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Identification and Treatment of Emerging Contaminants in Wet Weather Flows

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Abstract

This research report focuses on the identification and treatment of emerging contaminants in wet weather flows. It contains extensive literature reviews on the topic along with results from sample collections supporting the research. Investigations were conducted at a wastewater treatment plant treating separate municipal wastewater that received elevated flows during wet weather. Stormwater sheetflow samples were also obtained in the area for pharmaceutical, PAH, trace metals, bacteria, and pesticide analyses. Laboratory tests were also conducted investigating trace heavy metal leachate sources during material exposures, and the survival and re-growth of indicator bacteria in urban areas. The report also contains discussions on the treatability of these pollutants using traditional and advanced stormwater control practices.

Municipal wastewater treatment plants have traditionally been designed to treat conventional pollutants found in sanitary wastewaters. However, many synthetic pollutants, such as pharmaceuticals and personal care products (PPCPs), also enter the wastewater stream. Some of these nontraditional contaminants are not efficiently removed by the treatment process at the wastewater treatment plant. Some of the pharmaceuticals excreted from the human user's body are metabolized and are more toxic and untreatable than their parent compound. Emerging contaminants have been referred to by EPA as "contaminants of emerging concern (CECs) because the risk to human health and the environment associated with their presence, frequency of occurrence, or source may not be known."

In this EPA funded research, pharmaceuticals, PAHs and pesticides at the treatment plants were examined. The study focused on the effects of stormwater infiltration and inflow (I&I) into sanitary systems and the amounts and treatability of targeted pharmaceuticals and other compounds. Dry and wet weather samples were obtained from the city of Tuscaloosa's wastewater treatment plant for analyses. Samples were obtained from four locations within the treatment plant in order to determine if there are significant differences between influent quantities and removal characteristics for the different unit processes during periods of increased flows associated with wet weather compared to normal flow periods. The data generally show that treatability appears to remain similar during both wet and dry weather conditions under a wide range of flow conditions.

Another objective of this research was to examine how different drainage system and tank materials, water chemical characteristics, and exposure times affect trace heavy metal losses. Static leaching tests for eight pipe and gutter materials were conducted over two separate three month periods during which pipe and gutter test materials were exposed to roof runoff and stormwater buffered to pH 5 and 8 and for exposure to different salinity conditions. This research found that the metallic gutter and pipe materials released significant amounts of heavy metals, with galvanized steel materials being the most significant sources of lead and zinc, while copper materials were the

most important source of copper (as expected). Zinc, copper, and lead releases were detected during both short and long exposure times under low and high pH conditions and low and high salinity conditions.

Because of difficulties in the measurements of water-borne pathogens, the microbiological quality of stormwater runoff is often characterized on the basis of bacterial indicator species. These are assumed to derive from a common (sewage) source with pathogens of interest, and to arrive in, survive in, and move through watershed environments in numbers that correlate with the health risk from those pathogens. Commonly used indicator species (especially *E. coli,* and *Enterococcus* spp. or Enterococci), however, may derive from sources other than sewage, and survive in the (non-enteric) environment at rates different from those of the pathogens they are presumed to indicate. The studied indicator organisms (especially Enterococci) were found to be quite persistent (especially under environmental conditions that most closely approximate enteric conditions) on impervious surfaces subject to the extreme Tuscaloosa, AL environmental conditions. Moreover, under most conditions studied, the rate of disappearance of these organisms from the landscape slowed (or even reversed), rendering short term studies of their survival (or even the simple regression of long term studies) unreliable in predicting their environmental fate.

Stormwater treatment is entering a new phase with stormwater management systems being required to meet specific numeric objectives, as opposed to the historic approach of meeting guidance-document-provided percent removal rates. Meeting numeric discharge requirements will require stormwater managers to better understand and apply the physical, chemical, and biological processes underpinning these treatment technologies. This report concludes with a discussion of the treatability of these compounds by conventional sedimentation and chemically active media that can be used in biofilters or other stormwater treatment devices.

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Contents

Tables

Figures

List of Abbreviations

%	Percentage
<	Less Than
>	Greater Than
µg/L	Microgram per Liter
AL	Alabama
Al	Aluminum
ANOVA	Analysis of Variance
BDL	Below detection limit
BQ	Below quantification
Ca	Calcium
CAS	conventional activated sludge
CBZ	carbamazepine
Cd	Cadmium
cm	Centimeter
COD	Chemical Oxygen Demand
COV	Coefficient of Variation (standard deviation/mean)
Cr	Chromium
CSOs	Combined sewer overflows
Cu	Copper
DI water	Distilled Water
DL	Detection Limit
DO	Dissolved Oxygen
ECOC	Emerging contaminants of concern
ECs	Emerging contaminants
EDCs	endocrine disruptor compounds
Eh	The Half-cell Potential Relative to the Standard Hydrogen Electrode
EPSCoR	Experimental Program to Stimulate Competitive Research
E_{SHE}	The Half-cell Potential Relative to the Standard Hydrogen Electrode
EWRI	Environmental and Water resources Institute

Fe	Iron
FLX	fluoxetine
ft.	Feet
G.	Gutter material specimen
g/L	Gram per Liter
GAC	Granular Activated Carbon
GFB	Gemfibrozil
H^+	Hydrogen Ion
HDPE	High Density Polyethylene
HMW	High molecular weight
HNO_3	Nitric Acid
hr.	Hour
HRT	hydraulic retention time
IBP	Ibuprofen
IC50	Concentration Required for 50% Inhibition of Bacterial Fluorescence
K	Potassium
KCl	Potassium Chloride
kg	Kilogram
K_{SP}	Solubility Product Constant
L	Liter
LMW-	Low molecular weight
m	Meter
M	Molar
MBR-	membrane bioreactor
MDL	Method Detection limit
MDL	Method Detection Limit
Mg	Magnesium
mg/L	Milligram per Liter
mg/m^2	Milligram per Square Meter
mL	Milliliter
mm	Millimeter
mo	Month

mol/L	Mole per Liter
N	Nitrogen
na	Not Available
Na	Sodium
NaOH	Sodium Hydroxide
ND	Not Detected
Ni	Nickel
NO_3	Nitrate
NSF	National Science Foundation
OCP-	Organochlorine Pesticides
ORP	Oxidation Reduction Potential
P	Phosphorus
P.	Pipe material specimen
PAHs	polycyclic aromatic hydrocarbons
Pb	Lead
PCBs	polychlorinated biphenyls (Arochlor)
Pes	population equivalents
PhACs	Pharmaceutically Active Compounds
PO_4^{3-}	Phosphate Ion
POP	Persistent Organic Pollutant
PPCPs	Pharmaceuticals and personal care products
PPs	Pharmaceutical products
PVC	Polyvinyl Chloride
QAQC	Quality Control Quality Assurance
SD	Standard Deviation
SMZ	sulfamethoxazole
SRT	solids retention time
SSC	suspended sediment concentration
STPs	Sewage treatment plants
TCL	Triclosan
TDS	Total Dissolved Solids
TRM	trimethoprim
TSS	total suspended solids

US EPA	United States Environmental Protection Agency
WEFTEC	Water Environment Federation Technical Exhibition and Conference
WWTP	Wastewater treatment plant
Zn	Zinc
ZVI	Zero-valent Iron
Σ	Sum

Section 1. Executive Summary

This project and its many tasks had several inter-related activities focusing on source identification and treatment of emerging contaminants in wet weather flows. The direct goals and objectives of this project were to compile existing and related information pertaining to these under-represented contaminants that may occur in wet weather flows (such as separate stormwater and separate sewer overflows); to collect characterization information of these contaminants from a selection of these flows; and to evaluate these flows for their treatability using a variety of methods, including literature reviews, chemical characteristics, water chemistry modeling, and field testing. While much information exists in the literature pertaining to dry weather sewage treatment, industrial wastewater treatment, and drinking water treatment of some emerging contaminants, very little data are available concerning treatment of wet weather flows or the characterization of these contaminants in wet weather flows.

We were fortunate in being able to supplement the project resources with additional support for some of the graduate research assistants (and for the analytical costs) from Alabama EPSCoR and industrial clients. These other projects, while not directly involved in the original project tasks, allowed us to address several important elements that had direct benefits to this project. These other data and results were integrated in this project report and addressed several topics, including: survival and fate of stormwater indicator bacteria on impervious surfaces; leaching of trace heavy metals from different pipe materials and asphalts; and extensive testing of biofiltration media for the treatment of a broad range of organic, radioactive, and metallic contaminants. These supplemental projects have enabled us to greatly expand our originally planned project efforts to address these additional issues pertaining to sources and treatment of emerging and related contaminants.

Pharmaceuticals and Personal Care Product Characteristics in Wet Weather Flows and their Treatability

The U.S. Environmental Protection Agency (USEPA) sets guidelines for pollutant discharges from municipal and industrial treatment plants and for stormwater discharges based on the National Pollutant Discharge Elimination System (NPDES). These regulations mainly focus on discharges of conventional pollutants. However, new classes of unregulated contaminants have become an emerging environmental problem (Petrovic, *et al*. 2003). These pollutants have been found in waterways and in groundwater. Pharmaceuticals were first reported in surface waters during the investigation of U.S. waterways in the 1970s, although they are not regulated as legacy pollutants such as are PCBs and DDTs (Snyder, *et al*. 2006).

Researchers, including Watts, *et al.* (1983), first reported the occurrence of several selected antibiotics in river water samples. Since then, there have been many investigations of antibiotics as well as publications documenting their presence in groundwaters, surface waters, wastewaters and landfill leachates (Xu, *et al.* 2007).

The USEPA coordinated with the U.S. Geological Survey to compile a list of emerging contaminants found in the U.S. waterways (A National Reconnaissance). Samples were obtained from 139 U.S. streams and waterways to analyze ninety five organic wastewater contaminants (Koplin, *et al*. 2002). These emerging contaminants are used in large amounts in the US, yet many have no maximum concentration limits in discharge permits. Research on several contaminants investigated during the Reconnaissance Study is being conducted to quantify the potential effects of these compounds on aquatic wildlife and the environment, such as work by Campbell (2006) who conducted a study to investigate the effects of estrogen, an endocrine chemical disruptor, on aquatic wildlife.

Emerging contaminants, as defined by the U.S. Geological Survey, are “any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects.” The U.S. EPA describes emerging contaminants by the statement: “chemicals are being discovered in water that previously had not been detected or are being detected at levels that may be significantly different than expected that may cause a risk to human health and the environment.” The EPA refers to these pollutants as “contaminants of emerging concern” (CECs).

Little is known about the effects of these compounds in the environment or how they are transported into the environment. Researchers have studied how some pollutants affect wildlife. Endocrine disrupting chemicals, a sub-category of emerging contaminants, have caused sexual abnormalities in certain species of fish. Endocrine disrupting chemicals include a broad range of chemicals: natural and synthetic estrogens, pesticides and industrial chemicals (Campbell, *et al.* 2006). Low levels (ng/L) of waterborne estrogens lead to adverse effects such as the feminization of fish, impaired reproduction and abnormal sexual development (Sellin, *et al.* 2009).

Research on emerging contaminants has improved with new analytical methods that quantify these contaminants in very small trace quantities, as some emerging contaminants may cause adverse effects on the ecosystem even in small amounts. Some studies have been conducted to examine the fate and transport of these chemicals from their point (or non-point) sources to the environment and how to reduce their discharge quantities. For instance, disposing unused medications via toilet flushing may appear minor to consumers, but that activity could perhaps cause adverse environmental effects in large communities. Additionally, many of the pharmaceuticals used in human medical care are not completely transformed or absorbed in the human body and are often excreted in only slightly transformed conjugated polar molecules (e.g. as glucoronides) or even unchanged (Herberer 2002). Some of these conjugates can pass through a wastewater treatment plant untreated and enter into the receiving waters. Residuals of contaminants may leach into groundwater aquifers. Some of these pollutants have been reported in ground and drinking water samples from water works using bank filtration or artificial groundwater recharge downstream from municipal sewage treatment plants (Herberer 2002).

Pharmaceuticals, personal care products and endocrine disruption chemicals are the major categories of emerging contaminants. Polycyclic aromatic hydrocarbons (PAHs), pesticides, heavy metals and microbes are classified as priority pollutants, and are also discussed in this report due to their lack of general information in wet weather flows and possibly similar treatment behavior as PPCPs. Pharmaceuticals enter the treatment system either directly, or through fecal matter or urine (or by pet medication and stormwater). Personal care products could possibly enter the treatment plant through direct disposal or by shower or bath waters. Pesticides, PAHs, heavy metals and microbial material can be brought to the treatment plant through urban runoff that infiltrates the sewer lines or directly discharged to the sewers if a combined system.

Emerging contaminants are treated at variable rates at wastewater treatment facilities. Recent studies have demonstrates wastewater treatment plant removals of personal care products and pharmaceutical ranging between 60% and 90% for a variety of polar compounds (Carballa, *et al.* 2004). The removal rate is mostly contingent on the physical and chemical nature of the pollutant and the effects of the wastewater matrix. It also depends on the treatment plant itself, such as the retention time through each unit process and the specific unit processes used at the treatment facility (Mohapatra, *et al*. 2010). The effects of increased inflow rates and changes in influent concentrations during rain events on the treatability of these compounds were investigated during this study.

One of the purposes of this research was to quantify the effects of wet weather flows on the performance of different unit processes in the removal of emerging contaminants and to quantify the mass discharges to the wastewater treatment facility of the ECs. Wet weather causes an increase in the amount of wastewater flowing to the treatment plant due to inflow and infiltration of stormwater. This increased flow rate and possible characteristic changes of the wastewater may affect EC treatment.

The objectives of this research included:

- Understand how emerging contaminants, such as pharmaceuticals, personal care products, PAHs, and pesticides are eliminated by unit treatment processes during variable flow conditions.
- Examine the range of the chemical characteristics of the contaminants and confirm how they correspond to theoretical treatment potential based on actual monitoring observations.
- Determine how the increased flow rates and mass loads of the emerging contaminants during wet weather conditions affect their treatability.
- Determine the mass discharges of the ECs from the stormwater contributions to the treatment facilities.

During this research, multiple dry and wet weather sample series were obtained at four locations within the Hilliard N. Fletcher Wastewater Treatment plant. This treatment plant serves the municipality of Tuscaloosa as well as some areas of Tuscaloosa County, Alabama. Samples were obtained from the inlet, after the primary clarifier, following secondary treatment, and after UV-disinfection at the plant final discharge. These samples were analyzed and evaluated for selected ECs for comparison to literature information, and to understand how they would respond to similar treatment processes that are used for wet weather flows.

Many of the publications during the last two decades have reported the occurrences of pharmaceuticals and personal care products in a wide variety of waters. Most of these included municipal wastewater treatment influents and effluents, rivers, other surface waters, and drinking waters. However, very little information is available addressing these compounds in wet weather flows. Stormwater I&I can have a significant effect on wastewater treatment flows (and pollutant concentrations) and may in turn potentially affect treatment of wastewater pollutants. As an example, PAHs are more likely associated with stormwater in urban areas than in separate dry weather sanitary wastewater. Increases of PAHs in wastewater influent during wet weather suggest stormwater is entering the sewer system. Pesticides are also of interest for this study and are known pollutants associated with stormwater. Some pharmaceuticals have dual roles in both human and veterinary medicine. While many would enter the sanitary sewage system from human wastes, pet pharmaceuticals could enter the system through stormwater contaminated by fecal matter from treated animals.

Samples were collected during a range of flow and rain conditions to understand whether stormwater contributes ECs to the treatment plant. I&I are not likely significant until the daily rain depth is greater than about one-half inch, when the treatment plant flow can increase to greater than about 20 MGD. During the largest rain depth observed (2.67 inches), the treatment plant flow was also the largest observed (42.2 MGD). Mass loads were calculated based on the measured daily flow rates and the influent concentrations. The mass loads for the dry weather days were compared to the wet weather day mass loads. The differences were then related to the rain depth observed for the day to determine if stormwater contribute to the EC discharges to the treatment plant. Eight dry weather samples were taken in addition to nine wet weather samples at four locations at the treatment facility. Some of the constituents did not have values for some of the sample dates and in a few instances, insufficient sample volumes were available to complete the full suite of analyses.

There are few obvious sources of PPCPs in wet weather flows (beyond some associated with veterinarian drugs). However, regression analyses of influent concentrations vs. treatment plant flow rate indicated significant slope terms for all of the pharmaceutical compounds (increasing concentrations with increasing flow rates at the treatment facility), except for carbamazepine. Table 1-1 summarizes the observed concentrations during both low and high flow conditions. In general, the average concentrations for peak flows were about double the dry weather period concentrations, although there was substantial variability.

Table 1-1. Dry and Wet Weather Observed Pharmaceutical Concentrations at Tuscaloosa Wastewater Treatment Plant

	Average dry weather concentrations (at about 18 MGD at treatment plant)	Average wet weather concentrations (at about 40 MGD at treatment plant)
Gemfibrozil, µg/L	55	110
Ibuprofen, µg/L	35	60
Triclosan, µg/L	35	60
Carbamazepine, µg/L	8	15
Fluoxetine, µg/L	45	100
Sulfamethoxazole, µg/L	50	100
Trimethoprim, µg/L	12	25

The samples obtained at the influent at the Tuscaloosa Wastewater Treatment Plant were also analyzed for selected PAHs. The PAH concentrations all had statistically significant increasing concentrations with increasing daily average flow rates (except for acenapthtylene), although there were generally wide variations in concentrations observed. In general, the average concentrations for peak flows were also about double the dry weather period concentrations, although there was also substantial variability for the PAHs, as shown on Table 1-2.

Table 1-2. Dry and Wet Weather Observed PAH Concentrations at Tuscaloosa Wastewater Treatment Plant

	Average dry weather concentrations (at about 18 MGD at treatment plant)	Average wet weather concentrations (at about 40 MGD at treatment plant)
Naphthalene, µg/L	10	20
Acenaphthene, µg/L	6	12
Fluorene, µg/L	1	2
Fluoranthene, µg/L	0.8	2
Phenanthrene, µg/L	2	4
Anthracene, µg/L	1	2
Pyrene, µg/L	1	2

Table 1-3 shows the significant slope terms for the analyzed pharmaceuticals and PAHs, reflecting the increasing concentrations as the daily average wastewater treatment plant flow increased during different sized rains. These slope terms were used to calculate approximate influent concentrations for these increasing flows, and the loads, expressed as mg/km^2 for each rain category.

Table 1-3. Calculated Influent Mass Loadings for Pharmaceuticals during Different Sized Rain Events

Pharmaceutical compound	Slope term (µg/L/MGD)	Conc. (µg/L) during 0 to 0.5 inch rain (18 MGD; 1.5 hr duration)	Mass per event (mg/km^2)*	Conc. (µg/L) during 0.6 to 1.5 inch rain (23 MGD; 4 hr duration)	Mass per event (mg/km^2)*	Conc. (µg/L) during 1.6 to 2.5 inch rain (34 MGD; 12 hr duration)	Mass per event (mg /km^2)*
Gemfibrozil	2.81	51	1.1	65	4.9	96	32
Ibuprofen	1.85	33	0.74	43	3.2	63	21
Triclosan	1.86	34	0.74	43	3.2	63	21
Fluoxetine	2.44	44	0.97	56	4.2	83	28
Sulfamethoxazole	2.51	45	1.00	58	4.4	85	29
Trimethoprim	0.66	12	0.26	15	1.2	22	7.5

* 74 mi^2 (192 km^2) service area

Table 1-4 summarizes some of the reported influent pharmaceutical concentrations at wastewater treatment plants as reported in the literature compared to the concentrations observed at the influent at the Tuscaloosa wastewater treatment plant during this study. The gemfibrozil and ibuprofen values are within the range previously reported, but the triclosan, sulfamethoxazole, and trimethoprim observed concentrations seem larger than typically reported (by about one order of magnitude). However, the laboratory QA/QC results, including frequent testing of internal and external standards and extraction efficiencies, indicated that the results are acceptable. Most of the methods used during the reported studies in the literature were advanced procedures that had very low detection limits, while our methods used more basic HPLC units, and we used specially developed solid-phase extraction methods for enhanced recoveries. Our detection limits were suitable, but relatively close to the observed values. Therefore, the pharmaceutical concentrations reported during this project may have greater uncertainly than many of the reported sources. However, the analyses of the treatment results reported in the next section show consistent results and expected behavior, with similar values for the influent and after primary treatment, and most of the removals occurring during the secondary treatment phase, resulting in much lower effluent concentrations. Some compounds did not show any significant removals, so the repeated results helped establish the analytical performance. Table 1-5 is a similar calculation of influent mass loadings for PAHs.

Table 1-4. Observed Influent Pharmaceutical Concentrations Compared to Reported Concentrations

Pharmaceutical compound	**Concentrations reported for influents at wastewater treatment plants (µg/L)**	**Influent concentrations observed during this study (average µg/L)**
Gemfibrozil	0.1 to 36	59
Ibuprofen	4 to 84	28
Triclosan	0.9 to 4	28
Sulfamethoxazole	0.05 to 1.5	38
Trimethoprim	0.05 to 1.5	9

Table 1-5. Calculated Influent Mass Loadings for PAHs during Different Sized Rain Events

PAH compound	Slope term (µg/L/MGD)	Conc. (µg/L) during 0 to 0.5 inch rain (18 MGD)	Mass per event (mg/km^2)*	Conc. (µg/L) during 0.6 to 1.5 inch rain (23 MGD)	Mass per event (mg/km^2)*	Conc. (µg/L) during 1.6 to 2.5 inch rain (34 MGD)	Mass per event (mg/mi^2 and mg/km^2)*
Naphthalene	0.5	9.0	0.20	11.5	0.87	17.0	5.7
Acenaphthene	0.31	5.6	0.12	7.1	0.54	10.5	3.5
Fluorene	0.057	1.0	0.02	1.3	0.10	1.9	0.65
Fluoranthene	0.047	0.8	0.02	1.1	0.08	1.6	0.54
Phenanthrene	0.11	2.0	0.04	2.5	0.19	3.7	1.3
Anthracene	0.055	1.0	0.02	1.3	0.10	1.9	0.63
Pyrene	0.059	1.1	0.02	1.4	0.10	2.0	0.67

* 74 mi^2 (192 km^2) service area

Table 1-6 compares the observed influent PAH concentrations during this study with some reported PAH values from the literature. The concentrations reported in the wastewater literature are again much lower than observed during this research. During our prior PAH studies in wet weather flows (Pitt, *et al.* 1999, for example). We have commonly seen even higher PAH concentrations in separate stormwater. We suspect the main differences are associated with the extraction methods. The use of solid-phase extraction methods for PAHs in the presence of particulates results in very low recoveries. More effective extraction methods use multiple extractions with separation funnels instead, as used during this study. Most of the PAHs are strongly associated with particulates which are difficult to extract by some methods. For groundwater samples, where little of the PAHs are associated with particulates and the particulate content in the samples is very low, so solid phase extraction can work well; for surface water samples (and wastewater samples), the particulate matter significantly interferes with PAH extractions using solid-phase extraction methods.

Table 1-6. Observed Influent PAH Concentrations Compared to Reported Concentrations

PAH compound	**Concentrations reported for influents at wastewater treatment plants (range µg/L)**	**Influent concentrations observed during this study (average µg/L)**
Naphthalene	0.1 to 7	11
Acenaphthene	0.02 to 0.4	11
Fluorene	0.04 to 0.7	5
Fluoranthene	0.1 to 0.2	5
Phenanthrene	0.3 to 2	3
Anthracene	0.03 to 0.1	75
Pyrene	0.1 to 0.5	5

Treatment of Pharmaceuticals and PAHs

Tables 1-7 and 1-8 summarize the chemical characteristics and their treatability as reported in the literature review for the emerging contaminants examined during this research. These tables shows the most likely means of removal, the reported ranges of influent and effluent concentrations, and the ranges of the percentage removals for each constituent.

The pharmaceuticals gemfibrozil, ibuprofen, triclosan and fluoxetine were reported to be best reduced by biodegradation (secondary treatment). The overall range of influent concentrations ranged from 0.3 to 14.6 µg/L. The removals for these compounds varied. Ibuprofen showed the highest level of treatability ranging from 82 to 95 percent. Triclosan had reduction rates of 75 percent and gemfibrozil had a reduction range from 38 to 76 percent.

Carbamazepine had the lowest reported reduction rates of zero to 30 percent. . Carbamazepine is difficult to treat, as it is resistant to biodegradation. Because carbamazepine is soluble in water, it is also not treatable by sedimentation in the primary unit processes. Carbamazepine concentration increases in the effluent compared to the influent were observed. Possible treatment mechanisms of carbamazepine are not clearly understood.

Sulfamethoxazole is highly soluble in water and therefore difficult to remove. Photodegradation removes sulfamethoxazole at some treatment facilities. The reported influent concentrations ranged from 0.25 to 0.35 µg/L, and the effluent concentrations ranged from 0.11 to 0.23 µg/L. The reduction rates of sulfamethoxazole ranged from 17 to 66 percent.

Low molecular weight (LMW) PAHs (naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, and anthracene) had reported reduction rates between 31 and 91 percent. Naphathlene had the lowest reduction rates ranging from 31 to 40 percent. Naphthalene has a Henry's Law constant of 0.019 atm-m^3/mol, making it more volatile than the other PAHs and more likely to volatize during wastewater treatment. Acenaphthene, acenaphthylene, fluorene, phenanthrene and anthracene have Henry's Law constants of about 10^{-3}, and their solubilities range from 0.045 to 16.1 mg/L. Volatization and oxidation were the primary means of reported treatment for PAHs having lower molecular weights. High molecular weight (HMW) PAH compounds (such as pyrene, fluoranthene, chrysene, and benzo(a)pyrene) had higher reduction percentages ranging from 83 to 91 percent. Adsorption is a primary removal factor for the HMW compounds. Influent concentrations for LMW PAHs ranged from 0.016 to 7.3 µg/L, and effluent concentrations ranged from 0.002 to 0.7 µg/L. Influent concentrations for the HMW PAHs ranged from 0.044 to 0.47 µg/L, and effluent concentrations ranged from 0.013 to 0.06 µg/L.

Table 1-7. Summary of Characteristics and Treatability of Targeted Pollutants

Constituent	Log Kow	Solubility (mg/L)	pka	Biodegradation half-life * **rate	Toxicity
Pharmaceuticals					
Gemfibrozil	4.78	5.0	4.7	1.5 hours	EC 50 D. Magna 22.85 mg/L
Ibuprofen	3.5-4.0	41.5	4.9	2 hours	EC 50 Daphnia. 108 mg/L
Triclosan	4.8-5.4	2-4.6	7.8	125 hours	IC 50 P. subcapitata. 1.4 μg/L
Carbamazepine	2.25	17.7	13.9	10-20 hours	LC 50 D. magna >100 mg/L
Fluoxetine	4.05	38.4	9.5	24-72 hours	LC 50 P. subcapitata 24 μg/L
Sulfamethoxazole	0.9	600	5.7	10 hours	IC 50 P. subcapitata. 1.5 mg/L
Trimethoprim	0.79	400	6.8	8-10 hours	IC 50 P. subcapitata. 80.3 to 130 mg/L

Table 1-7. Summary of Characteristics and Treatability of Targeted Pollutants (continued)

Polycyclic Aromatic Hydrocarbons	**Log kow**	**Solubility**	**Volatility**	**Biodegradation rate**	**Toxicity**
Napthalene	3.37	31.7	4.6 x 10^{-4}	0.8-43 days	LC 50 Pimephales promelas 7.76 mg/L
Acenaphthene	4.02	1.93	7.91 x 10^{-5}	1-25 days	LC 50 Salmo gairdneri 1570 μg/L
Fluorene	4.12	1.68-1.98	1.0 x 10^{-4}	2-64 days	EC 50 V. fischeri 4.10 μg/mL
Fluoranthene	5.14	0.20-0.26	6.5 x 10-^{6}	880 days	EC 50 S. capricornutum 54,400 μg/L
Acenaphthylene	3.89	3.93	1.5 x 10^{-3}	21-121 days	Did not find
Phenanthrene	4.48	1.20	2.56 x 10^{-5}	19 days ; 35-37 days;	Did not find
Anthracene	4.53	0.0076	1.77 x10^{-5}	108-139 days	EC 50 D.magna 211 μg/L;
Pyrene	5.12	0.0.077 (Dabestani and Ivanov 1999, 10-34)	4.3 x 10^{-4}	34 to 90 weeks	EC 50 D.magna 67000 μg/L
Benzo(a) anthracene and chrysene	5.61-5.71	0.0016-0.011	n/a	n/a	n/a
Benzo(b) fluoranthene, Benzo(k) fluoranthene, Benzo(a) pyrene, and indeno(1,2,3,cd) pryene			n/a	n/a	n/a
Benzo(a,h) anthracene and Benzo(g,h,i) perlene			n/a	n/a	n/a

Table 1-7. Summary of Characteristics and Treatability of Targeted Pollutants (continued)

Pesticides	Log kow	solubility	Reported most important treatment method	Biodegradation rate	Toxicity
Methoxychlor	4.68-5.08	0.1	Adsorption/ biodegradation	7 to 29 days	D. magna EC 50=1800 µg/L
Aldrin	6.5	0.027	Adsorption/ biodegradation	20-100 days	Salmo gairdneri LC 50 2.6 µg/L
Dieldrin	6.2	0.1	Adsorption/ biodegradation	None found	Salmo gairdneri LC 50 1.2 µg/L
Chlordane	~5.54	insoluble*	Adsorption/ biodegradation	60 days	Chironomus plummosus LC 50 10 µg/L
Arochlor Σ	5.6-6.8	insoluble*	Adsorption/ biodegradation	Variable. Depends on chlorination of compound	P. subcapitata 182nmol/L
Lindane	3.8	17	Adsorption/ biodegradation	69.41 hours	D. magna EC 50=1.64 mg/L
Heptachlor	6.10	0.056	Adsorption/ biodegradation	6 months-3.5 years	S. capricornutum LC 50 26.7 µg/L
Heptachlor-epoxide	5.40	not found	Adsorption/ biodegradation	None found; metabolite	None found
	4.68-5.08	0.1	Adsorption/ biodegradation		

Table 1-8. Summary of Characteristics and Treatability of Targeted Pollutants

Constituent	**Reported most important treatment method**	**Range of influent concentration (µg/L)**	**Range of effluent concentration (µg/L)**	**Range of removal at conventional wastewater treatment facility**
Gemfibrozil	Biodegradation	1.5-3.5	0.4-0.8	38%-76%
Ibuprofen	Biodegradation	0.45-15	0.02-2.0	82%-95%
Triclosan	Biodegradation	0.38-1.9	0.11-0.22	60%-75%
Carbamazepine	Not widely known due to increase in effluent	0.13-1.9	0.12-1.6	0%-30%
Fluoxetine	Biodegradation			
Sulfamethoxazole	Adsorption (minor), photodegradation	0.25-0.35	0.11-0.23	17%-66%
Trimethoprim	Chlorination (UV was not effective) Batt et al	0.10-0.45	0.10-0.11	70%-75%
	Reported most important treatment method	**Range of influent concentration (µg/L)**	**Range effluent concentration (µg/L)**	**Range of removal at conventional wastewater treatment facility**
Napthalene	Volatization/oxidation	0.147-7.3	0.088-0.7	31%-40%
Acenaphthene	Oxidation/Sorption	0.016-0.7	0.005-0.11	67%-85%
Fluorene	Oxidation/sorption	0.037-0.7	0.015-0.23	59%-68%
Fluoranthene	Sorption	0.15-0.24	0.02-0.03	86%-88%
Acenaphthylene	Oxidation/sorption	0.021	0.002	91%
Phenanthrene	Oxidation/sorption	0.333-1.7	0.11-0.2	67%-89%
Anthracene	Oxidation/sorption	0.028-0.09	0.007-0.012	75%-87%
Pyrene	Adsorption	0.14-0.47	0.023-0.06	83%-88%
Benzo(a) anthracene and chrysene	Adsorption	0.21	0.019	91%
Benzo(b) fluoranthene, Benzo(k) fluoranthene, Benzo(a) pyrene, and indeno(1,2,3,cd) pryene	Adsorption	0.42	0.076	82%
Benzo(a,h) anthracene and Benzo(g,h,i) perlene	Adsorption	0.044	0.013	71%
Heptachlor	n/a	n/a	n/a	n/a
Heptachlor-epoxide	n/a	n/a	n/a	n/a

Observed Treatment of PPCPs at the Tuscaloosa Wastewater Treatment Plant

Table 1-9 summarizes the average concentrations obtained at each of the four sampling locations at the Tuscaloosa Earl N. Hilliard (ENH) wastewater treatment plant and indications of the likely most important unit treatment process. The pharmaceuticals have low to moderate removals (about 50%) while the PAHs show larger removals (about 90%), although the observed removals varied substantially for different compounds in each constituent group. A combination of unit treatment processes resulted in the best pharmaceuticals and PAH reductions, as expected.

Table 1-9. Performance Data for Earl Hilliard WWTP, Tuscaloosa, AL

Constituent	Avg Influent conc. (µg/L)	Avg Primary effluent conc. (µg/L)	Avg Secondary effluent conc. (µg/L)	Avg concentration after UV (final effluent) (µg/L)	Avg Overall Percentage Removal at ENH wastewater treatment facility	Apparent most Important treatment unit process
Pharmaceuticals						
Gemfibrozil (w)	32.4	31.7	18.1	17.1	45	Secondary
Gemfibrozil (d)	80.3	23.4	22.3	18.6	71	Primary
Ibuprofen (w)	21.6	21.0	17.6	9.6	58	UV
Ibuprofen (d)	44.7	35.3	20.8	15.3	67	Secondary
Triclosan (w)	33.9	16.9	15.0	12.3	63	Primary
Triclosan (d)	16.7	3.3	12.9	0.4	98	UV
Carbamazepine (w)	2.4	5.0	5.0	2.6	-8	UV
Carbamazepine (d)	15.9	10.5	2.5	1.4	94	Primary
Fluoxetine (w)	14.1	41.7	3.3	1.9	86	Secondary
Fluoxetine (d)	61.7	36.8	11.6	9.6	84	Secondary
Sulfamethoxazole (w)	10.4	18.4	14.1	13.1	-33	None
Sulfamethoxazole (d)	68.7	42.6	31.1	24.4	65	Secondary
Trimethoprim (w)	3.1	3.1	3.9	2.0	33	UV
Trimethoprim (d)	16.3	28.3	21.1	21.0	-31	None
Polycyclic Aromatic Hydrocarbons						
Naphthalene (w)	15.3	4.7	25	22.7	-47	None
Naphthalene (d)	7.1	11.1	3.8	1.3	82	Secondary
Acenaphthene (w)	16.9	5.1	0.4	0.6	96	Primary
Acenaphthene (d)	7.7	0.8	0.1	0.02	99	Primary
Fluorene (w)	10.3	1.0	0.6	0.6	91	Primary
Fluorene (d)	0.7	1.2	0.04	0.05	93	Secondary
Fluoranthene (w)	10.3	4.2	0.5	0.5	95	Primary
Fluoranthene (d)	0.3	0.5	0.02	0.04	87	Secondary
Acenaphthylene (w)	10.5	0.6	0.6	0. 7	92	Primary
Acenaphthylene (d)	0.1	0.6	0.01	0.02	75	Secondary
Phenanthrene (w)	6.1	4.4	0.05	0.2	98	Secondary
Phenanthrene (d)	1.6	0.8	0.2	0.1	90	Primary and secondary
Anthracene (w)	198	2.3	9.7	0.8	100	Primary
Anthracene (d)	60.1	0.2	0.2	0.2	100	Primary
Pyrene (w)	10.2	4.0	0.7	0.5	95	Primary and secondary
Pyrene (d)	0.7	1.0	0.1	0.1	80	Secondary

The largest reductions, for all but acenaphthene, occur during secondary biological treatment, where most of the removal of particulates occurs along with biological digestion of the solids. The primary sedimentation treatment had little direct benefit. Phenanthrene actually indicated an increase in concentrations with primary treatment, likely due to removal of particulates that interfered with the extraction of the compound during the laboratory tests. Acenaphthene is an example where all of the treatment processes were effective for partial removal of the compound, including the primary, secondary, and disinfection unit processes. For many of the samples, acenaphthene was not detected after the secondary treatment phase.

In most cases, the median concentration reductions for the ECs are modest; however, extremely large periodic influent concentrations are usually significantly reduced by the primary treatment unit process. The biological secondary treatment processes and the final ozone disinfection processes provided additional benefit, approaching “irreducible” concentrations. Secondary treatment did result in a very narrow range of effluent quality for acenaphthene, fluorene, fluoranthene, phenanthrene, and pyrene, although most of the removals for these compounds occurred with primary sedimentation treatment. No pesticides were detected at the 0.5 to 1 µg/L detection limit at any of the sampling locations at the treatment facility.

Emerging Contaminants Observed in Stormwater Sheetflows in Tuscaloosa, AL

Sheetflow samples were analyzed for selected PPCP concentrations, including trimethoprim, sulfamethoxazole, carbamazepine, fluoxetine, ibuprofen, gemfibrozil, and triclosan. Triclosan was not detected in any of the samples, while ibuprofen was only detected in 15% of the samples, and trimethoprim was only detected in 23% of the samples. The nonparametric Kurskal-Wallis one-way analysis of variance on ranks test was applied on these data using SigmaPlot version 11 (SYSTAT Software Inc.) to detect the presence of any significant differences in land use or source area grouping. For the PPCPs, only carbamazepine (detected in 95% of the sheetflow samples) was found to have at least one source area statistically significantly different from the other source area categories. None were found to have any significant differences by land use, for the number of samples available.

Grouped box and whisker plots (using SigmaPlot version 11) were also prepared for all of the PPCPs showing differences by source area and land use. Probability plots (Minitab version 16) were also prepared for the constituents having sufficient data (sulfamethoxazole, bacteriostatic antibiotic, often used with trimethoprim; carbamazepine, an anticonvulsant; fluoxetine, and antidepressant such as Prozac; and gemfibrozil, used to lower lipid levels).

The probability plots were prepared showing each source area separately for carbamazepine to also help distinguish the source areas that were likely different from the others. The probability plots indicate good fits of the data to log-normal statistical distributions, with some very large values and some low values observed, as generally seen for most stormwater constituents. These analyses clearly show that landscaped areas had the lowest average concentrations of carbamazepine (about 1 µg/L), while the other source areas (paved areas and roof runoff) had higher average concentrations at about 4 µg/L.

Polycyclic aromatic hydrocarbons (PAHs) were also analyzed in the sheetflow samples. Naphthalene was detected in 64% of the sheetflow samples, phenanthrene was detected in 29% of the sheetflow samples, and indeno(1,2,3-cd)anthracene was detected in 21% of the sheetflow samples. Anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(a,h)anthracene, and benzo(ghi)perylene were also included in the GC/MSD analyses for the PAHs, but were detected in less than 20% of the samples. The Kurskal-Wallis nonparametric ANOVA test did not identify any significant groupings by source area or land use, for the number of observed data available, for any of the PAHs. Naphthalene had the highest concentrations observed, with about half greater than 2 µg/L (maximum of about 9 µg/L), while phenanthrene and indeno(1,2,3-cd)anthracene were much lower (medians of about 0.3 µg/L and maximums of about 1 µg/L).

No sheetflow samples had detected cadmium (total or filtered), filtered chromium, and filtered lead, while less than 20 percent of the samples had detected total chromium, total lead, and total and filtered nickel. The average filtered percentages of the observed metals were 0% for chromium and lead (but few samples had detected values), and 50 to 100% for copper, zinc, aluminum, and iron. The Kurskal-Wallis non-parametric ANOVA tests indicated the following metal forms that had significant groupings by either source area or land use:

- Total aluminum ($p<0.001$) for source areas
- Total zinc ($p = 0.012$) for land uses
- Filtered zinc ($p = 0.007$) for land uses
- Total iron ($p = <0.001$) for source areas
- Filtered iron ($p = 0.013$) for source areas

The commercial areas had significantly higher concentrations (140 and 41 µg/L for total and filtered zinc) compared to the institutional (20 and 12 µg/L) and residential (19 and 9 µg/L) areas, apparently reflecting the greater use of galvanized metals in the commercial land use areas. The probability distributions for most of the observed metals fit log-normal statistical distributions.

Enterococci results indicated at least one significantly different source area compared to the others. The roof runoff (median 60 MPN/100 mL) samples appear to have significantly lower counts compared to the highest levels from the landscaped area (median of about 2,000 MPN/100 mL) samples, while the paved area (median of about 600 MPN/100 mL) samples had intermediate levels (but close to the landscaped area samples). The *E. coli* sheetflow values are much lower than typically observed for stormwater, with a median of only 17 MPN/100 mL, but with an observed maximum of about 18,000 MPN/100 mL).

Most of the sheetflow samples actually had an increase in fluorescent activity with exposure to the sample, with only a very few indicating barely moderate toxicity (up to 30 to 33% light decrease).

The Kurskal-Wallis nonparametric ANOVA tests indicated that at least one source area subgroup was significantly different from the others for total solids, TSS, and SSC. TDS did not indicate any differences between the source area groups for the number of samples available. From the box and whisker and probability distribution plots, it is apparent that the landscaped areas generate much more sediment than the paved areas or roof runoff. The median TSS concentration in the landscaped runoff was about 300 mg/L, while the paved area median TSS was about 18 mg/L and the roof runoff median TSS was about 3 mg/L. The SSC concentrations were slightly higher than the TSS values and showed the same pattern, as did the total solids values. The TDS concentrations were not separated statistically by source area and had a median value of about 23 mg/L.

Only one of the sheetflow samples (a pavement runoff sample from a large regional mall) had any of pesticides, while other paved areas also had several phthalate compounds and a few PAHs detected. Roof runoff and landscaped areas had fewer detections of these compounds.

Sources of Heavy Metals for Material Exposures and their Treatability

Another task of this project examined how stormwater heavy metals may originate from different exposed materials commonly used for conveyance or storage of stormwater, or through exposure as building materials. Currently, the discharged amounts of heavy metals originating from anthropogenic sources exceed those discharged from natural sources in the environment (NCSU Water Quality Group). Anthropogenic sources can include urban stormwater runoff (from roads and roofing materials), corrosion of stormwater drainage systems, mining discharges, and heavy metal particles emitted during the combustion of fossil fuels that return to the surface as part of atmospheric deposition and then subjected to washoff during rains (NCSU Water Quality Group).

Heavy metals do not degrade in the environment, and therefore have the potential to accumulate within living organisms and increase in concentration within each successive link in the food chain. Adverse effects of high concentrations or accumulations of these metals can lead to many diseases and even mortality (US EPA 2007a). The US Environmental Protection Agency (US EPA) has established aquatic life criteria and human health criteria for many heavy metals.

Population increases lead to concurrent increases in land development, with corresponding increases in rooftop areas and stormwater drainage system expansions, the metal sources being examined during this research task. Often, roof runoff systems are directly connected to the storm drainage system and then to the receiving waters. Contaminated roof runoff, due to heavy metal roofing or drainage system materials, can have detrimental effects on stormwater runoff and receiving water quality (Burton and Pitt 2002).

Heavy metals are commonly found in stormwater runoff, mostly from automobile related sources, but also from material degradation. Roofing and drainage system materials and their coatings can be made of metals or have metals as a component. Metal corrosion and paint have been identified as copper, lead, zinc, and chromium sources of stormwater contamination (U.S.EPA 2011; Wallinder, *et al*. 2002a, 2001; Davis and Burns 1999; Simmons, *et al*. 2001; Burton and Pitt 2002; Kingette Mitchell Ltd. And Diffuse Sources Ltd. 2003). Elevated metal concentrations in the runoff can contaminate water bodies, soils during infiltration, and subsequently contaminate groundwater (Veleva, *et al*. 2010; Gromaire-Mertz, *et al*. 1999).

In previous research, investigators found that water quality was greatly affected by the materials used in the manufacture of roofing materials and drinking water pipes and chemical water parameters such as pH, chloride content, etc. (Clark, *et al*. 2008a, b; Clark, *et al*. 2007; Dietz, *et al*. 2007;Sandberg, *et al.* 2006; Lasheen, *et al.* 2008; Al-Malack, *et al*. 2001; Lagos, *et al*. 2001; Edwards, *et al*. 1996; Edwards, *et al.* 2001; Merkel, *et al*. 2002; Pehkonen, 2002; Mansouri, *et al*. 2003; Schock, *et al*. 1995; US EPA, 1995; Boulay and Edwards, 2001). Burton and Pitt (2002) noted that zinc contributions from rooftops can make up about one fourth of the total zinc discharges in stormwater runoff. Notable roof runoff zinc sources are associated with galvanized roofing and drainage system materials (rain gutters and downspouts).

The main goal of this research task was to determine the metal releases from different gutter and pipe materials, and their associated toxicities, under a wide range of environmental conditions. This research task quantified the concentrations of these contaminants from different pipe and gutter materials for different conditions and predicted the forms of the leached metals. Statistical analyses were also conducted to identify the significant factors affecting the releases of these contaminants from the test samples as a function of time for the different materials.

Stormwater runoff from roofs and pipes can be contaminated with high heavy metal concentrations. The dissolution of roofing and pipe material is affected by rainwater pH, and other factors. Acidic rainwater can dissolve the $CaCO_3$ content of cement roofs and drainage systems, and metal ions from metal and plastic materials. These processes lead to weathering and degradation of the roofing and piping materials. Factors that affect material deterioration include the chemical composition of water and the time of contact with it. Many studies identified that the type of material influences heavy metal concentrations leaching into the water. Metal ions released from roofs are chiefly in the most bioavailable form, and therefore roof runoff can be a significant source of toxicity.

The greatest zinc concentrations were observed from exposure of zinc and galvanized materials (Förster 1999; Heijerick, *et al*. 2002; Clark, *et al*. 2008a, b, and 2007; Burton and Pitt 2002; Bannerman, *et al*. 1983; Pitt, *et al.* 1995; Good 1993; Tobiason and Logan 2000; Tobiason 2004; Veleva, *et al.* 2007, 2010; Gromaire-Mertz, *et al*. 1999;

Schriewer, *et al.* 2008; Wallinder, *et al*. 2001, 2000; Gromaire, *et al*. 2002). Coated galvanized steel materials released lower zinc concentrations compared to un-coated galvanized metals (Clark, *et al*. 2008a; Wallinder, *et al*. 2001, 2000; Mendez, *et al*. 2011). When exposed to the atmosphere, zinc material forms a protective layer (zinc oxides/hydroxides/carbonates), which serves as a physical barrier between the metal surface and the atmosphere (Legault and Pearson 1978; Zhang 1996). Clark, *et al*. (2008a, b, and 2007) noted that there can be elevated zinc concentrations form zinc and galvanized metal materials throughout their useful life. Clark, *et al*. (2008a), Good (1993), and Gromaire-Mertz, *et al*. (1999) found that zinc concentrations in stormwater frequently exceed the criterion for aquatic toxicity. Heijerick, *et al*. (2002), Clark, *et al*. (2008a), and Wallinder, *et al*. (2001) also determined that as the age of metal panels increased, zinc concentrations increased also.

Copper materials released high copper concentrations (Wallinder, *et al*. 2009, 2002a; Sandberg, *et al*. 2006; Zobrist, *et al*. 2000; Karlen, *et al*. 2002; Boller and Steiner 2002). Fresh copper sheets released greater copper concentrations compared to naturally patinated copper sheet (Sandberg, *et al*. 2006). The copper concentrations from galvanized metals and vinyl materials didn't exceed 25 µg/L (Clark, *et al*. 2008a, b; Mendez, *et al*. 2011). Copper-based paints are important sources of copper at marina basins (US EPA 2011). Corvo, *et al*. (2005) observed that the metal mass loss was proportional to chloride deposition rate. However Sandberg, *et al.* (2006) found that copper runoff rates were significantly lower at the marine site compared to data acquired in an urban environment even despite substantially higher chloride deposition rates at the marine site. Copper concentrations may continue to leach out in an acid rain environment during the material's useful life (Clark, *et al*. 2008b).

Galvanized steel and galvalume roofing materials were not major sources of lead (Tobiason and Logan 2000; Gromaire-Mertz, *et al*. 1999; Förster 1999; Gumbs and Dierberg 1985; Shahmansouri, *et al*. 2003; Mendez, *et al*. 2011). Clark, *et al.* (2007) determined that old galvanized metals released lead. It was found that lead was leaching out of PVC rain gutters and that lead concentrations in roof runoff samples surpassed the water quality criteria for the corresponding constituents (Good 1993). Davis and Burns (1999) found that lead can be released in stormwater runoff from painted structures. Lead concentrations were significantly affected by paint age and condition. Lead releases from washes of older paints were significantly higher than from fresh paints. It was found that old surface paints have the potential to release high masses of lead into a watershed. Such factors as stagnation time, pH of the water, pipe age, and the Cl/SO_4 ratio influence lead release from PVC, polypropylene, and galvanized iron pipes (Lasheen, *et al*. 2008). Al-Malack (2001) also found that pH of water, time of contact, UV-radiation affected the migration of lead and other metal stabilizers from unplasticized polyvinyl chloride (uPVC) pipes. The author observed the increase of lead concentrations leaching out of uPVC pipes with the time. Gromaire-Mertz, *et al*. (1999) found that lead concentrations in roof runoff exceeded level 2 of French water quality standards of 50 µg/L for practically all samples.

Galvanized iron and PVC can leach iron concentrations, with galvanized iron materials releasing higher concentrations compared to PVC materials (Lasheen, *et al.* 2008; Shahmansouri, *et al.* 2003; Wallinder, *et al.* 2002b). Lasheen, *et al.* (2008) found that water quality parameters (pH, Cl^-/SO_4^{2-} ratio), stagnation time, pipe age, and pipe material affect heavy metal concentrations. Stagnation time and pipe age increase iron concentrations. At low pH (pH = 6) the concentrations of iron increased. High Cl^-/SO_4^{2-} ratio increased iron concentrations in all pipes. Sarin, *et al*. (2004) observed that when oxidants were present in water, greater iron release was noted during stagnation in comparison to flowing water conditions. Corvo, *et al*. (2005) found that metal mass loss was proportional to chloride deposition rate.

Rainwater pH influences the degradation of roofing and gutter material. The acidic environment of the rainwater dissolves $CaCO_3$ content of cement roofs and drainage system, and metal ions from metal roofing materials. This results in corrosion and damage of the roofing and piping materials and the change of the roof runoff pH. In case of concrete and metal materials, pH of the roof runoff is usually higher than that of rainwater and attributed to the $CaCO_3$ and metal ions, but below neutral (Horvath 2011; Pitt, *et al*. 2004; Clark, *et al.* 2007; Clark, *et al*. 2008 a, b; Tobiason 2004; Tobiason and Logan 2000).

Periodic spikes in nutrients were noted from galvanized roofing materials (Clark, *et al*. 2007; Clark, *et al.* 2008 a, b). It was found that roof runoff can be highly toxic (Good 1993; Tobiason and Logan 2000; Bailey, *et al*. 1999; Heijerick, *et al.* 2002).
First flush was observed for heavy metals in the stormwater runoff and was dependent on the antecedent dry period and the rain intensity (Zobrist, *et al*. 2000; He, *et al.* 2001a; Schriever 2008; Gromaire-Mertz*, et al*. 1999; Horvath 2011).

Factors that affect runoff concentrations include time of exposure, runoff water composition (pH, Cl-, etc.), meteorological factors (climate, humidity etc.), and material characteristics such as composition of the metal itself, its age, condition (Faller and Reiss 2005; Schriewer, *et al*. 2008; He, *et al.* 2001a; He 2002; Cramer, *et al* 2002; Veleva, *et al*. 2010, 2007; Sarin, *et al.* 2004; Lasheen, *et al.* 2008; Horvath 2011).
The form of the metals affects their behavior and toxicity in natural waters. Ionic forms of metal are the most bioavailable forms.

This research task examined metal releases from different stormwater drainage and tank materials under various water conditions. It was found that galvanized steel materials released the largest amounts of lead, zinc, and iron, while copper materials were the most significant sources of copper. Zinc and lead releases from galvanized steel materials were observed during both short and long exposure times. During controlled pH tests, zinc releases in the samples with galvanized steel materials exceeded those at higher pH values during long exposure times. During short exposure times, zinc releases from galvanized materials were lower in river water samples compared to the bay water samples; however, during long time exposures, zinc concentrations in the river water samples were greater than in the bay water samples. Plastic and concrete materials were the least important sources of zinc. Galvanized pipes and gutters were found to be the only source of lead releases. During short exposure times, copper releases were noted only for copper materials at both low and high pH for controlled pH conditions and for bay and river water during un-controlled pH tests. During the first series of tests, copper releases from copper gutters increased as pH decreased. During the second test series, copper losses were greater in containers with bay water compared to containers with river water. The smallest copper release was noted from HDPE and galvanized materials. The highest aluminum concentrations were released from aluminum materials.

Medusa chemical modeling software was used to perform water chemistry modeling with the test data. Eh-pH and log Concentration-pH diagrams were constructed and metal forms present were determined. The results showed that metal releases range in form from being strongly charged (valence state +2 and -2) to zero valence. In some of the test containers zinc (copper) compounds precipitated and formed protective film, therefore zinc (copper) concentration in those waters would not be expected to increase since there would be equilibrium between ions dissolved in the water and the precipitated compounds. Langelier Index calculated for the containers with concrete pipes immersed in pH 5 and pH 8 waters indicated that the waters were undersaturated with respect to $CaCO_{3(s)}$ and the waters would have a tendency to dissolve $CaCO_{3(s)}$ from the concrete. The samples with concrete pipes immersed in bay and river waters were oversaturated with respect to $CaCO_{3(s)}$ indicating that waters in these samples had a tendency to precipitate $CaCO_{3(s)}$ from the solution and there was no degradation of the concrete pipe after 3 months of exposure.

Under the controlled pH 8 conditions, samples with pipes and roofing materials were found to be less toxic compared to the same materials at controlled pH 5 conditions during the buffered experiments. Copper materials were the most toxic. The concrete pipes were least toxic under both high and low pH conditions during buffered and natural pH tests.

At pH 5, samples with copper, aluminum, vinyl, and HDPE materials resulted in the highest toxicities and were attributed to low pH values. Under buffered pH 8 conditions copper, materials were the most toxic. PVC and galvanized steel materials were slightly toxic. Under natural pH conditions, only the samples with copper and galvanized steel materials were a source of toxicity. Copper and galvanized steel materials caused high toxicity during all tests with buffered and natural conditions.

Based on the toxicity analyses, copper materials should be avoided, and the use of galvanized materials should be limited. Concrete pipes can be used with a wide range of water pH values. In natural water environments with pH values from 7 to 8 and with low and high salinity values, PVC, HDPE, vinyl, aluminum materials also can be used with minimal toxicity issues.

High concentrations of heavy metals leaching out of pipe and gutter materials are toxic to the bacteria. However, the pH of the test water may also interfere with the tests. The pH of stormwater can change as it comes in contact with different drainage and roofing materials and may affect the water toxicity. Correlation matrices, cluster and principal component analyses examined simple and complex correlations between toxicity and other water chemistry parameters and full factorial analyses will evaluate the effect of the water pH, time of contact, material, and interactions of those factors during the first test series; and the effect of water conductivity, time of contact, material, and interactions of those factors during the second test series.

Spearman correlation analyses indicated that pH values and metal releases influence the water toxicity during these tests. Under natural pH conditions, the toxicity in the samples with galvanized steel materials was strongly associated with zinc losses, and the toxicity in the samples with copper materials was strongly associated with copper releases. Cluster analyses also confirmed that toxicities were affected by both metal releases and pH values, and the metal losses were influenced by pH, conductivity, and time of exposure.

Principal component analyses showed that the first four principal components explained about 78% of the total variance. Toxicity and pH have high loadings on the first principal component. The second principal component has high loadings of time, Pb, and Zn. Copper has a large loading on the third principal component. Conductivity, pH, and material type were the highest loadings on the fourth principal component. Principal component analysis showed groupings of samples with similar characteristic. Samples with concrete, plastic, and aluminum materials immersed in controlled pH 8 waters had low lead and zinc releases and low toxicities. The samples with controlled pH 5 waters were associated with high toxicities.

Full 2^3 factorial analyses showed that for the controlled pH conditions, three-way interactions of pH, material, and time of exposure all had significant effects on copper and zinc releases; while the two-way interactions of material and time were important for lead releases. The two-way interactions of pH and material and pH and time had significant effects on toxicity. During the natural pH tests, the three-way interaction of conductivity, material, and time had a significant effect on copper and lead releases. For zinc releases, the two-way interaction of material and exposure period was significant. The two-way interactions of conductivity and material, and material and time, both had significant effects of toxicity during the natural pH test series.

Full 2^2 factorial analyses that examined the type of material indicated that for copper materials under controlled pH conditions, pH had a significant effect on copper releases; under natural pH condition, time and conductivity had significant effects on copper concentrations. For zinc releases from galvanized steel materials under controlled pH conditions, the interaction of time and pH was significant. For zinc releases from galvanized materials under natural pH conditions, time had a significant effect on zinc releases. For lead releases from galvanized steel pipe, exposure time was significant, and for galvanized steel gutter materials, the interaction of pH and time was significant. The interaction of exposure time and conductivity had an effect of lead releases from steel pipe under during natural pH tests.

The results from the factorial analyses were used to build an empirical model using the significant factors (materials, exposure times, or their combinations) that influence pollutant releases. Copper and galvanized steel roof gutters and pipes should not be used when acidic water conditions are expected due to high copper (for copper materials) and high zinc (for galvanized steel materials) releases and high toxicity. For stormwater drainage systems (gutters and pipes) exposed to pH 5 and 8 conditions, concrete and plastic materials can be employed. Galvanized steel and copper materials are not advised for use in storage tanks applications due to very high metal releases and associated toxicity. For stormwater storage applications, concrete, HDPE, and vinyl materials can be used due to their little or non-detected metal losses.

Heavy Metal Treatability

Many heavy metals are associated predominantly with particulates, and therefore their treatability is influenced by the removal of the associated particulates. The association of heavy metals with particulates depends on pH, oxidation-reduction potential, and particulate organic matter. The treatability of stormwater solids and associated heavy metals is dependent on their size. The removal of dissolved contaminants may be needed to meet stringent numeric discharge permit requirements and reduce surface and groundwater contamination potentials.

The valence charge of a metal and its complexation, among other contaminant properties, influence the choice of stormwater treatment technology. Strongly charged, small molecules can be removed effectively by zeolites. Zeolites are not effective in the removal of compounds of zero valence and compounds with large size. Peat can be used as a filtration media for treatment of heavy metals and likely their complexes. Peat's effectiveness is due to the wide range of binding sites (carboxylic acid, etc.) present in the humic materials and ligands in the peat. An advantage of peat media is that it can treat many heavy metals during relatively short (as short as 10 minutes) contact times.

Tests were conducted over a three month exposure period of pipe, gutter, and storage tank materials. Generally, most of the lead was associated with the particulate fraction under pH 5 conditions and with the dissolved fraction (> 76%) under pH 8 conditions after three months of exposure. Most of the copper was associated with the dissolved fraction (>67 %) for all the pipes under pH 5 and pH 8 conditions after three months of exposure. For plastic PVC and HDPE pipes immersed in pH 5 buffered stormwater, almost all of the zinc concentrations were in dissolved forms. For metal pipes under pH 5 conditions, from 49% to more than 92% of the zinc was associated with particulates, with the exception of the aluminum gutter sample where all zinc was associated with the filterable fraction.

Prior research found that ionic fractions for zinc, copper, and cadmium in stormwater can range from 25 to 75%. These metals can be associated with very small particles, therefore the efficiency of physical filtration to remove metals will depend on size of associated particulates. Treatment technologies for metals associated with dissolved fractions include chemical methods. To remove dissolved metals from stormwater, peat moss, mixtures of peat moss and sand, zeolite, and compost can be used, especially with long contact times. These metals can form soluble complexes with different inorganic and organic ligands. The complex valences can range from -2 to +2. Organic and inorganic complexes may be treated by chemically active filtration through compost, peat, and soil. Also, granular activated carbon (GAC) can be used to remove complexes with organic matter.

Survival of Stormwater Bacteria on Impervious Surfaces

A full 2^3 factorial study (examining temperature, moisture, and UV-B exposure and their interactions) of the indicator-species' environmental survival factors was performed for enterococci and *E. coli*. Pet feces slurries (1 mL) were applied to salt-passivated paving blocks and incubated in controlled environmental chambers. The test chambers were freezerless refrigerators fitted with BOD-controllers/heaters for temperature control, dehumidifiers or humidifiers for moisture control, and UV-B enhanced fluorescents with Lexan panels to split the chambers into UV-exposed and UV-shielded regions. These represent conditions likely to be found in Tuscaloosa, AL. Active control of temperature (40 and 90 degrees F, representing cool and warm conditions) held the temperatures steady (+/- 2 degrees) over the study period. Relative humidity (25% and 80%, representing dry and wet conditions) varied over about +/- 4%. UV exposure was treated as present or absent (UV or dark conditions).

All treatments exhibited an initial lag or die-off for *E. coli*, as usually assumed. The rate of this die-off depends on the temperature and humidity, with the warm/wet conditions (those most like the enteric habitat, and exerting the least pressure for adaptation) showing the lowest initial rate of decline. All test conditions resulted in declines from two to three orders of magnitude within a day or so. The duration of the decline was from19 h to 27 h. After this decline, the *E. coli* populations exhibited a re-growth period lasting for several days, and then a second, but slower rate of decline.

Treatment analyses of the breakpoints were less complex for enterococci than for *E. coli*. The warm/wet/dark treatment for enterococci showed no evidence of a breakpoint. When the regrowth phases are recognized, none of the conditions show a net decline of more than about one order of magnitude over a two week period. It also should be noted that no enterococci test population was in decline at the end of the study period.

Laboratory experiments were also conducted that focused on initial die-off and subsequent re-growth (and later die-off) on concrete test specimens. These results also affect the fate of these organisms after their discharge. Disinfection of a wastewater containing the indicators *E. coli* and enterococci may result in significantly reduced populations initially, but are likely to undergo significant re-growth (and possibly another period of slower die-off) during subsequent periods. The re-growth may occur on surfaces or in the receiving water (although the specific rates may vary for different conditions).

One treatment (warm temperatures/humid moisture/dark conditions, similar to gut conditions of warm blooded hosts) showed no significant decreases in *E. coli* populations. Two treatments (warm/dry/UV and warm/wet/UV) showed an initial decline, a rebound of growth, and a subsequent second decline period. Cool treatments were nearly indistinguishable from each other, and resulted in more rapid declines than warm/shade treatments. All treatments exhibiting multiple declines showed slower declines later in the study period than in the initial die-off period. The initial declines occurred over a few days period, but were rarely sustained for longer periods. By the end of the study period (about two weeks) all of the *E. coli* populations were about 2 to 4 orders of magnitude lower than their original populations after a second die-off period.

Survival characteristics were less complex for enterococci than for *E. coli*. The warm/wet/dark test conditions had much lower declines in populations with time than for the other test conditions. The clear trend of greater net survival in warm treatments seen for *E. coli* is not evident for enterococci. All treatments exhibited an initial decline, with all three environmental factors (temperature, humidity, and UV exposure) contributing (either as main effects or within interactions). The rates of decline, however, are only about half of those shown by *E. coli*. By the end of the study period (about two weeks) all enterococci had rebounded to within about 10% of their original populations.

Advanced Treatment of Trace and Emerging Contaminants using Media in Stormwater Filters or Biofiltration Facilities

A number of literature references describe laboratory tests of media for the control of stormwater. However, conventional laboratory batch tests need to be interpreted carefully when selecting media and when completing the design of biofilters or bioretention facilities. Johnson, *et al.* (2003) ran stormwater batch tests at two concentrations: one typical of stormwater and one typical of low-to-medium strength industrial wastewater. The results showed the importance of testing at the anticipated runoff concentrations because, at higher concentrations, the isotherms had different shapes and were more favorable than those at typical runoff concentrations (Johnson, *et al*. 2003). Fixed-bed adsorber equations address the impact of contact time in the media. Applying batch testing results to a fixed-bed column requires assuming an instantaneous equilibrium, with all adsorption sites available to a pollutant during movement through the bed (Watts 1998; McKay 1996). However, for many media, not all active sites are available, especially the interstitial sites, when the contact time is minutes instead of many hours. Typical contact time for treating stormwater is much less than normally assumed for batch tests due to the small area and high flow rates. Necessary contact times are usually range from about 10 minutes to an hour, much longer than typically available with most high-rate stormwater media filters. Recent research has focused on diffusion limitations, assuming that adsorption is instantaneous once the pollutant reaches the active site. Clark (2000) showed the difficulty of applying fixed-bed models for the treatment of wet weather flows. These models assume a substantial concentration gradient between the pollutant and the media surface, with adsorption overwhelming desorption. Large concentration gradients often do not exist in stormwater runoff treatment (the influent concentrations of many pollutants of concern are usually much lower than the industrial applications for which these models were developed. In addition, pollutant removal, especially in natural systems, is due to many phenomena, most of which cannot currently be mathematically quantified. Therefore, long-term, intermittent flowing pilot-scale column testing of media performance using actual stormwater is needed to measure and compare the ability of alternative treatment media.

Sand without surface amendments, such as oxide coatings, is considered relatively inert compared to other media and minimal removal likely would occur for colloidally-sized pollutants. Sand, though, often is incorporated into stormwater media to provide structure and to minimize fluctuations in flow rate through the media (Clark 2000). Sand removal efficiencies typically increase as the media/filter ages because the trapping of particles typically decreases the pore openings, especially on the surface, allowing smaller particles to be captured, plus the coating of chemically active materials and biofilms on the inert sand particles occurs with time (Metcalf and Eddy 2003; Geesey, *et al.* 1998).

Clark and Pitt (2011) found that zeolites can be effective for metals in the +2 valence state. The effectiveness of ion exchange decreases as the valence charge approaches zero and as the size of the complex increases. Therefore, the overall effectiveness of zeolites, and potentially other ion-exchange media such as oxide-coated sands, is likely reduced because a substantial fraction of the metals likely exist in valence forms other than +2 due to complexation with inorganic ions and organic matter. Organic compounds and larger, less charged complexes of metals, can be chemically bonded with a media having strong sorption capacities. K_{OW} is an indication of the preference for the molecule to attach to an organic media (peat, compost, GAC) versus remaining in the stormwater runoff. K_S indicates the likelihood that the organic compound will remain dissolved in solution. The removal of some inorganic anions is difficult because most stormwater treatment media specifications stress high cation exchange capacities (CEC). High CEC media typically have low anion exchange capacities (AEC). CEC and AEC provide an estimate of the potential for exchanging a less-desirable compound with a pollutant whose chemical characteristics are more favorable. Table 1-10 lists some of the pollutants of concern in stormwater runoff and potential treatment options, based on their chemical properties and the results of laboratory, pilot-scale, and full-scale treatment tests.

Table 1-10. Selecting Treatment Technologies for Stormwater Pollutants (summarized from Clark and Pitt 2012)

Pollutant	**Treatment Process**	**Design Notes**
		Metals
Lead	Sedimentation or filtration, possibly followed with ion-exchange and chemically-active media.	Lead attaches strongly to solids. Substantial removal by sedimentation and/or physical filtration of solids to which lead is attached. Lead < 0.45 µm may be ionic and could be removed using ion-exchange with zeolites, but filtered, ionic lead is usually at very low concentrations and it would be unusual to require treatment. Lead complexes with hydroxides and chlorides to a certain extent. Removed in media with a variety of binding sites (peat, compost, soil) would be needed.
Copper, Zinc, Cadmium	Sedimentation or filtration, likely followed with chemically-active media.	These metals can attach to very small particles, with attachments being a function of the particulate organic content, pH, and oxidation-reduction conditions (filterable fractions vary from 25 to 75+%). Physical filtration may be limited depending on size association of the pollutants. These metals complex with a variety of organic and inorganic ligands to create soluble complexes of varying valence charges (-2 to +2). Typical major ions in the stormwater reduce ion-exchange effectiveness of targeted pollutants. Complexes require a variety of types of sorption/exchange sites. Organic complexes may be removed by GAC, Peat, compost and soil will remove most inorganic and organic complexes.
		Organics and Pesticides
PAHs/Oil and Grease (O&G)/Dioxin	Sedimentation or filtration, possibly followed with chemically-active media.	These compounds have high K_{OW} and low K_S and are strongly associated with particulates. Sedimentation's effectiveness is function of particle size association. Preferential sorption to organic media, such as peat, compost, soil. Some O&G components can be microbially degraded in filter media. Reductions to very low levels with filtration may be difficult if parent material is contaminated. If low permit limits, may have to use clean material such as GAC.
Organic Acids and Bases	Chemically-active filtration	Tend to be more soluble in water than PAHs and more likely to be transported easily in treatment media. Need media with multiple types of sorption sites, such as peat, compost and soil. GAC possible if nonpolar part of molecule interacts well with GAC or if GAC has stronger surface active reactions than just van der Waals strength forces.

Pollutant	**Treatment Process**	**Design Notes**
Pesticides	Chemically-active filtration	Tend to be soluble in water and need multiple reaction sites to be removed. Breakdown time in biologically-active filtration media is compound-dependent. Breakdown has the potential to restore surface-active sites, and may result in more soluble daughter products, which may or may not be more toxic. Organic media such as peat, compost, soil, GAC likely to be most effective since size of pesticide compounds will exclude substantial removal in ion-exchange resins such as zeolites.
		Microorganisms
Bacteria	Physical filtration and organic media (chemically-active) filtration	Most bacteria are in the lower limits of the size range for effective physical filtration using a sand medium. Removal not 100% effective, but can be important as the bacteria can be highly associated with larger particulates. However, as the filter ages, removals will tend to increase, partly due to reduction in the effective pore sizes and due to the exopolymers that many bacteria excrete. These exopolymers will provide surface reactive sites, even on a relatively-inert sand media. Exopolymers and surface active sites on cell membranes also enhance the attachment of bacteria to surface sites on filtration media. Because of negative surface charge, bacteria can be removed by media with high AEC, with potential for predation, but also regrowth. Organic media provide a location for captured bacteria to reside and grow. Challenge is encouraging capture and potential growth to create reactive sites, but without excessive growth that sloughs off the media and is washed out with successive storms.

Section 2. Site Descriptions and Sampling Methods

Introduction

The literature information contains some information pertaining to EC treatability at treatment facilities during dry weather, but little information is available describing treatment during wet weather at wastewater treatment facilities or for separate stormwater treatment. Field measurements were made at the wastewater treatment plant in the city of Tuscaloosa, AL, as described below, to obtain information on treatability of ECs during both wet and dry weather. Sheetflow samples during rains were collected at various locations near the campus of the University of Alabama to identify the types and magnitudes of ECs present in separate stormwater. The bacteria survival tests and the heavy metal leaching tests were conducted in UA environmental engineering laboratories, while the media treatment tests were conducted in environmental engineering laboratories at Penn State – Harrisburg, in Middletown, PA.

Tuscaloosa Wastewater Treatment Plant

The purpose of this project task was to determine treatability of emerging contaminants at wastewater treatment facilities during wet weather, to compare this performance to dry weather periods, and to quantify the discharges of the ECs associated with stormwater.

The Hilliard N. Fletcher Wastewater Treatment Plant is located in Tuscaloosa, AL, having a population of 90,500 according to the 2010 U.S. Census (US Census 2010). The total area of Tuscaloosa is 66.7 mi^2 with 10. 5 mi^2 being Lake Tuscaloosa and the Black Warrior River. The population density for Tuscaloosa is therefore about 1,610 people/mi^2, excluding the water area. Lake Tuscaloosa is the source of Tuscaloosa's drinking. The Tuscaloosa wastewater treatment system discharges its final effluent into the Black Warrior River and Crib Mills Creek.

The winter seasons are generally mild with temperatures between 20°F and 50 °F and the average monthly rainfall depths are about 5.1 inches. Spring seasons have temperatures between 50 °F and 80°F, and have similar rainfall depths. Summer temperatures range from 60°F to 90°F and can reach 100°F; average summer monthly rainfall depths are about four to five inches.

The Hilliard N. Fletcher Wastewater Treatment System is a conventional municipal wastewater treatment facility that utilizes activated sludge biological treatment. This system includes approximately 550 miles of City maintained collection sewers with another fifty miles of privately owned collection lines. Over sixty gravity and pump stations carry wastewater to the wastewater treatment plant. A $33 million expansion was designed in 1995, increasing the capacity of the treatment plant to 24 MGD. The treatment system will be expanded to 40 MGD by 2013. According to the NPDES permit, this treatment system services a population of approximately 110,000.The service area is estimated to be about 74 mi^2. It is a separate sanitary treatment system and is not designed for stormwater treatment. There are also industrial discharges entering the Tuscaloosa treatment facility.

The Hilliard N. Fletcher WWTP is located on Kauloosa Avenue and is surrounded by many industrial facilities, as shown on Figure 2-1. The treatment plant is in close proximity to Phifer Wire, Peco Foods, Metals Component Manufacturers, Wingard Custom Woodworks and Cahaba Truck and Equipment. The slope of the land near the treatment plant is generally from east to west. Cribbs Mill Creek and Friday Lake are behind the treatment plant. The Tuscaloosa treatment plant has two outfall locations: one to the Black Warrior River in the upper Black Warrior watershed, and the other discharges into Cribbs Mill Creek. The topographic map shows that the treatment plant is in a flat area with slightly higher elevations east of the facility. The area is close to a major interstate surrounding the treatment plant and adjacent are industrial sites encompassed by pervious cover consisting of grass and trees.

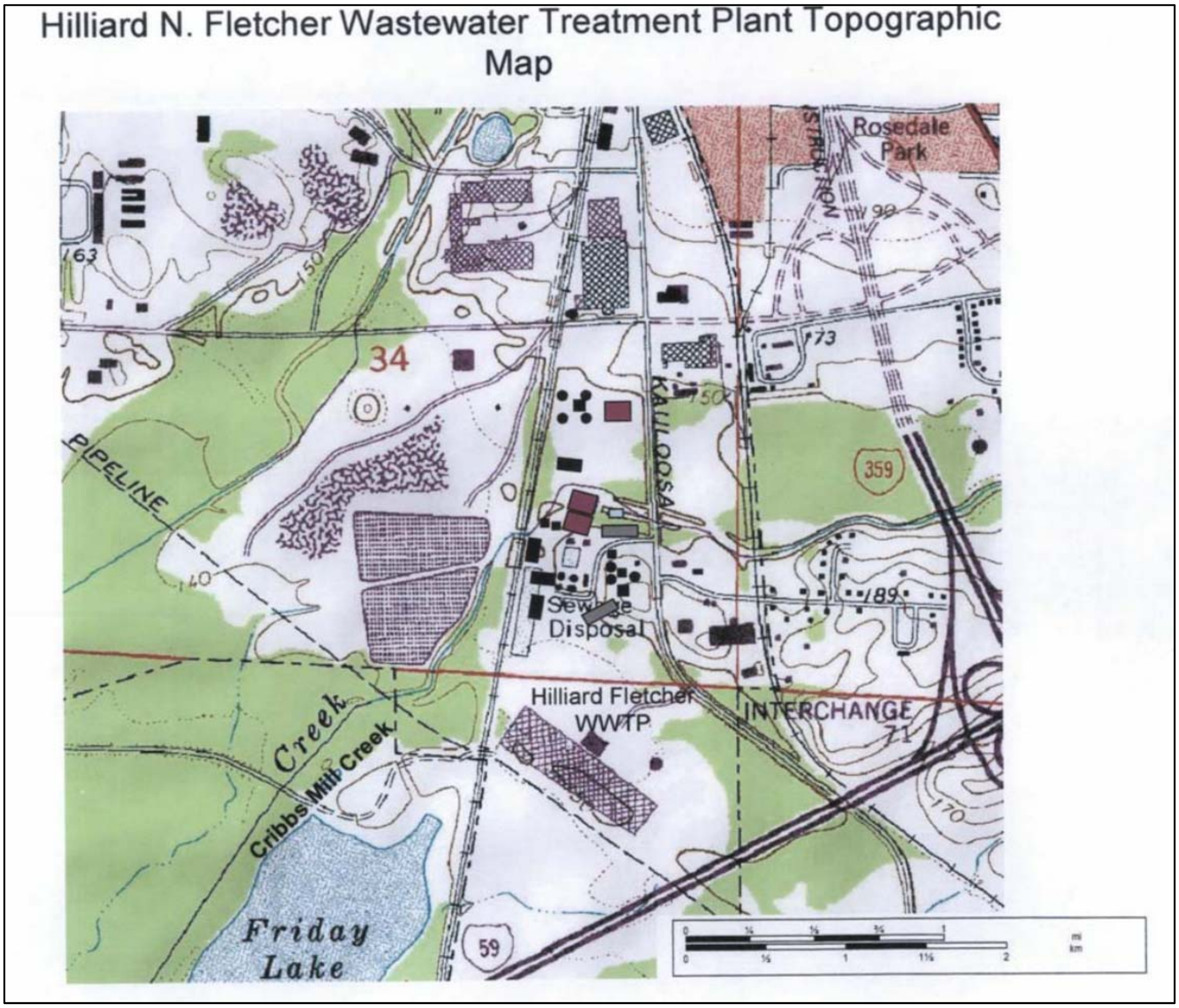
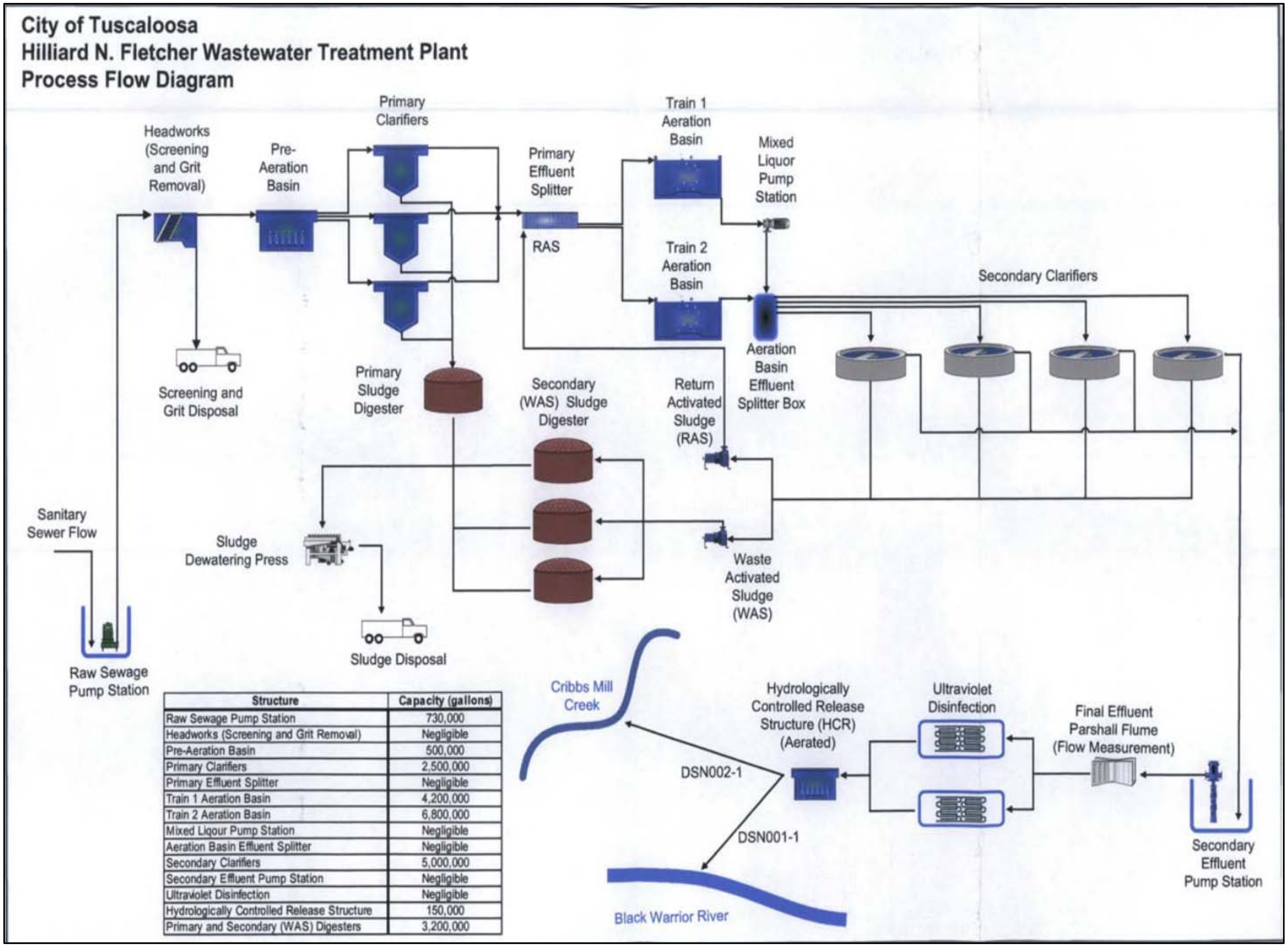

Hilliard N. Fletcher Wastewater Treatment Plant Topographic Map

Figure 2-1. Topographic map of area surrounding Tuscaloosa wastewater treatment plant.

Unit Processes at the Tuscaloosa Wastewater Treatment Plant

The Hilliard N. Fletcher Wastewater Treatment facility uses pre-treatment, primary sedimentation, biological treatment and UV disinfection, as shown on Figure 2-2. The treatment processes are duplicated in case of failure or maintenance shutdowns. Influent from the raw sewage pump stations goes through screening and grit removal, pre-aeration and enters into the primary clarifier. Effluent is split three ways for primary treatment. Primary treatment consists of sedimentation, where heavier solids sink to the bottom due to gravity and oil and grease floats to the top to be skimmed off for disposal. The primary effluent splitter then splits the effluent into two aeration basins where the mixed liquor in the basin contain the organisms used during biological treatment. After biological treatment, the effluent is divided into four secondary clarifiers by an aeration basin splitter box. The solids from the clarifiers are routed to the Waste Activated Sludge (WAS) system. Some of the activated sludge is recycled (RAS) to the primary effluent splitter box where it is reused for biological treatment. The secondary effluent is routed to a secondary effluent pump station where it enters a final effluent Parshall flume and undergoes UV disinfection. After disinfection, it is discharged to two outlets through a HCR or a Hydrologically Controlled Release Structure, which is aerated.



Structure	Capacity (gallons)
Raw Sewage Pump Station	730,000
Headworks (Screening and Grit Removal)	Negligible
Pre-Aeration Basin	500,000
Primary Clarifiers	2,500,000
Primary Effluent Splitter	Negligible
Train 1 Aeration Basin	4,200,000
Train 2 Aeration Basin	6,800,000
Mixed Liqour Pump Station	Negligible
Aeration Basin Effluent Splitter	Negligible
Secondary Clarifiers	5,000,000
Secondary Effluent Pump Station	Negligible
Ultraviolet Disinfection	Negligible
Hydrologically Controlled Release Structure	150,000
Primary and Secondary (WAS) Digesters	3,200,000

Figure 2-2. Schematic of Tuscaloosa's Hilliard N. Fletcher Wastewater Treatment Plant.

The Hilliard N. Fletcher wastewater treatment plant services a population of approximately 110,000. Table 2-1 shows that the current designed flow rate is 24 MGD, but the treatment plant averages between 15 MGD and 17 MGD. The maximum daily flow rates during 2008-2009, have periodically exceeded the design flow rate.

Table 2-1. Average and maximum flow rates from NPDES*

MGD	2008	2009	2010	2011	2012
Annual average flow rate	16.3	15.3	15.3	16.6	15.6
Maximum daily flow rate	38.1	36.5	23.0	42.2	30.3

* Flow rates from 2011 and 2012 are from treatment plant data and calculated by Goodson (2013); (Alabama Department of Environmental Management 2010)

The NPDES permit for the Hilliard N. Fletcher WWTP lists an estimated 1.5 MGD stormwater I&I that enters the treatment plant. This permit was recertified in 2010. The drainage area serviced by the wastewater treatment plant affects the potential stormwater I&I.

Industrial Influent to the Treatment Plant

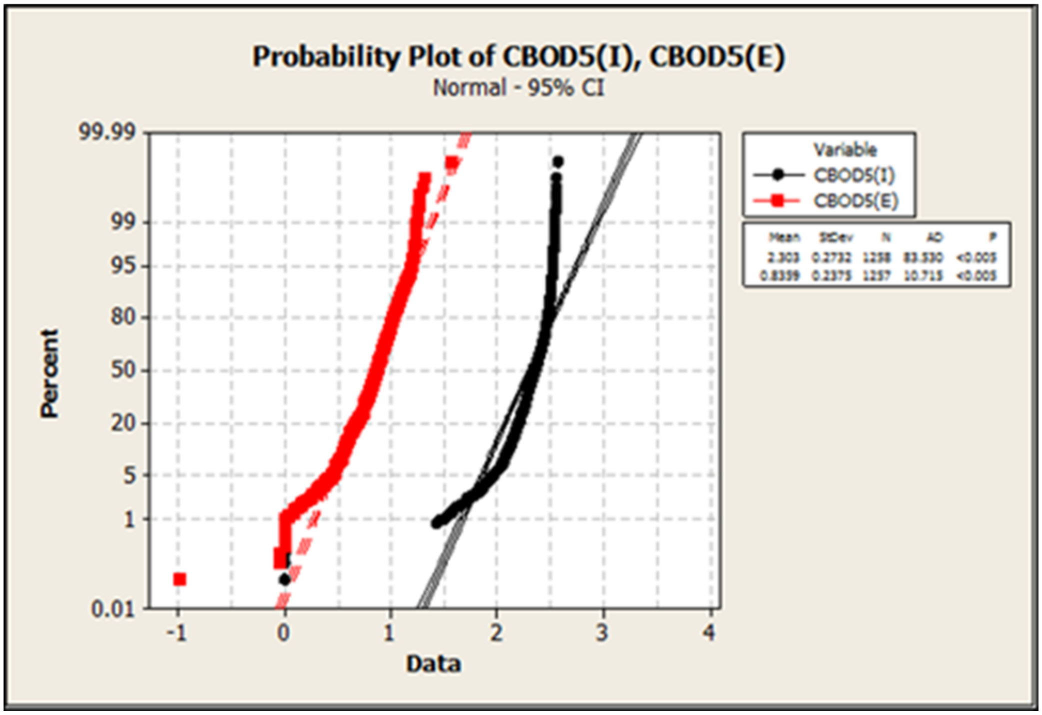
The Hilliard N. Fletcher wastewater treatment plant receives raw sewage from the surrounding municipal sanitary sewer system, along with some pre-treated industrial wastewaters (Table 2-2). These industrial facilities are described in the NPDES permit as SIUs (significant industrial users). Twenty seven percent of the permitted Tuscaloosa wastewater influent consists of these industrial wastewaters. Many of the industrial sites work with iron, steel and other metals. The metal industries contribute approximately 1.0 MGD to the municipal treatment plant. Roofing materials from manufacturers such as Tamko use a variety of materials for their products such as asphalt, slate, shake, tile and fiberglass. The largest contributors to the industrial wastewater flows that enter the Tuscaloosa treatment plant are Cintas Corp., Merichem Chemicals and Refinery Services, and Peco Foods. Each industrial effluent varies. Cinta’s major service is as a commercial laundry, which indicates their wastewater contains surfactants. Merichem recovers impurities such as sulfur byproducts, carbon dioxide and naphthenic acids. The Merichem wastewater treated by the Tuscaloosa treatment facility, according to the NPDES permit, includes contaminated stormwater from their previous operations. They possibly discharge PAHs and other hydrocarbons to the treatment facility. The Peco Food industrial wastewater contains chicken processing wastes. This wastewater contains mostly organic materials, but it may also contain chemicals such as pharmaceuticals and hormones used in chicken processing.

Table 2-2. List of Industrial Sites that Discharge to the Hilliard N Fletcher Treatment Plant

SIU	Industrial Processes	Contribution (gallons per day)
Nucor Steel	Iron and steel manufacturing	88
Mercedes Benz US Int.	Metal finishing operations from automobile manufacturing	1,860
Phifer Wire Products, Inc.	Manufacturer of miscellaneous wire products	16,770
JVC Disc America	Metal finishing operations	974,640
Cintas Corporation	Commercial laundry operations	1,040,750
Merichem Chemicals and Refinery Services, LLC	Stormwater runoff contaminated by previous operations	2,191,204
Tamko Roofing Products	Roofing products manufacturer	684,420
Peco Foods, Inc.	Poultry slaughtering and processing	1,573,270

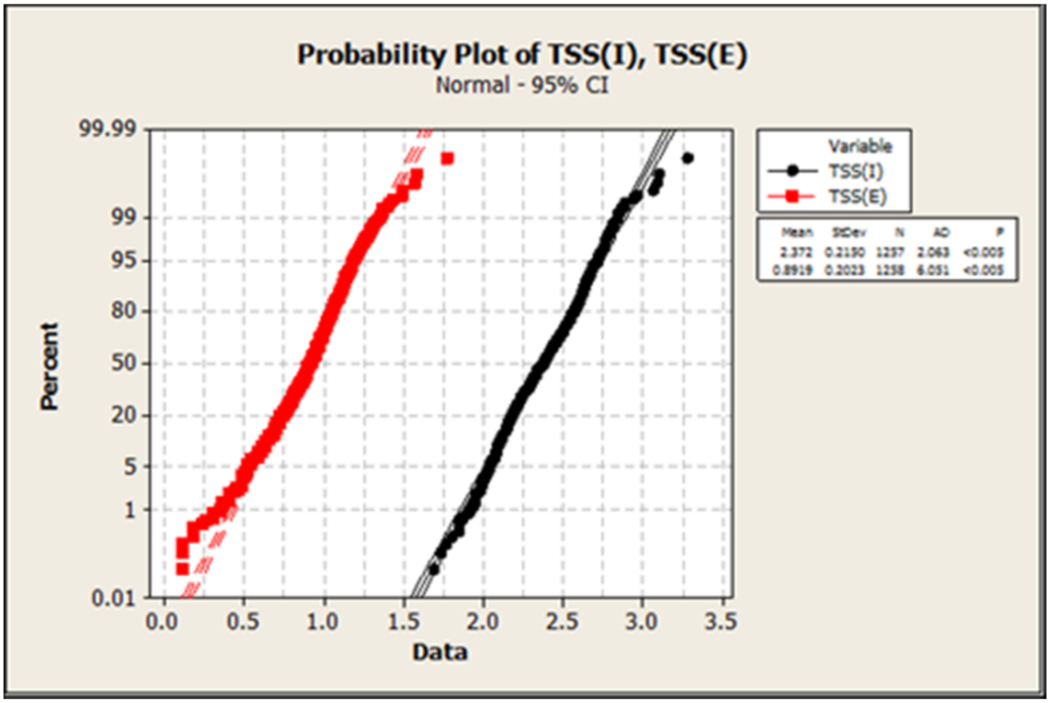
Monitored Performance at the Tuscaloosa WWTP

As previously noted, the Hilliard N. Fletcher wastewater treatment plant is a conventional activated sludge (biological) treatment system, but with UV disinfection instead of more common chlorination. The daily average flow rate for the treatment plant is 15 MGD, but has exceeded 40 MGD (the current design flow rate after expansion). Routinely monitored wastewater parameters to ensure treatment compliance at the wastewater treatment plant include $CBOD_5$, BOD_5, TSS, TKN, and fecal coliform bacteria. The historical removal rates for TSS and CBOD5 range between 80 and 99 percent. The pH levels for the influent and effluent range from 6 to 8. Figures 2-3 and 2-4 are influent and effluent probability plots for CBOD5 and TSS indicating the high level of removal from the treatment plant. These data from 2005 to 2008 were compared to reported rainfall information to identify any effects of increased flows on treatment efficiency. Figure 2-5 shows influent total suspended solids and oxygen demand compared to rainfall to identify any correlation. However, there are no apparent increases or decreases of TSS or oxygen demand during elevated rainfall.



Mean	StDev	N	AD	P
2.303	0.2732	1258	83.530	<0.005
0.8359	0.2375	1257	10.715	<0.005

Figure 2-3. Tuscaloosa Treatment plant CBOD influent and effluent data from 2005-2008.



Mean	StDev	N	AD	P
2.372	0.2150	1257	2.063	<0.005
0.8919	0.2023	1258	6.051	<0.005

Figure 2-4. Tuscaloosa Treatment plant TSS influent and effluent data from 2005-2008.

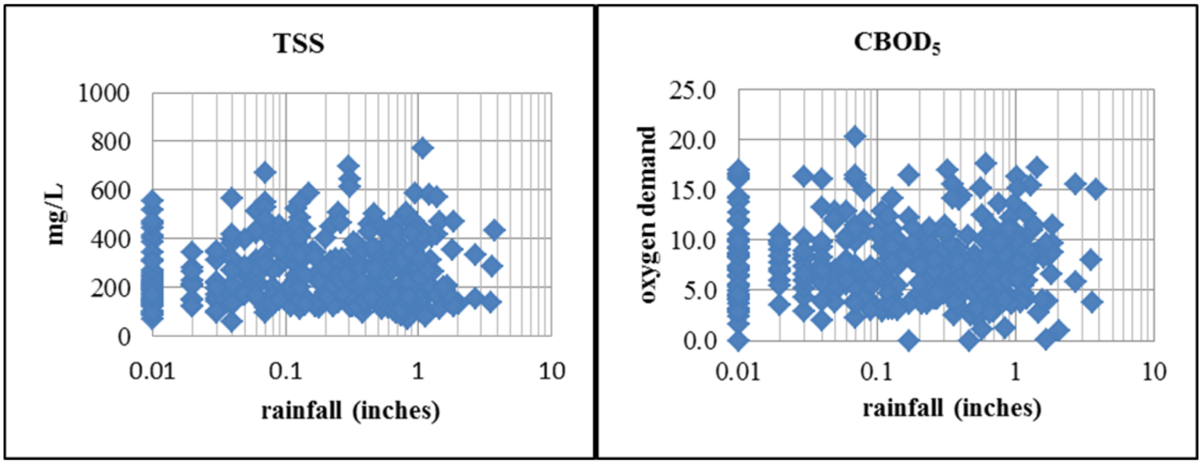


Figure 2-5. Scatterplots of TSS and CBOD concentrations vs. daily rain depths.

Figure 2-6 is a plot of daily average flow rates vs. total daily rainfall for 2005 through 2008. Due to the large scatter of flow values and the relative scarcity of large rains, a large trend is not apparent, but there does appear to be an upward trend of flow rates with increasing rainfall as the daily rainfall increases above about 1 inch (also associated with increased flow scatter).

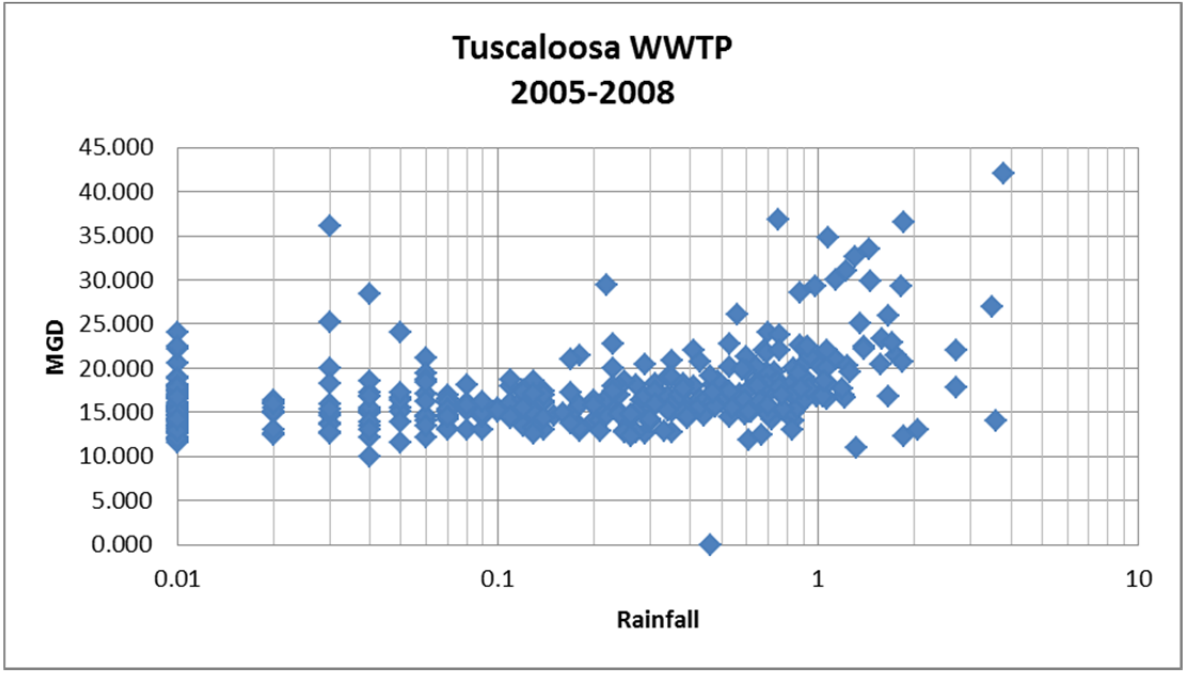


Figure 2-6. Comparison of rainfall and flow rates.

Figure 2-7 shows the rainfall and runoff data for 2010 through 2012. A Kurskal-Wallis one way ANOVA on ranks test indicated statistically significant differences between flow rates during periods with rainfall depths <1 inch, between 1 inch and 2 inches, and > 2.0.

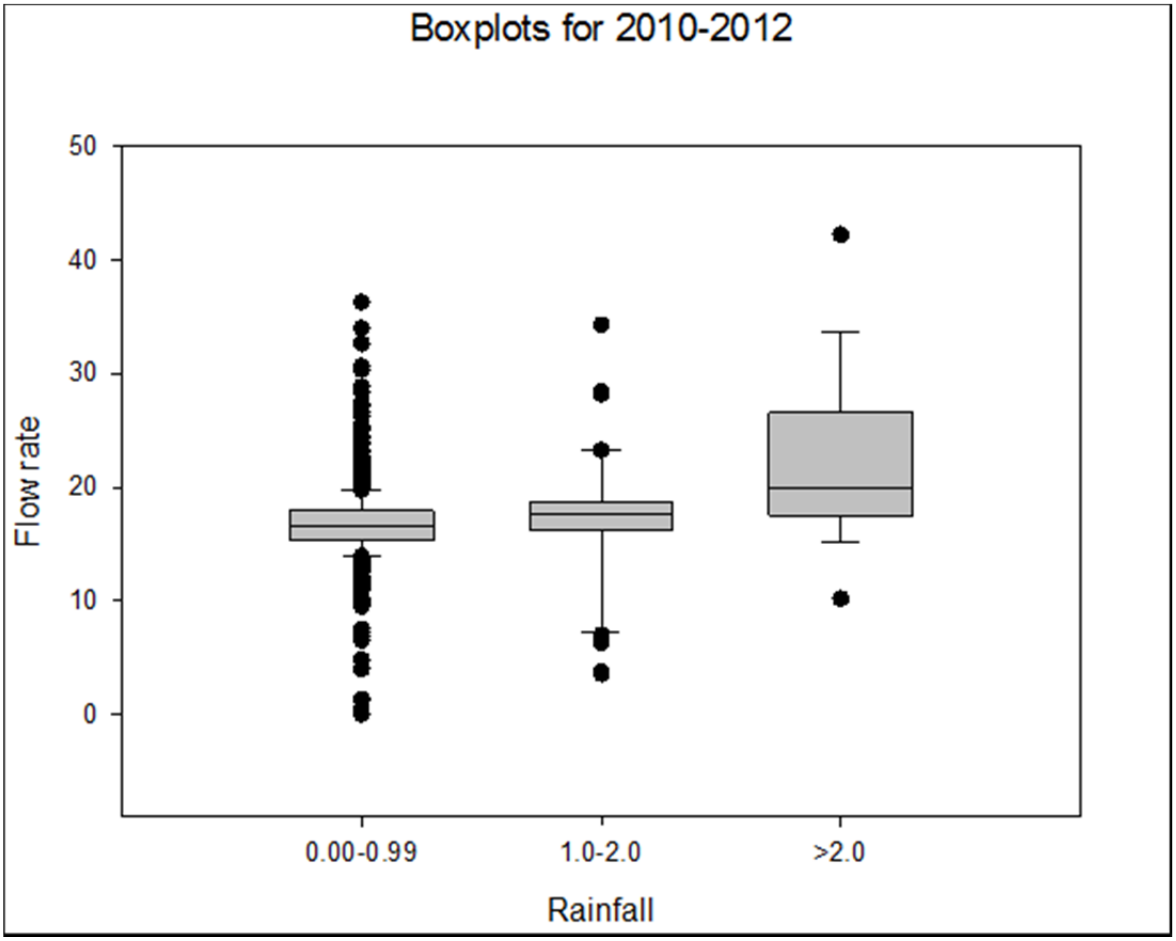


Figure 2-7: Boxplots showing rainfall vs. flows for 2010-2012.

Figure 2-8 is a box and whisker plot comparing the dry vs. wet weather rains for four rain categories during the days of sample collection for this research. Table 2-3 shows that most of the flow rates were obtained when the rainfall was less than 0.1 inches. The box plot shows there is an increase in the flow rates as the rainfall increases above 0.5 inches. However, a Kruskal Wallis 1-way ANOVA on ranks analysis resulted in a p value of 0.13, indicating that there is not enough data to indicate a statistically significant difference in the flow rates in the four different rain categories on the days of sampling.

Table 2-3. Flow rates by rainfall categories during days of sampling

Rainfall Ranges	Sample days for Tuscaloosa Treatment plants
< 0.1	9
0.1-0.55	3
0.56-1.0	3
>0.1	2

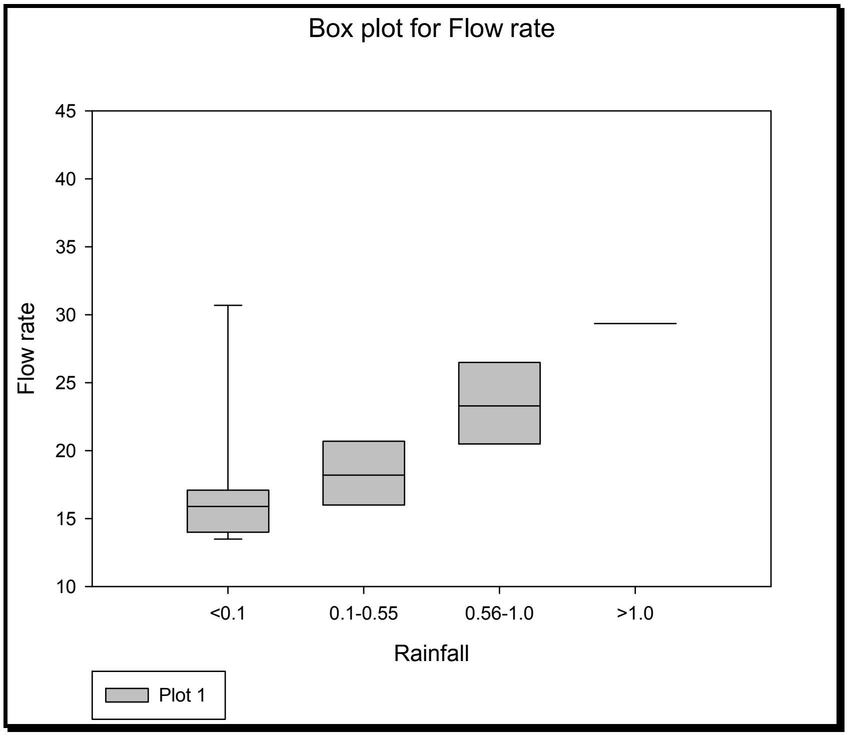


Figure 2-8. Box and Whisker plot for sampling events.

Studies have shown operational factors, such as the solids retention rate and the hydraulic retention rate, affect treatment plant performance. Both of these performance indicators are affected by the treatment flow rate. As an example, Clara, et al. (2005) shows longer solid retention times (SRT) is an important parameter increasing the growth of microorganisms which may increase treatment of certain micropollutants.

For each sample date during this study, the hydraulic retention time (RT) was calculated from the volume of the primary clarifiers (V) and the flow rates (Q):

$$RT=V/Q$$

The hydraulic retention time for each clarifier is therefore dependent on the flow rates. If there is a high flow rate, the holding times of the wastewater in each clarifier are decreased which may lead to decreased treatment.

As shown in Figure 2-9, the primary clarifier retention times for the sample dates vary from about 0.4 hours to 1.2 hours. Primary sedimentation involves the settling of settleable solids to the bottom of the clarifier and the oil and grease is skimmed off the top surface. The higher the flow rate, the less time the effluent remains in the clarifier. The longer the retention time, the more solids in the clarifier would settle by gravity in the bottom of the clarifier. Therefore, flow rate and clarifier volume affects sedimentation of particulate pollutants.

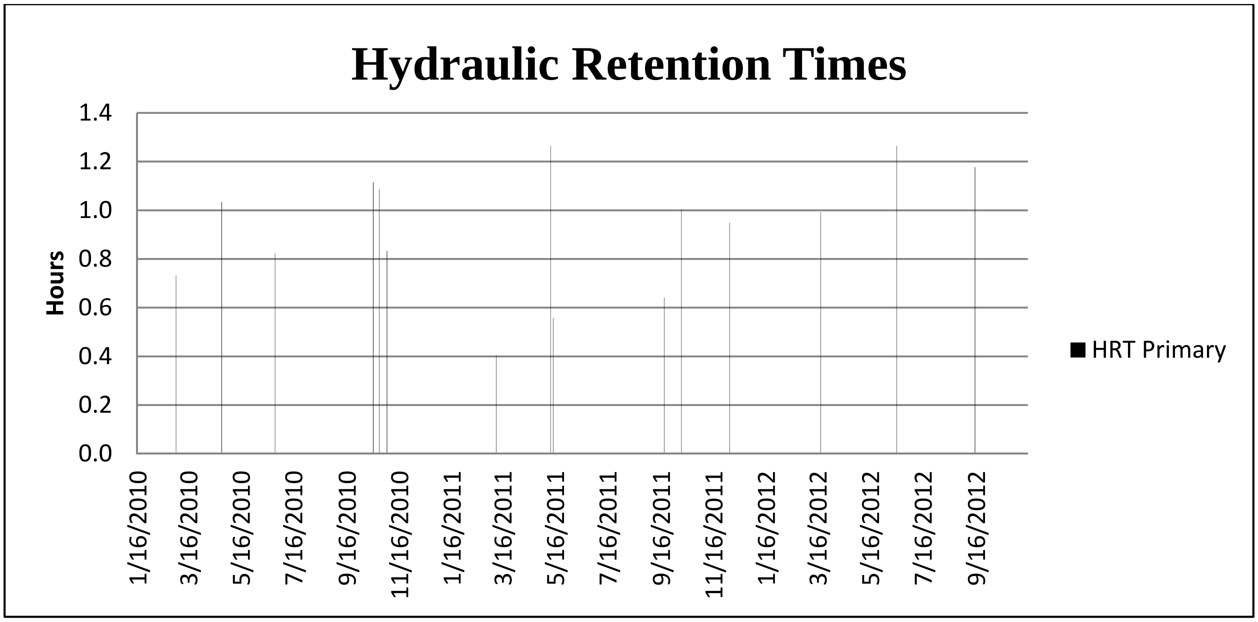


Figure 2-9. Primary clarifier hydraulic resident time (HRT) during days of sampling for the Hilliard N. Fletcher WWTP.

The sewage is treated biologically by activated sludge in the aeration basins. As shown in Figure 2-10, the aeration basins biologically treat the wastewater for approximately one to three hours on the days of sampling.

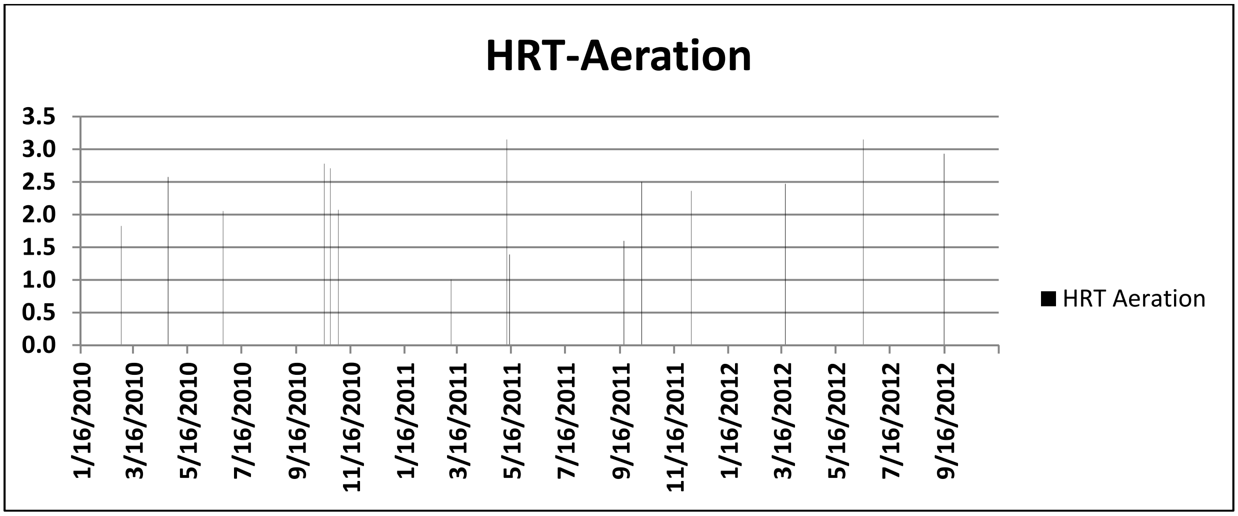


Figure 2-10. Graph of HRT for aeration basin during days of sampling for the Hilliard N. Fletcher WWTP.

The secondary clarifier receives the secondary effluent after biological treatment in the aerators. These clarifiers also operate by gravity and removes remaining sediment and debris from the biological treatment units. Figure 2-11 plots the HRT for the secondary clarifiers. The HRT for these units are seen to vary from about 0.6 to 1.9 hours on the sampling days.

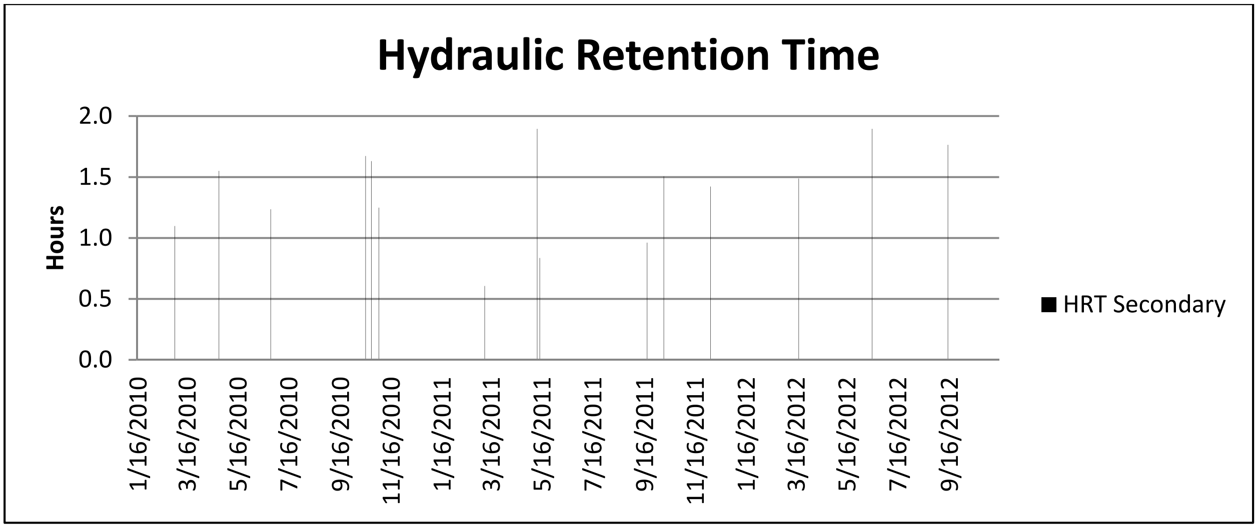


Figure 2-11. Graph of HRT for secondary clarifiers during days of sampling for the Hilliard N. Fletcher WWTP.

The hydraulic retention times determine how long chemical compounds have to react in the clarifiers and the aeration basin. The hydraulic retention times for the primary and secondary clarifying basins were two hours or less.

Sheetflow Sampling Locations

Stormwater runoff sheetflow samples were also collected at three main areas in the Tuscaloosa, AL, area for analyses. These were located in three general areas, corresponding to a park/institutional area, a commercial area, and a residential area. These are shown on the following maps and aerial photographs.

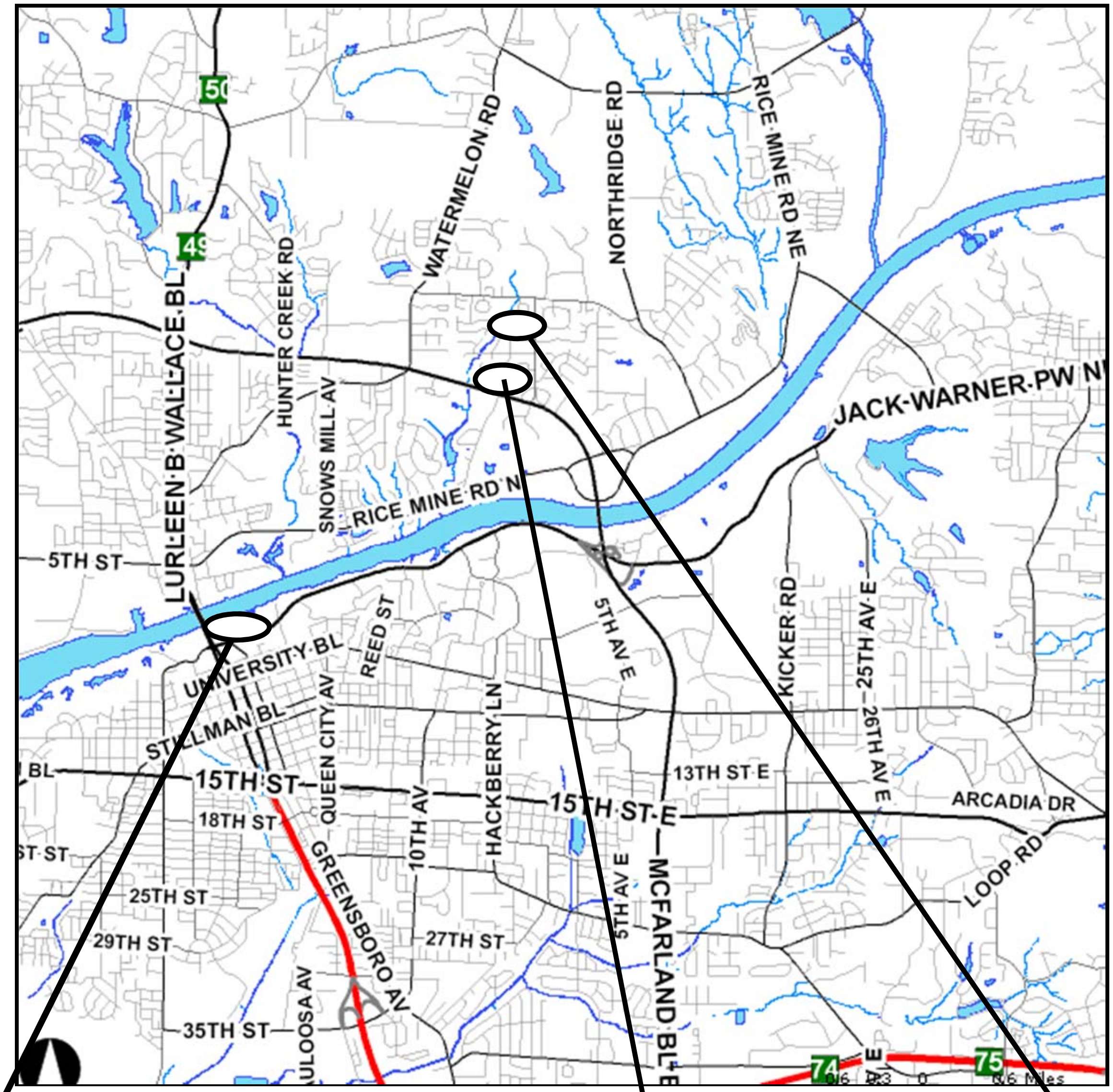
Tuscaloosa, AL, Sheetflow Sampling Locations

Samples were collected from clustered locations at three areas, as shown on Figure 2-12:

- The Bama Belle site is an institutional land use are, and consists of open space (partial tree cover, little constructed development), plus a large paved parking area and an entrance road, plus a small building. The site is part of a park/trail system adjacent to the Black Warrior River.

- The Galleria site is a commercial area and is sparse of tree cover. The buildings are single story and are surrounded by large paved parking areas with small amounts of peripheral landscaping.

- The Academy Drive area is a suburban residential development of split-level and two-story homes with considerable tree cover.



Institutional (Bama Belle) Site

Commercial (Galleria) Site

Residential (Academy Drive) Site

Figure 2-12. Map of Tuscaloosa, AL, showing sheetflow sampling areas.

Bama Belle (institutional open space) Site

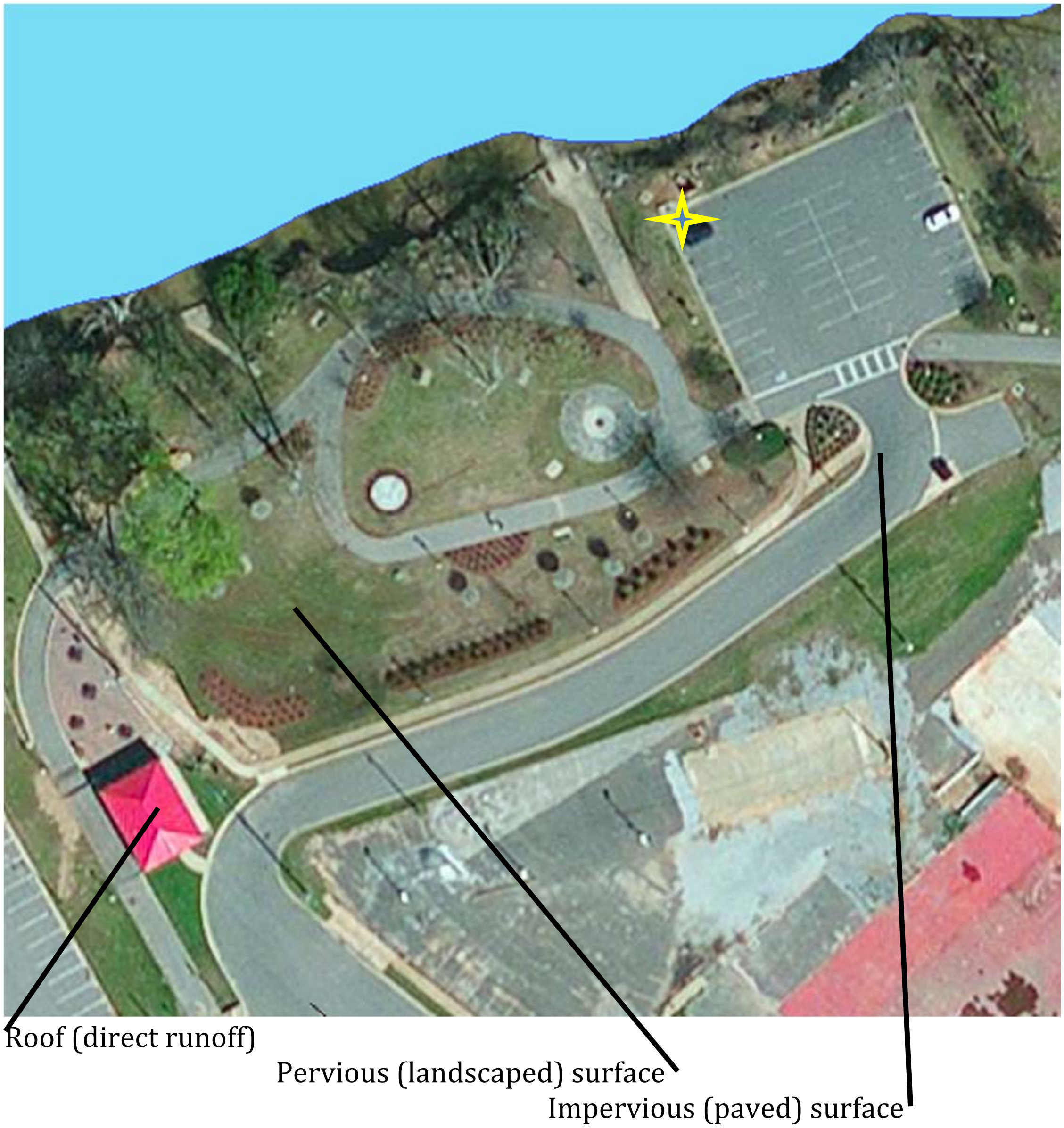
The BamaBelle site is the parking area for the linear park along the Black Warrior River, as shown in Figures 2-13 and 2-14. For the past several years, the parking area has been a test location for evaluation performance monitoring of the Up-flo filter^{tm}. The sheetflow sampling locations at this area include:

- The outfall samples represent a mixture of multiple source areas are the influent location for the Up-Flo filter.

- The road samples only include pavement runoff as the crown of the road was not topped during sampled rain events.

- A landscaped area sample was also obtained from grassed park areas.

- The roof sample was obtained from a small building that serves as a restroom for the adjacent park and as a police substation.



Yellow Star - Outfall (not a source area) was also sampled (upgradient of a test filtering device)

Figure 2-13. BamaBelle sheetflow sampling locations.

 Open space (park) landscaped (turf) sampling location (samples collected upgradient from walkway)	 Open space (park) roof sampling location (samples collected from direct runoff from overflowing gutters as downspouts were clogged)
 Open space (park) paved road sampling location	

Figure 2-14. Sampling locations at BamaBelle site.

Galleria (commercial, strip mall) Site

The Galleria shopping center is a small mall comprised of moderately large buildings surrounded by large paved areas, as shown on Figures 2-15 and 2-16. The sheetflow sampling locations are:

- paved parking area with moderate amounts of parked cars
- pervious landscaped areas adjacent to a building and parking area
- roof runoff from downspout from flat roof.

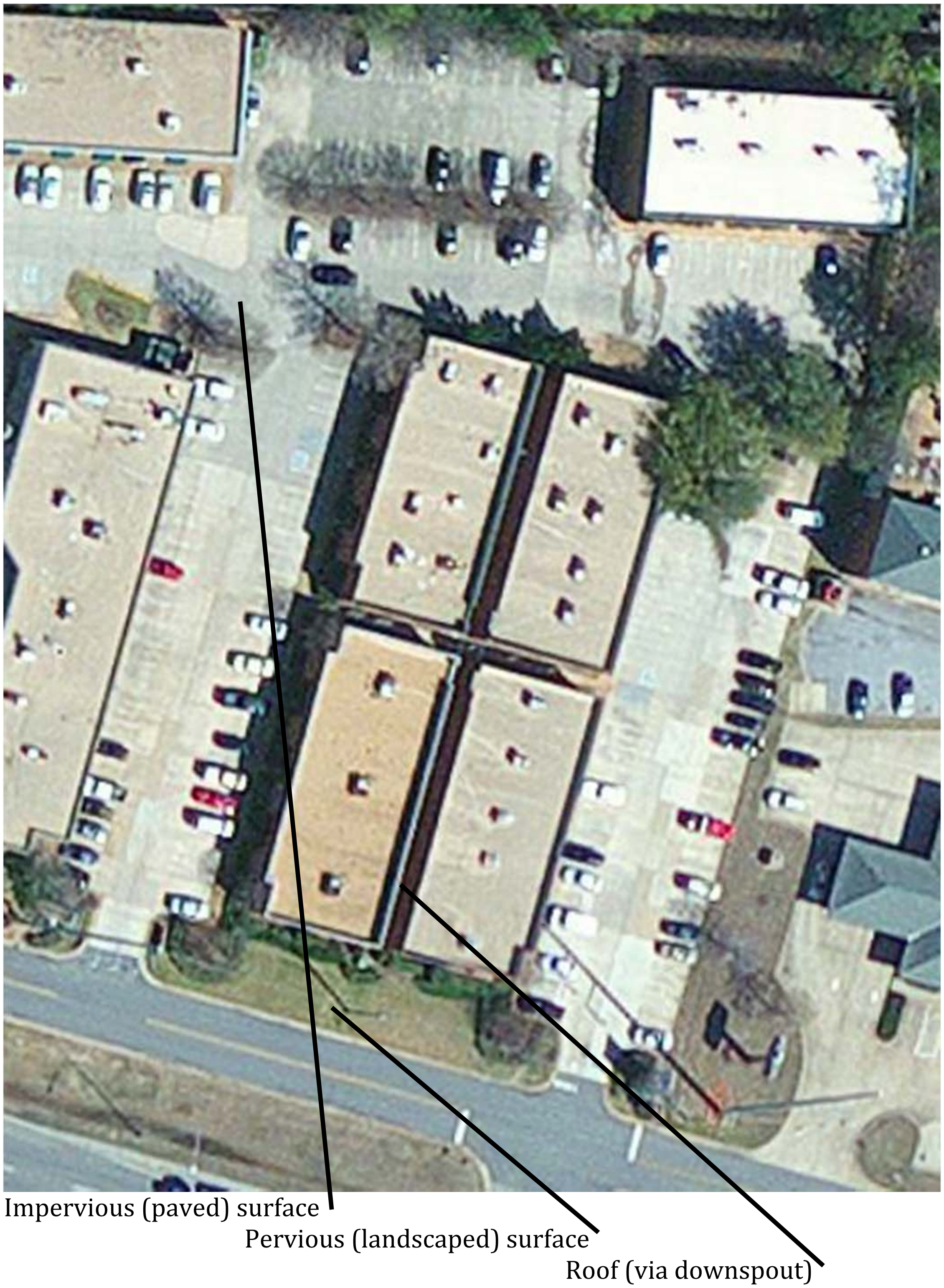


Figure 2-15. Galleria Shopping Center sheetflow sampling locations.

Commercial landscaped (turf) area sampling location

Commercial paved road runoff sampling location

Commercial roof runoff sampling location (from downspout)

Figure 2-16. Sampling locations at the Gallerie site.

Academy Drive (residential) Site

The Academy Drive location is a traditional medium density residential area, as shown in Figures 2-17 and 2-18. The sheetflow sampling locations are:

- the pervious landscaped area is a typical grass in the side yard of a home.

- the roof sample is from the front roof drain of a home.

- the paved area sample is from a road surface that does not receive runoff from other areas.

Figure 2-17. Academy Drive residential area sheetflow monitoring locations.

Residential landscaped (turf) area sampling location

Residential roof sampling location

Residential paved street sampling location

Figure 2-18. Sampling locations at the Academy Rd. site.

Sheetflow Sampling and Laboratory Processing Methods

Sheetflows were sampled using a household dustpan as a scoop. Dustpans were sterilized between uses (washed, isopropanol-wiped, allowed to air-dry covered at least overnight), and a separate dustpan was used for each sampling location. After twice thoroughly rinsing the dustpan with sheetflow runoff (to remove any potential dust or isopropanol remnant), biological samples (for *E. coli* and Enterococci analyses) were transferred to pre-sterilized 120-ml bottles. For other analyses, runoff was composited into pre-cleaned (scrubbed, tap-water rinsed, inverted and air dried) 5-gallon pickle jars of food-grade glass (Figure 2-19). The volume of the collected composite was rain-depth dependent – at least 2 gallons were required for later processing (minimum depth in the churn splitter to extract five 1-liter splits), but (rain-depth permitting) compositing was continued to 4 gallons (maximum allowed for complete transfer without overflowing the churn splitter, Figure 2-20).

Figure 2-19. Field equipment used in sheetflow sample collection.

Biological samples were processed immediately on return to the laB- Pickle-jar composites were kept refrigerated until further processing (typically the next day). Composites were divided, first by churn splitter, into five 1-liter subsamples; four subsamples were transferred to new, 1-liter amber-glass bottles for analysis elsewhere, and one subsample was transferred to a new, 1-liter Nalgene bottle for in-house processing.

Figure 2-20. Churn splitter for initial sample splitting into large portions.

The in-house subsample was further split using the cone-splitter (Figure 2-21), for analysis of particle/solids analysis, toxicity testing, and for metals analysis by others. Both sample splitters were thoroughly cleaned using tap water between uses.

Figure 2-21. Cone splitter for further sample splitting.

Site Description and Sampling Summary

Field measurements were made at the Tuscaloosa, AL, wastewater treatment plant to obtain information on influent quality and quantity and treatability of ECs during both wet and dry weather. Sheetflow samples during rains were also collected at various locations to identify the types and magnitudes of ECs present in separate stormwater. The bacteria survival tests and the heavy metal leaching tests were conducted in UA environmental engineering laboratories, while the media treatment tests were conducted in environmental engineering laboratories at Penn State – Harrisburg, in Middletown, PA.

The Hilliard N. Fletcher Wastewater Treatment Plant is located in Tuscaloosa, AL, having a population of 90,500 according to the 2010 U.S. Census (US Census 2010). The population density for Tuscaloosa is about 1,610 people/mi^2, excluding the water area. The Hilliard N. Fletcher Wastewater Treatment System is a conventional municipal wastewater treatment facility that utilizes activated sludge biological treatment. This system includes approximately 550 miles of City maintained collection sewers with another fifty miles of privately owned collection lines. Over sixty gravity and pump stations carry wastewater to the wastewater treatment plant. A $33 million expansion was designed in 1995, increasing the capacity of the treatment plant to 24 MGD. The treatment system will be expanded to 40 MGD by 2013. According to the NPDES permit, this treatment system services a population of approximately 110,000.The service area is estimated to be about 74 mi^2. It is a separate sanitary treatment system and is not designed for stormwater treatment. There are also industrial discharges entering the Tuscaloosa treatment facility. A Kurskal-Wallis one way ANOVA on ranks test indicated statistically significant differences between flow rates during periods with rainfall depths <1 inch, between 1 inch and 2 inches, and > 2.0, indicating important stormwater contributions to the treatment plant influent during large rains.

Stormwater runoff sheetflow samples were also collected at three locations at three main areas in the Tuscaloosa, AL, area for analyses. These were located in three general areas, corresponding to a park/institutional area, a commercial area, and a residential area. These samples were analyzed for PPCP, PAHs, trace heavy metals, and bacteria.

Section 3. Methodology and Experimental Design

Laboratory Analyses for the Detection of Emerging Contaminants

Much of the project effort was associated with method development for the analyses of the ECs in wet weather flows. The raw sewage and partially treated sewage matrices were especially troublesome concerning sample extractions, along with suitable detection limits for the analytical equipment available. The following discussion summarizes the methods used during this project, along with literature reviews of methods.

Emerging contaminants, unlike major pollutants, occur in extremely low levels and need special methods for their detection. The methods used for the detection of emerging contaminants are commonly not available in many laboratories. Some of the most commonly used analytical methods for their detection are High Performance Liquid Chromatography with Mass Spectrophotometer Detector (HPLC-MS), research grade Gas Chromatography with Mass Spectrophotometer Detector (GC-MS), and High Performance Liquid Chromatography with Electro Spray and Dual Mass Spectrophotometer Detectors (HPLC-ESI-MS-MS). This research utilized a more basic HPLC/UV with specialized extraction and concentration methods to enhance the detection limits. The following briefly describes these analytical methods, along with sample preparation methods.

Sample Extraction and Concentration

Solid Phase Extraction

Solid Phase Extraction (SPE) is an extraction and concentration process to remove and concentrate the analytes from the water matrix. It involves different steps which include dilution, buffer addition, pH adjustment and elution. SPE is considered to be the most effective extraction technique in comparison with the traditional techniques for dissolved pollutants compared to liquid- liquid extraction, soxhlet, automated soxhlet, and steam distillation; due to its accuracy, reproducibility, reliability (confirmation) of results, and capacity for multi-analyte determination. However it is not suitable when analytes to be extracted from particulates in the samples. Some of the most commonly used SPE cartridges include Oasis HLB, Oasis MCX, Strata-X, Lichrolut EN, and RP-C_{18}. At least one study has reported that Oasis HLB cartridges are efficient and resulted in high recoveries of the analytes investigated in the study (Zhang, et al. 2007). Most of the acidic compounds are recovered better at $pH < 3$, and the neutral and basic compounds are better recovered at pH values between 7 and 10. These pH ranges result in better adsorption of analytes onto the SPE cartridges (Miao, et al. 2002, Vieno, et al. 2006, Ternes, et al. 2001, Togola, et al. 2007, and Gibson, et al. 2007).

Analytical Methods for Detection of PPCPs

HPLC-ESI-MS-MS (High Performance Liquid Chromatography with Electro Spray and Dual Mass Spectrophotometer Detectors)

HPLC-ESI-MS-MS is an effective tool for the detection of most of the emerging contaminants because of their polar nature, low volatility and thermal instability. Electrospray Ionization is often used to convert the analyte into a sole ion which can be detected by a Mass Spectrometer. Tandem Mass Spectrometry involves multiple steps of mass selection for the detection of analyte ions. MS/MS involves the quantification of the ions in SIM (selective ion monitoring) and MRM (multiple reaction monitoring) modes which is helpful in increasing the specificity of detection. Some of the most commonly used HPLC equipment includes: Waters 2690 HPLC equipped with a Genesis C_{18} column, LC (Agilent 1100 system, which consists of a binary pump, a vacuum degasser, an autosampler, and a thermostated column), with a Waters 2695 HPLC separation module equipped with a Waters Symmetry C_{18} column.

HPLC-ESI-MS-MS is effective in analyzing most of the pharmaceutical compounds with retention times ranging between 2 and 35 min (Castiglioni, et al. 2005, Miao, et al. 2002, Vanderford, et al. 2003, Vieno, et al .2006, Zhang, et al. 2007). A few of the compounds may be poorly analyzed because of the signal suppression during the ESI step, requiring more efficient sample preparation steps (such as addition of surrogate standards) in order to achieve better recoveries of the analytes.

GC-MS (Gas Chromatography with Mass Spectrophotometer Detector)

Gas Chromatography, although less selective when compared to HPLC, is less complex and more cost effective. It is more often used for the analysis of compounds that are volatile in nature, and thermally stable. Gas Chromatography often involves the conversion of analytes into derivatives which helps in altering the molecule to have less polarity and high volatility. The most common derivatizing steps include using, trimethylsilyl (TMS), N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA), N-(t-butyldimethylsilyl)-N-methyltrifluoroacetamide (MTBSTFA) and pentafluorobenzyl bromide (PFBBr). The respective derivatives are then analyzed by GC-MS (Gibson, et al. 2007, Lee, et al. 2003, Reddersen, et al. 2003, Thomas, et al. 2004, Togola, et al. 2007), and showed appreciable recoveries for most of the compounds studied, although some poor recoveries for some of the compounds were observed due to ineffective sample preparation and storage steps.

Recoveries and detection limits for some of the pharmaceuticals using the above listed analytical methods are summarized in Table 3-1.

Table 3-1 Analytical Methods and Extraction Recoveries of pharmaceuticals and personal care products

Analyte	Extraction Method	Recovery (%)	Analytical Method	LOD (ng/L)	LOQ (ng/L)	Reference
Ibuprofen	SPE	92±3.7[a]	HPLC-MS-MS		1.38[a]	Castiglioni, et al. 2005
	SPE	71[a]	HPLC-MS-MS	5		Miao, et al. 2002
	SPE	96±15	HPLC-MS-MS	1		Vanderford, et al. 2003
	SPE	93±7[c],96±5[d],46±2[a],68±9[b]	HPLC-MS-MS		1[c,d],5[a,b]	Lindqvist, et al. 2005
	SPE-Derivatization	67[f],110[d]	GC-MS	3.5		Sacher, et al. 2001
	SPE-Derivatization	97±3[g],92±6[a]	GC-MS	10		Lee, et al. 2003
	SPE-Derivatization	87±4[g]	GC-MS	10		Lee, et al. 2005
	SPE-Derivatization	108±5[g]	GC-MS	10		Thomas, et al. 2004
	SPE-Derivatization	67±18	GC-MS	36 (full scan mode), 0.6 (SIM)	104(full scan mode), 1.6 (SIM)	Koutsouba, et al. 2003
	SPE-Derivatization	86.4±11[g]	GC-MS		30	Moldovan, et al. 2006
Naproxen	SPE	68.4[a]	HPLC-MS-MS		10	Castiglioni, et al. 2005
	SPE	91±9	HPLC-MS-MS	1		Vanderford, et al. 2003
	SPE	87±6[c],89±4[d],81±6[a],86±6[b]	HPLC-MS-MS		5[c,d],25[a,b]	Lindqvist, et al. 2005
	SPE	50±16[a],50±10[b],25[e]	HPLC-MS-MS	15[e]		Pedrouzo, et al. 2007
	SPE-Derivatization	68[f],105[d]	GC-MS	3.8		Sacher, et al. 2001
	SPE-Derivatization	101±4[g],93±5[a]	GC-MS	10		Lee, et al. 2003
	SPE-Derivatization	101±3[g]	GC-MS	10		Lee, et al. 2005
	SPE-Derivatization	101±4[g]	GC-MS	9		Thomas, et al. 2004
Clofibric acid	SPE	81±1.8[a]	HPLC-MS-MS		0.36[a]	Castiglioni, et al. 2005
	SPE	82.2	HPLC-MS-MS	10		Miao, et al. 2002
	SPE	54±20[a],33±20[b],61[e]	HPLC-MS-MS	5[e]		Pedrouzo, et al. 2007
	SPE-Derivatization	77[f],103[d]	GC-MS	5.3		Sacher, et al. 2001

Continuation of Table 3-1

Analyte	Extraction Method	Recovery (%)	Analytical Method	LOD (ng/L)	LOQ (ng/L)	Reference
	SPE-Derivatization	99±2[g],95±5[a]	GC-MS	10		Lee etal 2003
	SPE-Derivatization	98±3[g]	GC-MS	10		Lee etal 2005
	SPE-Derivatization	90±15	GC-MS	244 (full scan mode),1.8 (SIM)	714(full scan mode), 5 (SIM)	Koutsouba etal 2003
Diazepam	SPE	96±5.1[a]	HPLC-MS-MS		1.08	Castiglioni etal 2005
	SPE	80±19	HPLC-MS-MS	1		Vanderford etal 2003
	SPE-Derivatization	77[f],93[d]	GC-MS	6.9		Sacher etal 2001
	SPE-Derivatization	78.9±5.4[g]	GC-MS		30	Moldovan etal 2006
Carbamazepine	SPE	98±7.2	HPLC-MS-MS		1.3	Castiglioni etal 2005
	SPE	91±12[a]	HPLC-MS-MS	1		Vanderford etal 2003
	SPE	67±10[a],34±26[b],101[e]	HPLC-MS-MS	3[e]		Pedrouzo etal 2007
	SPE-Derivatization	80[f],74[d]	GC-MS	9.6		Sacher etal 2001
	SPE-Derivatization	103±5[f],99±7[c],108±10[e],79±2[a]	GC-MS		8	Lin etal 2005
	SPE-Derivatization	109.7±16.4	GC-MS		30	Moldovan etal 2006
Bezafibrate	SPE	76±2.6[a]	HPLC-MS-MS		0.1[a]	Castiglioni etal 2005
	SPE	67.1[a]	HPLC-MS-MS	10		Miao etal 2002
	SPE	73±4[c],64±2[d],58±1[a],64±2[b]	HPLC-MS-MS		1[c,d],5[a,b]	Lindqvist etal 2005
	SPE	59±20[a],5±38[b],82[e]	HPLC-MS-MS	5[e]		Pedrouzo etal 2007
	SPE-Derivatization	93[f],151[d]	GC-MS	7.5		Sacher etal 2001
Diclofenac	SPE	62.8[a]	HPLC-MS-MS	10		Miao etal 2002
	SPE	83±11	HPLC-MS-MS	1		Vanderford etal 2003
	SPE	75±11[c],77±6[d],64±1[a],77±6[b]	HPLC-MS-MS		1[c,d],5[a,b]	Lindqvist etal 2005
	SPE	57±18[a],37±2[b],47[e]	HPLC-MS-MS	5[e]		Pedrouzo etal 2007

Continuation of Table 3-1

Analyte	Extraction Method	Recovery (%)	Analytical Method	LOD (ng/L)	LOQ (ng/L)	Reference
	SPE-Derivatization	70[f],70[d]	GC-MS	8.7		Sacher etal 2001
	SPE-Derivatization	80±2[g]	GC-MS	45		Thomas etal 2004
	SPE-Derivatization	80±9[f],81±9[c],63±4[e],54±7[a]	GC-MS		2	Lin etal 2005
	SPE-Derivatization	76±9		38(Full scan mode), 1(SIM)	108(Full scan mode), 2(SIM)	Koutsouba etal 2003
Ketoprofen	SPE	83.9	HPLC-MS-MS	20		Miao etal 2002
	SPE	95±6[c],83±5[d],69±2[a],83±5[b]	HPLC-MS-MS		5[c,d],25[a,b]	Lindqvist etal 2005
	SPE-Derivatization	80[f],104[d]	GC-MS	4.8		Sacher etal 2001
	SPE-Derivatization	96±3[g],93±6[a]	GC-MS	10		Lee etal 2003
	SPE-Derivatization	102±4[g]	GC-MS	10		Lee etal 2005
	SPE-Derivatization	50±6[f],59±5[c],77±7[e],83±2[a]	GC-MS		2	Lin etal 2005
Gemfibrozil	SPE	78.2[a]	HPLC-MS-MS	5		Miao etal 2002
	SPE	94±10	HPLC-MS-MS	1		Vanderford etal 2003
	SPE-Derivatization	49[f],89[d]	GC-MS	5.2		Sacher etal 2001
	SPE-Derivatization	100±3[g],98±6[a]	GC-MS	10		Lee etal 2003
	SPE-Derivatization	99±4[g]	GC-MS	10		Lee etal 2005
Atenolol	SPE	106±6[a]	HPLC-MS-MS		1.07[a]	Castiglioni etal 2005
	SPE	81±3[c],90±6[d],101±4[a],108±10[b]	HPLC-MS-MS		6.5[c],11.8[d],21[a], 49[b]	Vieno etal 2006
	SPE	86[f],67[d]	HPLC-MS-MS	2.4		Sacher etal 2001
Triclosan	SPE	79±17	HPLC-MS-MS	1		Vanderford etal 2003
	SPE-Derivatization	89±2[g],84±6[a]	GC-MS	10		Lee etal 2003
	SPE-Derivatization	93±5[g]	GC-MS	10		Lee etal 2005

Continuation of Table 3-1

Analyte	Extraction Method	Recovery (%)	Analytical Method	LOD (ng/L)	LOQ (ng/L)	Reference
	SPE-Derivatization	79.2±7.3	GC-MS		30	Moldovan etal 2006
Fenoprofen	SPE	91.5	HPLC-MS-MS	10		Miao etal 2002
	SPE-Derivatization	71[f],99[d]	GC-MS	3.3		Sacher etal 2001
	SPE-Derivatization	95±4[g],96±5[a]	GC-MS	10		Lee etal 2003
	SPE-Derivatization	98±3[g]	GC-MS	10		Lee etal 2005
Caffeine	SPE	93±10	HPLC-MS-MS	1		Vanderford etal 2003
	SPE	84±7[a],50±1[b],45[e]	HPLC-MS-MS	3[e]		Pedrouzo etal 2007
	SPE-Derivatization	34±11[g]	GC-MS	9		Thomas etal 2004
	SPE-Derivatization	64.1±6.5	GC-MS		30	Moldovan etal 2006
Estrone	SPE	97±6.4[a]	HPLC-MS-MS		1.5[a]	Castiglioni etal 2005
	SPE-Derivatization	105±6[g]	GC-MS	10		Lee etal 2005
Erythromycin	SPE	50±5.1[a]	HPLC-MS-MS		0.4[a]	Castiglioni etal 2005
	SPE	71±10	HPLC-MS-MS	1		Vanderford etal 2003
Indomethacin	SPE	58.5±10	HPLC-MS-MS	10		Miao etal 2002
	SPE-Derivatization	86[f],114[d]	GC-MS	5.4		Sacher etal 2001
	SPE-Derivatization	93±4[g],83±7[a]	GC-MS	10		Lee etal 2003
	SPE-Derivatization	107±5[g]	GC-MS	10		Lee etal 2005

a: spiked with STP effluent, b: spiked with STP influent, c: spiked with ground water, d: spiked with surface water, e: spiked with river water, f: spiked with tap water, g: spiked with distilled water

Analytical Methods used during this Research

Pharmaceuticals Analytical Methods

EPA standard analytical processing (storage, extraction, and analysis) procedures for each category of compound were used. For the pharmaceuticals evaluated during this study, EPA method 1694 was used. The pharmaceuticals were held in a cooler at 4 C before extraction. The pharmaceutical samples were tested for acidic compounds. The method describes the pH adjustment solutions and extraction solvents to be used: HCl and MeOH. Hydrochloric acid (HCl) was used to acidify the sample and the methanol (MeOH) was used for extraction. For the analysis, two different elution solvents were used on a solids phase extraction (SPE) setup. One was used for the first set of four pharmaceuticals: carbamazepine, sulfamethoxazole, fluoxetine, and trimethoprim. The compounds in the other set were triclosan, gemfibrozil and ibuprofen. Formic acid (1%) /ammonia formate and formic acid (1%)/in methanol:water was used as the two extraction solvents. The instrument was calibrated and blanks were analyzed for detection limits. The final effluent was also spiked to determine extraction recovery efficiency. The pharmaceuticals were quantified using a HPLC/UV (Figure 3-2), as outlined below.

Sample Preparation:

The pH of a 1-L sample aliquot is adjusted to 2 with acid. The pH of a second 1-L aliquot of sample is adjusted with 10 with base. Stable pharmaceutical analogs of the analytes of interest are spiked into their respective acid or base fraction. The acid fraction is stabilized with tetrasodium ethylenediamine-tetraacetate dihydrate ($Na_4EDTA \cdot 2H_2O$).

Sample cleanup:

The acid and base fraction solutions are separately cleaned up using solid-phase extraction (SPE) with hydrophilic-lipophillic balance (HLB) cartridges. After cleanup, the fractions are exchanged to methanol, and the final volume is adjusted to 4 mL with the LC elution solvent.

Determination by HPLC/UV:

The acid extract is analyzed in three runs, each specific to a subset of the analytes of interest. The base extract is analyzed as a single subset. An individual compound is identified by comparing the LC retention time. The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and HPLC/UV systems.

Method References:

U.S. Environmental Protection Agency, 2007, Method 1694: Pharmaceuticals and personal care products in water, soil, sediment, and biosolids by HPLC/MS/MS: USEPA, Washington, DC, EPA-821-R-08-008, 77 p.

Columbia Analytical Services, Pharmaceutical testing, Technical Resources, Washington Laboratory, Washington

Interferences:

“Solvents, reagents, glassware, and other sample processing hardware may yield artifacts, elevated baselines, matrix enhancement or matrix suppression causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinse. Proper cleaning of glassware is extremely important, because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption on the glass surface. All materials used in the analysis must be demonstrated to be free from interferences by running reference matrix method blanks initially and with each sample batch. Interferences co-extracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the analytes of interest”. .

QA/QC

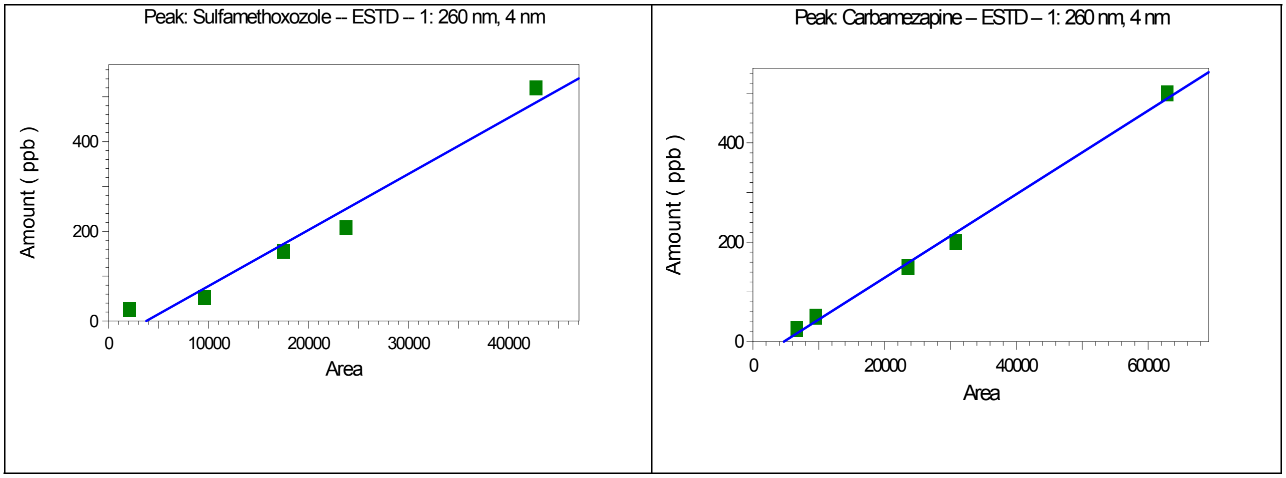
“Analysis of samples spiked with pharmaceutical analogs, compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method”.

Maximum Holding Time:

Extract within 48 hours of collection and analyze extract within 40 days. Freeze sample to minimize degradation and increase holding time to 7 days; if frozen, extract within 48 hours of removal from freezer.

Detection:

The detection limits of the compounds in the water samples are dependent on the sample volume extracted and the final volume of the extract. Using 1 mL of extract from 1 L of water sample, the detection limits for the compounds are expected to be in the range of 50 to 100 ng/L (Figure 3-1).



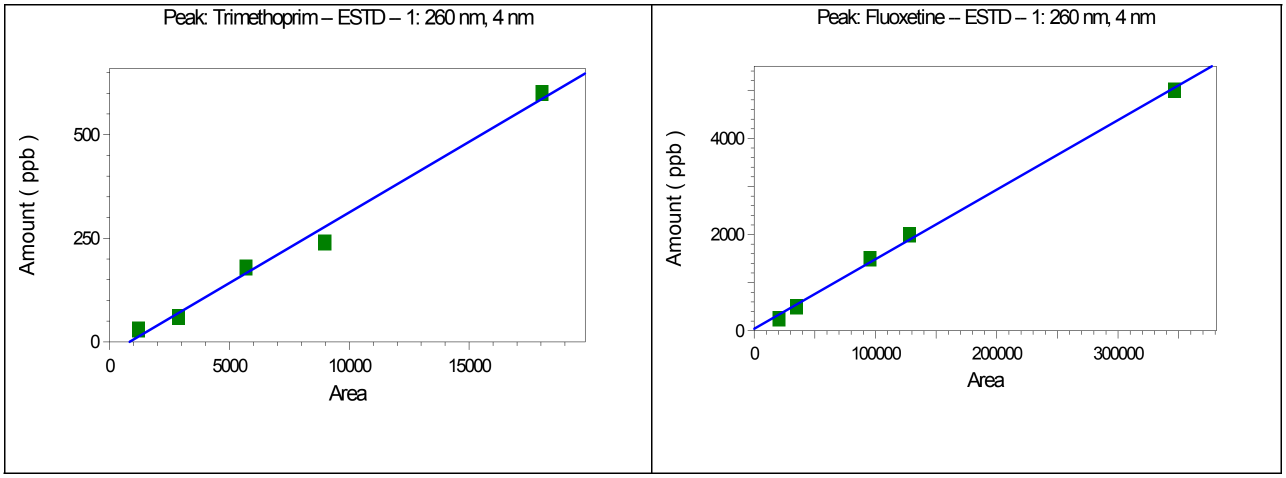


Figure 3-1. Selected standard curves for EC compounds.

LC/UV instrument for PPCP analyses

Loading automatic sampler tray for LC/UV

Figure 3-2. HPLC equipment used for PPCP analyses.

PAH Analytical Methods

For PAHs, EPA method 8310 was used. The initial calibration was conducted using a minimum blank and 5 points for each analyte. The calibration was verified by internal calibrations. Method blanks were analyzed for every 20 samples. The PAHs were extracted using methylene chloride in 2L separation funnels. The extracts were condensed from 120 ml to 2 ml using Kuderna Danish (KD) equipment. The extract was analyzed using a GC-MS.

The pesticides were sent to Penn State Harrisburg for extractions in a cooler with the separation funnel extractions completed within the allowable holding time of 7 days. The pesticides were analyzed using EPA 525 method. Calibration liquids, containing each of the analytes were prepared. After the samples were collected, they were dechlorinated using sodium thiosulfate, iced and sent to the laB- Field blanks were analyzed along with samples. QA/QC was demonstrated by the consistent analysis of laboratory reagent blanks, laboratory fortified blanks (LFB), and laboratory fortified matrix (LFM) samples. The pesticides were analyzed using a GC-ECD.

The quality control objective for the laboratory blank is to obtain results in a concentration less than the specified detection limit. If the blank concentration is greater than the field samples, the values will be rejected or re-analyzed.

Detection of Pesticides (EPA Method 508)

In EPA Method 508, the analytes of interest are extracted manually or by auto extraction and then analyzed in a Gas Chromatograph with an Electron Capture Detector (GC/ECD). Methylene chloride is used as the extracting solvent. As in all very low level analyses, care is needed to overcome interferences and matrix effects. This method has been proven to be very effective and sensitive. Recovery values and method detection limits for the targeted pesticides listed for Method 508 are shown in Table 3-2.

Table 3-2 Single Laboratory Accuracy, Precision, Method Detection Limits (Mdls) for Analytes from Reagent Water (National Exposure Research Laboratory Office of Research and Development U.S. Environmental Protection Agency, Cincinnati, Ohio, 1995)

Analyte	Fortified Conc (µg/L)	N[a]	Recovery (%)	RSD %	MDL (µg/L)
Aldrin	0.075	7	66	9	0.014
Chlordane-alpha	0.015	7	117	8	0.0041
Chlordane-gamma	0.015	7	109	3	0.0016
Chloroneb	0.5	7	47	34	0.25
Chlorobenzilate	5	8	99	5	2.2
Chlorothalonil	0.025	7	119	12	0.011
DCPA	0.025	7	112	4	0.0032
4,4'-DDD	0.025	7	115	5	0.0044
4,4'-DDE	0.01	7	127	6	0.0025
4,4'-DDT	0.06	7	87	23	0.039
Dieldrin	0.02	7	77	22	0.011
Endosulfan I	0.015	7	78	25	0.0092
Endosulfan Sulfate	0.015	7	129	4	0.0024
Endrin	0.015	7	72	18	0.0062
Endrin Aldehyde	0.025	7	95	15	0.011
Endosulfan II	0.015	7	148	35	0.024
Etridiazole	0.025	7	96	17	0.013
HCH-alpha	0.025	8	94	8	0.0053
HCH-beta	0.01	7	95	12	0.0036
HCH-delta	0.01	7	84	7	0.002

Continuation of Table 3-2

Analyte	Fortified Conc (µg/L)	N[a]	Recovery (%)	RSD %	MDL (µg/L)
HCH-gamma	0.015	7	80	16	0.006
Heptachlor	0.01	7	67	7	0.0015
Heptachlor Epoxide	0.015	7	71	18	0.0059
Hexachlorobenzene	0.005	7	115	43	0.0077
Methoxychlor	0.05	7	120	11	0.022
cis-Permethrin	5	7	64	24	0.25
trans-Permethrin	5	7	122	9	0.18
Propachlor	5	7	90	18	0.25
Trifluralin	0.025	7	108	3	0.0026

[a] N = Number of sample replicates.
RSD: Relative Standard Deviation (absolute value of the coefficient of variation expressed as a percentage).
MDL: Method Detection Limit (minimum amount of substance that can be detected with a given confidence).

Toxicity Screening using Microtox

Osmotic Pressure (Salinity) Adjustment

Granular NaCl was used to adjust the salinity (osmotic pressure) of the samples. Previously developed protocols used granular NaCl to adjust the salinity of the samples to 2%. This protocol recommended 0.2g of NaCl per 10mL sample. Tests were conducted to determine if there was a difference in illuminescence of the test bacteria with changing NaCl concentration and to determine the optimum concentration of NaCl required when adjusting to acceptable range of salinity of a sample. These toxicity tests were conducted by adding eight different concentrations of NaCl to a composite of three stormwater samples. NaCl concentrations were 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 mg per 10 ml of sample. Figure 5.1.1 shows the bacteria response to these eight NaCl concentrations at 5, 15, 25, and 45 min of exposure times.

The graphs show the fluorescence of the bacteria is significantly influenced by changing the osmotic pressure of the samples. The previously developed protocol recommended adjusting the salinity to 2%. According to the graph 2% salinity corresponds to 33%-46% reduction in fluorescence during 5 to 45 min exposure. Figure 3-3 shows that the minimum light reduction is at 0.3 g which corresponds to 3% salinity. The percent of toxicity effect was the smallest for the NaCl concentration of 0.3 g per 10 ml of sample and the data points for this concentration at different exposure times are very close together. The toxicity effect is nearly the same for 5, 15, 25, and 45 minutes for all the NaCl concentrations with the exception 0.4 mg of NaCl per 10 ml of sample, for which the toxicity effect ranged approximately between 35 to 37% at 5 min of exposure and 56 to 61% at 45 min of exposure. Slight change in quantities of salt added has an effect of the osmotic pressure and results in reduction of light output, therefore precision is necessary weighing salt additions. Because 0.3 g of NaCl per 10 mL corresponded to a minimum fluorescence reduction, this concentration was used for future experiments.

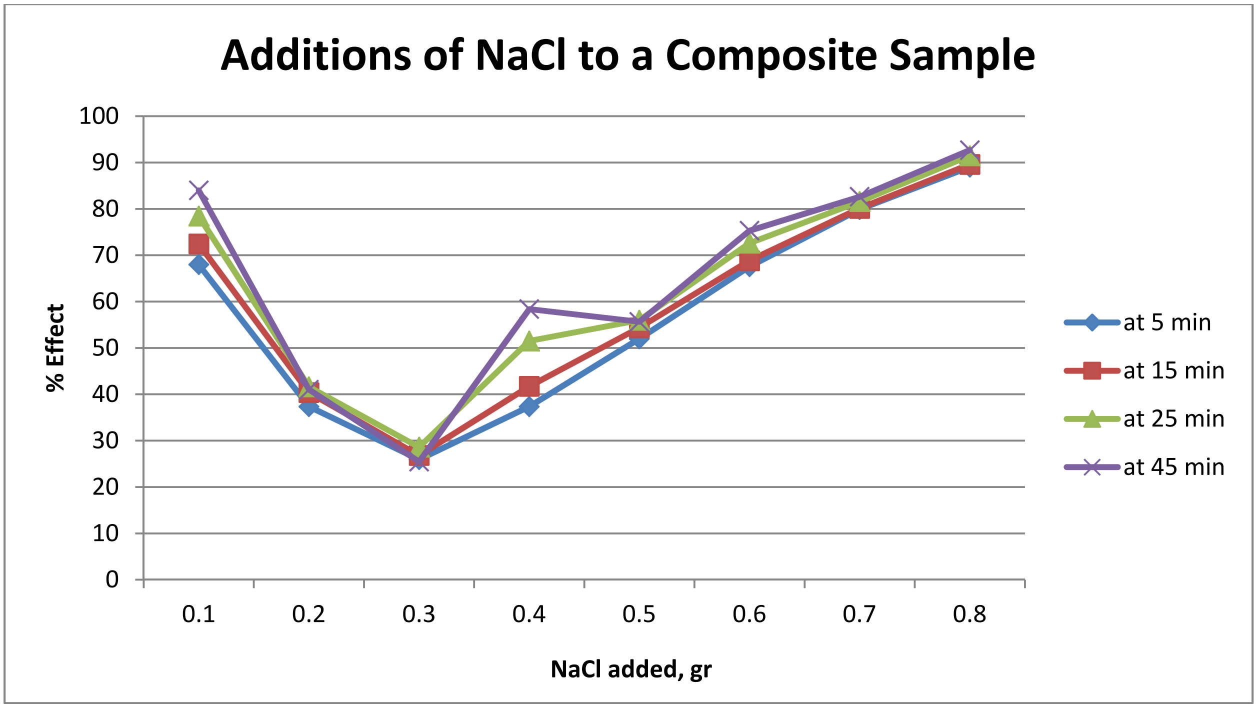


Figure 3-3. Toxicity effect (%) after additions of eight different NaCl concentrations to a composite sample. (X-axis: grams of NaCl per 10 ml of sample. Each point is an average of 2 replicates.)

$ZnSO_4$ and Phenol Toxicity Standards

Figures 5.2.1and 5.2.2 show the toxicity effects of two replicates of varying $ZnSO_4$ and phenol concentrations. As can be seen from the graphs, $ZnSO_4$ has an IC_{50} (inhibition concentration resulting in 50% inhibition) at approximately 0.7 mg/L, while phenol has an IC_{20} of approximately 5 mg/L at 15 min. All further tests used ZnSO4 and phenol as reference toxicants at concentrations of 0.7 mg/L and 5 mg/L, respectively, which were analyzed along with each sample batch. Figure 3-4 shows that toxicity associated with ZnSO4 increases more with bacteria exposure time compared to toxicity associated with phenol in Figure 3-5.

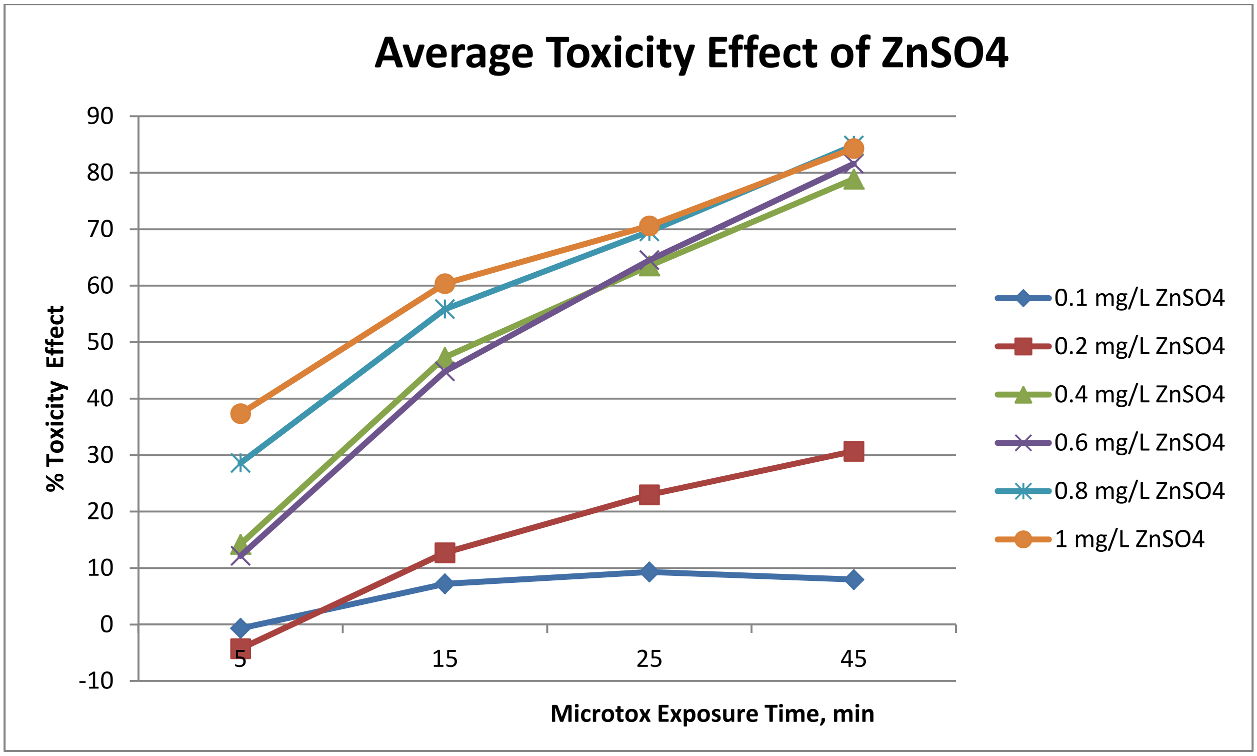


Figure 3-4. Toxicity effect (%) of different ZnSO4 concentrations at various exposure times. (Each point is an average of 2 replicates.)

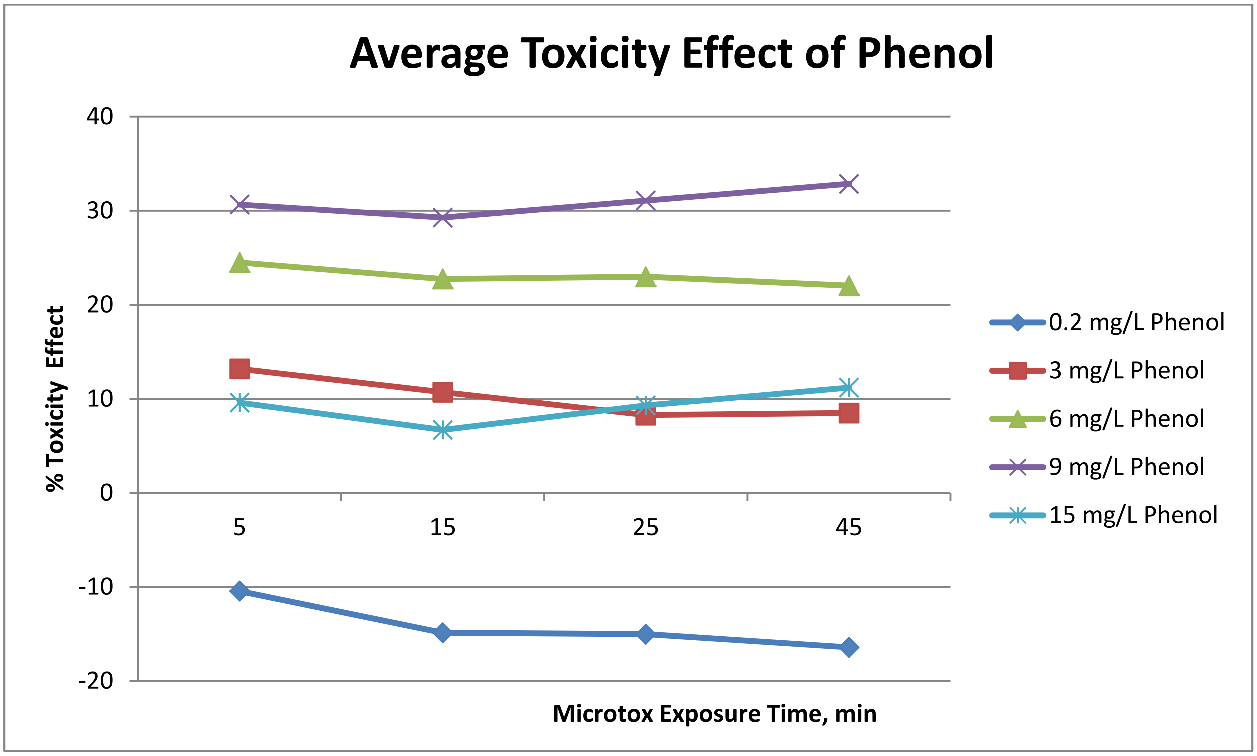


Figure 3-5.Toxicity effect (%) of different Phenol concentrations at various exposure times. (Each point is an average of 2 replicates.)

Bacterial Cultivation and Enumeration Methods

A full factorial study (2^3, Temperature/Moisture/UVB exposure, the latter being ultraviolet-B radiation) of the indicator species' environmental survival factors was performed for each taxon (Enterococci and E. coli). Pet feces slurries (1 mL) were applied to salt passivated paving blocks and incubated in controlled environmental chambers (freezerless refrigerators fitted with commercial biological oxygen demand (BOD) controllers and heaters for temperature control, desiccant or humidifiers for moisture control, and UVB enhanced fluorescents with Lexan panels to split the chambers into UV exposed and UV shielded regions) at conditions encompassing those likely to be found in Tuscaloosa.

The raw concrete paving blocks had been prepared by an overnight soak in mild brine (1/4 cup table salt into 40-gallon trash can of tap water), followed by thorough tap-water rinse and air drying, to provide an unreactive, "passive" surface. Slurries were produced by blending dog feces with distilled water (to assure microbiological purity and absence of bactericidal components) and immediately applied (with a 3-ml sterile, disposal syringe) to the passivated blocks (to quickly relieve any potential osmotic stress of the distilled water). No additional nutrients (other than fecal materials) were added. Active control of temperature (40 ºF and 90 ºF, 4.4 ºC and 32 ºC, cool or warm) held the parameter steady (±2 ºF, 1.1 ºC) over the study period. Relative humidity (25% and 80%, dry or wet) varied over about ±4%. UV exposure was treated as present or absent (UV or dark).

Over an extended period (about two weeks), duplicate inoculated paving blocks were subjected to mechanical biofilm disruption by consistently applied and timed toothbrush abrasion (three scrubs of one minute each, with intervening wetting between scrubs), washing the slurry debris into sample bottles and dilution to 100 mL (with distilled water). Method-development comparisons of wash-off MPN to inoculant MPN showed incomplete but consistent (within 95% confidence bands of MPN measurement) recovery of the inoculant by this abrasion/rinse technique.

Washed-off samples were immediately mixed with defined-substrate formulations (Colilert/Enterlert) for relief of osmotic stresses. The most probable numbers (MPN) of surviving E. coli and Enterococci colony forming units (CFU) per 100 mL were measured using IDEXX (IDEXX Laboratories, Inc.) methods and normalized to the inoculation date (Day 0) MPN (also acquired from brush-off samples from blocks inoculated and brushed in the same way). IDEXX reagents (Colilert and Enterolert) provide for selective incubation of the taxons of interest, and colorimetric and fluorometric indicators of viable colonies within 24 h, and are recognized water assays under Standard Methods for the Examination of Water and Wastewater (21st Edition, sections 9223 and 9230b, respectively). MPN measurement values with three orders of magnitude ranges (from 1 to 2 420 MPN/100 ml) are directly available with the reagents when used in conjunction with Quantitray 2000 units. Additional dilutions of each sample were incubated to ensure that all samples were quantified over even wider ranges.

Experimental Design

Emerging Contaminants at the Tuscaloosa Wastewater Treatment Plant

One of the objectives of this research was to determine if treatment at a conventional municipal wastewater system is reduced during periods of increased flows associated with stormwater I&I, and whether or not these increased flows affected the influent concentrations of the ECs. Specifically, we were most interested in identifying which unit processes were most effective for EC removal and how those process could be translated to wet weather flow treatment. The wet weather flow EC mass loadings were also quantified.

Each unit treatment process therefore needed to be examined during a range of flow conditions. Factors that affect the unit operations at a treatment plant include flow rate (and associated hydraulic retention time), treatability characteristics of the constituents and solids retention time. These factors were investigated during this research for both dry and wet weather conditions. The constituents analyzed included:

-Pharmaceuticals
trimethoprim
sulfamethoxazole
fluoxetine
carbamazepine
ibuprofen
gemfibrozil
triclosan

-Pesticides
lindane aldrin
dieldrin
heptachlor
heptachlor-epoxide
methoxychlor
arochlor

-PAHs
naphthalene
phenanthrene
anthracene
fluoranthene
pyrene
fluorene
acenaphthene
chrysene
Acenaphthylene

Eight sets of four samples were obtained at the wastewater plant during wet weather and nine sets of four samples were collected during dry weather to compare concentrations and performance as a function of flow rates.

A total of 24 samples were collected for PAHs, pharmaceuticals and pesticides during wet weather conditions. Twenty-eight samples were collected for PAHs, pharmaceuticals and pesticides during dry weather conditions. As this study was designed to measure the effects of wet weather on wastewater treatment of these ECs, the wet and dry conditions are the causal or independent variables. The dependent variables, or the outcome variables, are the influent and effluent concentrations for each unit process. The wet weather samples were weather dependent and were therefore obtained as a judgmental sample design (when it was predicted to have moderate to large amounts of rainfall for the area). The dry weather samples were taken randomly, increasing variability. Samples were obtained manually as composite grab samples. All treatment plant samples were taken over a six hour period. Grab samples were taken at the sampling locations as time composites over a two hour period, staggered to correspond to flow time at the treatment plant. The samples were obtained at: (1) inlet; (2) primary clarifier effluent; (3) secondary clarifier effluent; and (4) after disinfection at the plant effluent. Each sample was obtained in one liter, pre-washed amber glass bottles having Teflon-lined lids.

Heavy Metal Sources and Pollution Prevention

Eight gutter and pipe materials (some also used in tank construction) were subjected to long-term static leaching tests under different water conditions: buffered low and high pH waters and natural bay and river waters having different conductivities. The gutter materials included vinyl, aluminum, copper, and galvanized steel. The pipe materials included concrete, PVC (polyvinyl chloride), HDPE (high density polyethylene), and galvanized steel. Materials that are also commonly used in water tank construction include: aluminum, galvanized steel, concrete, PVC, and HDPE. All of the material samples for these tests were obtained as new specimens from a local building material supplier. The specimens used for the two controlled pH tests and bay and river water tests were nearly identical, with the exception of the concrete pipes. The two concrete samples for the pH tests were the same, but larger than the two smaller, but identical concrete samples for the bay and river water tests.

The tests were performed in two stages. During the first testing stage, the materials were immersed into locally collected roof runoff and parking lot runoff that were adjusted to pH values of 5 and 8 using buffer chemicals added to the runoff water (disodium phosphate dehydrate $Na_2HPO_4 * 2H_2O$ and potassium phosphate monobasic KH_2PO_4). These buffered waters therefore had high phosphate concentrations (2,065 mg/L as P) and high conductivity values (greater than 10 mS/cm) that can affect the metal speciation during the tests. Each section of pipe and gutter material was submerged into the runoff water in 16 L plastic buckets, or 80 L containers for the concrete specimens. During the first test, the effects of pH, time, and material type on contaminant leaching from the drainage system materials were investigated. A second series of tests were conducted to investigate the metal releases under natural pH conditions, but with varying conductivity values associated with natural brackish bay water and river water. During the second testing stage, un-buffered waters from Mobile Bay (saline) and the Black Warrior River (non-saline) were used. Saline water was used to study the effect of salinity on metal releases, such as when pipe materials are exposed to snowmelt containing salt in stormwater runoff during spring months and for pipe crossings or outfall structures in brackish or saline waters.

The pH 5 and 8 values were chosen for the test conditions based on the studies summarized by Pitt, et al. (2004). The authors found that pH varied widely for different source areas, with the pH of roof runoff being on the lower end of the reported pH range between 4.4 and 8.4, and a mean value of 6.9. The highest pH was observed for storage areas at a concrete plant with reported pH values ranging between 6.5 and 12, with a mean of 8.5. The pH 5 and 8 conditions were therefore within the ranges of the two extreme groups of sample sets and could be controlled by known buffer systems. Each specimen of pipe and gutter material was submerged into containers with pH values of 5 and 8 during the first series of tests; the gutter materials were submerged in buffered roof runoff (at both 5 and 8 pH) and the pipe materials were submerged in the buffered parking lot runoff (also at both 5 and 8 pH). For the second series of tests, new specimens of the same samples were submerged in containers having un-buffered bay and river waters. The pH and conductivity values for the first and second series of tests at time zero (waters without specimens) are listed in Table 3-3.

Table 3-3.Initial pH and conductivity values for buffered and natural water tests.

	pH 5	pH 8	Bay	River
pH	5	8	8	8
Conductivity, mS/cm	6.1	10.1	10.1	0.4

Water samples from each leaching container were periodically collected and analyzed over a three month period for selected heavy metals, nutrients (during first stage of the experiments), toxicity (using Microtox screening methods); pH, conductivity, and Eh. Eh is the half-cell potential relative to the standard hydrogen electrode (see Langmuir 1997 and Garrels and Christ 1990 for a complete definition and descriptions of how it is used in water chemistry modeling).The samples from the first series of tests were analyzed at time 0 (water with adjusted pH without pipes), 0.5 hour, 1 hour, 27 hours, 1 month, 2 months, and 3 months for total concentrations of cadmium, chromium, lead, copper, and zinc. The samples were also analyzed for total aluminum and iron, along with filterable concentrations of lead, copper, zinc, and aluminum after 3 months of exposure. Analyzed nutrients included ammonia nitrogen, total nitrogen, and nitrate plus nitrite. Since phosphates were a major component of the buffers, they were not considered during the leaching tests (except as possible films to protect the materials). Chemical Oxygen Demand (COD) was also measured. During the second series of tests, 14 L leaching containers with un-buffered bay and river waters were sampled at time 0(natural bay or river waters without pipes), 1 hour, 27 hours, 1week, 1 month, 2 months, and 3 months for total concentrations of lead, copper, and zinc, and also screened for toxicity. Concentrations in mg/L were converted to mg of constituent per surface area of a pipe or gutter in order to account for different area surfaces of the pipes and water volumes. Water samples were also analyzed for total aluminum and iron, and filterable iron, at time zero and at 3 months. Alkalinity, total hardness as $CaCO_3$, and calcium hardness as $CaCO_3$ concentrations were measured after 3 months during first stage of the experiments and at time zero and after 3 months during the second stage of the experiments. Additionally, Cl^- and SO_4^{2-}were analyzed after 3 months of exposure during the first and the second series of tests. Bay and river waters were analyzed for fluoride, nitrate, total phosphorus, bromide, and manganese, boron as BO_3^{3-}, silicon, sodium, and potassium. Shavings from pipe and gutter materials were also analyzed for Pb, Cu, Zn, Al, and Fe. Metal analyses were performed using inductively coupled plasma mass spectroscopy (ICP-MS). The detection limits for zinc, copper, and lead concentrations were20, 2, and 5 µg/L, respectively. The detection limits for cadmium and chromium were 5µg/L and 20 µg/L, respectively, and for aluminum and iron 100 µg/L and 20 µg/L, respectively. Analytical methods used and method detection limits are shown in Table 3-4.

Table 3-4. Analytical methods and method detection limits.

Analyte	Analytical Method	Method Detection Limit (MDL), µg/L
Zinc, Copper, Chromium, Iron, Manganese, Boron (outside laboratory*)	Inductively Coupled Plasma Mass Spectrometry (ICP-MS). EPA Method 200.8	20
Lead, Cadmium (outside laboratory)	Inductively Coupled Plasma Mass Spectrometry (ICP-MS). EPA Method 200.8	5
Aluminum (outside laboratory)	Inductively Coupled Plasma Mass Spectrometry (ICP-MS). EPA Method 200.8	100
Chloride, Sulfate, Fluoride, Nitrate, Bromide (outside laboratory)	Ion Chromatography. Standard Methods. Method 4110B	20
Phosphorus (outside laboratory)	Ascorbic Acid Method. Standard Methods. Method 4500P-E	20
Silicon (outside laboratory)	Standard Methods. Method 3111D. Metals by Flame Atomic Absorption Spectrometry	10,000
Sodium (outside laboratory)	EPA Method 273.1 Flame Atomic Emission Spectrometry	20
Potassium (outside laboratory)	EPA Method 258.1	20
Alkalinity (outside laboratory)	Standard Methods. Method 2320B Titration	100
Ca Hardness as $CaCO_3$ and Total Hardness as $CaCO_3$ (outside laboratory)	Standard Methods. Method 2340B Hardness by Calculation.	20
Ammonia Nitrogen	HACH Method 10023. Test ‘N Tube	61 as N**
Total Nitrogen	HACH Method 10071 TNT Persulfate Digestion.	734 as N **
Nitrate	HACH Method 8171 Using Accuvac Ampule	95 asN**
Chemical Oxygen Demand	HACH Method 8000. Colorimetric Determination.	1,530as COD**

* the outside commercial laboratory was Stillbrook Environmental Testing Laboratory in Fairfield, AL.

** at95% confidence level

A full 2^2 factorial experiment examined the direct effects and interactions of pH and exposure time for each material for the data collected during the first testing stage and the effects and interactions of conductivity and time for each material for the data collected during the second testing stage. Also, a full 2^3 factorial experiment identified the effects and interactions of exposure time, pH, and material during the first series of tests and the effects and interactions of exposure time, conductivity and material during the second series of the experiments.

Pipe and Gutter Material Descriptions

All samples were purchased new and were typical materials used in new construction. The gutter samples were obtained from the local Lowes store; the HDPE, PVC, and galvanized steel pipe samples were obtained from Summit Pipe and Supply Co., and the concrete pipe samples were obtained from Hanson Pipe and Precast. The gutters were rectangular in shape (with the exception of galvanized steel gutter which was rounded), while the pipes were round. All the pipe and gutter segments were new and were 30.5 cm long, with the exception of the concrete pipe samples, which were 15.3 cm long in the first testing stage (a smaller portion of the new concrete pipe was used during the second testing stage) (Figure 3-6 and 3-7). Tables 3-5 and 3-6 describe the test specimens.

Table 3-5. Round pipe section descriptions.

Material	Outer Diameter, cm	Wall thickness, cm	Length, cm	Weight, g	Surface Area, m^2
Concrete Pipe	41.2 (20% section of cylinder)	5.5	15	22,400 (4,400)	0.47 (0.10)
PVC Pipe	15.7	0.5	30.5	1,096	0.30
HDPE Pipe	17.5	1	30.5	409	0.65
Galvanized Steel Pipe	16.4	0.6	30.5	8,000	0.32

Note: the values in parenthesis are for the second testing stage

Table 3-6. Rectangular gutter section descriptions.

Material	Outer Diameter or Cross-sectional Dimensions, cm	Wall thickness, cm	Length, cm	Weight, g	Surface Area, cm^2
Galvanized Steel Gutter	15	0.05	30.5	704	0.29
Vinyl Gutter	5 x 8	0.1	30.5	100	0.07
Aluminum Gutter	8.4 x 5.6	0.05	30.5	79	0.08
Copper Gutter	10.58 x 7.2	0.07	30.5	503	0.10

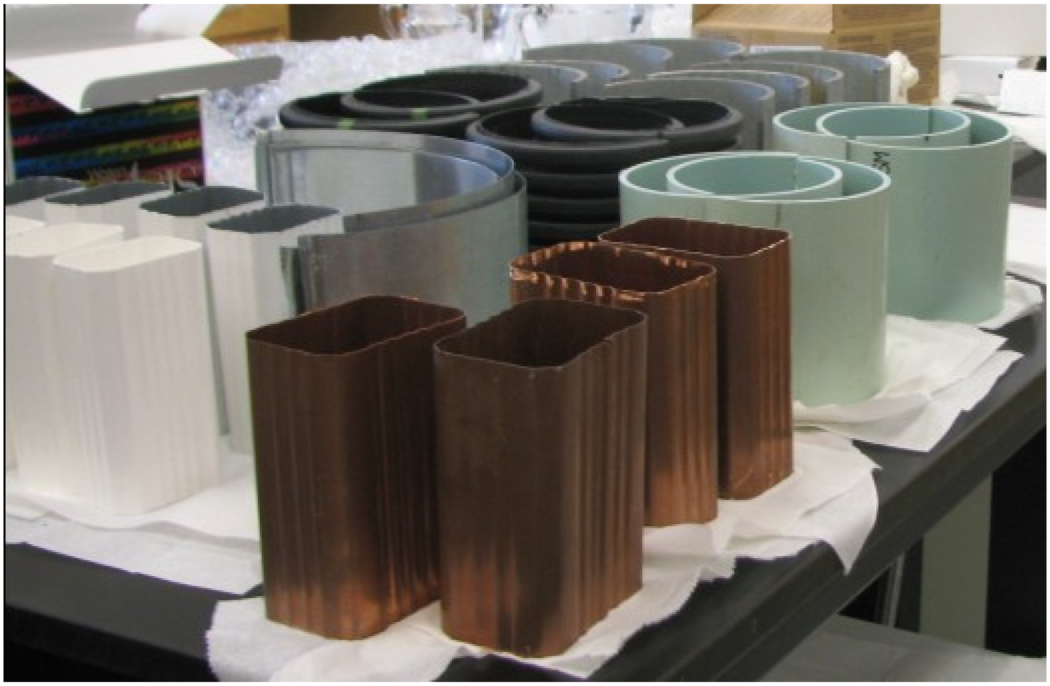


Figure 3-6. Pipe and gutter samples

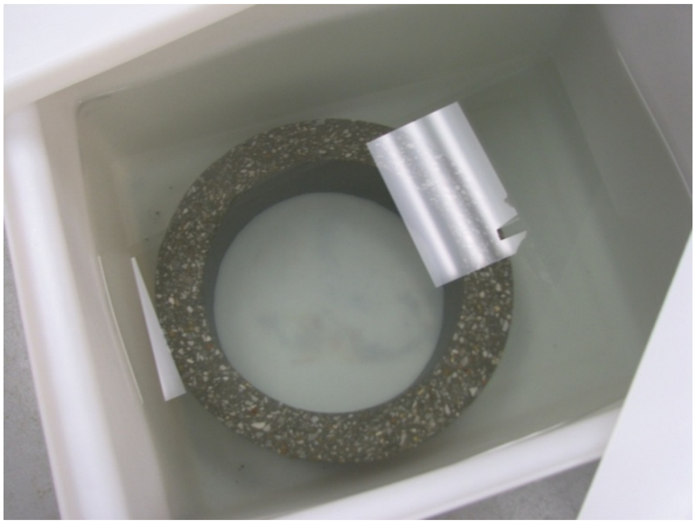


Figure 3-7. Concrete pipe sample submerged in test solution.

The shavings of the pipe and gutter materials were acquired by drilling the samples which were then chemically analyzed for lead, copper, zinc, aluminum, and iron (Appendix D). Lead was a constituent in concrete, galvanized steel, aluminum, and copper materials. Galvanized steel pipe and gutter materials had similar metal content concentrations. Galvanized steel pipes had slightly higher lead and zinc content compared to the galvanized steel gutter samples. Iron concentrations were 970 and 980 g/kg for galvanized steel pipes and gutters respectively; zinc concentrations were28 and

18 g/kg for galvanized steel pipes and gutters respectively. Copper materials had 998g/kg copper concentrations. Copper was also detected in the concrete, HDPE, galvanized steel, and aluminum materials, but the concentrations were much lower (≤0.52 g/kg). Besides galvanized steel materials, zinc was also detected as a component in concrete, aluminum, and copper materials.

Buffer Preparation

Roof runoff was collected from the flat roof from the H.M. Comer engineering building to use as the base for the buffer solutions for the gutter samples, while parking lot runoff from behind the building was collected to use as a base for the buffer solutions for the pipe samples. These runoff samples were used as they represented the basic types of waters that the materials would be exposed to during typical use. The following describes how the buffer solutions were prepared (very large volumes of the buffers were prepared by adjusting the quantities in the following description):

$Na_2HPO_4 * 2H_2O$ and KH_2PO_4 can be used for the buffers with the values of pH between 4.8 and 8.00:

To prepare a buffer having pH 5:
dissolve 11.866 g of $Na_2HPO_4 * 2H_2O$ in 1 L H_2O, take 0.95 mL from the solution
dissolve 9.073 g of KH_2PO_4 in 1L H_2O, take 99.05 mL from the solution
combine the 0.95 mL portion from the first solution with the 99.05 mL portion from the second solution to produce 100 mL of buffer having a pH of 5

To prepare buffer having pH 8:
dissolve 11.866 g of $Na_2HPO_4 * 2H_2O$ in 1 L H_2O, take 96.9 mL from the solution
dissolve 9.073 g of KH_2PO_4 in 1L H_2O, take 3.1 mL from the solution
combine the 96.9 mL portion from the first solution with the 3.1 mL portion from the second solution to produce 100 mL of buffer having a pH of 8

More than 450 liters of roof runoff and parking lot runoff buffers were prepared for the first series of tests.

Method Detection Limit Determination

The analytical method detection limit (MDL) for ammonia nitrogen, total nitrogen, nitrate nitrogen, and Chemical Oxygen Demand were determined in the UA lab using standards with known low concentrations (about twice the expected MDL value). Seven replicates were analyzed to determine the standard deviation of the analyses (Eaton, et al. 2005). The MDL was calculated using the measured standard deviation times the value of t from a table of the one-sided t distribution for 7-1 = 6 degrees of freedom at for the desired confidence level (for the 99% level t = 3.14) (Eaton, et al. 2005). The calculated method detection limits are shown in Appendix C. For example, to determine the method detection limit for ammonia nitrogen, a standard having a known concentration of 1 mg/L as N was used. The expected MDL was 0.5 mg/L as N, or lower. Seven replicates of the ammonia nitrogen Standard 1 mg/L as N were analyzed. The values observed are shown in Table 3-7.

Table 3-7. Observed values for nitrogen ammonia standard with concentration 1 mg/L as N

Value Observed, mg/L as N
0.88
0.92
0.92
0.94
0.96
0.97
0.96
Standard deviation: 0.032

The standard deviation of the seven samples was 0.032 mg/L N. The MDL was the calculated standard deviation times the coefficient at the specified confidence level. The calculated MDLs at different confidence intervals are listed in the Table 3-8.

Table 3-8. Method detection limits for ammonia nitrogen at different confidence levels.

MDL	Confidence Level, %
0.099	99
0.061	95
0.045	90

HACH states that a standard deviation of 0.03 mg/L as N for ammonia nitrogen was obtained using a 1.5 mg/L as N ammonia nitrogen standard, a similar standard deviation as found during the UA lab tests. The analytical method detection limits for the rest of nutrients are shown in Appendix D.

Quality Control and Quality Assurance

QA/QC data are shown in Appendix D. Figures 3-9 and 3-10 are plots of pH values with time in the containers with initial pH 5 and pH 8, respectively. The graphs show that pH values in the containers were fairly constant throughout the experiments. The pH change with time did not exceed 1 pH unit, with the exception of the containers with concrete samples and initial pH 5. In those conditions, the pH increased from 4.98 to 6.37 due to the increased alkalinity from the immersed concrete sample. Figures 3-10 and 3-11 show changes in conductivity values with time. The metal releases in the containers with immersed concrete samples were below or just above the detection limits, while the conductivity values in those containers were fairly constant with time. The increase in conductivity values with time in the rest of the containers can be explained by the increase in metal concentrations released from the immersed samples.

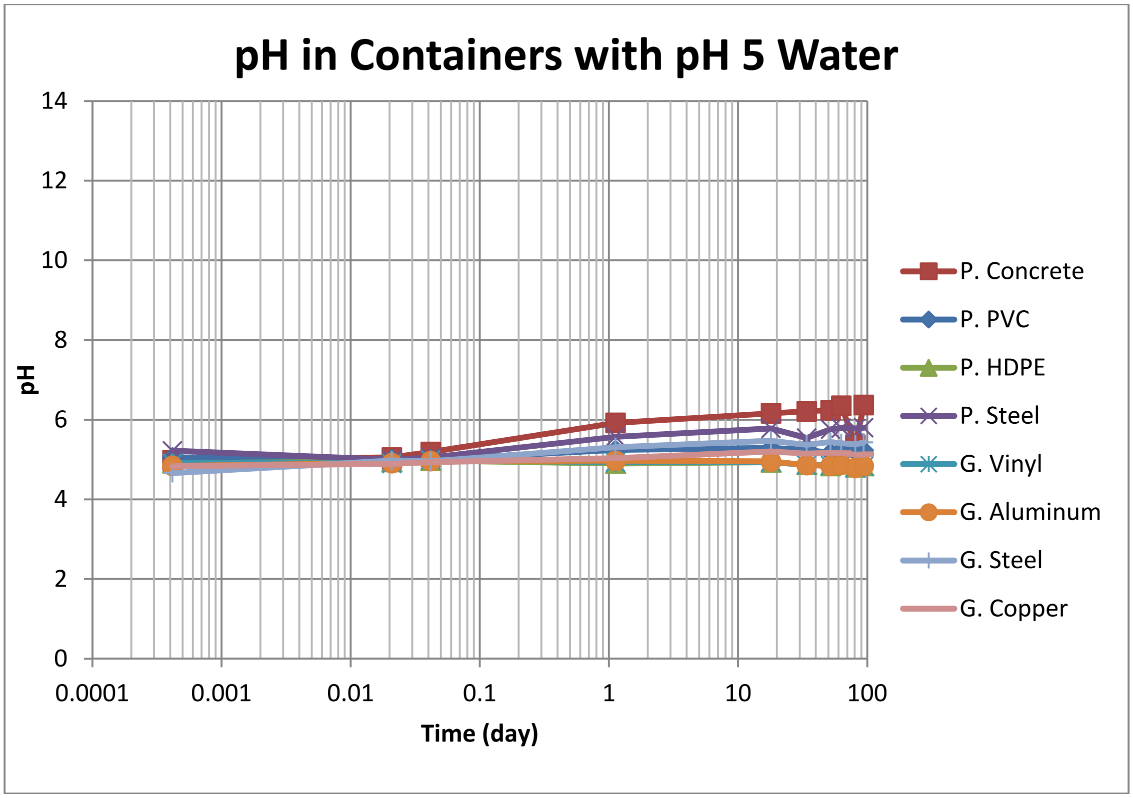


Figure 3-8. pH measurements in the containers with pH 5 water.

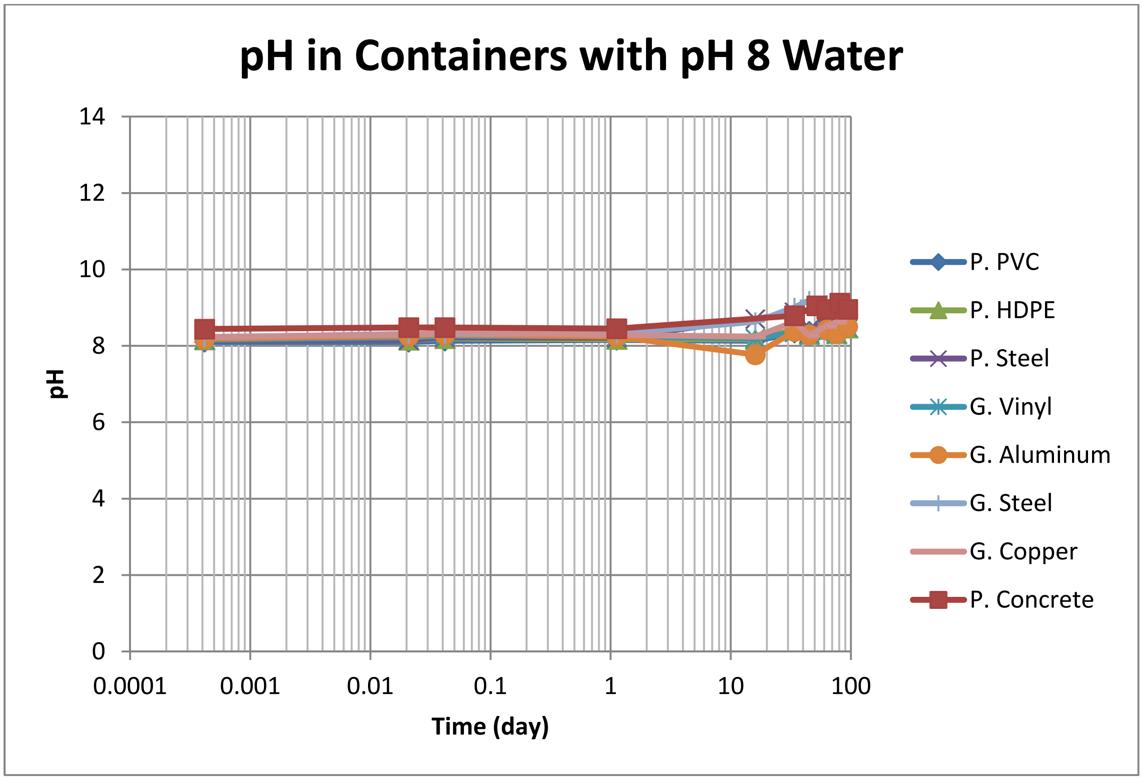


Figure 3-9. pH measurements in the containers with pH 8 water.

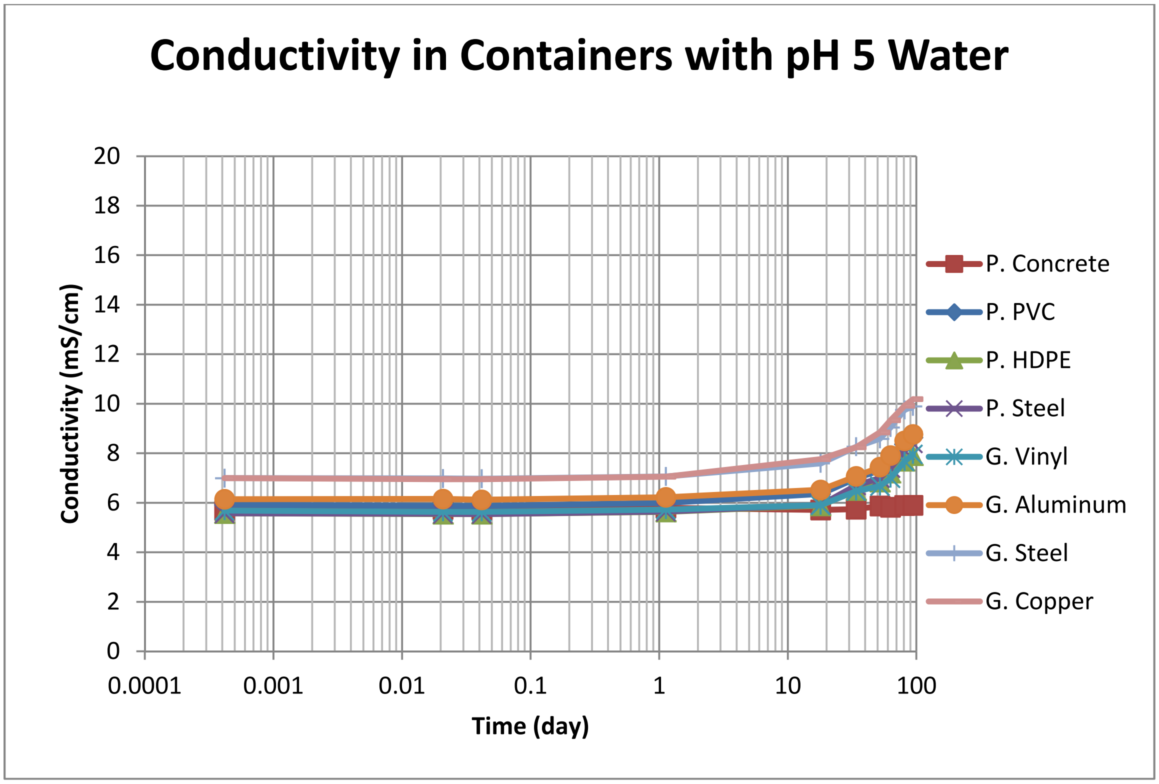


Figure 3-10. Conductivity measurements in the containers with pH 5 water.

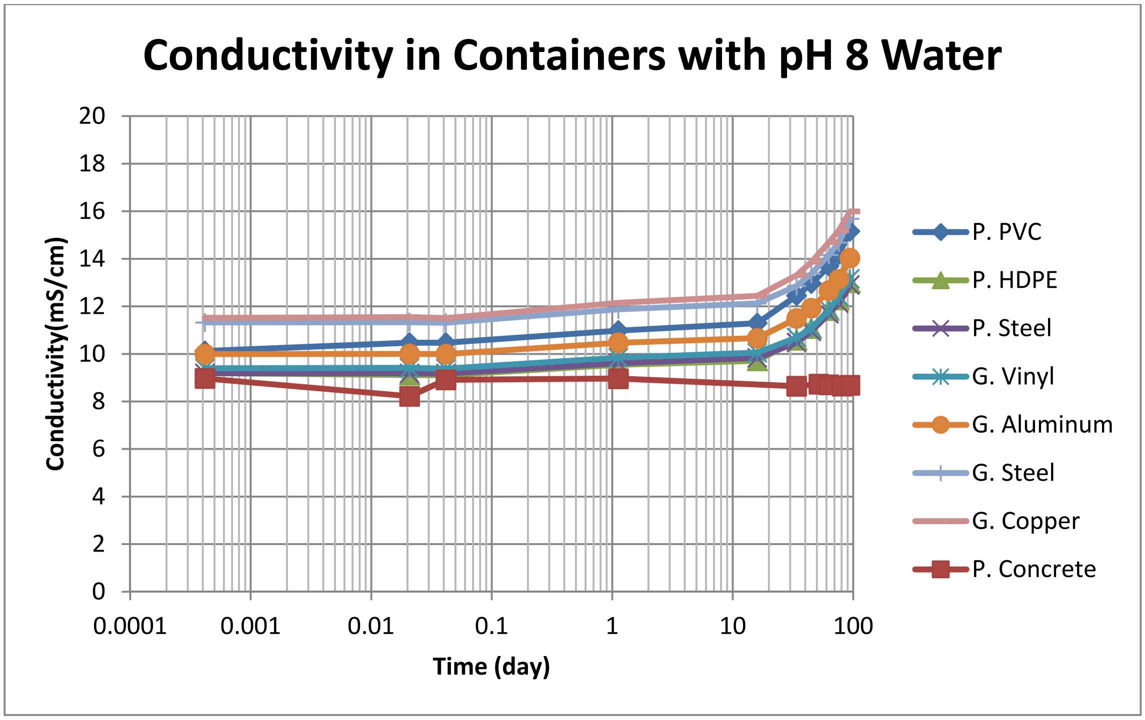


Figure 3-11. Conductivity measurements in the containers with pH 8 water.

Metal analyses and associated laboratory quality control procedures were performed by Stillbrook Environmental Lab, in Fairfield, AL using inductively coupled plasma mass spectroscopy (ICP-MS).Stillbrook Environmental Lab also conducted analyses on major constituents using analytical methods listed in Table 3-9. QA/QC results are shown in Appendix D.

The lab ware used for sample collection and storage was made of polyethylene and was soaked in 10% nitric acid for at least 24 hours before use and rinsed off with 18mΩ water to avoid heavy metal contamination. High-density polyethylene (HDPE) containers were used for sample storage. Leaching buckets were washed using warm tap water and laboratory phosphate-free detergent, rinsed with tap water, washed with 10% nitric acid, then distilled water, followed by 18mΩ water. Polyethylene bottles were washed using warm tap water and laboratory phosphate-free detergent, rinsed with tap water, then deionized water, soaked in a 10% solution of reagent grade nitric acid for at least 24 hours before use, and rinsed with laboratory grade 18mΩ water. The glassware used for sample collection was also cleaned with phosphate-free detergent, rinsed with tap water, deionized water, and soaked in a 10% nitric acid bath at least overnight before use and rinsed with 18mΩ water. Glassware used for toxicity analysis also was rinsed with sampled water. 18mΩ water was also used for method blanks. If not immediately analyzed, water samples were adjusted to pH <2, as required, and placed in a refrigerator at 4^{o}C until they were analyzed. During this research, the labware preparation and sample storage and preservations requirements that were followed were from Eaton et al (2005) and Burton and Pitt (2002).The instruments were calibrated prior to each data collection. Calibration techniques are listed in Table 3-9.

Table 3-9. Instrument calibration.

Instrument	Calibration
pH meter Model IQ 160, conductivity meter model sensION5 by HACH, DR 2010 (for nitrate, nitrogen ammonia, total nitrogen, chemical oxygen demand analysis)	used known standards
ORP meter HI 98120, salinity meter YSI 30	factory calibrated, checked with standard solution
Dissolved oxygen meter YSI Model 57	air calibration
Microtox	$ZnSO_4$ and phenol solutions used as reference toxicants

Toxicity analyses were conducted in duplicate for each water sample. Standards were run together with the samples for nutrient and toxicity analyses to confirm the instrument performance, and methods blanks were used (Appendix D). The observed nutrient values were reasonably close to the standard values. For phenol standards, the toxicity responses were generally constant with bacteria exposure time during each individual experiment. For the majority of the samples, toxicity associated with the ZnSO4standardsincreased with bacteria exposure time. In some cases, there was a change in the sensitivity of the bacteria that can be explained by change in Microtox reagent, as also reported by Morquecho (2005).

Analyses of the Data

The metal masses released per surface area of a pipe or gutter (expressed as mg/m^2) were calculated to account for the loss of water due to sample extraction and for varying sample specimen sizes. Eh-pH diagrams were constructed for the test water systems; the measured values of pH and Eh were placed on the diagrams to determine the predominant metal species expected. Also, log concentration – pH and fraction – pH diagrams were plotted to illustrate the concentrations of chemical species in the test waters. Other analyses of the data are described in the following subsections.

The Langelier Index

The Langelier Index was calculated to determine whether the leaching water for the concrete specimens is in equilibrium with $CaCO_{3(s)}$ (Snoeyink and Jenkins, 1980). The Langelier Index is the difference between the actual pH of the water and the pH the water would have if it were in equilibrium with $CaCO_{3(s)}$. If the Langelier Index has a positive value, the water is oversaturated with $CaCO_{3(s)}$ and will tend to precipitate $CaCO_{3(s)}$, with no degradation of the concrete. If the Langelier Index has a negative value, the water is undersaturated with $CaCO_{3(s)}$ and will tend to dissolve $CaCO_{3(s)}$ from the concrete. If the Langelier Index of the water is zero, it is in the equilibrium with $CaCO_{3(s)}$.

Toxicity

Toxicity analyses were conducted using the Microtox® Test System (Strategic Diagnostics, Inc.). In this test, bioluminescent marine bacteria (Vibrio fischeri) were exposed to water samples and the reduction of light output by the bacteria was measured at specific times. Vibrio fischeri emits light during its normal respiration. The toxicity was calculated by comparing the light output in a sample to that of a control. The bacteria have been freeze-dried, with one vial of freeze-dried reagent containing approximately one million test organisms. Reconstitution solution (specially prepared nontoxic ultra pure water) was used to rehydrate the bacteria. Zinc sulfate ($ZnSO_4$) and phenol were used as reference toxicants to check the performance of the test system.

Statistical Analyses of the Data

The following discussion presents several examples of the statistical tests conducted during different project phases. The results discussions and appendices present the complete data.

Basic Data plots

Exploratory data analyses were used to identify relationships between contaminant concentrations (metal leaching) and gutter and piping material samples, water conditions, and time. These initial tests were followed by statistical tests to determine the significance of the observations (Burton and Pitt 2002). Time series plots were constructed to examine the data. For example, Figure 3-12 shows time series plots of lead releases from different pipe and gutter materials under controlled pH 5 conditions.

For containers with galvanized steel materials, detectable amounts of lead were released after 27 hours of exposure. Lead releases were greater associated with galvanized steel pipe compared to galvanized steel gutter samples. Lead was not detected in the containers having any of the other test materials the entire during three months exposure time.

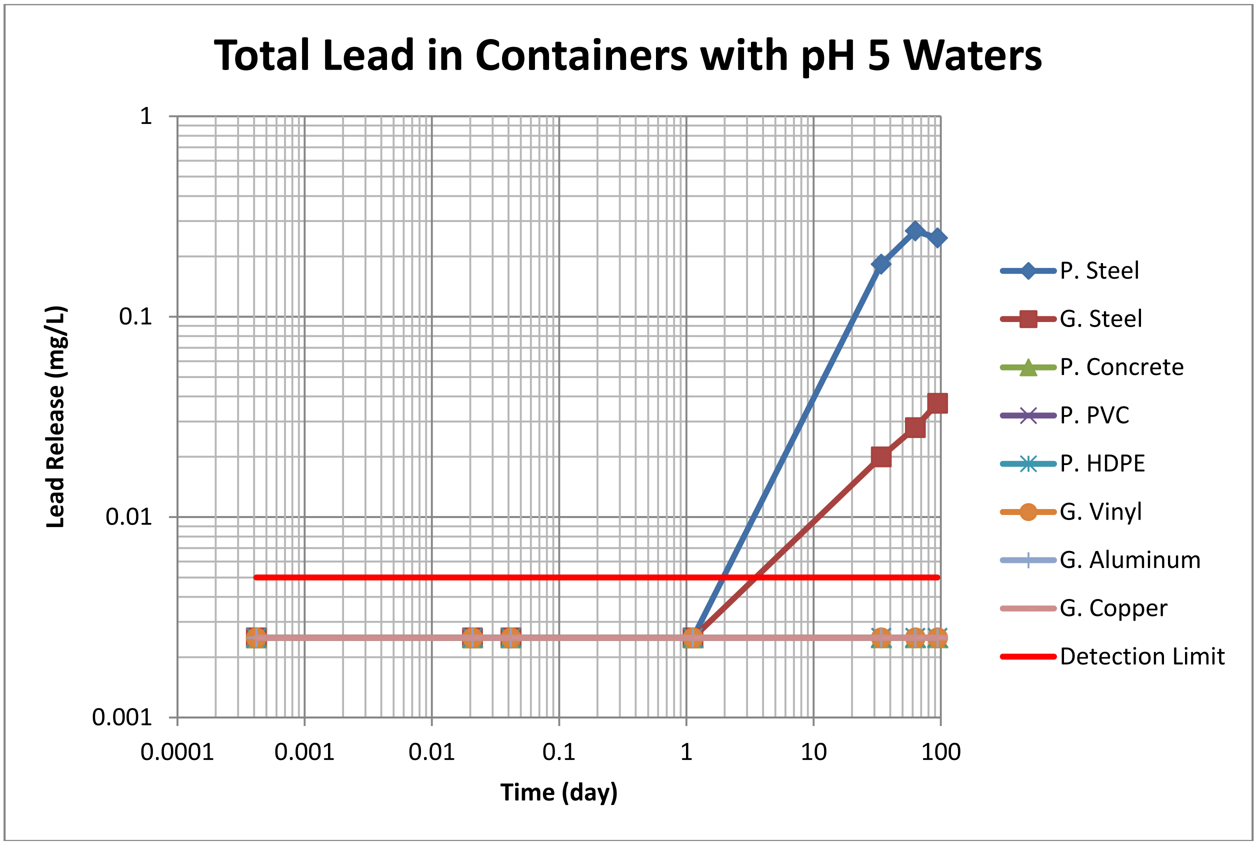


Figure 3-12. Time series of lead releases from various gutter and pipe materials under controlled pH 5 conditions (Ogburn, et al. 2012).

The water quality parameters were plotted as a function of time for different pipe and gutter materials on the same graph. Figure 1.16 is another exploratory data analysis plot: group box and whisker plots for zinc releases from various pipe and gutter materials immersed in bay and river waters during different exposure times. The box plot for the plastic materials (vinyl, PVC, and HDPE) represent all the data combined (for bay and river waters and for short and long exposure times). As expected, zinc releases from plastic materials were significantly lower than from galvanized materials. The 75thpercentile lines of the box and whisker plot for plastic materials are located much lower than the medians of box and whisker plots for galvanized materials, therefore the pairs of groups of plastic materials and galvanized materials are likely significantly different at the 95% confidence level. However, there was no statistically significant difference between the box plots of galvanized steel pipe and gutter materials during short exposure time, and also there was no statistically significant difference between box plots of galvanized pipe and gutter materials during long exposure times. Zinc releases from galvanized materials increase with exposure time. There were statistically significant differences between zinc releases from galvanized materials during short and long exposure times, as indicated on Figure 3-13.

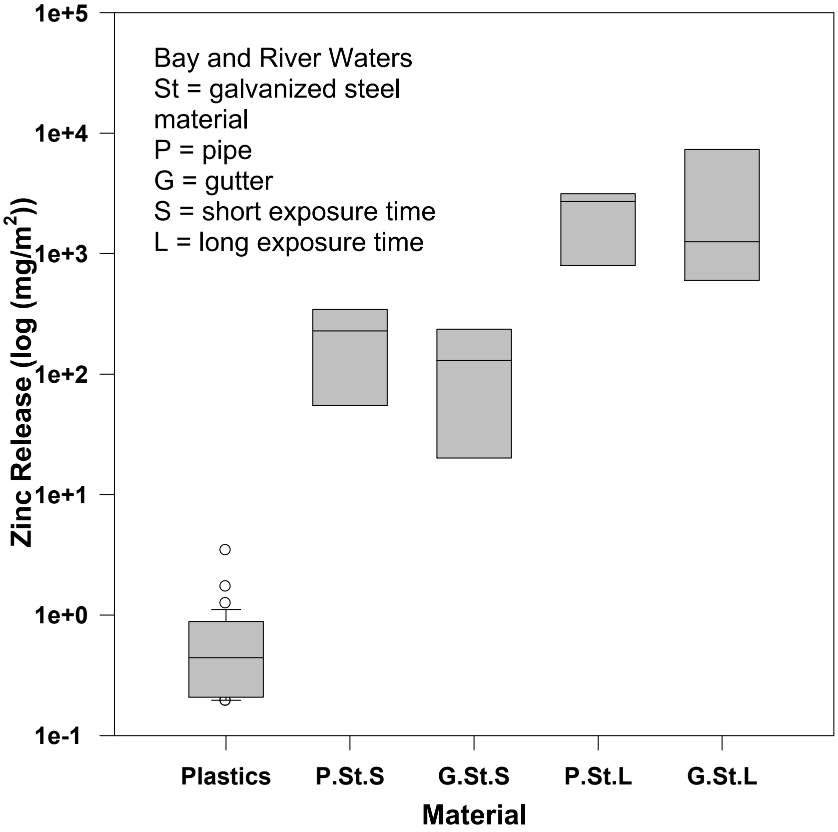


Figure 3-13. Group box plot of zinc releases from different construction materials.

Probability plots show the possible range of the values expected, their likely probability distribution type, and the data variation (Burton and Pitt 2002). Figure 3-14 is a normal probability plot of zinc releases from a galvanized steel pipe section submerged in bay water. The p-value of the Anderson Darling test for normality is greater than 0.05, indicating that the data population distributions not statistically different from a normal population distribution, allowing certain categories of statistical analyses (after appropriate log transformations).

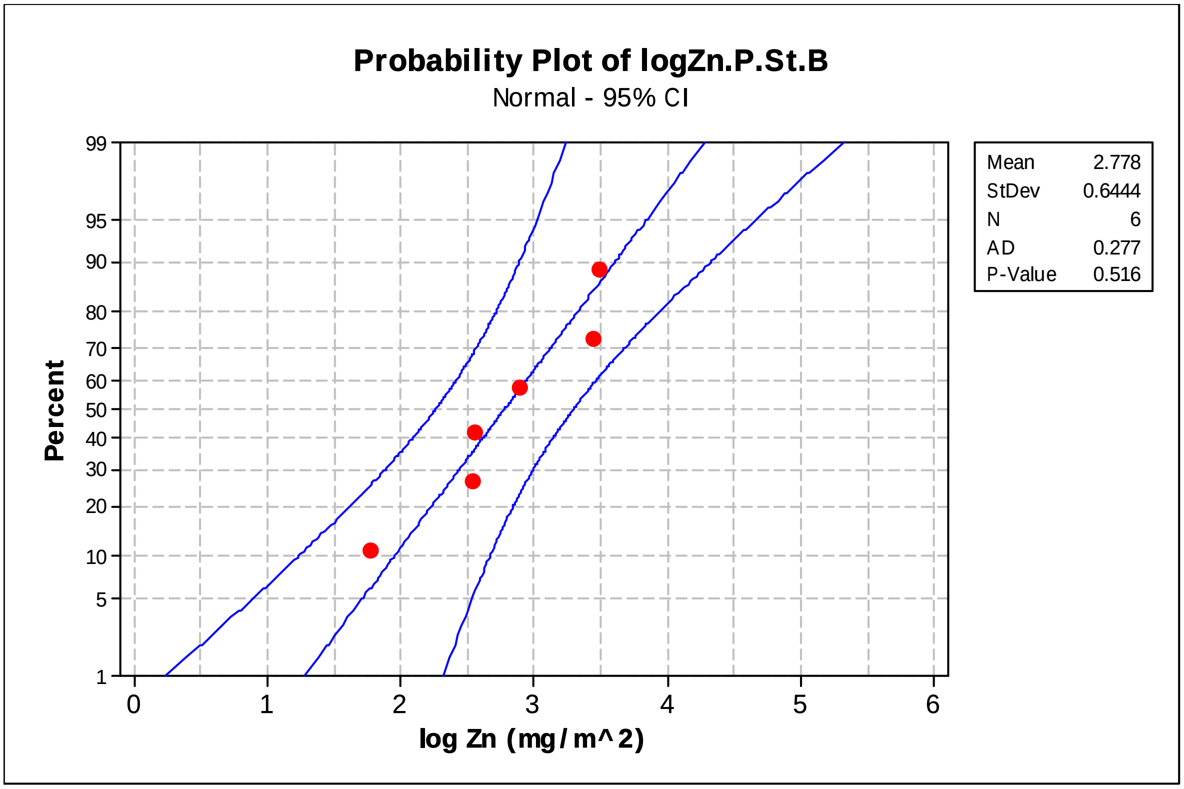


Figure 3-14. Probability plot of zinc releases from galvanized steel pipe immersed in bay water.

Statistical Significance Measures and Power Analysis

A Type I error refers to rejecting the null hypnosis when the null hypothesis is actually true (a false positive) (Burton and Pitt 2002, Devore 2008). The calculated alpha (α) from statistical tests is the probability of making this Type I error. The alpha value is often referred to as the significance level, or confidence, of the test. The typical alpha value of 0.05 is usually chosen, meaning accepting a 5% risk of having a Type I error. Consequently, the confidence of not having a false positive is 1 – α (or 95% if the alpha is 0.05). A Type II error is not rejecting the null hypnosis when the null hypothesis is actually false (a false negative) (Burton and Pitt 2002, Devore 2008). Beta (β) is the probability of making a Type II error. Power is the certainty of not having a false negative = 1 – β (Devore, 2008; Burton and Pitt, 2002, http://www.minitaB-com/en-US/training/tutorials/accessing-the-power.aspx?id=1742&langType=1033). A common level of beta is 0.20 with a resulting power of 80%. If ignored (unfortunately common), the false negative rate then becomes 50%. The statistical power, or the sensitivity of a statistical test, is the probability that the test will detect a significant difference or an effect among the groups if a difference or effect truly exists. The closer the power is to unity, the more sensitive the test. The power is the sensitivity of the test for rejecting the hypothesis. For example, for an ANOVA test, it is the probability that the test will detect a difference amongst the groups if a difference really exists (Burton and Pitt 2002).

During a statistical test of previously obtained data, alpha and beta values cannot be distinguished: a decrease in the alpha value reduces the Type I error but also results in a larger value of beta increasing the probability of making a Type II error. Therefore α and β values need to be chosen during the experimental design phase such that to have the smallest β at the largest α values that can be tolerated (Devore 2008). The experimental design (selecting the sample numbers needed, for example), needs to ensure that both adequate confidence and power can be achieved.

A p-value reveals information about the strength of evidence against the null hypothesis and permits a conclusion at any specified level of α. If the p-value is below the specified significance level α, the null hypothesis is rejected and the results are considered to be statistically acceptable at that level of significance (Devore 2008). Failure to reject the null hypothesis does not mean that the sample sets are the same (if doing a comparison test), only that insufficient numbers of data observations are available to detect the significance difference for the conditions being examined.

Normality Tests

The applicability of most statistical tests is dependent on their probability distribution types. Probability plots and the Kolmogorov-Smirnov tests can be used to determine if the data are normally distributed (Systat Software, Inc., 2008) and therefore able to use a broad range of standard statistical tests. If not normally distributed, the statistical tests available are more limited. Using incorrect statistical tests results in very low power.

Data are plotted on normal probability graphs in order to visually identify whether the data are normally distributed. If the observations are roughly normal (from the normal distribution), then the points plotted on normal probability graphs will roughly plot as a straight line (Burton and Pitt, 2002). If observations do not fit reasonably well on a straight line, the data are not normally distributed. Typically, data transformations (log10) are also used to identify possible log-normal probability distributions.

The Kolmogorov-Smirnov test uses a P value to determine whether the data passes or fails the normality test (Systat Software, Inc., 2008). If the computed P value is greater than the selected alpha value (usually 0.05), the test of normality passes (the data cannot be shown to be significantly different from the normal distribution), however, if the computed P value is less than or equal to the critical alpha value, the hypothesis of normality is rejected and we can conclude with 95% confidence that the observations do not follow the normal distribution.

Comparison Tests with More than Two Groups using Analysis of Variance

Analysis of Variance (ANOVA) tests are used to test the hypothesis that the means among two or more groups (treatments) are equal (Systat Software, Inc., 2008; Devore 2008). This test is valid if the treatment populations are normal and have the same variance. Assumptions of normality and equal variance need to be checked. It is often recommended to transform the data to meet the ANOVA assumptions of homogeneity of variance and normality. The square root, log, and arcsin-square root transformation are used most often, with log10 transformations being most common for water quality analyses (Burton and Pitt 2002).

One-way ANOVA can be used to see if varying the levels of one factor affects the response (if the data are normally distributed) (Devore 2008). One–way ANOVA were used to determine whether the samples collected after 1, 2, and 3 month of exposure could be combined together as replicates into a single “long term” exposure group for each constituent for some of the comparison tests, and to determine if the samples collected after 0.5 hr, 1 hr, and 27 hrs of exposure during first testing stage (and after 1hr, 27 hrs, and 1 week during the second testing stage) could be combined together as replicates of “short term” exposure periods. If the normality assumption doesn’t hold, the Kruskal-Wallis test can be used. A P-value of 0.05 was used to reject the hypothesis. This test identifies if there are at least one subset that is significantly different from the other subsets. Unfortunately, the test does not identify which subgroup(s) are different from the others (Navidi 2006). Post-hoc tests are used to determine which groups are different from the others (Burton and Pitt 2002).

If the assumptions of normality and equal variance do not hold, the Kruskall-Wallis test can be used to determine if there is a statistically significant difference between the median values among the treatment groups affected by a single factor (Systat Software, Inc., 2008). The populations that samples are drawn from do not have to be normal or have equal variances. The P-value of 0.05 was used.

Two-way Analyses of Variance (ANOVA) is used to determine whether varying the levels of either the row factor, the column factor, or both factors affect the treatment means (response) (Navidi, 2006). ANOVA requires that within any treatment, the observations are a simple random sample from a normal population with roughly equal variances for all treatments. The test will tell if there are differences among the groups, i.e. if at least one group is statistically different from another one, but it will not tell which groups are different. Post-hoc procedures must be used to determine which groups are different from one another. Post-hoc tests discussion can be found in section 3.5.5.

Post-Hoc Tests

An ANOVA or Kruskal-Wallis tests determines whether at least one treatment statistically differs from the others; however, they do not identify which are different (Navidi 2006). Post hoc tests can be used to identify the significant treatments that are different from the others (Burton and Pitt 2002).

The Mann-Whitney test can be used as a post hoc test. The Mann-Whitney Test was performed to see if there is a statistically significant difference between the medians of two groups affected by a single factor (pairwise comparisons). This is a nonparametric test and does not require normality or equal variance (Systat Software, Inc., 2008). Group box and whisker plots were also prepared showing the ranges and comparisons between the different groups. These plots show many important characteristics of the data: center, spread, the extent of departure from symmetry (skewness), and unusual conditions. The advantage of a boxplot is that it is unsusceptible to a few unusually large values because it is based on medians and forth spread (which is the difference between the median of the largest half of the observations and the median of the smallest half of the observations) (Devore 2008). The grouped box and whisker plots were used to examine the range of water quality parameter within and between different piping/gutter/tank materials. If the 25 and 75 percentile lines of a box and whisker plot are located higher or lower than the medians of other box and whisker plots, then the groups are likely significantly different at the 95% confidence level, for moderate numbers of samples (Burton and Pitt, 2002). The group box and whisker plots were also used to examine the overlapping and separation of some groups relative to others to see if some data groups could be combined.

Comparison Tests with Two Groups

The paired t-test is a commonly used standard parametric statistical method that has high power if used correctly. It assumes that the observed treatment effects are normally distributed. The test examines the changes that occur before and after a treatment on the same individuals and determines whether or not the treatment had a significant effect (Systat Software, Inc., 2008). This test examines the changes rather than the values observed before and after the treatment. The paired t-test can be used to see if the effect of a single treatment on the same individual is significant. For paired t-tests, the number of data observations in each set must be the same, and they must be organized in pairs, in which there is a definite relationship between each observation in each pair of the data points (such as concurrent before and after treatment samples).

The sign test can be used as a simple paired test for non-normally distributed data (Burton and Pitt 2002). However, a test with more power is the Wilcoxon Signed Rank Test. This test is a nonparametric paired test and is used to determine whether the effect of a single treatment on the same individual is significant. As noted, this is a non-parametric test and should be used when the distribution of the observed effects are non-normal (Systat Software, Inc., 2008).

Spearman Correlation Analyses

Spearman correlation analyses were conducted to measure the degree of association between water quality parameters, toxicity of the samples, time of exposure and the material type. Nonparametric Spearman correlation tests were used because some of the data were not normally distributed (a requirement for the similar Pearson correlation analyses). Parameters examined were Pb, Cu, and Zn concentrations, pH, conductivity, and toxicity at 5, 15, 25, and 45 minutes of bacteria exposure, plus the time of material exposure to the experimental water. Metal concentrations that were below detection limit were substituted with half of the detection limit. Appendix D shows the correlation matrix for the associations between these parameters for different drainage materials during the buffered and natural pH tests. High spearman correlation coefficients (at or above 0.75) are highlighted in bold.

For all materials during the buffered pH tests, toxicity was negatively correlated with water pH (toxicity increased as the pH decreased). However during the natural pH experiments, positive correlations were observed (toxicity increased as the pH

increased) for all the materials, with the exception of galvanized steel pipes and gutters. These toxicity relationship results are likely associated with thepH values being outside of the optimum range for the test bacteria for many of the test conditions and are not related to other experimental factors. For galvanized steel materials under natural pH conditions, there was a strong positive correlation between the toxicity and zinc releases, and for copper materials the toxicity was associated with copper losses. It was found that for majority of the materials (galvanized steel, copper, PVC, aluminum) under controlled pH conditions the toxicity is highly correlated with water conductivity. Toxicities at different times of bacteria exposure were highly correlated to each other, with no apparent change in toxicity mechanism with exposure time (as sometimes occurs if both organic and metallic toxicants are present). For galvanized steel materials, zinc concentrations were strongly associated with the exposure time, and similarly, for copper materials, the copper concentrations were also highly correlated with exposure times. Spearman correlation analyses showed that for galvanized steel materials under natural pH conditions, zinc releases were responsible for most of the toxicity (correlation coefficient >0.77). For the copper materials immersed into natural pH bay and river waters, the toxicity was mainly associated with copper releases.
The identified correlations between pH and metal releases, pH and toxicity, conductivity and metal releases, conductivity and toxicity, exposure time and metal releases, and exposure time and toxicity, were used in empirical model building covering all of the experimental and exposure conditions.

Cluster Analyses

Cluster analyses were performed to further investigate how pH, conductivity, material, and time of exposure affect the metal releases and toxicity of the samples. This analysis was conducted to examine complex associations between these parameters. The variables were standardized to a common scale to diminish the effects of scale range differences. Appendix D shows the results of the cluster analyses. Figure 3-15 is a dendrogram prepared from the cluster analyses for different water quality parameters for steel pipe sections during buffered pH tests (pH 5 and 8 test conditions).This figure shows that lead and copper concentrations were highly correlated with pH and conductivity. Metal releases, pH, and conductivity influenced the toxicity. The toxicity was also affected by time of exposure. Conductivity was closely associated with pH and metal releases.

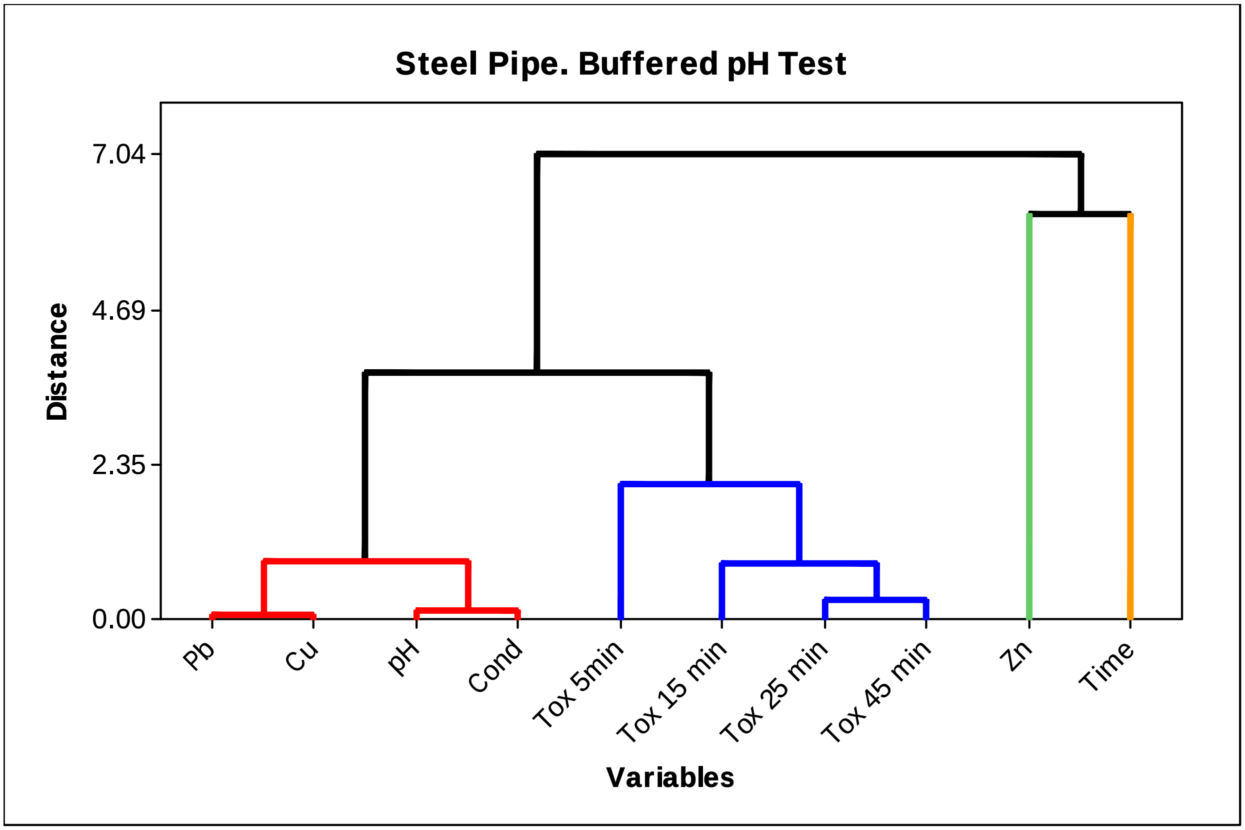


Figure 3-15. Dendrogram from cluster analysis for water quality parameters. Galvanized steel pipe. Buffered tests.

Cluster analyses were performed for each gutter and pipe material examining the data for buffered and natural pH tests. The dendrograms (Appendix D) were constructed for the same data that were used to compute the correlation matrices. Spearman correlation analyses confirmed that metal releases, conductivity, pH, and time of exposure all influence the toxicity. There were also high correlations between toxicity and pH, toxicity and metal releases, toxicity and conductivity, metal releases, and time of exposure. Cluster analyses showed that pH also affected the metal releases. The toxicities measured at 5, 15, 25, and 45 min of bacteria exposure to the sample water were closely related, as expected, due to the toxicity being mainly associated with heavy metals. Pb, Cu, and Zn concentrations were highly correlated with pH and conductivity for all materials, with the exception of galvanized materials for which zinc was in a separate cluster. The correlations between toxicities and pH and metal concentrations were greater for galvanized steel materials compared to the other materials.

Also, cluster analyses were used to determine groups of similar materials. These analyses were performed for all pipe and gutter materials using buffered and natural pH test results (Figure 3-16). Materials of galvanized steel pipe were similar to galvanized steel gutter, as expected. Generally, PVC, HDPE, vinyl, and aluminum materials also were closely associated; concrete and copper materials were in separate groups from the rest of the materials.

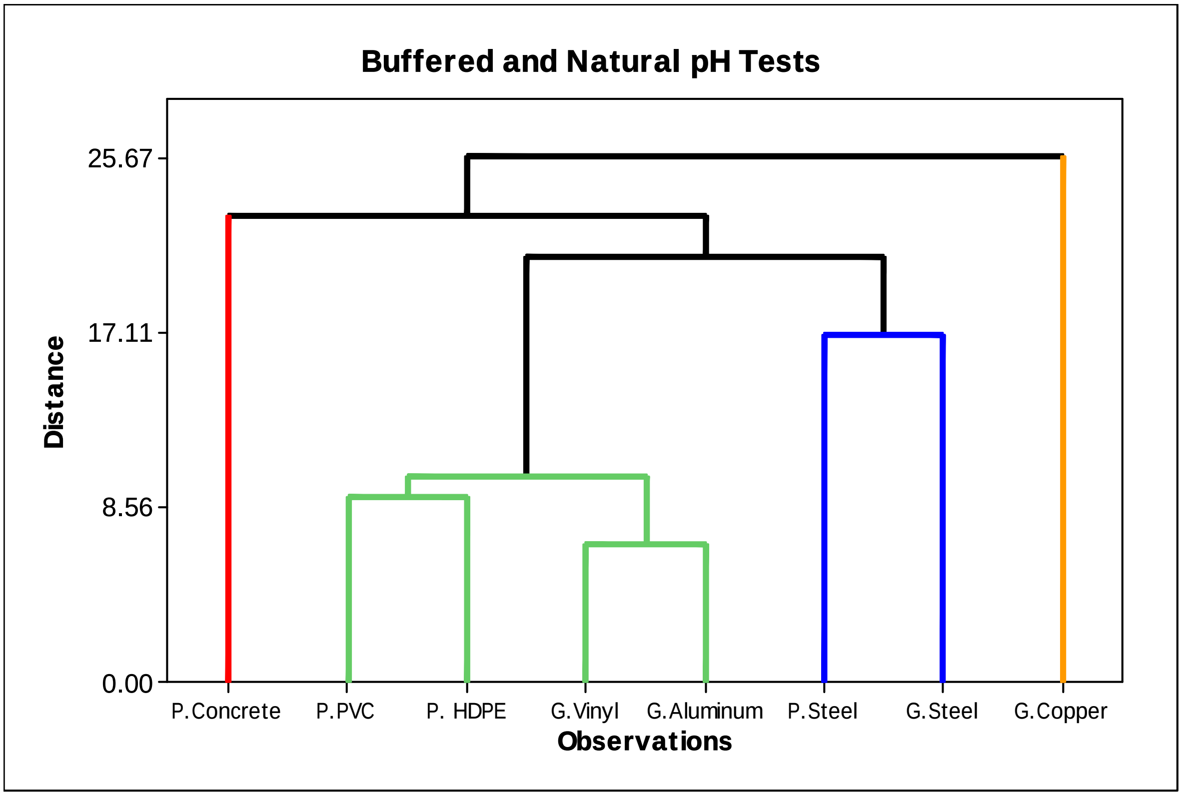


Figure 3-16. Dendrogram from cluster analysis for pipe and gutter materials. Buffered and Natural pH Tests.

The influence of pH, conductivity, and time of contact on toxicity and metal concentrations, as well as groupings of similar materials, resulted in supporting their use in model building.

Principal Component Analyses

Next, Principal Component Analyses (PCA) were performed to identify groupings of samples having similar characteristics. PCA transforms the original set of variables into a smaller set of variables that represents most of the information present in the original dataset (Jensen 2005). Principal components are derived from the original variables such that the first principal component explains the largest proportion of the variance of the data, with subsequent components explaining smaller fractions of the data variance. PCA was conducted on the data on all pipe and gutter materials under buffered and natural pH conditions. Minitab 16 (Minitab, Inc.) software was used for these analyses.

Scree plots (Figure 3-17) show eigenvalues of the correlation matrix of eleven sample variables, while Table 3-10 shows how much of the total variance is explained by each principal component group. The first four principal components accounts for about 78% of the total variance and can reasonably represent the data set. The fifth principal component explains another 8% of the total variance. Table 3-11 shows loadings of the first four principal components. Toxicity values have high loadings on the first principal component. The second principal component has high loadings of time, Pb, and Zn. Copper and Zn have large loading on the third principal component, while pH, conductivity, and material type are included in the fourth principal component.

The relationships between loadings of the first two principal components (that account for approximately 57% of the total variance) are shown in Figure 3-18.The vectors on this plot correspond to examined parameters. A vector's length is comparable to its component loading. Figure 3-18 shows that the first principal component has a large loading associated with toxicity. The second principal component has high loadings associated with time, lead, and zinc, and accounts for exposure time and lead and zinc releases. High loadings of principal components are highlighted in bold. Score plots of the first two principal components (Figures 3-19) show groupings of samples with comparable principal component loadings and similar water quality characteristics. The group "other materials" on the graphs includes concrete, PVC, HDPE, vinyl, and aluminum materials. The circled group of data on Figure 3-19 is mostly comprised of the samples with all materials that are exposed to pH 5 water conditions and is located in the upper corner of the graph indicating large loadings of toxicity and pH associated with the first principal component.

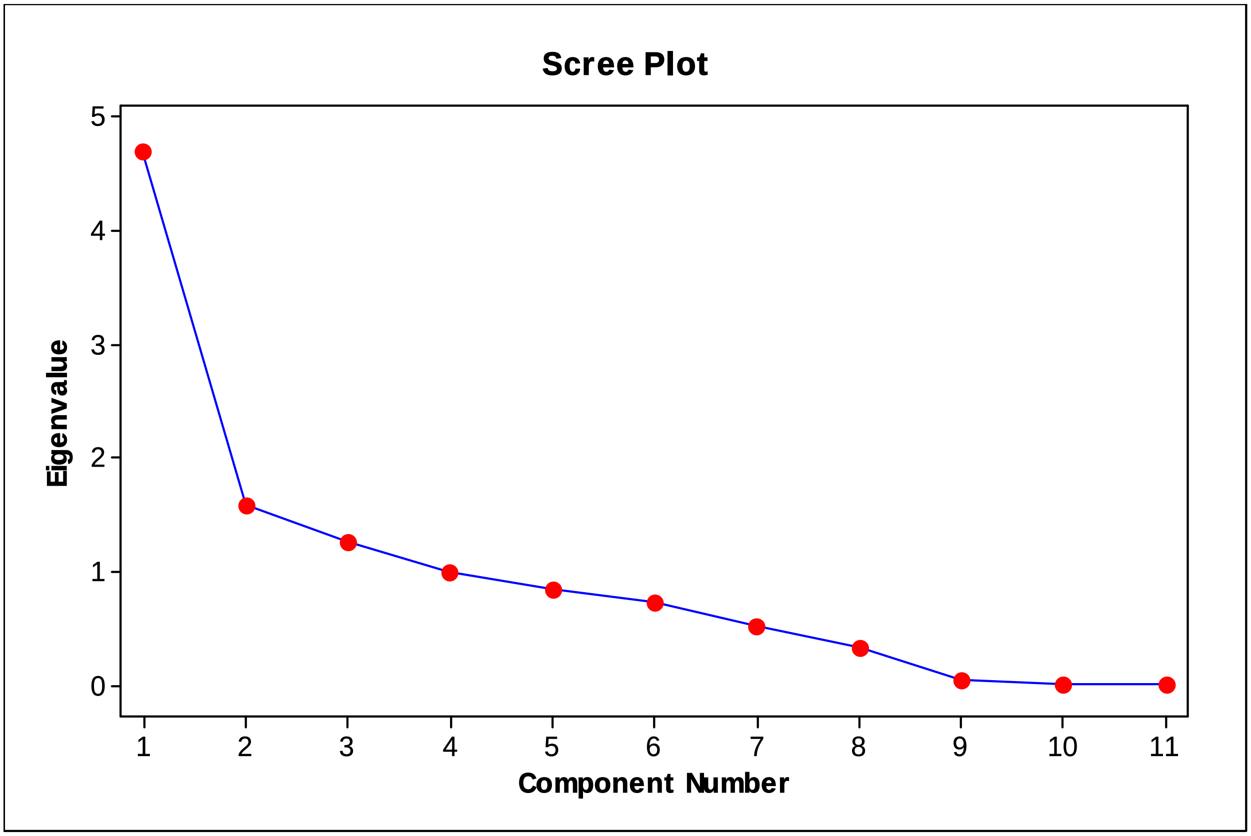


Figure 3-17. Scree plot of sample characteristics. All samples combined.

Table 3-10. Percent of total variance explained by the first six principal components.

Principal Component	Eigenvalue	Variance Explained by a Component, %	Cumulative Variance, %
1	4.7	42.8	42.8
2	1.57	14.3	57.1
3	1.26	11.5	68.6
4	1.00	9.1	77.6
5	0.84	7.7	85.3
6	0.72	6.6	91.9

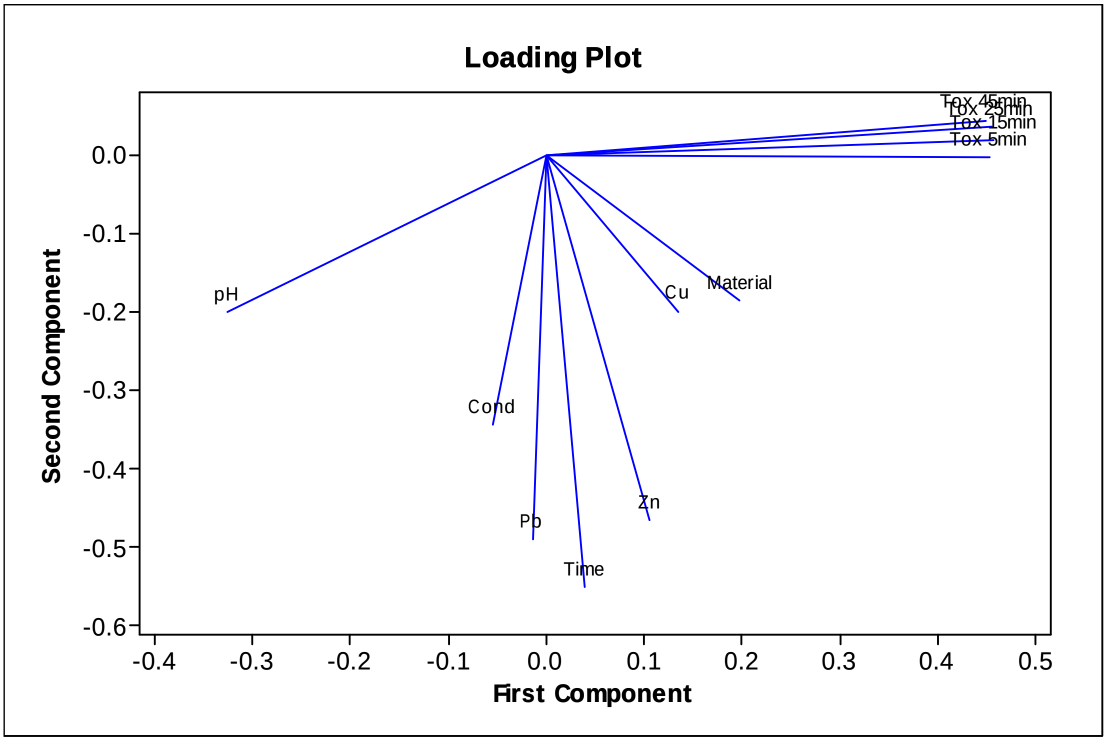


Figure 3-18. Principal component loadings for sample characteristics. All samples combined.

Table 3-11. Loadings of the principal components. All samples combined.

Variable	PC1	PC2	PC3	PC4
Pb	-0.013	**-0.491**	0.318	0.110
Cu	0.135	-0.199	**-0.606**	-0.181
Zn	0.106	**-0.467**	**0.426**	-0.352
pH	-0.325	-0.201	-0.127	**-0.474**
Cond	-0.055	-0.344	**-0.425**	**0.561**
Tox at 5min	**0.452**	-0.003	0.002	0.096
Tox at 15min	**0.457**	0.019	0.024	0.025
Tox at 25 min	**0.454**	0.036	0.040	-0.023
Tox at 45 min	**0.448**	0.045	0.048	-0.045
Time	0.039	**-0.552**	0.023	0.242
Material	0.198	-0.186	-0.385	**-0.470**

Footnote: High principal component loadings are highlighted in bold.

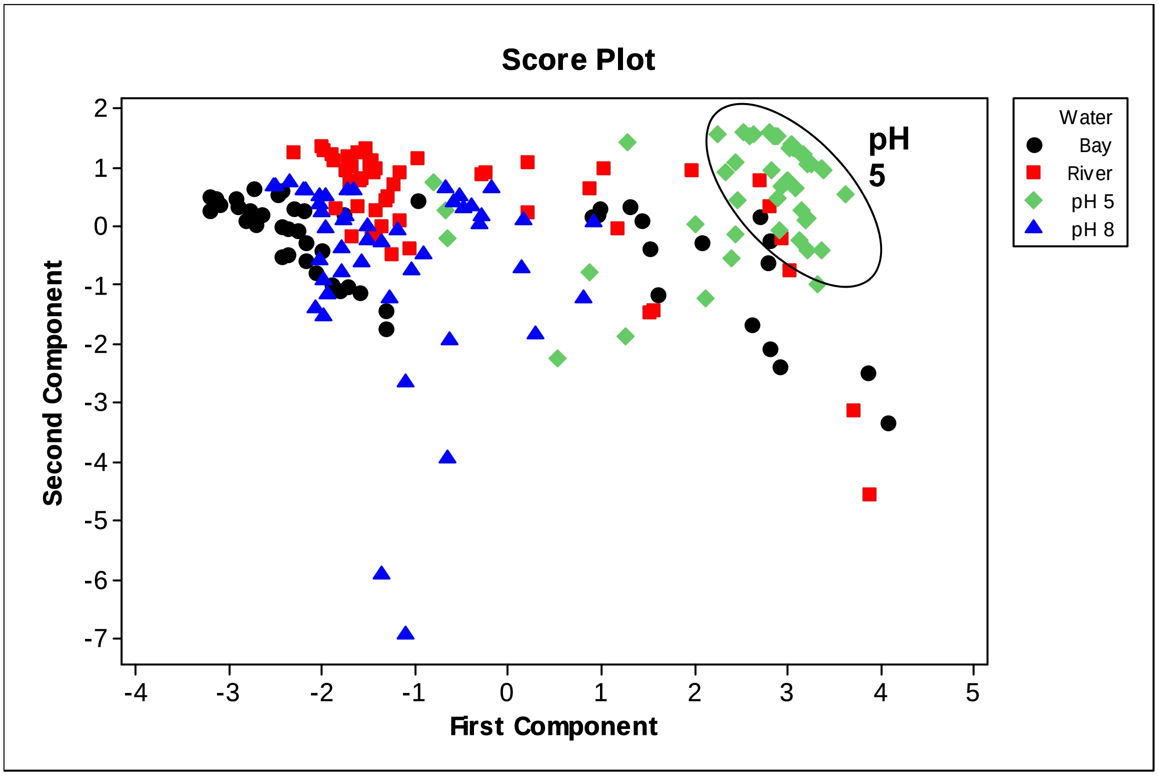


Figure 3-19. Score plot of principal components for sample characteristics. All samples combined.

Principal component analysis helped to indentify groupings of samples with similar characteristic. Samples with concrete, plastic, and aluminum materials under controlled pH 8 conditions had low lead and zinc releases and low toxicities. On the other hand, the samples with controlled pH 5 waters were associated with high toxicity.

Factorial Experiment

Factorial experiments are used to examine a set of factors that are independent variables and identify which of them (singly or in combinations) are significant factors in explaining the magnitude of the variability produced by the experimental factors. The test results were used to build an empirical model (Berthouex and Brown 2002). The basic experimental design for testing two factors (pH and time) is shown in Table 3-12.

Table 3-12. Factorial experimental design for two factors.

Experiment No.	pH	Time	pH*Time
1	+	-	-
2	+	+	+
3	-	-	+
4	-	+	-

Full 2^2 factorial experiments will therefore require four experiments representing all combinations of conditions in order to examine the main effect and all possible interactions of those factors (only one interaction term for this simple two-way test). The plus and minus signs represent different levels (such as high and low values) for each main factor during the experiments. This table of contrasts shows the main factors and the one possible two-way interaction.

Factorial analyses are used to determine which factors and their interactions have an important effect on the outcome (are significant) (Navidi 2006). The null hypothesis for each factor was tested assuming that the effect is equal to 0. If the null hypothesis is rejected, a conclusion can be made that the factor affects the outcome (the factor is significant) (Navidi 2006, Devore 2008).

For each pipe and gutter material, full 2^2 factorial analyses were conducted for each material to determine whether exposure time (the data sorted by short and long exposure periods), pH value (5 and 8), and the interaction of these factors affect the pollutant releases in mg per area of the material(during the first stage of the experiment). Effects of pH, time, and pH x time interactions were estimated along with the pooled standard error. The two factors that were studied: pH of rain water at 2 Levels (5 -, 8 +) and time of contact at 2 Levels (short -, long +). pH values for the design were chosen based on studies summarized by Pitt, et al. (2004).

The replicates for each experiment were averaged and the value entered into a table of contrast coefficients (or Yates's algorithm methods can be used) (Box, et al. 1978). Two Way-ANOVAwas used to determine if the effects were significant. Also, the effects can be plotted on normal probability graphs in order to identify which effects and interaction terms are significant. If the observations are roughly normal (from the normal distribution), then the points plotted on normal probability graphs will roughly plot as a straight line. If any of the extreme values plotted do not fit reasonably well on a straight line, they are likely causing significant effects on the predictions of interest, while those effects that roughly fall on the straight line are likely random noise (not causing any significant effect) (Boxet al., 1978).

Models were developed which contain the significant factors affecting the parameter outcome (Burton and Pitt 2002). Residuals were also examined to determine if the model was reasonable and met the calculation requirements. Residuals are the unexplained variation of a model and must satisfy the assumptions of being independent, having zero mean, having constant variance σ^2, and be normally distributed (Burton and Pitt 2002). Graphical analyses of model residuals were conducted to determine if these requirements are met.

The model was checked by plotting the residuals on normal probability graphs. If all the points from this residual plot lie close to a straight line, this would confirm the assumption that effects (other than those off the straight line in the normal probability plot of the effects) are readily explained by random noise (Box, et al. 1978). To check if there is a trend of residuals and if the residuals are homoscedastic and have zero mean, the graph of residuals vs. fitted (predicted) values were also constructed. To check the independence of the residuals, the plot of residuals vs. order in which the observations were made is necessary (Navidi 2006).The models can be used to predict the contaminant concentration for each pipe and gutter material by focusing on the significant factors.

If a factor does not interact with another one(s), then the main effect of that factor will be considered individually. However, if one factor interacts with another one(s), then the factors with interactions will be interpreted jointly. The effects of the row levels depend on which column levels they are paired with, and vice versa, and the main effects can be misleading (Navidi 2006, p. 669).

The standard errors were also calculated as estimates of the standard deviation of the effects under consideration and were used to help identify the significant effects (Box, et al. 1978).The pooled estimate of run variance were calculated using the following formulas (Box, et al. 1978):

$S^2 = (v_1 * S_1^2 + v_2 * S_2^2 + \dots + v_g * Sg^2) / (v_1 + v_2 + \dots + v_g) =$
$= ((n_1-1) * S_1^2 + (n_2-1) * S_2^2 + \dots + (n_g-1) * Sg^2) / ((n_1-1) + (n_2-1) + \dots + (n_g-1))$
with $v = v_1 + v_2 + \dots + v\ g$ degrees of freedom

Where:
g = the number of sets of experimental conditions that were replicated.
ni = the number of replicate runs made at the ith set yield an estimate si^2 of σ^2 having vi = ni-1 degrees of freedom.
di = the difference between the duplicate observation for the ith set of conditions.
If there are two replicates (ni = 2, vi = 2 – 1 = 1), the equation for ith variance:
$Si^2 = di^2/2$
Si^2=ith variance, then
$S^2 = \Sigma\ di^2/2g$
S = sqrt (S^2) = (the pooled estimate of run standard error) with v degrees of freedom
The variance of each effect was calculated using the formula:
V (effect) = $4 * \sigma^2/N$
σ^2 will be estimated with S^2
N = the number of runs
The estimated standard error of an effect was calculated using the formula:
St. error = sqrt (V (effect))

Using the P-value of the ANOVA Analysis (or Factorial Effect/Pooled Standard Error Ratio of the Factorial Analysis), the observations were combined into groups for each pipe and gutter according to whether there was or was not an effect of pH, time, and interaction of those factors.

Correlation Analyses

Simple correlation analyses (such as the Pearson correlation matrix) measure the strength of association between two variables, and can be a measure of the certainty of prediction. The correlation coefficient r is a number between -1 and +1 (Navidi 2006). A correlation of -1 indicates that there is a perfect negative relationship between the two variables, with one always decreasing as the other increases. A correlation of +1 indicates there is a perfect positive relationship between the two variables, with both always increasing simultaneously. A correlation of 0 indicates no relationship between the two variables (Systat Software, Inc., 2008).

Pearson product moment correlations were used to determine the strength of the associations between pairs of variables without regard to which variable is dependent or independent. This is a parametric test that assumes a normal distribution and constant variance of the residuals. This procedure was used to evaluate the strength of association between water quality characteristics and released contaminant concentrations. High correlation coefficients between variables indicate that one variable can be predicted by the other one (Systat Software, Inc., 2008).

Model Building using Statistical Results

To build an empirical model, factorial experiments were utilized to determine the significant factors, materials, exposure times, and their combinations affecting contaminant concentrations. The data were combined into groups based on the calculated effects from the factorial analysis. Based on this test, materials were identified that can be used for long term storage of water and for short term exposures such as for roof gutters and piping of water. Also, cluster and principal component analyses were performed on raw data to determine associations between different materials and water quality conditions and contaminant loads. Pearson correlations were calculated to quantify associations between significant materials and water quality parameters and contaminant concentrations. Finally, regressions were performed on time series plots to predict pollutant release with time. A model identifying critical materials and exposure conditions or critical combinations of materials and exposure conditions was finally developed based on these prior analyses.

Regression Analyses

Regression methods use the values of one or more independent variables to predict the value of a dependent variable. The regression coefficients are determined by minimizing the sum of the squared residuals (Systat Software, Inc, 2008). Regression is a parametric statistical method that assumes that the residuals (differences between the predicted and observed values of the dependent variables) are normally distributed with constant variance. The residuals must be independent, and have zero mean, constant variance, and be normally distributed (Systat Software, Inc., 2008). The normal probability plot (and related statistical tests, such as the Anderson-Darling test (Minitab, Inc.) of the residuals can be used to determine whether the residuals are normally distributed. To determine whether the residuals have constant variance and zero mean, the scatterplots of the residuals versus the predicted values can be used and the plots need to indicate a relatively constant width of a flat band of residuals (Burton and Pitt

2002, Navidi 2006, Berthouex and Brown 2002). If the requirements of normality and constant variance hold, then the fitted model can be assumed to be correct (but only if it makes physical sense!). The coefficient of determination (R^2) is the proportion of the variance in y explained by the regression equation (Navidi 2006, Burton and Pitt 2002). ANOVA can also be used to test the significance of the regression coefficients (Burton and Pitt 2002, Berthouex and Brown 2002).

Bacteria Breakpoint Analyses

There is considerable reason to expect that the growth or decline (change in MPN over time) of bacterial populations is a first order (log-linear) relationship, arising as the sum of binary fission and death of individual cells (both dependent on the number of viable cells at any given time). This pattern, well established in textbooks currently in use (e.g., Madigan, et al. 2002) is of the form:

$$\log(MPN / \text{initial } MPN) = k * t \qquad \text{(X.1)}$$

where:

k = net growth constant (slope of the function), and
t = time (hours).

Changes in the slope of log(*MPN*) versus time are likely caused by a change in environmental conditions or a change in the makeup of the subject population.

Introduction of a viable bacterial inoculant to a new (habitable) medium (batch style) typically results in up to four distinct phases of population behavior: lag, exponential growth, stationary, and exponential death (Madigan, et al. 2002):

Lag Phase

The lag phase is characterized as a period of adaptation to the new environment, in which little or no population growth occurs, and its length is dependent on differences between the environmental history of the inoculant and the environmental conditions of the new medium. Inoculants transferred to environments similar to their historical conditions may exhibit little or no lag time; for transfers to a very different environment, lags may be considerable. Of course, if new conditions are so foreign to members of the inoculant population as to render it uninhabitable, individual cell death may occur until remnants of the inoculant population are viable (Madigan, et al. 2002: 144–5).

Growth phase

In the growth phase, the adapted (or naturally selected) population grows exponentially; population at any given time is dependent on the number of actively dividing members of the population present at previous times. Rate of growth is dependent on environmental conditions and genetic (metabolic mechanisms available) make-up of the population (Madigan, et al. 2002: 144–5).

Stationary Phase

The stationary phase (in which the population is static) represents conditions in which available nutrients (either from the original inoculant or from release by the lysis of dying cells) is balanced by a buildup of refractory (and often inhibitory) waste products (Madigan, et al. 2002: 144–5).

Death Phase
The death phase (dominated by waste build-up) is exponential.

Any or all of these phases may occur (or, of course, may be missed by insufficient time density of sampling) and both environmental conditions and the genetic makeup of the population are relevant (Madigan, et al. 2002: 144–5). The four main environmental factors influencing bacterial growth are temperature, pH, and the availability of water and oxygen (Madigan, et al. 2002: 151). For terrestrial environmental surfaces, oxygen is unlikely to be a factor. For dry weathered pavements (without liquid moisture, between rains), pH is likewise probably unimportant. An important factor in cell death, however, is that of UVB exposure (Madigan, et al. 2002: 272–3), which is bactericidal, especially during cell division.

Because we cultivated our samples at constant conditions, a change in slope of log(*MPN*) versus time must be viewed as a population change. Population change may arise either through induction of new enzymes in individual cells, or through natural selection in the overall population.

Each combination (2^3 = 8 combinations of temperature, humidity, and UV exposure) of environmental conditions (treatments, combinations of environmental factors) was treated as a log-linear (first order) segmented (with unknown break points) model of normalized MPN with respect to time, and with continuity between the segments imposed (as shown below in Figure X.3, for example).The statistical analysis of such models is not straightforward. Hudson (1966) provides a graphic algorithm (for minimization of overall sum of squares of error, SSE, in the segmented model) and shows that the algorithm generally provides the maximum likelihood estimate (MLE) of the abscissa of an unknown breakpoint (*tBP*); he provides no information as to how likely that estimate may be (rendering inferences impossible). Feder (1975a; 1975b) proves that, provided the model is identified (i.e. includes no more hypothesized breakpoints than are present in the real population), and if no hypothesized tBP coincides with an abscissa of observation in the sample, then minimization of *SSE* (the MLE function) converges asymptotically to the true population breakpoint (BP). In the unidentified case (i.e. too many BPs assumed), the MLE function becomes indeterminate (estimates are not asymptotically normal). Feder’s second condition arises because a discontinuity exists in the SSE function at each observation point, rendering it non-differentiable there, allowing for a possible true BP existing between the MLE tBP and an adjacent sample observation point (i.e. the MLE function becomes unstationary). For the unstationary case, he proves that, as the number of sample observations increases, minimization of SSE of a pseudocase (in which the observation point coinciding with the tBP is removed from the dataset) still converges (at a known rate) to the true BP. Lerman (1980) adapts Feder’s work into a grid-search algorithm (again, only for the identified case, and incorporating the pseudocase approach when necessary) in which proposed tBPs are mapped across the range of the observations and the SSE at each is determined. Progressive refinement (finer grain) of the grid provides the tBP (minimization of the SSE versus proposed-tBP function). The exercise also provides an estimate of the variance of that tBP estimate, corresponding to the range (which need not be continuous or symmetrical) of proposed-tBPs. The range includes all time in which SSE is less than the minimum SSE plus its associated mean square of error (minSSE + MSE). Finally, Bai and Perron (1998) derive a log-likelihood ratio by which it can be determined whether the addition of a new breakpoint to an identified model results in a new model which is also identified, and publish critical values for that ratio.

We found the grid search method amenable to spreadsheet implementation. We first modeled each treatment by simple linear regression, resulting in a one-segment (R = 1, no breakpoints) model. We then hypothesized a breakpoint, and searched for it by Lerman's grid method. If the resulting MLE did not coincide with an observation point, we accepted the tBP and associated uncertainty indicated by the search (e.g. see Figure 3-21 below). We found grid search of the (asymptotically converging) pseudocase, however, problematic for the limited number of data points we had for each treatment (typically about 35). In one case, analysis of the pseudocase resulted in the tBP jumping about 100 hours (and across multiple observation points, an impossible situation) because of the slower convergence of the smaller, highly variable dataset. In these cases we retained the grid derived tBP and accepted the greater uncertainty inherent; we conducted a one-sided grid search solution around the tBP to establish one side of the variance range and took the adjacent observation point as the other (e.g. see Figure 3-22). Note that since we generated our grid search left-to-right (increasing t), the segment containing the discontinuity occurred between our tBP and the immediately preceding (adjacently left) observation. In both situations, the new model was tested against Bai and Perron's criteria for identification and, if it was identified, repeated the sequence. For the final model of each treatment, we numbered each tBP and intervening segments left-to-right (e.g. see Figure 3-23).

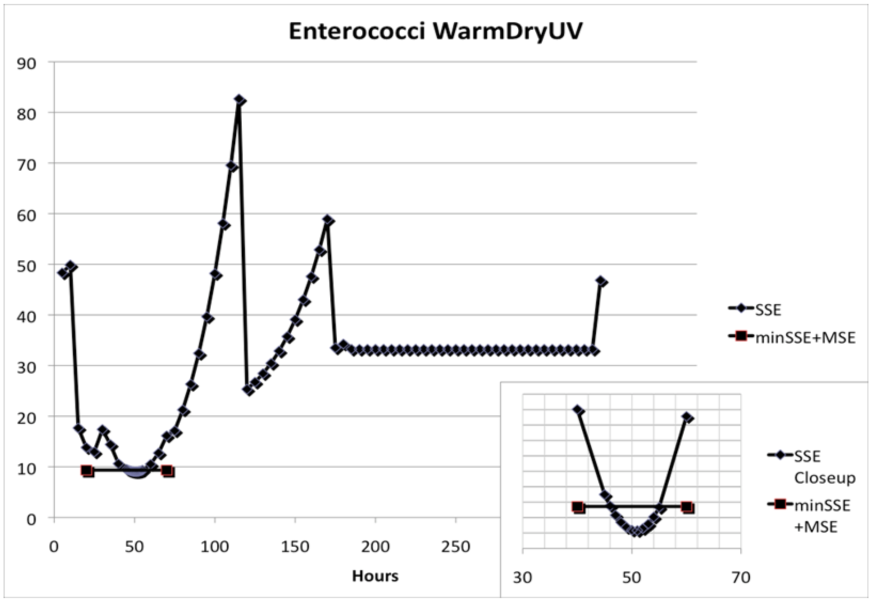


Figure 3-21. Example of graphic derivation of estimated tBP variance, normal case (with closeup inset).

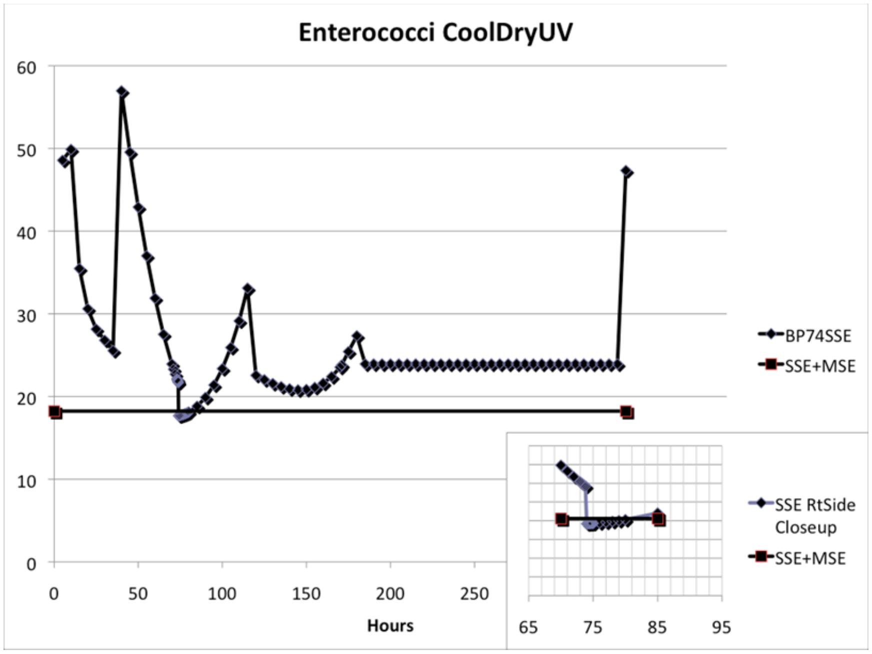


Figure 3-22. Example of right-sided graphic derivation of tBP variance, discontinuity on the left (with closeup inset).

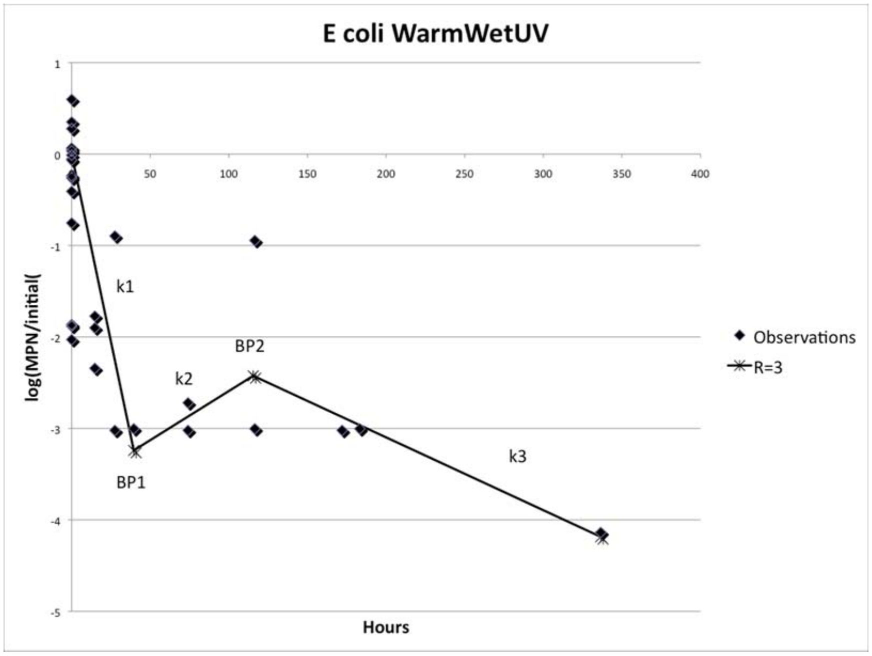


Figure 3-23. Example of a three segment (R = 3) treatment model with segment and breakpoint designations.

Methodology and Experimental Design Summary

Sampling

One of the objectives of this research was to determine if treatment at a conventional municipal wastewater system is reduced during periods of increased flows associated with stormwater I&I, and whether or not these increased flows affected the influent concentrations of the ECs. Specifically, we were most interested in identifying which unit processes were most effective for EC removal and how those process could be translated to wet weather flow treatment. The wet weather flow EC mass loadings were also quantified.

A total of 24 samples were collected for PAHs, pharmaceuticals, and pesticides during wet weather conditions, while 28 samples were collected during dry weather conditions. The wet weather samples were weather dependent and were therefore obtained when it was predicted to have moderate to large amounts of rainfall for the area. The dry weather samples were taken randomly, increasing variability. Samples were obtained manually as composite grab samples taken over a six hour period. Each sample was taken at the sampling locations as time composites over a two hour period, staggered to correspond to flow time at the treatment plant. The samples were obtained at: the inlet; at the primary clarifier effluent; at the secondary clarifier effluent; and after UV disinfection at the plant effluent. Each sample was obtained in one liter, pre-washed amber glass bottles having Teflon-lined lids.

Sheetflow samples were obtained at three sites in each of three land use locations during several rains. During many rains, no flows occurred at the turf areas. These samples were manually obtained using a scoop sheetflow sampler and poured into large glass sample bottles. The samples were then subdivided in the laboratory for the PPCP, PAHs, pesticides, trace metals, and indicator bacteria.

Eight gutter and pipe materials (some also used in tank construction) were subjected to long-term static leaching tests under different water conditions: buffered low and high pH waters and natural bay and river waters having different conductivities. The gutter materials included vinyl, aluminum, copper, and galvanized steel. The pipe materials included concrete, PVC (polyvinyl chloride), HDPE (high density polyethylene), and galvanized steel. Materials that are also commonly used in water tank construction include: aluminum, galvanized steel, concrete, PVC, and HDPE. All of the material samples for these tests were obtained as new specimens from a local building material supplier. The specimens used for the two controlled pH tests and bay and river water tests were nearly identical.

Analytical Methods

Much of the project effort was associated with method development for the analyses of the ECs in wet weather flows. The raw sewage and partially treated sewage matrices were especially troublesome concerning sample extractions, along with suitable detection limits for the analytical equipment available. Emerging contaminants, unlike major pollutants, occur in extremely low levels and need special methods for their detection. The methods used for the detection of emerging contaminants are commonly not available in many laboratories. Some of the most used analytical methods are High Performance Liquid Chromatography with Mass Spectrophotometer Detector (HPLC-MS), research grade Gas Chromatography with Mass Spectrophotometer Detector (GC-MS), and High Performance Liquid Chromatography with Electro Spray and Dual Mass Spectrophotometer Detectors (HPLC-ESI-MS-MS). This research utilized a more basic HPLC/UV with specialized extraction and concentration methods to enhance the detection limits.

For the pharmaceuticals evaluated during this study, EPA method 1694 was used. The pharmaceuticals were quantified using a HPLC/UV. The pharmaceuticals were held in a cooler at 4 C before extraction. The pharmaceutical samples were tested for acidic compounds. HCl and MeOH. Hydrochloric acid (HCl) was used to acidify the sample and the methanol (MeOH) was used for extraction. For the analysis, two different elution solvents were used on a solids phase extraction (SPE) setup. One was used for the first set of four pharmaceuticals: carbamazepine, sulfamethoxazole, fluoxetine, and trimethoprim. The compounds in the other set were triclosan, gemfibrozil and ibuprofen. Formic acid (1%) /ammonia formate and formic acid (1%)/in methanol:water was used as the two extraction solvents. The HPLC/UV was calibrated and blanks were analyzed for detection limits. The final effluent samples were also spiked to determine extraction recovery efficiency.

For PAHs, EPA method 8310 was used and analyzed with a GC/MS. The initial calibration was conducted using a minimum blank and 5 points for each analyte. The calibration was verified by internal calibrations. Method blanks were analyzed for every

20 samples. The PAHs were extracted using methylene chloride in 2L separation funnels. The extracts were condensed from 120 ml to 2 ml using Kuderna Danish (KD) equipment.

The pesticides were sent to Penn State Harrisburg for extractions in a cooler with the separation funnel extractions completed within the allowable holding time of 7 days. The pesticides were analyzed using EPA 525 method. Calibration liquids, containing each of the analytes were prepared. After the samples were collected, they were dechlorinated using sodium thiosulfate, iced and sent to the laB- Field blanks were analyzed along with samples. QA/QC was demonstrated by the consistent analysis of laboratory reagent blanks, laboratory fortified blanks (LFB), and laboratory fortified matrix (LFM) samples. The pesticides were analyzed using a GC-ECD.

Microtox was used to investigate sample toxicity of some samples. Granular NaCl was used to adjust the salinity (osmotic pressure) of the samples. Previously developed protocols used granular NaCl to adjust the salinity of the samples to 2%. This protocol recommended 0.2g of NaCl per 10mL sample. Tests were conducted to determine if there was a difference in illuminescence of the test bacteria with changing NaCl concentration and to determine the optimum concentration of NaCl required when adjusting to acceptable range of salinity of a sample.

A full factorial study (2^3, Temperature/Moisture/UVB exposure, the latter being ultraviolet-B radiation) of the indicator species' environmental survival factors was performed for Enterococci and *E. coli*. Pet feces slurries were applied to salt passivated paving blocks and incubated in controlled environmental chambers (freezerless refrigerators fitted with commercial biological oxygen demand (BOD) controllers and heaters for temperature control, desiccant or humidifiers for moisture control, and UVB enhanced fluorescents with Lexan panels to split the chambers into UV exposed and UV shielded regions) at conditions encompassing those likely to be found in Tuscaloosa.

Statistical Analyses

Exploratory data analyses were initially used for reviewing all of the data. These analyses generally included time series plots, probability plots, and box and whisker plots. Measures of statistical significance were mostly nonparametric due to the typical non-normality of the observations.

To build an empirical model, factorial experiments were utilized to determine the significant factors affecting contaminant concentrations. The data were combined into groups based on the calculated effects from the factorial analysis. Cluster and principal component analyses were performed on raw data to determine associations between different conditions and contaminant loads. Pearson correlations were calculated to quantify associations between significant water quality parameters. Finally, regressions were performed on time series plots to predict pollutant release with time.

Section 4. Occurrences and Characteristics of Emerging Contaminants

Introduction

This report section contains information concerning characteristics (mainly concentrations and frequency of observations) of emerging contaminants examined in wet weather flows during this research. Literature information supplements the new data. The major subsections address pharmaceuticals and personal care products (PPCP), PAHs, pesticides, trace heavy metals, and indicator bacteria features of special interest in wet weather flows. The next section (Section 6) discusses treatability of these contaminants, both from literature and field studies supporting this research. The information in these two sections was supplemented by outcomes from parallel research projects (mainly supported by Alabama NSF – EPSCoR) which focused on characterization and treatment of toxicants associated with natural disasters, along with sources and fates of these materials.

Much of the material in these sections was part of several PhD dissertations by recent and current University of Alabama (Dept. of Civil, Construction, and Environmental Engineering) graduate students. These students were funded by a combination of this EPA project and the NSF projects, leveraging and coordinating research to meet the broad tasks of this emerging contaminant project. Three students that have completed their research are:

Bathi, Jejal. Ph.D. *Associations of Polycyclic Aromatic Hydrocarbons (PAHs) with Urban Stream Sediments*. 2008.
Goodson, Kenya. Ph.D. *Treatability of Emerging Contaminants in Wastewater Treatment Plants during Wet Weather*. 2013.
Ogburn, Olga. Ph.D. *Urban Stormwater Contamination Associated with Gutter and Pipe Material Degradation*. 2013.

In addition, Brad Wilson is expected to complete his Ph.D. research on urban bacteria survival and re-growth soon.

Pharmaceuticals and Personal Care Products (PPCP)

The most commonly occurring pharmaceuticals and personal care products are from different therauptic classes. Some as listed as follows:

Antibiotics: Erythromycin, Clarithromycin, Ciprofloxacin, Ofloxacin, Amoxycillin.
Analgesics: Ibuprofen, Naproxen, Ketoprofen, Fenoprofen, Indomethacin.
Estrogens: Estrone, 17β-estradiol.
Lipid Generators: Bezafibrate, Gemfibrozil.

Many of the publications during the last two decades have reported the occurrences of pharmaceuticals and personal care products in a wide variety of waters. Most of these included municipal wastewater treatment influents and effluents (Castiglioni, et al. 2005, Miao etal. 2002, Lindqvist, et al. 2005, Pedrouzo, et al. 2007, Lee, et al. 2005, Thomas, et al. 2004), rivers (Lindqvist, et al. 2005, Kosjek, et al. 2005), other surface waters (Hao, et al. 2006, Pedrouzo, et al. 2007, Togola, et al. 2007) and drinking waters (Kosjek, et al. 2005). Representative occurrences of PPCPs, along with observed concentrations, are shown in Table 4-1.

Table 4-1. Observed Concentrations of Pharmaceuticals in different waters

	Observed Concentrations (ng/L)												
Compound	**STP influent**			**STP effluent**			**River waters**			**Surface waters**			**Reference**
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Ibuprofen				nd	nd	nd							Castiglioni etal 2005
Ciproflaxin				27	514								
Clofibric acid				0.5	82								
Diazepam				nd	nd								
Carbamazepine				33	1318								
Bezafibrate				0.3	117								
Atenolol				27	1168								
Ibuprofen				10	15								Miao etal 2002
Naproxen				25	300								
Bezafibrate				20	65								
Diclofenac				25	65								
Gemfibrozil				30	60								
Fenoprofen				20	25								
Carbamazepine	290	310		380	470		20	66					Vieno etal 2006
Atenolol	510	800		40	440		12	25					
Metoprolol	980	1350		910	1070		20	116					
Diazepam			nd			nd		33					Ternes etal 2001
Caffeine			147000			190		880					
Naproxen												41	Hao etal 2006

Continuation of Table 4-1

	Observed Concentrations (ng/L)												
Compound	**STP influent**			**STP effluent**			**River waters**			**Surface waters**			**Reference**
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Carbamazepine												1.5,4.2,16	
Gemfibrozil												13	
Erythromycin												1.9,6.9	
Ibuprofen			13100	80	3920								Lindqvist etal 2005
Naproxen			4900	160	1920								
Bezafibrate			420	20	840								
Diclofenac			350	160	360								
Ketoprofen			2000	40	1280								
Ibuprofen	1610	5990		20	690					18	44		Pedrouzo etal 2007
Naproxen	340	8620		20	450								
Clofibric acid	30	2020		10	120					11	14		
Carbamazepine	60	480		80	290					9	37		
Bezafibrate	Nd	nd		70	340								
Diclofenac	120	550		10	460					25	41		
Caffeine	420	40120		20	1010					106	240		
Ibuprofen	2740	9210		40	970								Lee etal 2003
Naproxen	1100	6060		210	1110								
Diclofenac	30	200		20	210								
Ketoprofen	30	700		30	150								

Continuation of Table 4-1

	Observed Concentrations (ng/L)												
Compound	**STP influent**			**STP effluent**			**River waters**			**Surface waters**			**Reference**
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Gemfibrozil	100	750		20	540								Lee et al 2003
Triclosan	370	3240		30	740								
Indomethacin	50	200		30	240								
Ibuprofen				2.4	197.6					3	610.6		Togola etal 2007
Naproxen				13.6	2666.8					2.6	274.6		
Carbamazepine				30.9	2519.3					1.8	82.7		
Diclofenac				26.3	918.6					7.1	172.5		
Ketoprofen				15.2	1136.5					4.4	33.2		
Gemfibrozil				4.3	108.8					2.7	85.8		
Caffeine				2.6	3257.2					3.5	159.8		
Ibuprofen	4100	10210		110	2170								Lee etal 2005
Naproxen	1730	6030		360	2540								
Diclofenac	50	2450		70	250								
Ketoprofen	60	150		40	90								
Gemfibrozil	120	36530		80	2090								
Triclosan	870	1830		50	360								
Estrone	8	52		<1	54								
Indomethacin	30	430		40	490								
Ibuprofen						18							Thomas etal 2004
Naproxen						31							
Diclofenac						nd							
Ketoprofen						23							
Triclosan						72							
Caffeine						36							

nd: not detected

Veterinary Pharmaceuticals

Veterinary pharmaceuticals are also a class of emerging contaminants that are likely associated with separate stormwater and other wet weather flows. However, there were no specific literature references available for these compounds. Interviews were held with local veterinarians (personal communications) to determine the most commonly used pet medicines, and their uses. Table 4-2 lists these pet pharmaceuticals, and their use.

Table 4-2. Veterinary Pharmaceuticals and their Usage

Compound	Usage
Nystatin	Anti-infective
Thiabendazole	Anti-infective
Dexamethasone	Anti-infective
Metronidazole	Anti-infective
Clindamycin	Anti-infective
Permethrin	Flea preventative
Fipronil	Flea preventative
Imidacloprid	Flea preventative
Methoprene	Flea preventative
Prednisone	Anti Inflammatory
Betamethasone	Anti Inflammatory
Ketoconazole	Anti-fungal
Ivermectin	Heart worm preventative
Amoxicillin	Antibiotic
Tetracycline	Antibiotic
Gentamicin	Antibiotic

Pesticides

Pesticides are another class of emerging contaminants and are frequently detected in wet weather flows. The usage of pesticides in urban areas is mostly for weed and insect control near homes, along roads and railway rights-of-way, parks, lawns and golf courses (Recke et al 1993). Kunimatsu et al (1992) reported that the concentrations of pesticides varied for each storm runoff event and no clear correlation was observed with precipitation; instead the loading rates depended on the length of period after application, drainage system, application method, volatilization, microorganisms and sunlight. Schiff et al (2004) also identified first flush effects for pesticides. Pesticides are commonly analyzed using EPA Method 508.

Presence of PPCPs at Wastewater Treatment Facilities

Stormwater I&I can have a significant effect on wastewater treatment flow rates (and pollutant concentrations) and may in turn potentially affect treatment of wastewater pollutants. The increases of volume during a large rain event may cause a dilution effect for pollutants more associated with sewage than with stormwater (such as expected for many of the pharmaceuticals), causing the concentrations to be significantly lower. Lower concentrations of a pollutant can reduce the removal rates of targeted pollutants. However, stormwater I&I can be a major source of some pollutants entering the treatment plant. As an example, PAHs are more likely associated with stormwater in urban areas than in separate sanitary wastewater. Increases of PAHs in wastewater influent during wet weather suggest stormwater is entering the sewer system. Pesticides are also of interest for this study and are known pollutants associated with stormwater. Some pharmaceuticals have dual roles in both human and veterinary medicine. While many would enter the sanitary sewage system from human wastes, pet pharmaceuticals could enter the system through stormwater contaminated by fecal matter from treated animals.

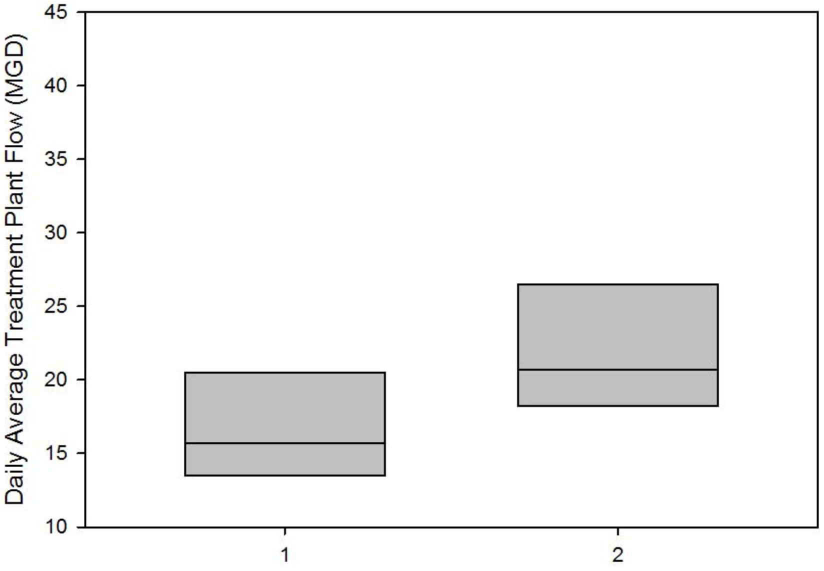
As described in the methodology discussion, samples were collected during a range of flow and rain conditions to understand whether stormwater contributes ECs to the treatment plant. Mass loads were calculated based on the measured daily flow rates and the influent concentrations. The mass loads for the dry weather days were compared to the wet weather day mass loads. The differences were then related to the rain depth observed for the day to determine if stormwater contribute to the EC discharges to the treatment plant. Eight dry weather samples were taken in addition to nine wet weather samples at four locations at the treatment facility. Some of the constituents did not have values for some of the sample dates and in a few instances, insufficient sample volumes were available to complete the full suite of analyses. Therefore, the final number of data observations varied. Each sample set was tested for selected pharmaceuticals, PAHs, and pesticides. Daily average flow rates were obtained from the treatment plant operators and the rainfall data were obtained from Accu-Weather for the Tuscaloosa Municipal Airport rain gauge, as shown on Table 4-3.

Table 4-3. Treatment Plant Average Daily Flow Rates and Daily Total Rain Depth on Days of Sampling

Weather events for sampling	Tuscaloosa Municipal Airport Total Daily Rainfall (inches)*	Treatment Plant Average Daily Flow Rate (MGD)
01/16/10 (wet)	0.55	18.2
03/02/10 (wet)	0.68	23.3
04/24/10 (wet)	1.01	16.5
06/25/10 (wet)	0.59	20.7
11/02/10 (wet)	0.88	20.5
03/09/11 (wet)	2.67	42.2
05/11/11 (dry)	0	13.5
05/14/11 (dry)	0	30.7
09/20/11 (wet)	0.64	26.5
10/10/11 (dry)	0.07	16.9
03/20/12 (dry)	0	17.1
06/16/12 (dry)	0	13.5
09/15/12 (dry)	0	14.5
11/01/12 (dry)	0	17.1
11/04/12 (dry)	0.05	15.4
11/08/12 (dry)	0	15.9
11/12/12 (wet)	0.44	16.0

* historical rain data obtained from Accu-Weather for the Tuscaloosa Municipal Airport

The average flow during the dry weather sampling days was about 18 MGD, while the average daily flow during the wet weather sampling days was about 24 MGD. Figure 4-1 is a box and whisker plot comparing the dry weather and the wet weather observed flows. Most of the wet weather flows are larger than the dry weather flows, but there is some overlap (the Mann-Whitney rank sum test only indicates a marginal significance that they are different at p = 0.07, likely due to the small number of observations: 6 dry weather samples and 7 wet weather samples having both rainfall and flow data).



1: Treatment plant flows during dry weather; 2: treatment plant flows during wet weather

Figure 4-1. Treatment plant flows during dry and wet weather.

Figure 4-2 is a plot of these rain depth values compared to the daily average treatment plant flows (with the zero rain data removed to enable log-transformations). This plot indicates I&I are not likely significant until the daily rain depth is greater than about one-half inch, when the treatment plant flow can increase to greater than about 20 MGD. During the largest rain depth observed (2.67 inches), the treatment plant flow was also the largest observed (42.2 MGD). This plot has a reasonably fit, but it also indicates a large variability. The rain depth is available only for a single location in the large service area (Tuscaloosa Municipal Airport) and it is likely that the rains vary greatly over the service area, especially for the smaller rains. In addition, there are relatively few larger rains compared to the smaller rains, so there is not very much information available to verify the upper range of this relationship. In addition, elevated flow rates are also noted during dry weather, which indicates that other factors are involved in some of the elevated flow rates, such as the industrial flows entering the treatment facility.

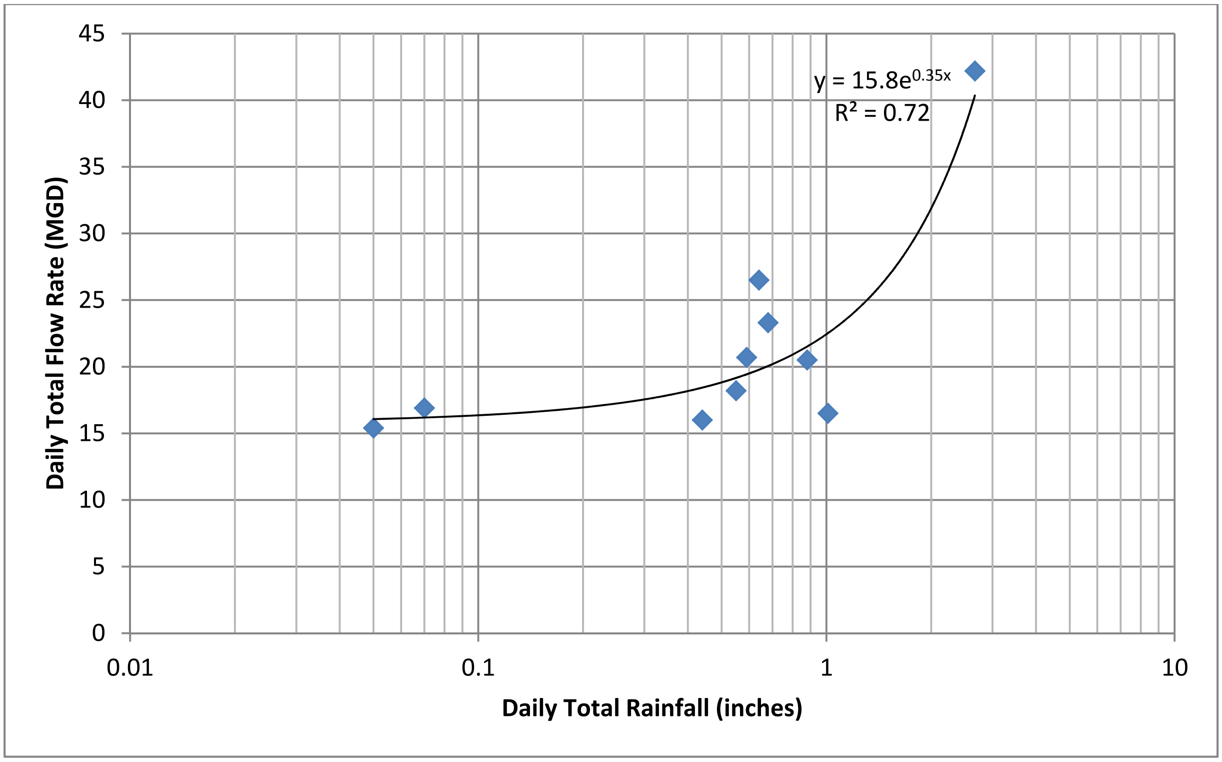


Figure 4-2. Treatment plant flow compared to rain total.

Table 4-4 includes estimated calculations describing the amount of stormwater I&I that could affect the treatment plant for different rain categories. As noted above, there is some uncertainty associated with these calculations, but they indicate that the rainfall fraction entering the sanitary sewer system and causing increased flows is very small (<2% even for the largest rains). The total sewage flow entering the treatment plant during large rains could be affected by large amounts of stormwater that entered the system by inflow (rapid entry) or infiltration (slower entry).

Table 4-4. Estimated Stormwater Infiltration and Inflow (I&I) for Different Rain Categories

Rain range (in)	Average treatment plant flow (MGD)	Increase over base treatment plant flow assumed due to stormwater I&I (MGD)	Percentage of total treatment plant flow associated with stormwater I&I (%)	Estimated stormwater I&I (MGD/mi^2)*	Estimated stormwater I&I (watershed inches)	Estimated stormwater I&I as a percentage of the rain depth (%)
0 to 0.1	17.7	0	0	0	0	0
0.2 to 0.5	18	0.3	2	0.027	0.0015	0.43
0.6 to 1.5	23	5.3	23	0.31	0.018	1.7
1.6 to 2.5	34	16.3	48	0.65	0.037	1.8

* Service area: 74 mi^2; the population served: 110,000; the total length of sewers: 600 miles

As noted previously, there are few obvious sources of PPCPs in wet weather flows (beyond some associated with veterinarian drugs). However, regression analyses of influent concentrations vs. treatment plant flow rate indicated significant slope terms for all of the pharmaceutical compounds (increasing concentrations with increasing flow rates at the treatment facility, except for carbamazepine (complete statistical analyses are presented in Appendix A). Figures 4-3 through 4-9 are plots of the generally increasing concentrations with increasing daily average flow rates.

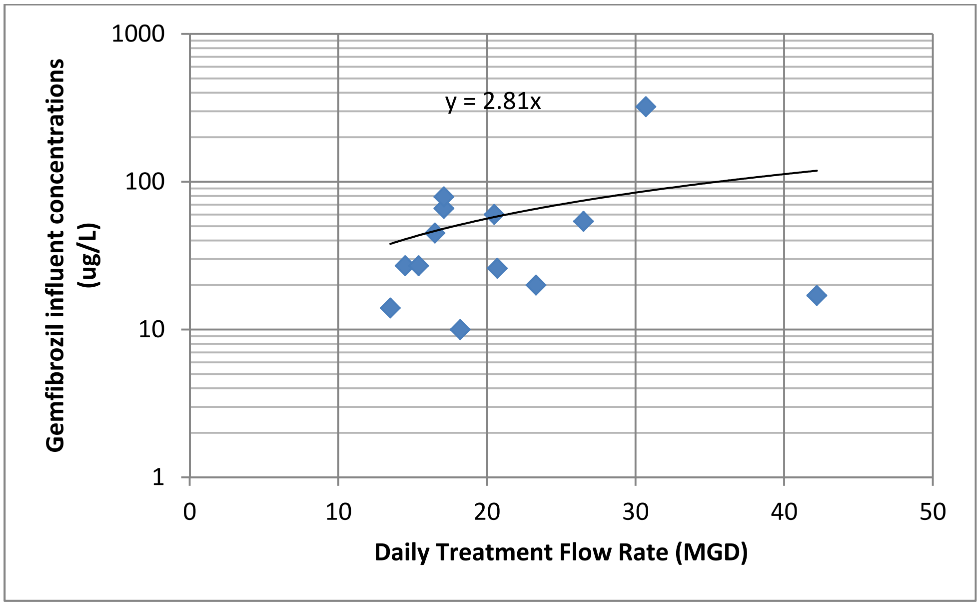


Figure 4-3. Overall regression p = 0.013 and slope term p = 0.013, both significant

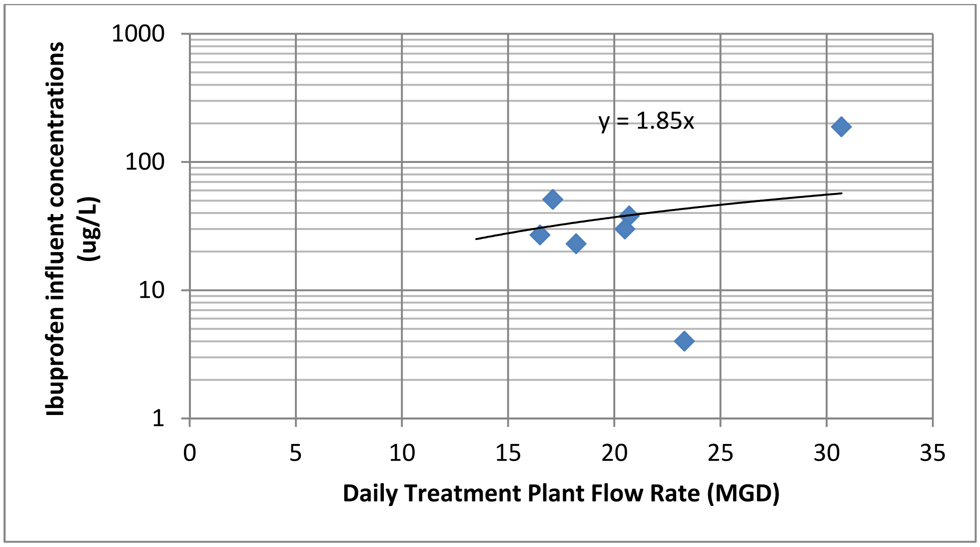


Figure 4-4. Overall regression p = 0.02 and slope term p = 0.02, both significant

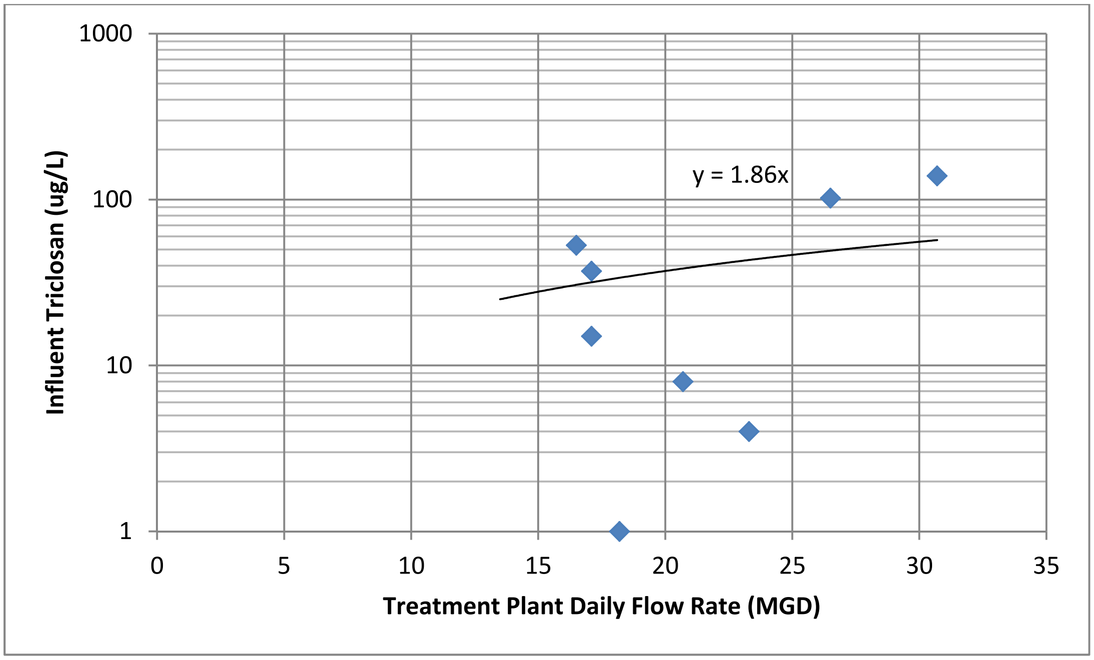


Figure 4-5. Triclosan influent concentrations vs. treatment plant flow rates (overall regression p = 0.004 and slope term p = 0.004, both significant).

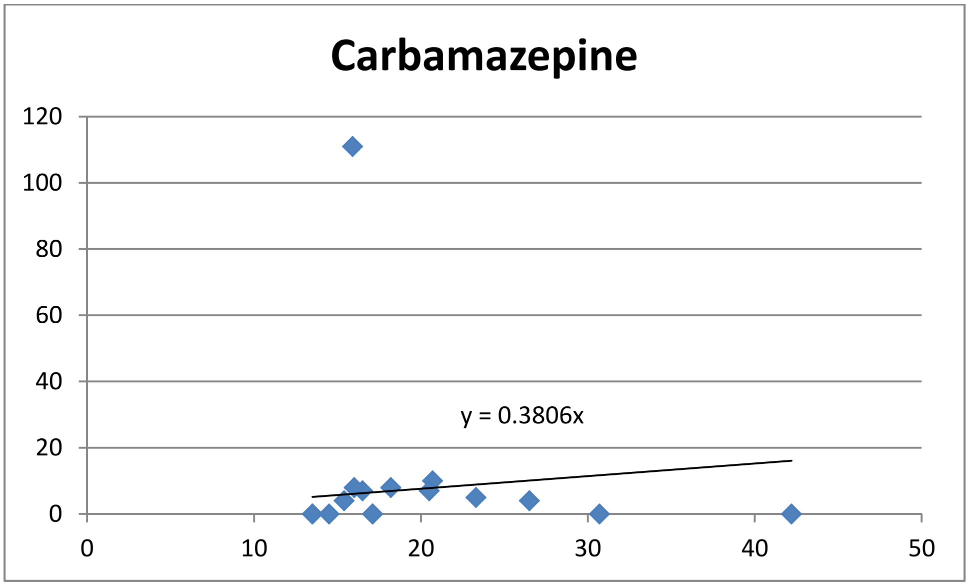


Figure 4-6. Regression and coefficients are not significant based on the ANOVA analysis.

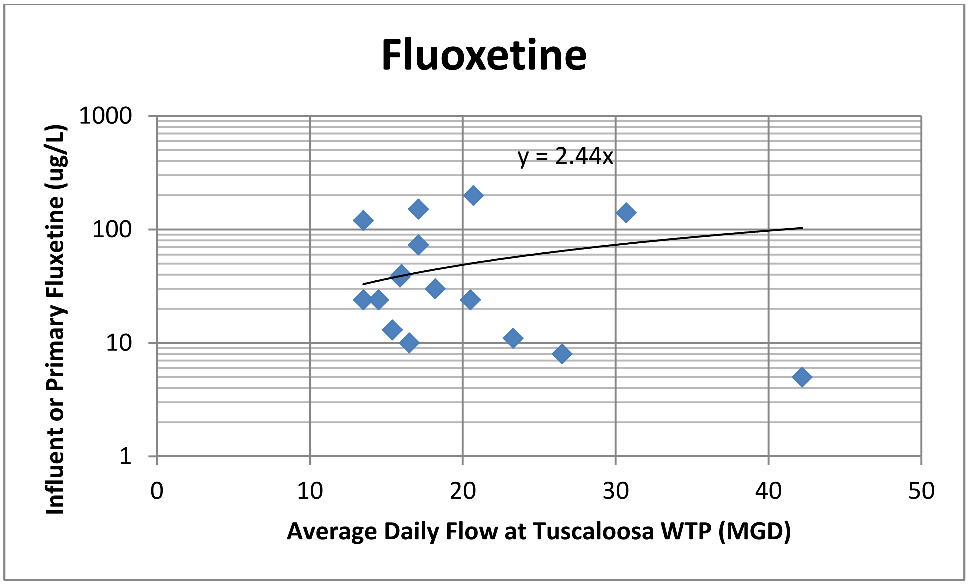


Figure 4-7. Overall equation and slope term are both significant (p = 0.006) based on ANOVA.

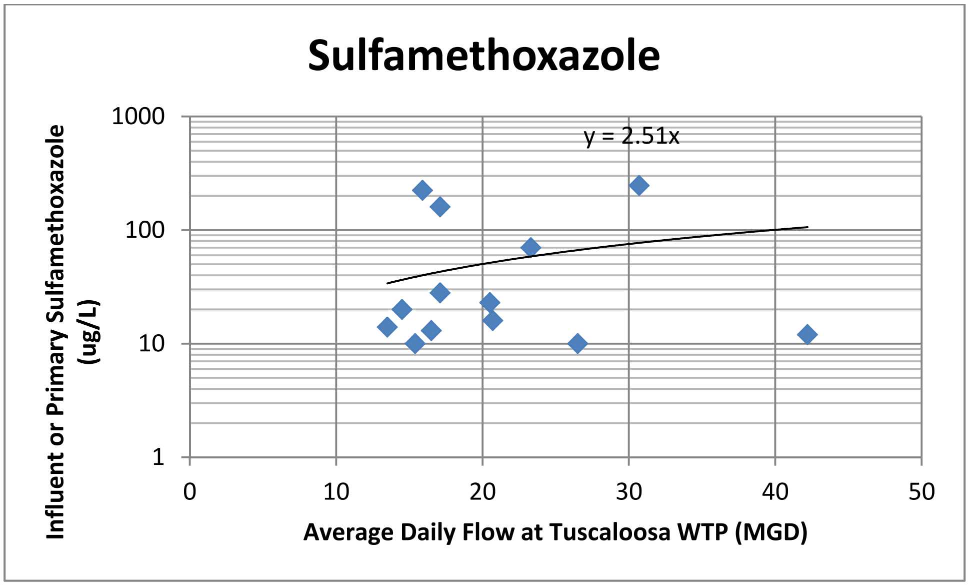


Figure 4-8. Equation and slope term both significant (p = 0.02) based on ANOVA.

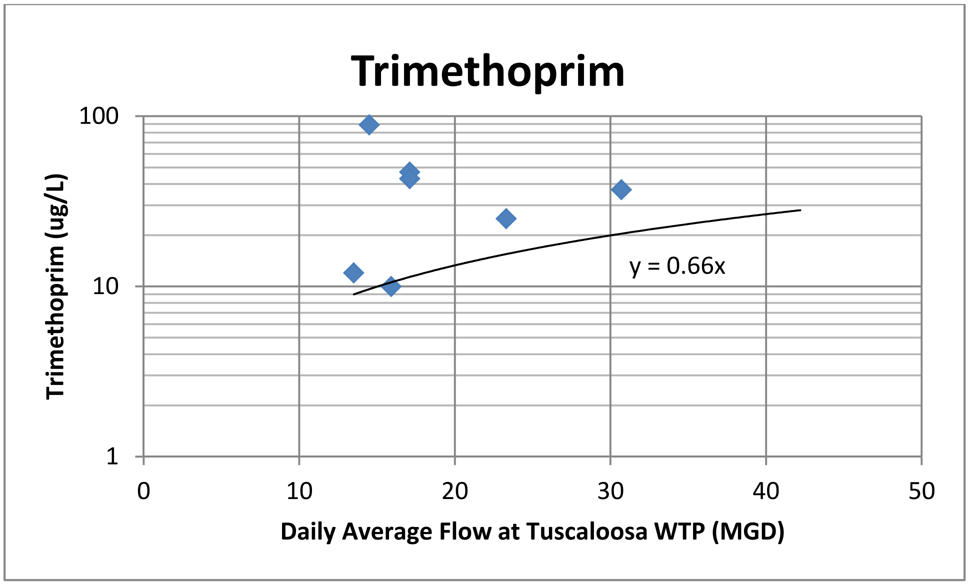


Figure 4-9. Both equation and slope term are marginally significant (p = 0.054), based on ANOVA (zero values are not plotted on the log scale).

Table 4-5 summarizes the observed concentrations during both low and high flow conditions, along with the overall observed range. In general, the average concentrations for peak flows were about double the dry weather period concentrations, although there was substantial variability.

Table 4-5. Average PPCP Influent Concentrations at Tuscaloosa Wastewater Treatment Plant during Dry and Wet Weather Conditions

	Average dry weather concentrations (at about 18 MGD at treatment plant)	Average wet weather concentrations (at about 40 MGD at treatment plant)	Overall observed range (dry and wet weather)
Gemfibrozil, µg/L	55	110	10 – 300
Ibuprofen, µg/L	35	60	4 – 200
Triclosan, µg/L	35	60	1 – 150
Carbamazepine, µg/L	8	15	1 – 110
Fluoxetine, µg/L	45	100	5 – 200
Sulfamethoxazole, µg/L	50	100	10 – 250
Trimethoprim, µg/L	12	25	10 – 100

Polycyclic Aromatic Hydrocarbons

The samples obtained at the influent at the Tuscaloosa Wastewater Treatment Plant were also analyzed for selected PAHs. Similar plots and regression analyses (with

ANOVA) for these are shown in Figures 4-10 through 4-17. All had statistically significant increasing concentrations with increasing daily average flow rates (except for acenapthtylene), although there were generally wide variations in concentrations during dry weather (possibly affected by the industrial discharges to the treatment facility.

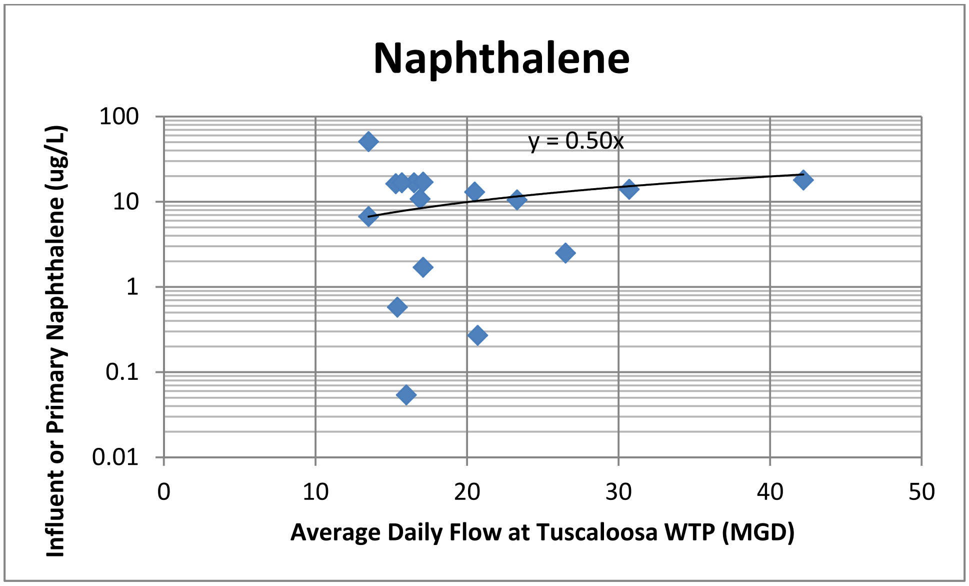


Figure 4-10. Regression equation and slope coefficient are both significant (p = 0.003) based on ANOVA (removed very large single value).

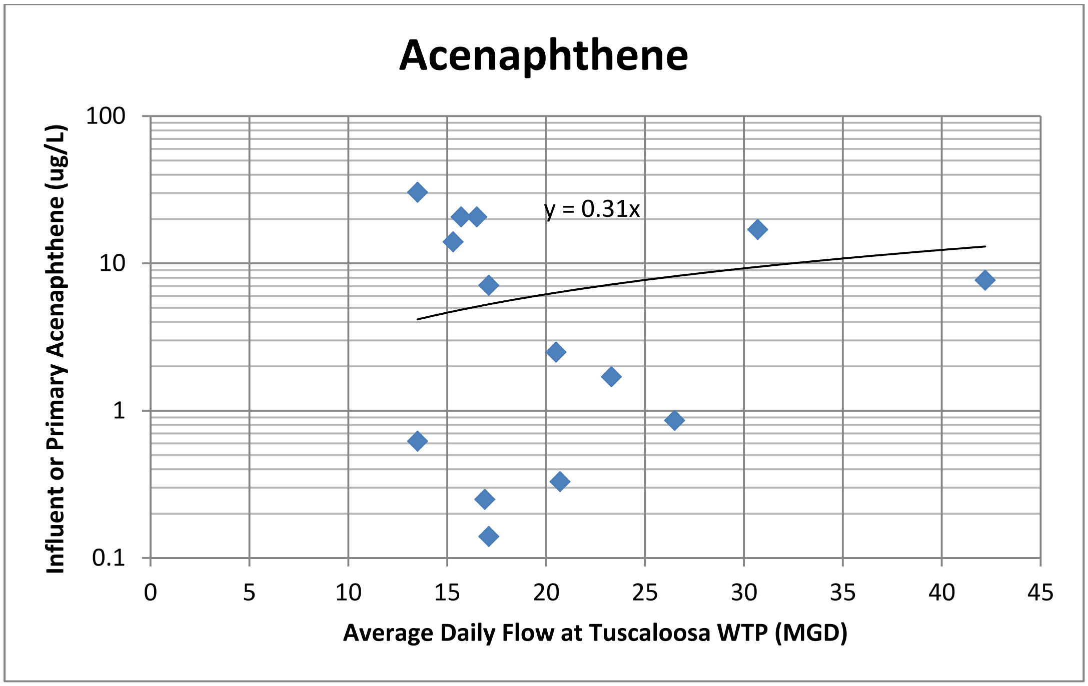


Figure 4-11. Regression equation and slope coefficient are both significant (p = 0.01) based on ANOVA (removed very large single value).

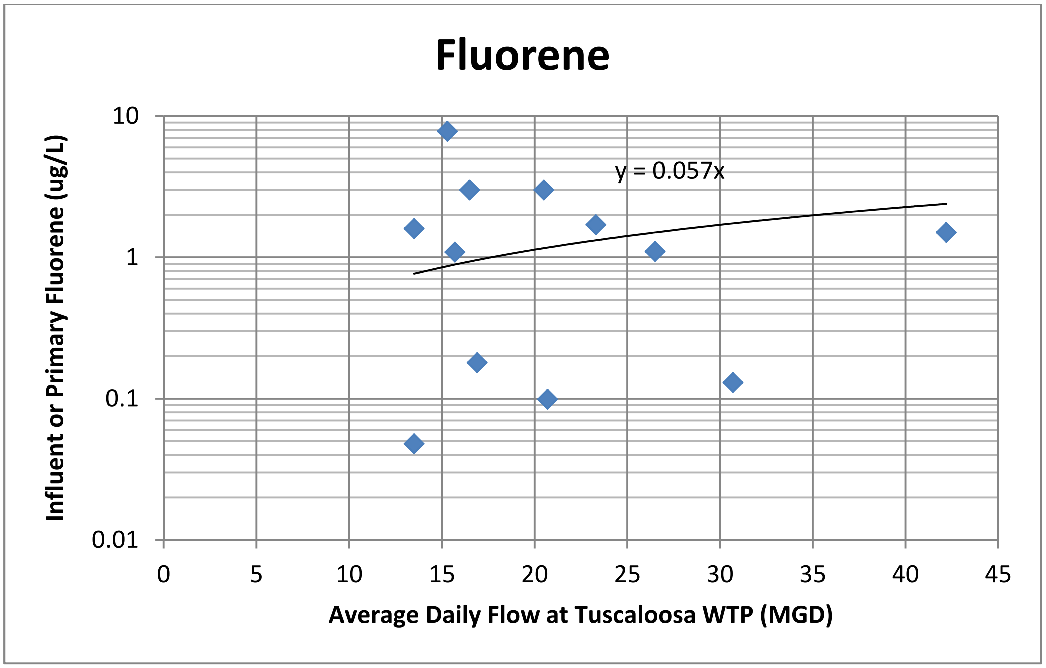


Figure 4-12. Regression equation and slope coefficient are both significant (p = 0.02) based on ANOVA (removed very large single value).

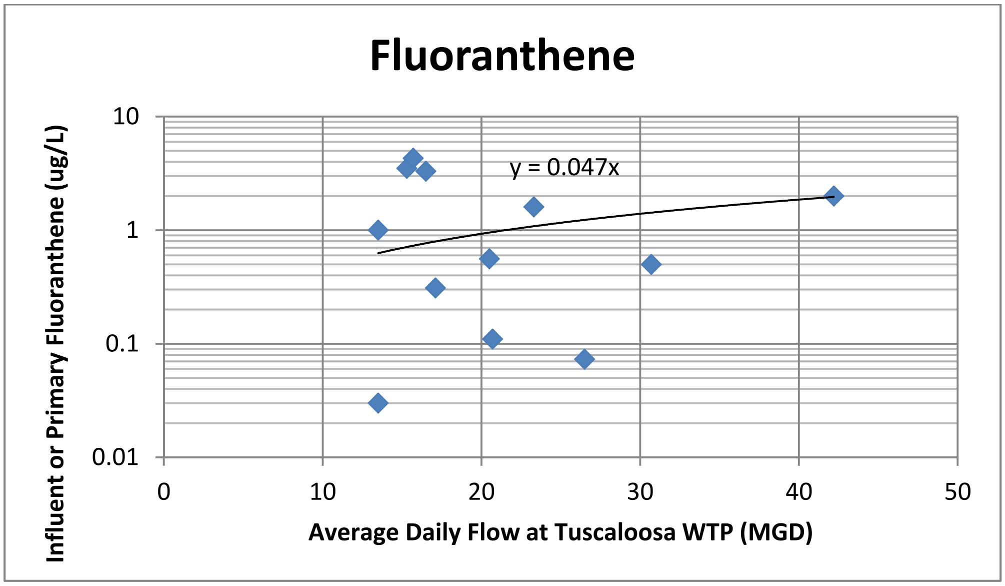


Figure 4-13. Regression equation and slope coefficient are both significant (p = 0.01) based on ANOVA (removed very large single value).

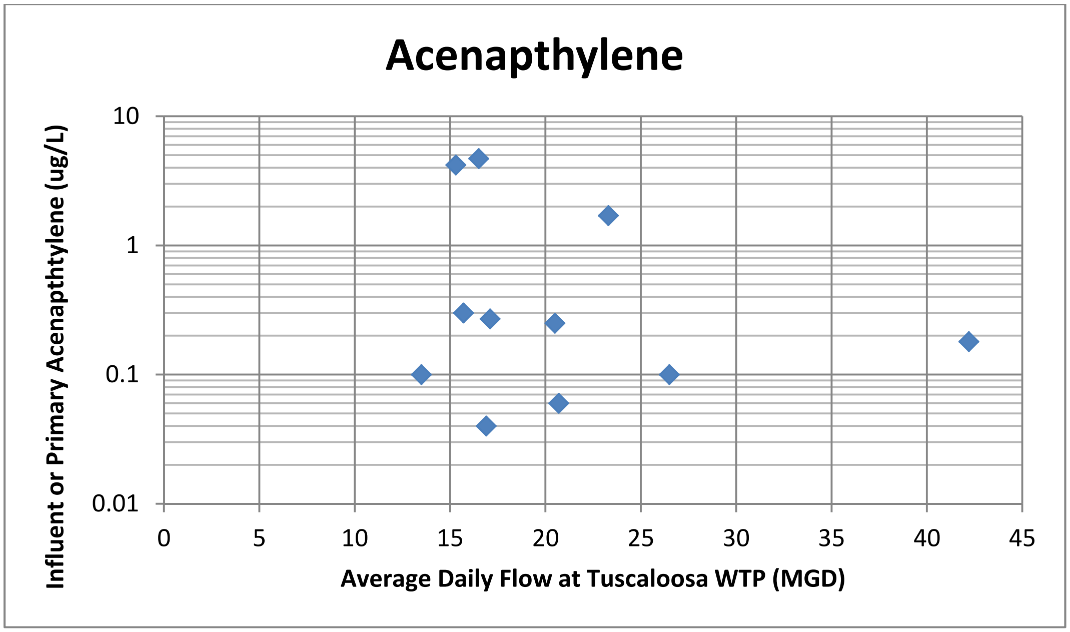


Figure 4-14. Regression equation and coefficients are all insignificant (p = 0.11) based on ANOVA (even with removal of single very large value).

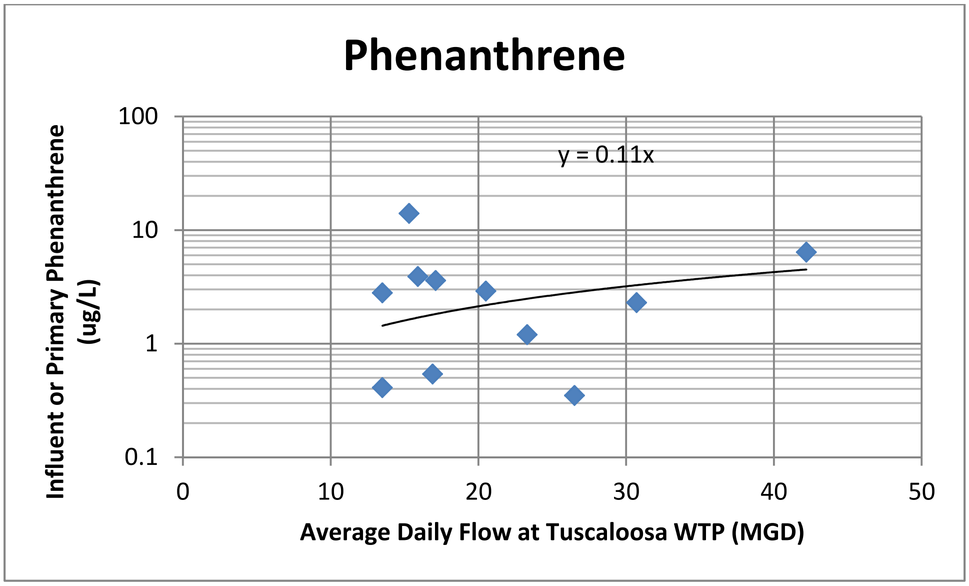


Figure 4-15. Regression equation and slope coefficient are both significant (p = 0.01) based on ANOVA (removed very large single value).

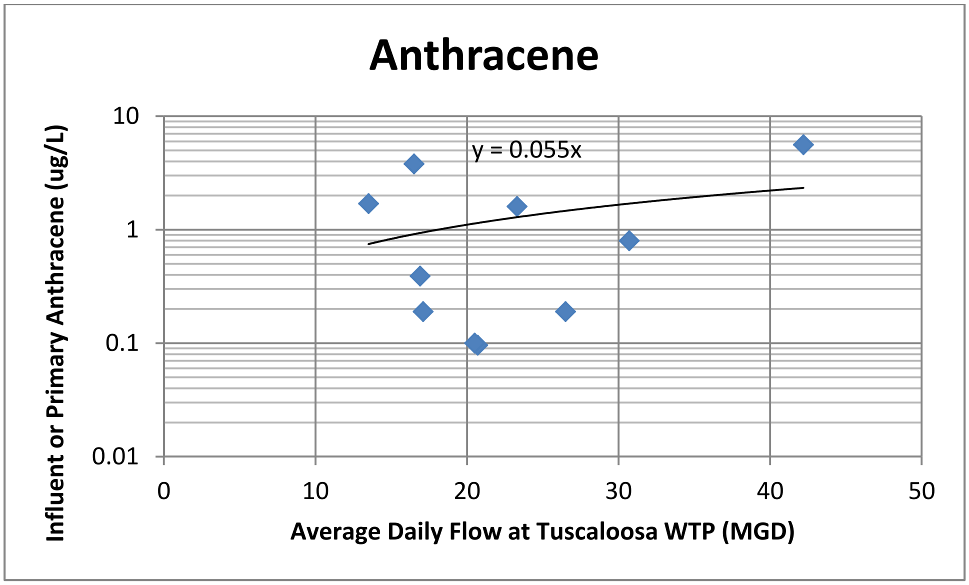


Figure 4-16. Regression equation and slope coefficient are both significant (p = 0.004) based on ANOVA (removed very large single value).

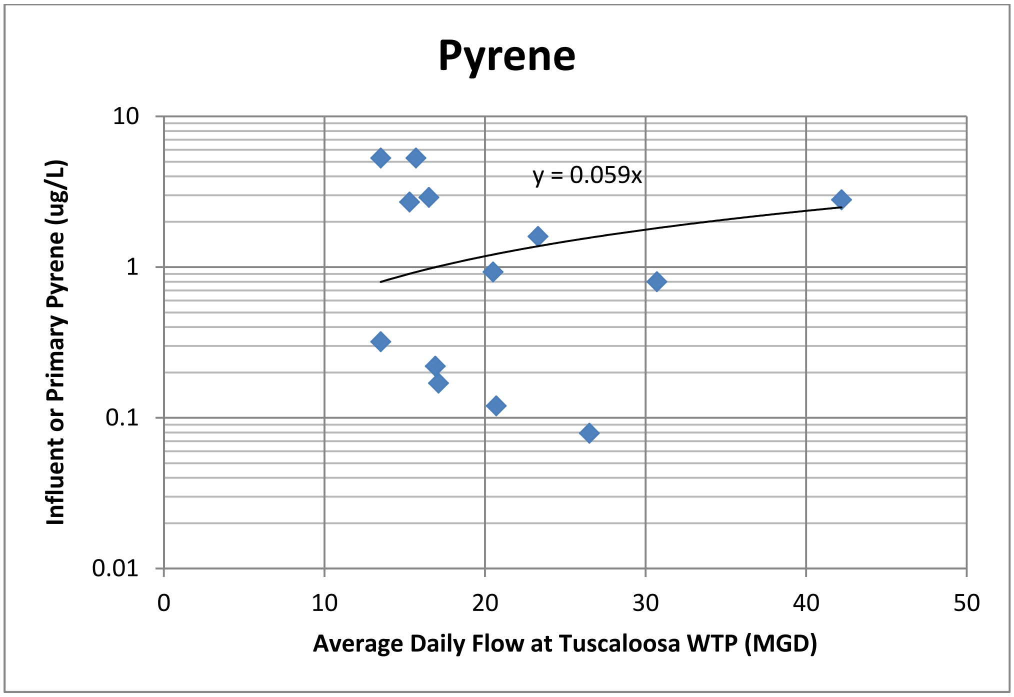


Figure 4-17. Regression equation and slope coefficient are both significant (p = 0.01) based on ANOVA (removed very large single value).

In general, the average concentrations for peak flows were also about double the dry weather period concentrations, although there was also substantial variability for the PAHs, as shown in Table 4-6.

Table 4-6. Average Dry and Wet Weather PAH Concentrations at Tuscaloosa Wastewater Treatment Plant

	Average dry weather concentrations (at about 18 MGD at treatment plant)	Average wet weather concentrations (at about 40 MGD at treatment plant)	Overall observed range (dry and wet weather)
Naphthalene, µg/L	10	20	0.004 – 50
Acenaphthene, µg/L	6	12	0.15 – 30
Fluorene, µg/L	1	2	0.05 – 7
Fluoranthene, µg/L	0.8	2	0.03 – 6
Phenanthrene, µg/L	2	4	0.3 – 12
Anthracene, µg/L	1	2	0.1 – 6
Pyrene, µg/L	1	2	0.08 – 5

Fate of Emerging Contaminants in Surface Waters

Any compound released into the environment will tend to partition between solid, liquid and gaseous phases. The partitioning of a compound into different phases depend on the physical and chemical properties of the phases and as well as the properties of the compound itself. Usually pollutants with high Koc and Kow values tend to adsorb onto the solid phase and with the lower values, associate with the liquid phase. A fugacity model developed by Mackay, et al. (1992) is used to predict the partition of pollutants into different phases and its approach is described in the following section

Fugacity Approach for Predicting the Partitioning of PPCPs and Pesticides with Different Phases

Fugacity literally means the “tendency to flee”. Fugacity modeling is based on chemical equilibrium and is used to determine the relative concentrations of a chemical in air, water, and soil phases. Level I Fugacity models shown by Mackay, et al. (1992) were used to calculate the likely fate of representative emerging compounds, based on set volumes for each media compartment. A Level I Fugacity model assumes the equilibrium distribution of a fixed quantity of conserved chemical, in a closed environment at equilibrium, with no degrading reactions, no advective processes and no intermediate transport processes. The characteristics of different compartments used in the calculations were as shown in Table 4-7

Table 4-7. Level 1 Fugacity Parameters for Emerging Contaminants (Mackay Method)

Compartment	Air	Water	Soil	Sediment	Suspended sediment	Fish
Volume, V (m^3)	1E+14	2E+11	9E+09	1E+08	1E+06	2E+05
Depth, h (m)	1000	20	0.1	0.01		
Area, A (m^2)	1E+11	1.E+10	9E+11	1E+10		
Fraction OC			0.02	0.04	0.2	
Density, ρ (kg/m^3)	1.2	1000	2400	2400	1500	1000
Adv. Residence time, T (hrs)	100	100		5E+04		
Adv. Flow, G	1E+12	2E+09		2000		

The fugacity of compound is calculated as $f = M/\Sigma V_i Z_i$ (eq. 5.1)
Where M is the total amount of chemical (mol)
V_i is the medium volume (m^3)
Z_i is the corresponding fugacity capacity for the chemical in each medium
The number of moles partitioned into each respective phase is in turn calculated as:
$M = f^* \Sigma V_i Z_i$
The equations for phase Z values used in Level I calculations are as shown below:

Air: $$Z_1 = \frac{1}{RT} \qquad \text{(eq. 5.2)}$$

Water: $$Z_2 = \frac{1}{H} \qquad \text{(eq. 5.3)}$$

Sediment: $$Z_3 = Z_2 * \mathrm{P}_3 * \phi_3 * \frac{K_{OC}}{1000} \qquad \text{(eq. 5.4)}$$

Suspended Sediment: $$Z_4 = Z_2 * \mathrm{P}_4 * \phi_4 * \frac{K_{OC}}{1000} \qquad \text{(eq. 5.5)}$$

Fish: $$Z_5 = Z_2 * \mathrm{P}_5 * L * \frac{K_{OW}}{1000} \qquad \text{(eq. 5.6)}$$

Where:
R = gas constant (8.314 J/mol K)
T = absolute temperature (K)
H = Henry's law constant (atm*m^3/mol)
Kow = Octanol-water partition coefficient
Koc = Organic-carbon partition coefficient
ρ_i = density of phase i (kg/m^3)
φ_i = mass fraction of organic fraction in phase i (g/g)
L= lipid content of fish

The physical and chemical properties of the compounds included in the study are shown in Tables 4-8 and 4-9.

Table 4-8. Physical and Chemical Properties of PPCPs Examined

Compound	Log Kow	Koc	Henrys constant (atm m^3/mole)
Nystatin	7.08	170	2E-07
Dexamethasone	1.83	240	7.2E-08
Methoprene	5.5	23000	6.9E-06
Prednisone	1.46	150	2.8E-10
Metronidazole	-0.02	23	1.7E-11
Clindamycin	2.16	360	2.9E-22
Ketoconazole	4.34	8970	5.6E-20
Carbamazepine	2.45	510	1.1E-10
Caffeine	-0.07	22	3.6E-11
Ibuprofen	3.97	3400	1.5E-07
Diclofenac	4.51	830	4.7E-12
Acetaminophen	0.46	42	6.4E-13
Triclosan	4.76	9200	1.5E-07
Ciprofloxacin	0.28	61000	5.1E-19
Metoprolol	1.88	62	2.1E-11
Salicylic acid	2.62	65,104	7.34E-09
Dioxin	6.8	24000000	5.0E-05

Table 4-9. Physical and Chemical Properties of PPCPs Examined

Compound	Log Kow	Koc	Henrys constant (atm-m^3/mole)
Aldrin	7.08	22909	4.4E-05
Chloroneb	2.47	1260	1.0E-04
Chlorothalonil	1.83	1800	2.5E-07
DDD	6.5	724436	6.6E-06
DDE	4	50118	4.2E-05
DDT	5.5	239883	8.3E-06
Dieldrin	1.46	8730	1.0E-05
Endosulfan	-0.02	2884	6.6E-05
Endrin	2.16	10000	6.4E-06
Etridiazole	4.34	1000	3.0E-05
HCH-α	2.45	2089	6.7E-06
HCH-β	-0.07	9550	4.4E-07
HCH-δ	3.97	661	4.3E-07
HCH-γ	4.51	1071	5.1E-06
Heptachlor	0.46	23988	2.9E-04
Heptachlor epoxide	4.76	7800	3.2E-05
Methoxychlor	0.28	80000	2.0E-07
Permethrin	1.88	10715	1.9E-06
Propachlor	2.62	79	3.6E-07
Trifluralin	6.8	7943	1.0E-04
Aroclor 1016	7.08	17783	1.3E-04
Aroclor 1221	2.47	5754	2.3E-04
Aroclor 1232	1.83	7079	3.1E-04
Aroclor 1242	6.5	66070	3.4E-04
Aroclor 1248	4	275423	4.4E-04
Aroclor 1254	5.5	1000000	2.8E-04
Aroclor 1260	1.46	6760830	3.4E-04
Toxaphene	-0.02	7244	6.0E-06
Chlordane	2.16	21380	4.9E-05

The fugacity calculations assumed that 100,000 kg of each compound was released into the environment and the percentage partitions into different phases were as shown in Table 4-10 and 4-11.

Table 4-10. Partition of PPCPs into Different Phases

		Partition into different phases				
Compound	fugacity	% in air	% in water	% in sediment	% in suspended sediment	% in fish
Nystatin	6.7E-14	0.25	61.97	0.51	0.02	37.25
Dexamethasone	9.1E-14	0.15	98.68	1.14	0.04	0.00
Methoprene	4.8E-12	6.14	43.57	48.10	1.50	0.69
Prednisone	3.9E-16	0.00	99.26	0.71	0.02	0.00
Metronidazole	5.0E-17	0.00	99.89	0.11	0.00	0.00
Clindamycin	3.4E-28	0.00	98.25	1.70	0.05	0.00
ketoconazole	3.6E-26	0.00	69.20	29.79	0.93	0.08
Carbamazepine	2.3E-16	0.00	97.54	2.39	0.07	0.00
Caffeine	9.3E-17	0.00	99.89	0.11	0.00	0.00
Ibuprofen	3.1E-13	0.26	85.34	13.93	0.44	0.04
Diclofenac	7.6E-18	0.00	95.90	3.82	0.12	0.16
Acetaminophen	2.1E-18	0.00	99.79	0.20	0.01	0.00
Triclosan	1.8E-13	0.21	68.43	30.22	0.94	0.20
Ciprofloxacin	1.9E-25	0.00	24.88	72.84	2.28	0.00
Metoprolol	3.9E-17	0.00	99.69	0.30	0.01	0.00
Salicylic acid	6.3E-15	0.00	23.68	74.00	2.31	0.00
Dioxin	6.5E-14	0.09	0.08	96.78	3.02	0.03

Table 4-11. Partition of Pesticides into Different Phases

		Partition into different phases				
Compound	fugacity	% in air	% in water	% in sediment	% in suspended sediment	% in fish
Aldrin	1.9E-11	28.18	31.33	34.46	1.08	4.95
Chloroneb	7.8E-11	66.24	31.78	1.92	0.06	0.00
Chlorothalonil	4.3E-13	0.47	91.39	7.90	0.25	0.00
DDD	2.8E-13	0.36	2.70	93.78	2.93	0.22
DDE	1.4E-11	17.76	20.89	50.25	1.57	9.53
DDT	8.7E-13	1.26	7.43	85.61	2.68	3.02
Dieldrin	8.0E-12	12.43	60.81	25.48	0.80	0.48
Endosulfan	3.3E-11	54.13	40.13	5.56	0.17	0.01
Endrin	5.1E-12	7.96	61.24	29.40	0.92	0.49
Etridiazole	3.6E-11	36.88	60.15	2.89	0.09	0.00
HCH-α	9.3E-12	11.01	80.63	8.08	0.25	0.03
HCH-β	5.1E-13	0.61	67.48	30.93	0.97	0.02
HCH-δ	7.1E-13	0.84	95.95	3.04	0.10	0.07
HCH-γ	7.6E-12	9.07	86.33	4.44	0.14	0.02
Heptachlor	4.8E-11	73.23	12.19	14.03	0.44	0.11
Heptachlor epoxide	2.0E-11	31.86	48.72	18.24	0.57	0.61
Methoxychlor	5.9E-14	0.08	20.12	77.26	2.41	0.12
Permethrin	1.4E-12	2.21	57.91	29.79	0.93	9.16
Propachlor	8.4E-13	0.73	98.89	0.37	0.01	0.00
Trifluralin	4.4E-11	59.99	28.50	10.87	0.34	0.31
Aroclor 1016	5.6E-11	58.54	22.03	18.81	0.59	0.03
Aroclor 1221	1.0E-10	78.53	16.71	4.61	0.14	0.01
Aroclor 1232	9.1E-11	82.41	13.01	4.42	0.14	0.02
Aroclor 1242	5.8E-11	62.14	8.86	28.11	0.88	0.01
Aroclor 1248	3.2E-11	37.93	4.22	55.77	1.74	0.33
Aroclor 1254	7.7E-12	10.26	1.77	85.13	2.66	0.18
Aroclor 1260	1.3E-12	2.03	0.29	94.63	2.96	0.09
Toxaphene	4.8E-12	8.19	66.80	23.23	0.73	1.06
Chlordane	1.9E-11	31.80	32.01	32.85	1.03	2.31

These fugacity calculations show that the compounds are predominantly partitioned into either the water or sediment phases except for some into the air phase. The compounds associated with particulates can likely be significantly reduced using traditional sediment practices, either in wastewater treatment plants, or in stormwater detention ponds.

Media filtration may reduce the compounds predominantly found in the water phase, especially with suitable selection of media (activated carbon).

The Effects of Environmental Factors on PPCP and Pesticide Associations with different Phases using Fugacity Calculations

The effect of different environmental factors on the partitioning of emerging contaminants into different media was studied using a full 2^3 factorial design. The number of runs and possible interactions of the factors were shown in Table 5.6. The high value of a factor is shown by a '+' and the low value by a '-'sign. The high and low values of the factors are based on the available literature. Table 4-12 is the 2^3 factorial design showing experimental conditions for eight runs (Box, et al. 1978).

Table 4-12. Factorial Design for PPCP and PAH Associations

Run	A	B	C	AB	AC	BC	ABC
1	+	+	+	+	+	+	+
2	+	+	-	+	-	-	-
3	+	-	+	-	+	-	-
4	+	-	-	-	-	+	+
5	-	+	+	-	-	+	-
6	-	+	-	-	+	-	+
7	-	-	+	+	-	-	+
8	-	-	-	+	+	+	-

A: Concentration of contaminant
B: Concentration of Suspended Sediment
C: Organic Fraction of Suspended Sediment

The high and low values of the factors considered in the design were shown in Tables 4-13 and 4-14.

Table 4-13. 2^3 Full Factorial Design Values for PPCPs

Variable	Low value	High value
Concentration of Carbamazepine (A), µg/L	0.002	0.083
Concentration of Caffeine (A), µg/L	0.004	0.24
Concentration of Ibuprofen (A), µg/L	0.003	0.6
Concentration of Diclofenac (A), µg/L	0.007	0.18
Concentration of Acetaminophen (A), µg/L	0.012	0.03
Concentration of Triclosan (A), µg/L	0.03	0.74
Concentration of Ciprofloxacin (A), µg/L	0.027	0.5
Concentration of Metoprolol (A), µg/L	0.02	0.12
Concentration of Salicylic acid (A), µg/L	0.013	0.22
Concentration of Dioxin (A), µg/L	0.004	0.071
Concentration of Nystatin(A), µg/L	0.002	0.74
Concentration of Dexamethasone(A), µg/L	0.002	0.74
Concentration of methoprene(A), µg/L	0.002	0.74
Concentration of prednisone (A), µg/L	0.002	0.74
Concentration of Metronidazole (A), µg/L	0.002	0.74
Concentration of Clindamycin (A), µg/L	0.002	0.74
Concentration of Ketoconazole(A), µg/L	0.002	0.74
Concentration of Suspended solids (B), mg/L	10	500
Organic Fraction of Suspended Solids (C)	0.05	0.2

Table 4-14. 2^3 Full Factorial Design Values for Pesticides

Variable	Low value	High value
Concentration of Contaminant (A), µg/L	0.002	0.083
Concentration of Suspended solids (B), mg/L	10	500
Organic Fraction of Suspended Solids (C)	0.05	0.2

The effects of selected factors on partitioning of emerging contaminants into water, sediment and suspended sediment were analyzed. As an example, the results of the nystatin and chloroneb analyses calculations are shown below in Tables 4-15 through 4-18 and Figures 4-18 through 4-23.

Table 4-15. Model Predicted Portioning of Nystatin with 2^3 Factorial Design Variables

Factor Value			Moles of Analyte Partitioned Into		
A	**B**	**C**	**Water**	**Sediment**	**Suspended Sediment**
+	+	+	5.0E+07	4.0E+05	4.2E+03
+	+	-	5.0E+07	4.0E+05	1.1E+03
+	-	+	5.0E+07	4.0E+05	8.4E+01
+	-	-	5.0E+07	4.0E+05	2.1E+01
-	+	+	1.3E+05	1.1E+03	2.8E+00
-	+	-	1.3E+05	1.1E+03	2.8E+00
-	-	+	1.3E+05	1.1E+03	2.3E-01
-	-	-	1.3E+05	1.1E+03	5.7E-02

Table 4-16. Calculated Effects of Factors and their Interactions on the Associations of Nystatin with Different Media

Factors/Interactions	Effect		
	Water	**Sediment**	**Suspended Sediment**
A	2.0E+08	1.6E+06	5.4E+03
B	-3.2E+03	-2.6E+01	5.2E+03
C	-2.0E+03	-1.6E+01	3.2E+03
AB	-3.2E+03	-2.6E+01	5.2E+03
AC	-2.0E+03	-1.6E+01	3.2E+03
BC	-1.9E+03	-1.6E+01	3.1E+03
ABC	-1.9E+03	-1.6E+01	3.1E+03

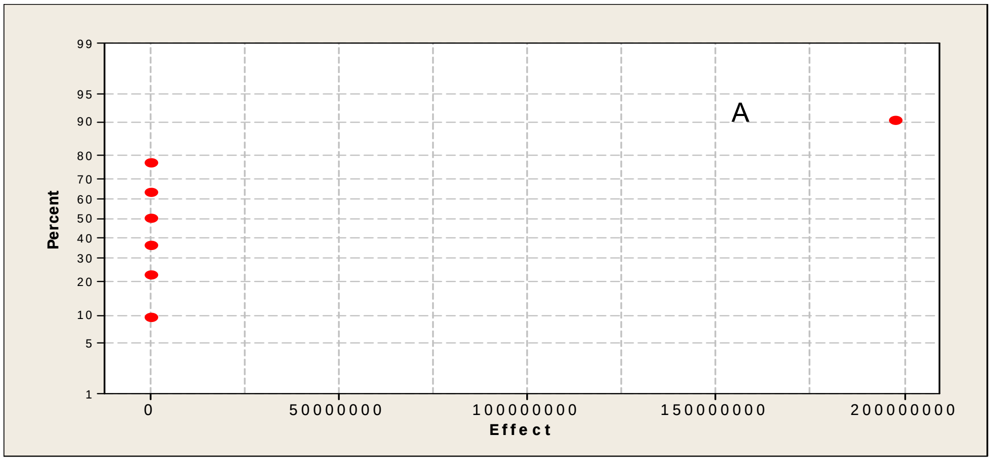


Figure 4-18. Probability plot of effects of partitioning of Nystatin with water

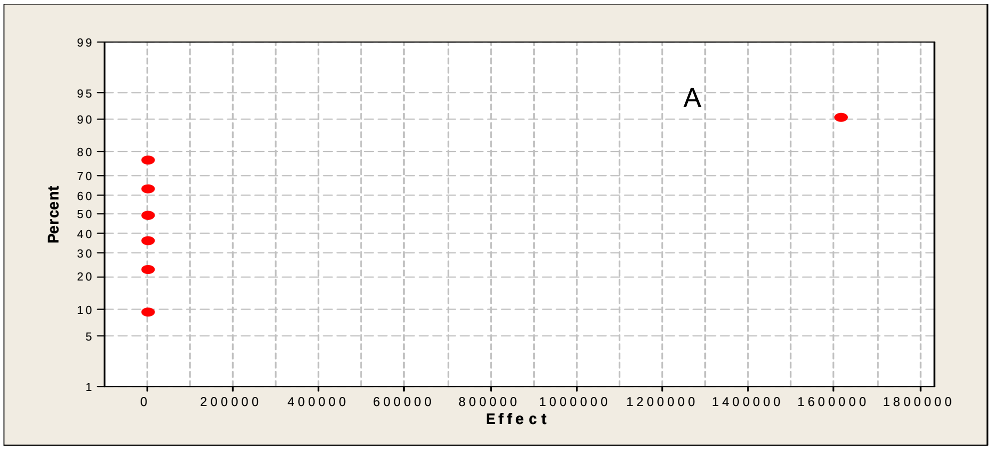


Figure 4-19. Probability plot of effects of partitioning of Nystatin with sediment.

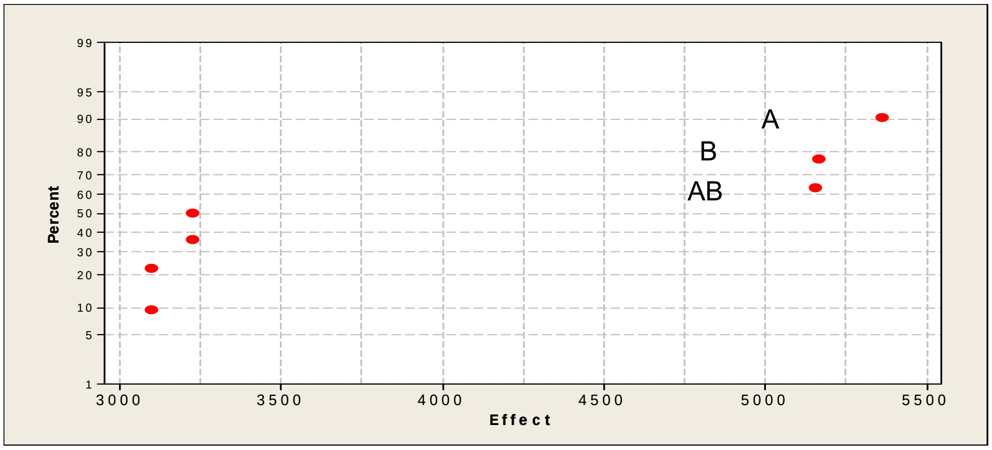


Figure 4-20. Probability plot of effects of partitioning of Nystatin with suspended sediment.

Table 4-17. Model Predicted Portioning of Chloroneb with 2^3 Factorial Design Variables

Factor Value			**Moles of Analyte Partitioned Into**		
A	**B**	**C**	**Water**	**Sediment**	**Suspended Sediment**
+	+	+	1.5E+09	9.3E+07	9.7E+05
+	+	-	1.5E+09	9.3E+07	2.4E+05
+	-	+	1.5E+09	9.3E+07	1.9E+04
+	-	-	1.5E+09	9.3E+07	4.8E+03
-	+	+	1.5E+07	9.3E+05	9.7E+03
-	+	-	1.5E+07	9.3E+05	2.4E+03
-	-	+	1.5E+07	9.3E+05	1.9E+02
-	-	-	1.5E+07	9.3E+05	4.8E+01

Table 4-18. Calculated Effects of Factors and their Interactions on the Associations of Chloroneb with Different Media

Factors/Interactions	**Effect**		
	Water	**Sediment**	**Suspended Sediment**
A	6.1E+09	3.7E+08	1.2E+06
B	-3.8E+05	-2.3E+04	1.2E+06
C	-2.4E+05	-1.4E+04	7.5E+05
AB	-3.7E+05	-2.3E+04	1.2E+06
AC	-2.3E+05	-1.4E+04	7.3E+05
BC	-2.3E+05	-1.4E+04	7.2E+05
ABC	-2.2E+05	-1.4E+04	7.0E+05

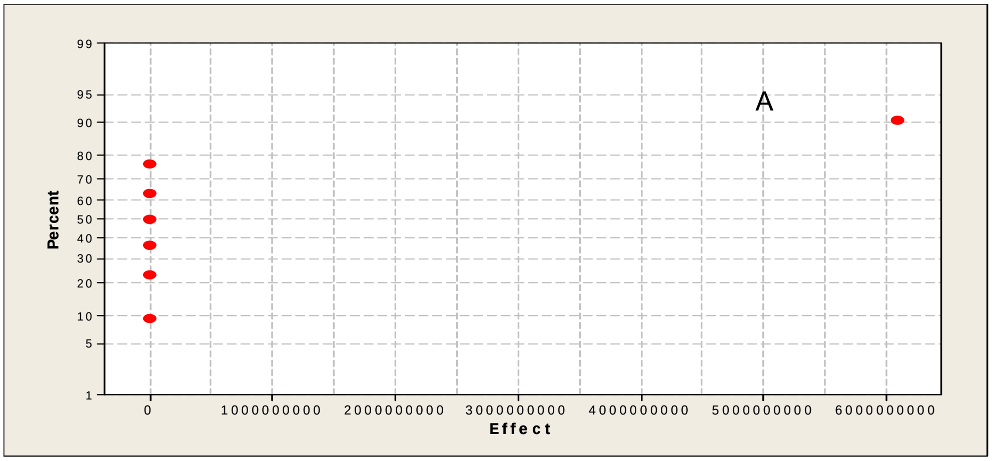


Figure 4-21. Probability plot of effects of partitioning of Chloroneb with water.

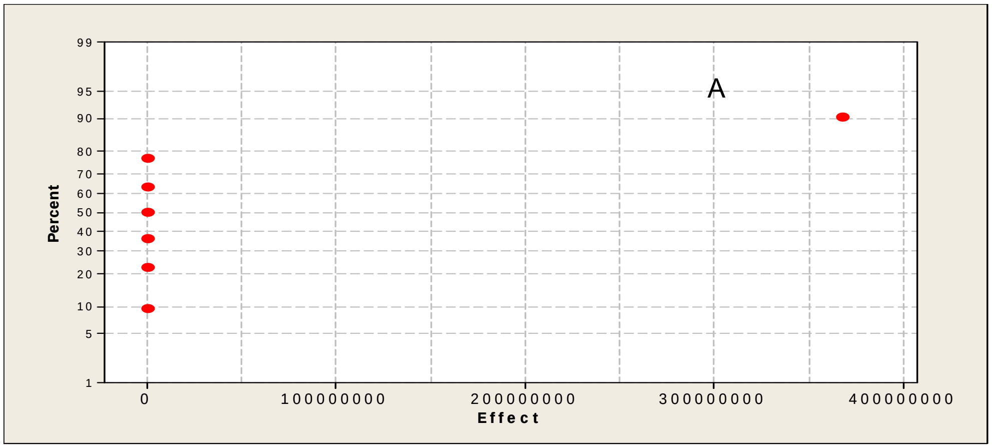


Figure 4-22. Probability plot of effects of partitioning of Chloroneb with sediment.

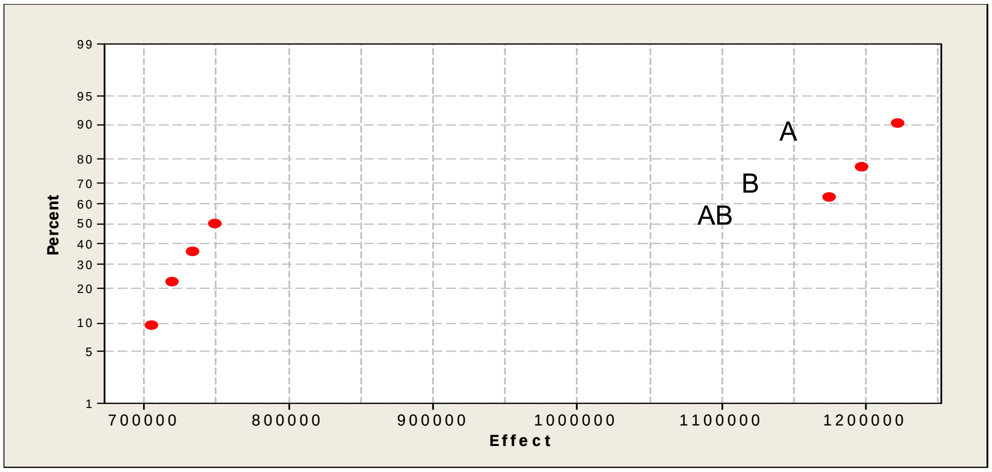


Figure 4-23. Probability plot of effects of partitioning of Chloroneb with suspended sediment.

Tables 5.8 and 5.10 show the predicted portioned moles of nystatin and chloroneb into water, sediment and suspended sediment under different combinations of the factors of the 2^3 factorial design. Tables 5.9 and 5.11 show the calculated effects of different combinations of the factors in portioning of nystatin and chloroneb with water, sediment and suspended sediment. Figures 5.1 – 5.6 are probability plots of the effects of the factors and their interactions on partitioning of nystatin and chloroneb into the three main phases.

The probability plots for the water and sediment phases (Figures 5.1, 5.2, 5.4, 5,5) indicate that the concentration of contaminant (A) in the system have positive effects in partitioning of those compounds into water and sediment phases. In the case of partitioning into the suspended sediment phase (Figures 5.3, 5.6), the concentrations of contaminant (A), concentration of suspended sediment (B),and combination of suspended sediment concentration and concentration of contaminants (AB) were found to have the greatest positive effect. Similar results were also found during the factorial analyses and Fugacity modeling portioning of all the other PPCPs and pesticides (Appendices A &B).

Fate of Emerging Contaminants in Groundwater

There is a potential threat of groundwater contamination by ECs, when stormwater is infiltrated. In the recent years, there have been extensive studies, on the fate and transport of various organic and inorganic pollutants in the saturated and unsaturated layers of the soil. Various computer models have been developed to determine the movement of the pollutants in the sub surfaces of the soil. SESOIL (Waterloo Hydrogeologic Inc) was selected as a suitable model that could consider all the physical and chemical processes involved for these contaminants during the wet weather flows.

An Overview of SESOIL

The Seasonal Soil Compartment Model (SESOIL) is an integrated screening-level soil compartment model, which is used to model the water transport, sediment transport and the fate of the pollutants in the subsurface. It simulates contaminant transport and fate based on diffusion, adsorption, volatilization, biodegradation, and hydrolysis. Arthur D. Little, Inc (ADL), developed it for EPA's Office of Water and the Office of Toxic Substances (OTS) in 1981 and later in 1984, it was fortified with a fourth soil compartment along with the existing three. During the end of 80's, it was integrated with the Graphical Exposure Modeling System for the PC (PCGEMS) that was later named RISKPRO.

SESOIL was developed as a screening-level model, using soil, chemical, and meteorological values as input information. The data requirements for SESOIL were generally less than needed for most other similar models. As it accepts time varying pollutant loading, it has a capability of simulating chemical releases into soil from various sources such as landfill sites, accidental leaks, agricultural applications, leaking underground storage tanks, or deposition from the atmosphere.

The various processes modeled by SESOIL are subdivided into three cycles, which constitute the hydrologic cycle, the sediment cycle and the pollutant fate cycle. The hydrologic cycle deals with moisture movement, the sediment cycle deals with runoff from the soil surface, and the pollutant fate cycle deals with the movement of the pollutant through the soil.

Hydrologic Cycle

The hydrologic cycle simulates the movement of the moisture through the soil compartment. Only vertical movement is considered here. We can obtain the hydrology of the site from the output, which is then passed onto the sediment washload cycle. This submodel is based on the adaptation of the water balance dynamics theory of Eagleson (1978). The water balance equations used by Eagleson are:

$$P - E - MR = S + G - Y \qquad \text{(eq. 6.1)}$$
$$I = P - S \qquad \text{(eq. 6.2)}$$

where the yield (Y) is equal to the sum of the surface runoff (S) and groundwater recharge (G). Yield is also a function of the total precipitation (P), evapotranspiration (E), and moisture retention (MR). And infiltration (I) equals to the difference of total precipitation and the surface runoff.

Sediment Washload Cycle

This submodel is used to estimate the erosion and sediment yield on watersheds. This model utilizes the runoff results from the hydrologic cycle and the sediment transport is estimated. This erosion model is comprised of the three basic processes of soil detachment, transport, and deposition. The Universal Soil Loss Equation (USLE) is employed in the detachment process. The USLE is used to predict the annual sediment erosion which was subjected to sheet and rill erosion. The various parameters involved in the USLE are rainfall factor (R), soil erodibility (K), slope length (L), slope degree factor (S), crop practice factor (C), and the conservation practice factor (P).

Pollutant Fate Cycle

The pollutant fate cycle uses the output obtained from the hydrologic and sediment washload cycles and stimulates the fate and transport of the pollutants considered. This model is based on the following mass balance equation.

$$O(t-1) + I(t) = T(t) + R(t) + M(t) \qquad \text{(eq. 6.3)}$$

Where

O (t-1) = the amount of pollutant originally in the soil compartment at time t-1(μg/cm^2),
I (t) = the amount of pollutant entering the soil compartment during a time step (μg/cm^2),
T (t) = the amount of pollutant transformed within the soil compartment during the time step (μg/cm^2),
R (t) = the amount of pollutant remaining in the soil compartment at time t (μg/cm^2),
M (t) = the amount of pollutant migrating out of the soil compartment during the time step (μg/cm^2)

The fate of the pollutant considered, is comprised of the movement of the pollutant as well as the transformation of the pollutant. These transformations involve the partitioning of the component across the three phases: soil air, soil moisture and soil solids. The concentration of the component in one phase is used to calculate the concentrations in the other two phases as equilibrium exists between all three phases.

The concentration in the soil air is calculated via the modified Henry's law:

$$C_{sa} = cH/R\,(T + 273) \qquad \text{(eq. 6.4)}$$

Where

C_{sa} = pollutant concentration in soil air (μg/ml); c = pollutant concentration in soil water (μg/ml); H = Henry's law constant (m^{3}atm/mol); R = Universal gas constant; T = soil temperature (^{o}C).

The concentration adsorbed to the soil is estimated using the Freundlich isotherm:

$$s = K_d c^{1/n} \qquad \text{(eq. 6.5)}$$

Where,

s = pollutant adsorbed concentration (μg/g); n = Freundlich exponent; K_d = pollutant partitioning coefficient (μg/g)/ (μg/ml); c = pollutant concentration in soil water (μg/ml)

The total concentration of the pollutant in the soil is computed as:

$$C_o = f_a * C_{sa} + \theta * C + \rho_b S \qquad \text{(eq. 6.6)}$$

Where,

C_o = overall (total) pollutant concentration (μg/cm^3);
$f_a = f - \theta$ = the air-filled porosity (mL/mL); f = soil porosity (mL/mL),
θ = soil water content (mL/mL); ρ_b= soil bulk density (g/cm^3).

Fate of Pharmaceuticals and Personal Care Products in Ground waters

The fate of PPCPs in ground water was studied using the SESOIL software (Waterloo Hydrogeologic Inc). A full 2^6 factorial design was used to determine the factors and their interactions effecting the pollutant movement in the vadose zone. Pollutant concentration, rainfall, vadose zone thickness, intrinsic permeability, organic content and pH were chosen as the possible factors and their effects were evaluated. The high and low values of the factors, except for the pollutant concentrations, used in the factorial analyses were acquired from a similar work conducted earlier (Mikula et al 2005) to predict the movement of inorganic pollutants in the vadose zone and are shown in Table 4-19.

Table 4-19. High and low values of controlling factors (Mikula et al 2005)

Factor	High	Low
Concentration of Nystatin (μg/L)	0.74	0.002
Concentration of Dexamethasone (μg/L)	0.74	0.002
Concentration of Methoprene (μg/L)	0.74	0.002
Concentration of Prednisone (μg/L)	0.74	0.002
Concentration of Metronidazole (μg/L)	0.74	0.002
Concentration of Clindamycin (μg/L)	0.74	0.002
Concentration of Ketconazole (μg/L)	0.74	0.002
Concentration of Carbamazepine (μg/L)	0.083	0.002
Concentration of Caffeine (μg/L)	0.24	0.004
Concentration of Ibuprofen (μg/L)	0.6	0.003
Concentration of Diclofanac (μg/L)	0.18	0.007
Concentration of Acetaminophen (μg/L)	0.03	0.012
Concentration of Triclosan (μg/L)	0.74	0.03
Concentration of Ciprofloxacin (μg/L)	0.5	0.027
Concentration of Metoprolol (μg/L)	0.12	0.02
Concentration of Salicylic acid (μg/L)	0.22	0.013
Rainfall Location and Depth (cm)	West Palm Beach	Phoenix
	153.59	6.71
Vadose zone thickness (cm)	1200	300
Intrinsic permeability (cm^2)	1.00E-07	1.00E-10
Organic content (%)	3	0.5
pH	7.2-8.0	4.3-5.0

The simulation run time was chosen to be 10 years and the rainfall and soil types were chosen for the SESOIL inbuilt data. Besides the controlling factors being examined, other factors (soil and pollutant chemical parameters) which were needed to predict pollutant movement are shown for each simulation in Appendix F. A total of 64 runs were conducted for each pollutant and the effects of different factors on the pollutant movement were evaluated by generating normal probability plots as shown in Appendix A. As an example, the results of the pollutant migration analyses for nystatin are shown in Figure 4-24.

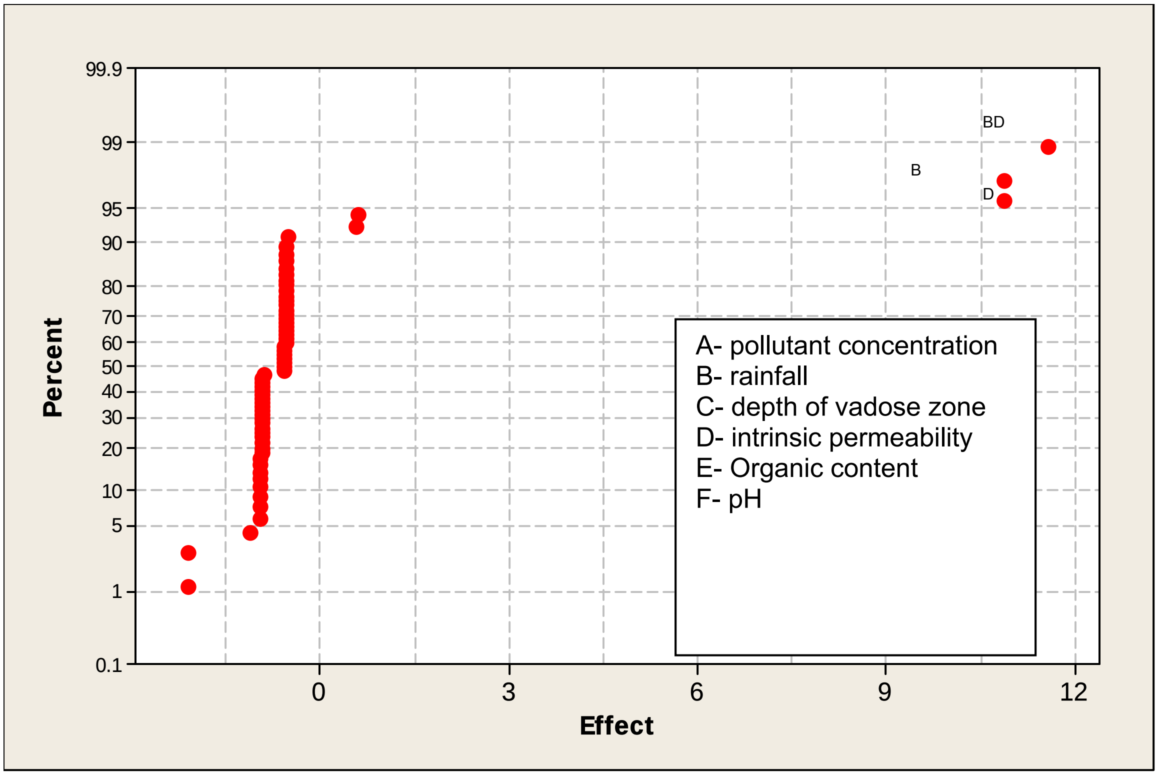


Figure 4-24. Estimated main effects and effect interactions on nystatin migration in vadose zone.

It can be seen from Figure 6.1, that rainfall, and intrinsic permeability were the significant factors effecting the migration of nystatin in the vadose zone. Similar results were observed for all the other studied compounds, as shown in appendix C.
The results generated by the SESOIL were useful and most of the PPCPs included in the study were predicted to move along with the infiltrating stormwater and didn't sorb to the soils and higher rainfall amounts naturally allowed them to migrate deeply into the vadose zone. The effect of intrinsic permeability was also identified as being significant, since increased rainfall, along with the soils, having high permeability would likely to be expected to increase the mobility of the pollutants through the vadose zone to ground water.

The retardation factors for the PPCPs are calculated to predict the movement of these compounds with respect to water movement. The retardation factors were calculated as the ratio of the saturated hydraulic conductivity of the soils to the pollutant migration rates. The minimum and maximum migration rates of the pollutants along with their retardation factors were shown in Table 4-20.

Table 4-20. Retardation Factors for the PPCPs in Saturated Zone

	Max. Sat. Hydraulic Conductivity		Min. Sat. Hydraulic Conductivity	
	0.634 m/hr		0.000462 m/hr	
Compound	Max. Migration Rate (m/hr)	Retardation Factor	Min. Migration Rate (m/hr)	Retardation Factor
Nystatin	3.05E-04	3279	7.54E-06	61
Dexamethasone	3.39E-04	2953	8.33E-06	55
Methoprene	8.98E-05	11142	2.23E-06	208
Prednisone	5.87E-04	1704	1.46E-05	32
Metronidazole	6.42E-04	1558	1.59E-05	29
Clindamycin	3.66E-04	2733	9.08E-06	51
ketoconazole	4.35E-04	2299	1.08E-05	43
Carbamazepine	4.07E-04	2455	1.01E-05	46
Caffeine	7.18E-04	1393	1.78E-05	26
Ibuprofen	1.52E-04	6585	3.77E-06	123
Diclofenac	2.76E-04	3622	6.85E-06	67
Acetaminophen	7.46E-04	1341	1.85E-05	25
Triclosan	1.10E-04	9054	2.74E-06	169
Ciprofloxacin	1.31E-04	7624	3.26E-06	142
Metoprolol	6.14E-04	1628	1.52E-05	30
Salicylic acid	3.11E-04	3219	7.71E-06	60

It can be seen from Table 6.2 that the retardation factors of pollutants in the saturated zone were in the range of 25 to more than 11000, indicating their very slow movement rate in the saturated zone.

The disposal of pesticide contaminated stormwater to the subsurface should receive special attention. Pitt, et al. (1995) identified pesticides as having moderate to high groundwater contamination potentials due to their mobility through the vadose zone with little soil attenuation and difficulty of treatment before discharge.

Several studies have investigated pesticide movement through soil and it was found out that the mobility depends on several significant factors including soil texture, pesticide persistence, total organic carbon content, depth of the water table (Shirmohammadi etal 1989), solubility, and adsorption rates (Bucheli etal 2007). Usually, pesticides with low water solubility and high K_{ow}, especially in organic rich soils, are less mobile. It has also been observed that biological degradation can be an effective mechanism for the decomposition of some pesticides retained in the soil (Takemetsu etal 1985), although most are resistant to degradation.

Trace Heavy Metals in Wet Weather Flows

Another project task associated with this project investigated sources of heavy metals in wet weather flows (and their chemical characteristics and associated treatability). This section shows that many of the heavy metals in stormwater could be related to material selection and that use of proper materials could result in decreased heavy metals in wet weather flow. This section presents the results of an extensive literature review of heavy metal releases from different materials (mostly roofing types) and the results of several controlled leaching tests that examined a variety of roof gutter, piping, and storage tank materials.

Contaminants Associated with Rooftop and Pipe Materials and Parameters that Influence Metal Releases into the Environment

Roofing drainage systems are often made of metallic materials or may have metals as components, including aluminum, zinc, and copper. Researchers have determined these heavy metals are common contaminants in roof runoff at potentially high concentrations (Clark, et al. 2008 a, b; Wallinder 2001; Pitt, et al. 1995; Förster 1996; Morquecho 2005; Tobiason 2004). When released into the environment, metals can bioaccumulate and pose a threat because of their toxicity (US EPA 2007a). In the environment, metals are found in many forms including ionic, chemical complexes, colloidal, and particulate forms (Morquecho 2005), which all affect their toxicity levels and fates in the environment (Pitt, et al. 1995). The metal's chemical forms (speciation) are determined by such factors as pH, temperature, and inorganic and organic anionic complexation. The presence of other cations in the water also influences metal bioaccumulation and toxicity (US EPA 2007a; Morquecho 2005).

A number of studies have been conducted to obtain quantitative data on the metal runoff rates from new and naturally aged copper and zinc roofing materials which have been exposed to different atmospheric environments (He, et al. 2001a,b; Wallinder, et al. 2009, 2002 a,b; 2001, 2000, 1998, 1997; Cramer, et al. 2002; Faller and Reis 2005; Clark, et al. 2008a). Metal corrosion and paint were identified as copper, lead, zinc, chromium, iron, and aluminum sources (Burton and Pitt 2002; Gromaire, et al. 2002; Förster 1996; USEPA 2011; Davis and Burns 1999; Simmons, et al. 2001; Gumbs and Dierberg 1985, Lasheen, et al. 2008, Mendez, et al. 2011).

Zinc, copper, and other metals are frequently used in outdoor structures. For example, in southeastern Mexico, 63% of roofs and walls are made from galvanized steel sheets which undergo corrosion. As dew and rain dissolve zinc corrosion products, zinc ions leach from the corroded surfaces (Veleva, et al. 2010). Annually, runoff from Parisian zinc roofs generated approximately 34 to 64 metric tons of zinc which is about half the load produced by runoff from the total Paris area (Gromaire, et al. 2002).

The following discussions summarize key findings of metal releases from different exposure experiments, including summary tables containing observed concentrations from the different monitoring studies.

Zinc

When exposed to the atmosphere, metal material surfaces are in contact with many forms of moisture (condensed water from high humidity, rain, mist, dew, or melting snow) and the materials undergo corrosion (oxidation) processes (Veleva, et al. 2007). When zinc material is exposed to the atmosphere, a protective layer (zinc oxides/hydroxides/carbonates) called patina is formed, which serves as a physical barrier between the metal surface and the atmosphere, slowing down further oxidation (Legault and Pearson 1978; Zhang 1996). Patina can be removed physically by winds and sand erosion or by partial dissolution of some soluble patina components when exposed to rain or water condensation on the metal surface, re-exposing the material to continued oxidation. Zinc runoff can lead to zinc accumulations in the soils, and in surface and ground waters (Veleva, et al. 2007). In urban areas, the highest zinc runoff concentrations are found in roof runoff from roofs having galvanized steel components (such as roofing sheets, flashing, or gutters and downspouts) (Burton and Pitt 2002; Förster 1999; Bannerman, et al. 1983; Pitt, et al. 1995). Zinc contributions from rooftops can make up about one fourth of the total zinc discharges from an area's total stormwater runoff (Burton and Pitt 2002).

Clark, et al. (2008a) studied runoff water quality from uncoated galvanized steel roofing materials during four months of exposure to rain on the campus of Penn State Harrisburg and found that this material can be a significant source of zinc. Figure 1.1comparesrunoff zinc concentrations (after background correction) from different roofing materials (Clark, et al. 2008a). The greatest zinc concentrations were from runoff from galvanized materials. The authors didn't observe any consistent decreases in runoff concentrations during the four months of roof exposure. The median zinc concentrations in the runoff from uncoated galvanized metals were about 5.5 mg/L (about 1,400 times higher than the criterion established by the EPA for aquatic toxicity) with maximum concentrations about 10 mg/L. All other roofing materials tested had zinc runoff concentrations much less than 1 mg/L, as shown on Figure 4-25.

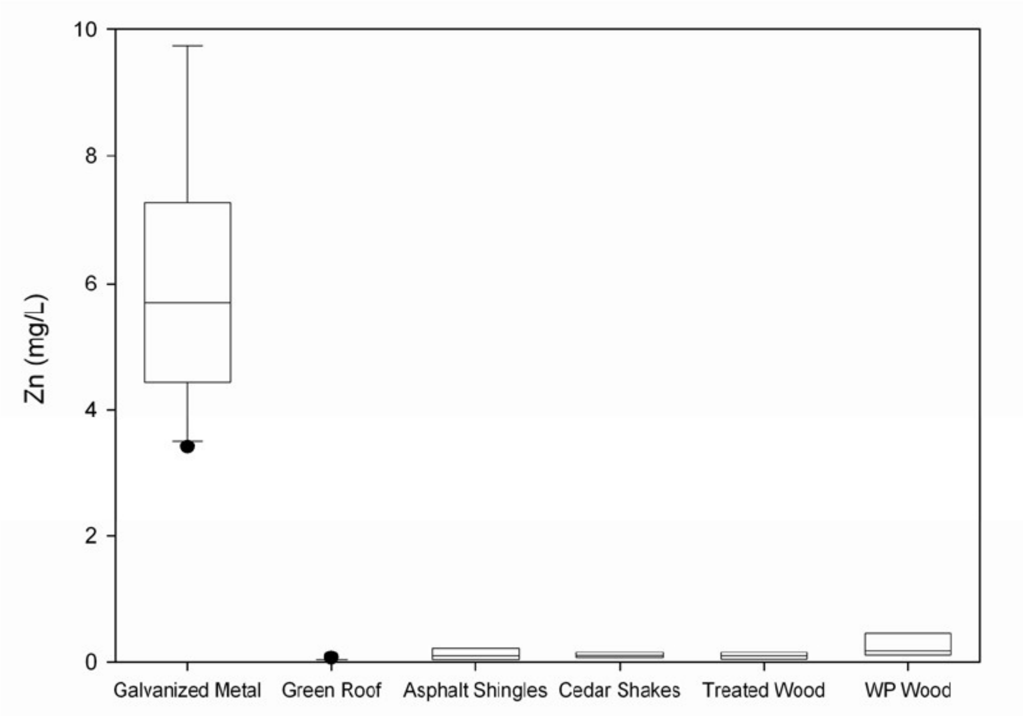


Figure 4-25. Runoff zinc concentrations from roofing materials. Background corrected. Source: Clark, et al. (2008a).

Clark, et al. (2007), based on their laboratory testing on aged galvanized roofing panels, concluded that there can be elevated concentrations of pollutants in roof runoff over a long period of time. Clark, et al. (2008b) further studied leaching of heavy metals from several materials including two 60year old painted galvanized metal roofing panels (one galvanized metal panel had been exposed to the weather for 60 years, while the other was stored in the barn for roof repairs) in the laboratory and in the field. They also studied galvanized corrugated aluminum, prepainted 55% aluminum-zinc alloy coated steel (Galvalume), and corrugated polyvinyl chloride panels. After monitoring runoff from a naturally-exposed pilot-scale test of these materials for 2 years, the authors noted substantial zinc release from uncoated galvanized metals during the early part of the materials' lifespan. Within two weeks of the installation, the authors noticed visible degradation on the galvanized metal (Clark, et. al. 2007). The authors also found that aged roofing panels have the potential for pollutant releases, even after 60 years of exposure.

Good (1993) studied heavy metal concentrations and aquatic toxicity of roof runoff from different roofing materials at a sawmill on the coast of Washington. The roofing materials included a rusty galvanized metal roof, a weathered metal roof that may have been coated with aluminum paint many years age, a tar roof sealed with aluminum paint, and a relatively new aluminum roof. Zinc concentrations in roof runoff samples surpassed the water quality criteria. Zinc was leaching out of each type of roofing material, however zinc concentrations were extremely high (up to 12.2 mg/L of total zinc and 11.9 mg/L of dissolved zinc) in the runoff samples from galvanized roofing materials.

Tobiason and Logan (2000) and Tobiason (2004) measured zinc concentrations in the runoff from an unpainted Galvalume metal roof at Seattle Tacoma International Airport. Zinc concentrations varied over an order of magnitude during the rain events ranging from 0.03" to 0.38" total rainfall, and decreased with rainfall volumes and possibly seasonal factors. The authors observed that such commonly used galvanized products such as fencing, guardrails, light poles and unpainted Galvalume metal roofing leach substantial concentrations of dissolved zinc in stormwater runoff. Galvanized material was contributing zinc concentrations ranging from 100's of µg/L to the 10's of mg/L (Tobiason 2004; Tobiason and Logan 2000; Good 1993).

Veleva, et al. (2007) studied zinc runoff due to atmospheric corrosion of products during exposure of pure Zn and hot dip galvanized steel materials in the Gulf of Mexico (urban and rural) during 18 months. High annual rates of zinc runoff were observed. The authors found that zinc runoff rates ranged between 6.5 to 8.5 ± 0.30 g Zn/(m^2yr). Gromaire-Mertz, et al. (1999) studied runoff from zinc roofs and gutters in an old densely populated district of central Paris, France, between July 1996 and May 1997. Roofing materials included clay tiles (70%) and zinc sheets. Zinc concentrations in roof runoff frequently exceeded level 2 of the French water quality standards of 0.05mg/L (observed zinc concentrations in the runoff were between 1 and 5 mg/L).

Schriewer, et al. (2008) studied runoff from 14 year-old zinc roofs in Germany for a period of 1 year. Roof runoff quality was affected by the titanium–zinc gutters and down spouts. Samples were collected directly in the gutter. The authors observed high zinc concentrations in the roof runoff. The flow-weighted average zinc concentration was 4.9 mg/L. Zinc runoff rates of 3.73 g/m^{2}were determined for the zinc roof during868 mm of precipitation during the 12 months of the study.

Zobrist, et al. (2000) measured the concentrations of heavy metals in runoff from tile, polyester, and gravel roofs located at a suburb of Zurich, Switzerland. The drainage system for the tile (clay) roof was made of 15-year old copper; new copper for the polyester roof, and PVC material for the gravel roof. Runoff from the polyester and gravel roofs was sources of zinc. Observed zinc concentrations were between 0.005 and 0.85 mg/L.

Wallinder, et al. (2001 and 2000) investigated zinc yields in the runoff from 15 different zinc panels or zinc coatings, which included new and naturally aged sheets, commercial zinc-based construction materials (different zinc panels or zinc coatings, which included new and naturally aged sheets) located in Stockholm, Sweden and Olen, Belgium during 1 year exposures. Zinc runoff yields ranged from 0.07 g/m^2/year (prepainted galvanized steel) to 3.5 g/m^2/year (40 year old zinc panels). Zinc runoff yields from hot dip galvanized steel panels were 2.7 g/m^2/year.

Faller and Reiss (2005) studied the exposure of different metallic materials to the open atmosphere in Dubendorf, Switzerland. The materials included: copper and zinc with different surface treatments, including tinned copper, galvanized steel, aluminum, stainless steel, tinned stainless steel, titanium, and lead. Zinc materials released measurable amounts of metallic ions. The largest source of zinc was prepatinated zinc sheets, while black phosphatated titanium-zinc sheets released the least zinc concentrations. The corrosion rates of the untreated zinc sheets decreased with time during the early exposure periods. However the runoff rate was relatively constant in time after one year of exposure. They concluded that the corrosion and runoff rates will equalize with time. The zinc runoff yield from untreated zinc sheets was approximately 80% of its mass corrosion rate. Metal runoff yield is the metal concentration in the runoff times the actual runoff water volume; corrosion rate is the rate of degradation of the metal based on the measured mass loss (He 2002).The runoff rate for the titanium-zinc sheet after 5 years exposure was 2.6 g/m^2/year, compared to 3.2 g/m^2/year for prepatinated zinc. At the Stockholm site, the runoff rate for zinc was 3.1 g/m^2/year and at the Hannover, Germany site, the runoff rate for zinc was 4.51 g/m^2/year measured after 3 years of exposure. Also, studies conducted by Wallinder, et al. (2000 and 2001) on zinc runoff yields from zinc coatings show that in general, at least during the first year of exposure, zinc runoff yields were substantially lower than the corresponding corrosion rates and constituted 50-90% during exposure times up to five years.

In contrast to the findings by Faller and Reiss (2005), Veleva, et al. (2010) (who studied zinc concentrations leaching from hot dip galvanized (HDG) steel that were exposed to the Gulf of Mexico environments for two years) observed that the annual zinc runoff yields in both test sites decreased by 50% during the second year and ranged between 2.70 and 3.28 g m^{-2}/year compared to the first year's yields that were between 6.52–7.98 g m^{-2}/year. Zinc concentrations in the runoff appeared to diminish its rate of release with time, possibly due to the doubled rain amounts during the second year of the experiment. More frequent and intense rains wash off aggressive contaminants and shorten the dry period of time during which the corrosion products form (Veleva, et al. 2010).

Förster (1996 and 1999) studied heavy metals in roof runoff in Bayreuth, Germany. Förster found that metal flashings used on the roofs released very high concentrations of Zn and concluded that the best management practice would be to stop using exposed metal surfaces on roofs and walls of buildings. The differences in the pollution yields between different roofs were sometimes as high as three orders of magnitude. The variability was also high within a single roof and for different storm events. Roofing materials studied included concrete tiles, clay pantiles, fibrous cement, tar felt, and zinc sheet. Zinc and PVC gutters were used. Förster (1999) found that zinc concentrations in the zinc sheet roof runoff was two to three orders of magnitude above the concentrations measured in runoff from roofing materials that didn't have any metal components (fibrous cement roof). Zinc concentrations were elevated in the runoff from roofs that had metal gutters and downspouts. The total zinc concentrations in the zinc sheet runoff were approximately 18 mg/L. Total zinc concentrations from zinc gutters at Keuperstr and Konigsallee, Germany, were approximately 2 and 4 mg/L, respectively. Gumbs and Dierberg (1985) studied three components of 46 single-family rainwater storage cisterns with a domestic water delivery system (roof, cistern, and distribution system) on St. Maarten Island. The elements of the monitored cistern water supply system included the house roof, cistern, pressure tank, and water distribution system. The potential heavy metal sources were airborne soils and auto emissions, corrosion of galvanized iron roof and roof paint, dissolution of sediments in the cistern and corrosion within the distribution system. The metal concentrations in the harvested rainwater increased as it passed over the galvanized roofing surfaces and through gutter and downspouts connected to the cisterns. They observed that zinc concentrations (0.006 to 2.29 mg/L with an average of 0.192 mg/L) in the tap samples (water supplied by the distribution system from the cistern) were significantly higher than in the surface water (0.001 to 1.16 mg/L with an average of 0.084 mg/L) of the cisterns. The elevated levels of zinc concentrations at the tap were attributed to the corrosion of the galvanized metal components within the distribution systems that connected the cistern with the tap due to the longer residence time.

Mendez, et al. (2011) also studied the effects of roofing materials on water quality for rainwater harvesting systems. The authors examined the quality of harvested rainwater using several pilot-scale roofs (asphalt fiberglass shingle, Galvalume® metal, concrete tile, and a green roof that contained a substrate, drainage layer, and membrane roof barrier and native perennial plants) and three full-scale roofs (two asphalt fiberglass shingle and one Galvalume® metal). The full-scale site was located at the University of Texas at Austin Child Development Center and had a 7-year-old Kynar®-coated Galvalume® roof. Also, new and artificially aged coupons of asphalt fiberglass shingle, Galvalume® metal, and concrete tiles were examined in lab-scale studies to determine the potential for changes in harvested rainwater quality influenced by aged roofing materials. The authors found high zinc concentrations leaching out of pilot-scale Galvalume and full-scale Kynar®-coated Galvalume® roof. Zn concentrations in the harvested rainwater from the pilot-scale Galvalume® roofs ranged between 0.21 and 0.85 mg/L for the first flush sample, and between 0.08 and 0.36 mg/L for later samples. Ambient rain zinc concentrations were between 0.001 and 0.1 mg/L. Zn concentrations in the harvested rain water from full-scale Kynar®-coated Galvalume® roof ranged between 0.1 and 0.2mg/L for the first flush sample and between 0.06 and 0.18 mg/L for later samples.

Shahmansouri, et al. (2003) conducted a study on pilot scale drinking water distribution systems in Zarrinshahr and Mobarakeh, Iran. The piping system materials in houses and buildings were galvanized, the distribution piping systems were made of asbestos, polyethylene, and occasionally iron pipes. Copper brass taps and valves were possibly used in some homes. A minimum of 6 hours of retention time for tap water samples was used. The authors found that the samples analyzed along the domestic water distribution system showed significant increases in zinc concentrations. Zinc concentrations sometimes exceeded the recommended maximum contaminant levels (MCL).Zinc concentrations released in the drinking water distribution systems ranged between 0.001 and 0.006 mg/L in Zarrinshahr and between 0.0002 and 0.006 mg/L in Mobarakeh.

Heijerick, et al. (2002) studied the bioavailability of zinc in runoff from 15 different zinc-based roofing materials in Stockholm, Sweden. High zinc concentrations were released from roofing materials made using zinc, galvanized steel and galvalume materials. The highest zinc concentrations were found in runoff from 40 year old uncoated zinc roofing materials (up to 8.4 mg/L), while the lowest runoff concentrations were from prepainted galvanized steel materials (up to 0.63 mg/L).

Table 4-21 summarizes zinc concentrations or runoff yields from different materials found by various researchers.

Table 4-21. Zinc releases from various sources.

Materials	Test conditions	Zn concentrations or runoff yields	Reference
Uncoated Galvanized Steel Roofing Materials			
New uncoated galvanized steel roof	4 mo field test. Pilot Scale. Harrisburg, PA.	3.5 and 9.8 mg/L	Clark, et al. (2008a)
Galvanized metal roof	Field Seattle	0.09 and 0.48 mg/L	Tobiason and Logan (2000)
Hot dip galvanized steel	2 year field test. The Gulf of Mexico	6.52– 7.98 g m^{-2} during the 1st year 2.70 and 3.28 g m^{-2} during the 2nd year	Veleva, et al. (2010)
Hot dip galvanized steel panel	Stockholm, Sweden. 1 year test	2.7 g/m^2 per year	Wallinder, et al. (2001)
Hot-dip galvanized steel	5 years pilot scale test. Dubendorf, Switzerland	2.4 g/m^2 per year	Faller and Reiss (2005)
Galvanized steel roof	Stockholm, Sweden. 1 year test.	1.2-5.5 mg/L	Heijerick, et al. (2002)
Galvanized material	Hannover, Germany, 3 year test	4.51 g/m^2 per year	Lehmann (1995)
Pure Zn and hot dip galvanized steel	Urban and rural areas. The Gulf of Mexico, 18 mo test	6.5 – 8.5 ± 0.30 g/ m^2 per yr.	Veleva, et al. (2007)
14 year old zinc roof	Germany, 1 year test	0.3 - 30 mg/L 3.73 g/m^2 per year	Schriewer, et al. (2008)
40 year old zinc panel	Stockholm, Sweden. 1 year test	3.5 g/m^2 per year	Wallinder, et al. (2001)
Zinc roof	Filed test. Bayreuth, Germany.	17.6 mg/L	Forster (1999)
Zinc roof	Stockholm, Sweden. 1 year test.	3.8-4.4 mg/L	Heijerick, et al. (2002)
40 years old zinc roof	Stockholm, Sweden. 1 year test.	8.4 mg/L	Heijerick, et al. (2002)
Zinc materials	Stockholm, Sweden. 1 year test.	3.0 - 3.3 g/m/^{2} per year	He, et al. (2001a)
Zinc sheet (0.07% Ti, 0.17% Cu) panel	1 year field test. Olen, Belgium. Industrial area	4.5 and 5.7 g/m^2 per year	Wallinder, et al. (2000)
Clay tiles (70%) + zinc sheets, zinc sheets; roofs and gutters	Field test. Central Paris. July 1996 and May 1997	0.8 - 38 mg/L	Gromaire-Mertz, et al. (1999)
Zinc gutters	Filed test. Bayreuth, Germany.	2-4 mg/L	Forster (1999)
zinc roofing	Paris, France. 10 mo. test	34 - 64 metric tons per year for whole City	Gromaire, et al. (2002)

Table 4-21. Zinc releases from various sources (continued)

Coated Galvanized Steel Roofing Materials			
New coated galvanized metal roof	4 mo field test. Pilot Scale. Harrisburg, PA	< 0.5 mg/L	Clark, et al. (2008a)
60 years old painted galvanized metal roof in the field	Leaching test in the lab	5 - 30 mg/L	Clark, et al. (2008b)
60 years old painted galvanized metal roof stored in the barn	Leaching test in the lab	5 - 30 mg/L	Clark, et al. (2008b)
Prepainted galvanized steel panel	Stockholm, Sweden. 1 year test	0.07 g/m^2 per year	Wallinder, et al. (2001)
Zinc with different surface treatment	5 years pilot scale test. Dubendorf, Switzerland	1.9 to 3.2 g/m^2 per year	Faller and Reiss (2005)
Prepatinated zinc	5 years pilot scale test. Dubendorf, Switzerland	3.2 g/m^2 per year	Faller and Reiss (2005)
Prepainted galvanized steel roof	Stockholm, Sweden. 1 year test.	0.16-0.63 mg/L	Heijerick, et al. (2002)
Uncoated Galvanized Aluminum Roofing Materials			
Galvalume roofs	Pilot-scale scale in Austin, Texas. Several rain events in 2010	0.208 – 0.852 mg/L during the first flush; 0.077 – 0.362 mg/L for later samples	Mendez, et al. (2011)
Galvalume roof	Stockholm, Sweden. 1 year test.	0.6-1.6 mg/L	Heijerick, et al. (2002)
Unpainted Galvalume roof	Field	0.42 - 14.7 mg/L	Tobiason (2004)
Coated Galvanized Aluminum Roofing Materials			
Kynar®-coated Galvalume®	Full scale in Austin, Texas. Several rain events in 2010	0.098 – 0.179 mg/L during first flush, 0.058 – 0.177 mg/L for later samples	Mendez, et al. (2011)
New prepainted 55% aluminum-zinc alloy coated steel (Galvalume) roof	2 years field test. Pilot Scale. Harrisburg, PA	<0.25 mg/L	Clark, et al. (2008b)
Other Roofing Materials			
Black phosphatated titanium-zinc	5 years pilot scale test. Dubendorf, Switzerland	1.9 g/m^2 per year	Faller and Reiss (2005)
Titanium-zinc sheet after 5 years exposure	5 years pilot scale test. Dubendorf, Switzerland	2.6 g/m^2/year	Faller and Reiss (2005)
Aluminum, stainless steel and titanium	5 years pilot scale test. Dubendorf, Switzerland	< detection limit (0.01 mg/L)	Faller and Reiss (2005)
Polyester roof	Zurich, Switzerland. 2 year test	<0.160 mg/L	Zobrist, et al. (2000)
Gravel roof	Zurich, Switzerland. 2 year test	<0.035 mg/L	Zobrist, et al. (2000)

Table 4-21. Zinc releases from various sources (continued)

Drinking Water Distribution Systems (DWDS)			
At the tap after galvanized metal parts in distribution systems	St. Maarten Island, Netherlands	0.006 to 2.29 mg/L (average of 0.19 mg/L)	Gumbs and Dierberg (1985)
DWDS made of asbestos, polyethylene, and iron pipes; piping system materials in houses and buildings were galvanized	DWDS in Zarrinshahr, Iran	$0.73*10^{-3}$ - $5.80*10^{-3}$mg/L	Shahmansouri, et al. (2003)
DWDS made of asbestos, polyethylene, and iron pipes; piping system materials in houses and buildings were galvanized	DWDS in Mobarakeh, Iran	$0.20*10^{-3}$ - $5.80*10^{-3}$ mg/L	Shahmansouri, et al. (2003)

The largest sources of zinc in stormwater runoff are zinc-based roofing materials (Clark, et al. 2008a, b; Good 1993; Tobiason and Logan 2000; Tobiason 2004; Faller and Reiss 2005; Schriewer, et al. 2008; Förster 1996, 1999; Gromaire-Mertz, et al. 1999; Gumbs and Dierberg 1985; Heijerick, et al. 2002), galvanized roof drainage systems (Burton and Pitt 2002; Bannerman, et al. 1983; Pitt, et al. 1995; Förster 1996 and 1999), and galvanized pipes (Gumbs and Dierberg 1985; Shahmansouri, et al. 2003). Galvanized materials have a large potential for contributing zinc to runoff during their useful life (Clark, et al. 2008a, b; Wallinder, et al. 2001, 2000; Heijerick, et al. 2002). Zinc runoff yields were generally observed to increase with the age of the material (Clark, et al. 2008b; Schriewer, et al. 2008; Wallinder, et al. 2001; Heijerick, et al. 2002). Zinc concentrations in runoff from galvanized materials ranged from 100’s of µg/L to 10’s of mg/L (Tobiason 2004; Tobiason and Logan 2000; Clark, et al. 2008a, b; Heijerick, et al. 2002; Good 1993). Zinc concentrations in roof runoff samples frequently exceeded the water quality criteria established by the U.S. EPA and regulatory agencies from other countries (Good 1993; Clark, et al. 2008a; Gromaire-Mertz, et al. 1999).

Copper

Clark, et al. (2008 a and b) monitored runoff from a pilot-scale set upon the campus of Penn State Harrisburg examining various roofing and building materials for 2 years under natural rain conditions and noted substantial copper releases from pressure treated and waterproofed woods. The copper concentrations from non-copper metal and vinyl materials did not exceed 25 µg/L (a typical toxicant value for certain aquatic plants). The results from laboratory leaching tests showed that copper concentrations may continue to leach out in an acid rain environment during the material’s useful life (Clark, et al. 2008b).

Wallinder, et al. (2000) studied the effect of exposure direction and inclination on the runoff rates of zinc and copper from roofs located in Olen, Belgium (Zn measurements) and Stockholm, Sweden (Cu measurements).For copper, the yearly runoff rate on the average ranged between 1.3 and 1.5 g/m^2. The copper runoff yield constituted 20-50% of the observed corrosion rate during exposure times up to two years. The mass loss due to corrosion was estimated by the difference between the weights before exposure and after chemical removal of the corrosion patina.

Sandberg, et al. (2006), Wallinder and Leygraf (1997), and Leuenberger-Minger, et al. (2002) also noted that the copper runoff rate is significantly lower than the corrosion rate. The runoff rate is lower than the corrosion rate because the runoff does not wash away all the corrosion products that are formed, such as the patina. For example, the annual total copper runoff rate was 1.5 g/m^2/year from fresh copper sheet and was substantially lower than the annual copper corrosion rate (19 g/m^2/year) (which was decreasing with time).

Sandberg, et al. (2006) examined corrosion-induced copper concentrations in the runoff from copper sheet, naturally patinated copper, and pre-patinated copper in a chloride-rich marine environment near Brest, France during one year. For some roof panels a comparison was made with results from an urban site in Stockholm, Sweden. At similar rain quantities, copper runoff rates were significantly lower at the marine site compared to data acquired in an urban environment, despite substantially higher chloride deposition rates at the marine location. For naturally patinated copper, there were no large variations noted in runoff rates with time. However, for the fresh copper sheet, the runoff rate increased from a fairly constant rate of 1.1 g/m^2/year, during the first 4 months of exposure, to a relatively constant rate of 1.5 g/m^2/year during the remaining exposure period as a result of the formation of paratacamite ($Cu_2(OH)_3Cl$).

For fresh copper sheet, cuprite (Cu_2O) was the main crystalline patina constituent during the first 12 weeks of exposure, followed by the formation of paratacamite ($Cu_2(OH)_3Cl$) after that exposure period. Formation of paratacamite was a result of significantly higher deposition rates of chlorides between 12 and 26 weeks. After months of atmospheric exposure, basic copper compounds like ($Cu_2(OH)_3Cl$), brochantite ($Cu_4SO_4(OH)_6$) and cuprite (Cu_2O) and Posnjakite ($Cu_4SO_4(OH)_6 \cdot H_2O$) can be formed depending on the contamination in the environment (Sandberg et. al. 2006; Faller and Reiss 2005; Kratschmer, et al. 2002). Brochantite ($Cu_4SO_4(OH)_6$) and posnjakite ($Cu_4SO_4(OH)_6 \cdot H_2O$) are common compounds in sulfate containing environments; ($Cu_2(OH)_3Cl$) are often found in chloride rich environments (Kratschmer, et al. 2002). The brochantite phase was still detected after one year of exposure (Sandberg, et al. 2006). The bioavailable portion (available for uptake by an organism) of the released copper was a small fraction (14–54%) of the total copper concentration due to Cu complexation with organic matter in impinging seawater aerosols (Sandberg, et al. 2006).

Faller and Reiss (2005) studied the exposure of different metallic materials to the open atmosphere in Dubendorf, Switzerland. Figure 4-26 shows copper, lead, and zinc runoff rates from different materials (listed on the left side of the figure) after 5 years of exposure. Copper runoff rates were high for copper materials. After 5 years of exposure, the Cu runoff yield from the untreated rolled copper sheet was 1.3 g/m^2/year, which was about 30% of the corrosion rate. The Cu corrosion rate decreased with time; however the runoff rate was relatively constant with time. The authors noted that the corrosion and runoff rates would likely equalize with time. At the Stockholm site, the copper runoff rate observed after 2 years of exposure was similar to that at the Dubendorf site. Stockholm and Dubendorf test sites have similar atmospheric SO_2 concentrations.

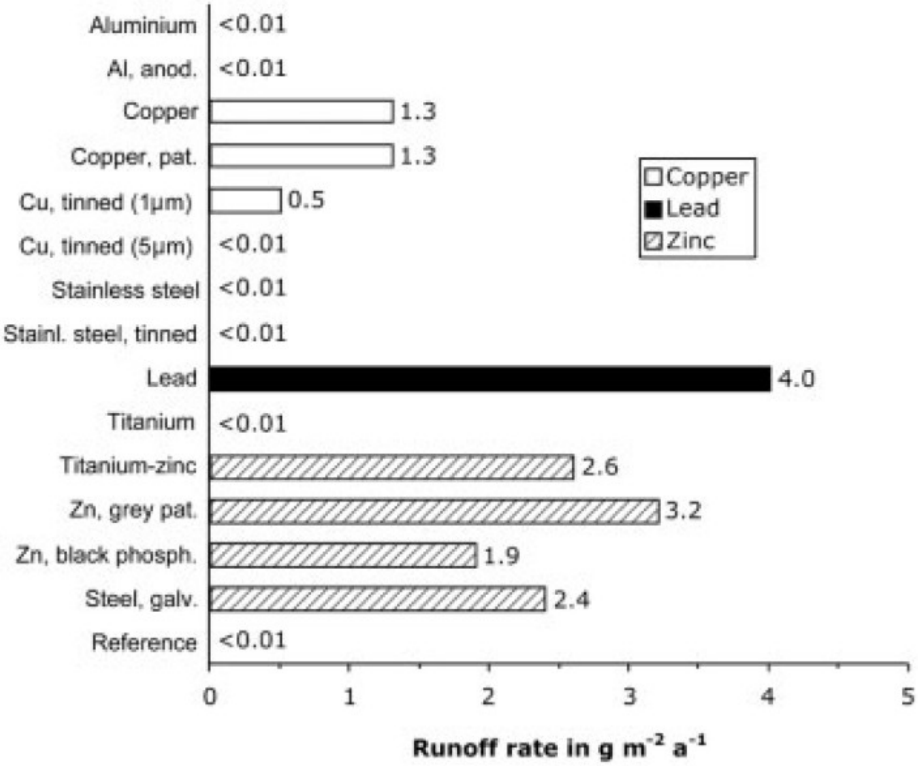


Figure 4-26. Runoff rates of copper, lead, and zinc from different materials after 5 years of exposure (Faller and Reiss 2005).

Wallinder, et al. (2009) studied the copper releases from a naturally aged copper roof on a shopping center building in a suburban site near Stockholm, Sweden, along with the interactions of copper with the internal drainage system and storm drains made of cast iron and concrete. Annual runoff rates of copper from the naturally oxidized copper roof ranged from 0.74 to 1.6 g/m^2/year (with the median being 1.0 g/m^2/year). The authors also studied runoff from a copper roof at a shopping center in Farsta, another suburban area near Stockholm. Roof runoff was sampled after transport through the internal drainage system consisting of downspouts made of cast iron and concrete (site A) and after approximately 50 m in a storm drain pipe made of concrete (site B). Generally, total copper concentrations at sites A and B were very similar. The total copper concentrations ranged between 5 to 101 µg/L (with a median of 15 µg/L) and between 2 to 175 µg/L (with a median of 18 µg/L), for sites A and B respectively. The majority of the copper released from the roof was retained in the runoff during transport through the internal drainage system of the building. However, the internal drainage system changed the chemical speciation of the released copper and its bioavailable fraction. Most of the copper in the runoff flowing through the cast iron and concrete pipes was complexed with organic matter, significantly reducing the bioavailable fraction. Bertling, et al. (2006), Boulanger and Nikolaidis (2003), and Wallinder, et al. (2009) also found that the interaction of copper released from outdoor structures with different solid surfaces resulted in changes in the chemical speciation of the released copper and subsequently greatly reduced the bioavailable copper fraction. In another study, Michels, et al. (2003) studied the impact of stormwater runoff from a copper roof on the environment. The authors found that the toxicity of the stormwater roof runoff decreased as it passed through the drainage system.

Other laboratory and field studies have shown that concrete pipes and concrete-based pavement materials have a high capacity to retain copper released from roofs by forming corrosion product malachite, $Cu_3(CO_3)_2(OH)_6$ (Bahar, et al. 2008a,b; Sundberg 1998; Boulanger and Nikolaidis 2003; Wallinder, et al. 2009).For a given rainfall quantity, the amount of copper retained on concrete surfaces increases with decreasing rain intensity as a result of prolonged contact time (longer duration rains). At a given rainfall quantity, low rain intensities also result in a higher released amount of copper from a copper roof (He, et al. 2001; He 2002; Wallinder, et al. 2009).

Good (1993) investigated chemical concentrations and aquatic toxicity of roof runoff from different roofing materials at a sawmill on the coast of Washington. Copper leached from tar-covered roofs at concentrations averaging 166 μg/L. The authors concluded that copper maybe a component in the roof coating.

Dietz, et al. (2007) investigated copper releases from distribution systems made of various materials. Water was passed through copper pipes with embedded lead coupons to simulate residential systems. The use of phosphate-based inhibitors reduced the copper concentrations by more than 50% (the concentrations of copper were between 200 and 800 μg/L when using the inhibitors). Gumbs and Dierberg (1985) reported in a literature review that heavy metal concentrations in drinking water can increase due to the corrosion of the distribution system and household plumbing. They reported that other researchers found significantly higher copper concentrations in tap water compared to cistern water.

Gromaire-Mertz, et al. (1999) studied runoff from roofs and gutters in an old, densely populated district of central Paris, France, between July 1996 and May 1997. Roofing materials included clay tiles, zinc sheets, and slate. Copper concentrations observed in the roof runoff ranged between 3 and 247 μg/L, with a median of 37 μg/L.

Zobrist, et al. (2000) measured the concentrations of heavy metals in runoff from tile, polyester, and gravel roofs located in the suburb of Zürich, Switzerland. The roof drainage system for the tile (clay) roof was made of 15-year old copper, the polyester roof had new copper drainage, and the gravel roof had PVC material drainage. The average runoff copper concentrations from the tile roof were 304 μg/L and from polyester roof 842 μg/L. Higher copper concentrations were associated with smaller rain depths.

Mendez, et al. (2011) studied the effects of roofing material on water quality for rainwater harvesting systems using five pilot-scale (asphalt fiberglass shingle, Galvalume® metal, concrete tile, cool, and green) roofs and three full-scale roofs (two asphalt fiberglass shingle and one 7-yar-old Kynar®-coated Galvalume® metal). The flat cool roof consisted of a white, acrylic-surfaced 2-ply atactic polypropylene (APP) modified bituminous membrane.

The test site was located at University of Texas in Austin. Cu concentrations in the harvested rainwater from the full-scale Kynar®-coated Galvalume® roof were lower than from pilot-scale uncoated Galvalume roofs. Cu concentration in the harvested rainwater from pilot-scale Galvalume roofs ranged between <0.6 and 9.9µg/L for the first flush sample, and between <0.6 and 4.8 µg/L for later samples. The rain water quality was between <0.6 and 12 µg/L. Cu concentrations in harvested rainwater from full-scale Kynar®-coated Galvalume® roof were <0.02µg/L for the first flush sample, for later samples, and for the ambient rain (Mendez, et al. 2011).Mendez, et al. (2011) also examined the contaminants in harvested rainwater from coupons of new and artificially aged roofing materials in lab-scale studies. The aging process did not significantly affect Cu concentrations from the Galvalume® metal roofing coupons.

Förster (1996) studied heavy metals and major ions in roof runoff in Bayreuth, Germany. He found that copper flashings used on the roofs released very high concentrations of Cu (up to 640 µg/L) and concluded that the best management practice would be not to use exposed metal surfaces on roofs and walls of buildings. Also, copper-based algaecide paints can be significant sources of copper as was shown during investigations conducted in several boat marinas (US EPA 2011).

Karlen, et al. (2002) studied runoff rates from naturally patinated copper roofs of varying age (0 and 30 years) during a three-year field exposure study in Stockholm, Sweden. Annual runoff rates for naturally patinated copper of varying ages ranged between 1.0 and 1.5 g/m^2 year and have been found to increase slightly with patina age which was attributed to the enhanced first flush noted on thicker patina layers. The major portion of the released copper (60 – 100%) was present as the free hydrated cupric ion, $Cu(H_2O)_6^{2+}$, which is the most bioavailable copper species. Other copper species in the roof runoff water ($Cu(OH)^+$ and $Cu_2(OH)_2^{2+}$), were also bioavailable.

Wallinder, et al. (2002a) examined the atmospheric corrosion of naturally and pre-patinated copper roofs in Singapore and Stockholm. Similar copper runoff rates between fresh and brown-patinated copper roof sheet and between green naturally patinated and green pre-patinated copper roof sheet at each site were linked to similar morphology and composition of the patina.

Boller and Steiner (2002) studied the release and control of copper from roofs and roads in urban stormwater in Basle and Zürich, Switzerland. A large copper building facade was examined for copper concentrations in the runoff. The concentrations ranged from 1 to 10 mg/L during the first year of investigation.

Corvo, et al. (2005) investigated changes in Cu corrosion rates caused by chloride ions in rain. Test materials included copper and steel that were exposed in two atmospheric test stations located in Havana, Cuba and Medellin, Colombia. The samples were subjected to accelerated outdoor tests by intermittent spraying of a salt solution. The addition of salt spray at Havana increased the corrosion rate of the copper material (33 g/m^2 of Cu) compared to the samples at the same location but under natural conditions (9.4g/m^2 of Cu) .Metal mass losses were proportional to the chloride deposition rate. The authors found that the acceleration of copper corrosion caused by chloride ions was notably higher at Havana(33 g/m^2 of Cu) compared to Medellin(17 g/m^2 of Cu) and was explained by lower frequencies and amounts of rain at Havana during the 1 year of exposure. A higher washing and cleaning effect took place at Medellin. Additionally, rain diminishes chloride surface concentrations; the acceleration rate caused by chloride ions is likely to lessen with the increase of rain amount at constant exposure time.

Atmospheric-induced corrosion causes an alternately growing and decreasing layer of electrolyte, which is often very thin. In the presence of corrosion products at the metal–atmosphere interface, the sorption properties of these products and salts (usually hygroscopic) deposited or formed by corrosion, determine the possibilities of superficial wetness. The amount of water on the corroding surface plays an important role in the corrosion rate. The formation of green rust in the presence of chloride ions involves an incorporation of the chloride ions from solution into the inter-layers of green rust and an oxidation of Fe (II) to Fe (III) without any structural changes (Corvo, et al. 2005).

Table 4-22 summarizes copper concentrations or runoff yields from different materials found by various researchers.

Table 4-22. Copper Releases from Various Sources

Material	Test descriptions	Cu concentrations or runoff yields	Reference
Uncoated Copper Roofing Materials			
Copper roof	2 year field test. Stockholm, Sweden	Average 1.3 - 1.5 g/m^2/year	Wallinder, et al. (2000)
Copper roof	Stockholm, Sweden. 2 year test	1.3 g/m^2/year	Faller and Reiss (2005)
Fresh copper sheet	Brest, France. 1 year test	1.5 g/m^2/year	Sandberg, et al. (2006)
Untreated rolled copper sheet	Dubendorf, Switzerland. 5 year test	1.3 g/m^2/year	Faller and Reiss (2005)
After copper roof and cast iron and concrete downspouts	Field. Suburban Farsta, Stockholm. Several rains during 2006-2008	5-101 µg/L (median 15 µg/L)	Wallinder, et al. (2009)
After copper roof and cast iron and concrete downspouts and concrete drain system pipe	Field. Suburban Farsta, Stockholm .Several rains during 2006-2008	2 -175 µg/L (median 18 µg/L)	Wallinder, et al. (2009)
Copper material	(salt spray) Medellin, Colombia. 1 year test	16.0 g/m^2/year mass loss	Corvo, et al. (2005)
Copper material	(salt spray) Havana, Cuba. 1 year test	32.8 g/m^2/year mass loss	Corvo, et al. (2005)
Copper material	(natural conditions) Havana, Cuba. 1 year test	9.4 g/m^2/year mass loss	Corvo, et al. (2005)
Copper materials	Stockholm, Sweden	1.0 - 2.0 g/m^2/year	He, et al. (2001a)
Other Roofing Materials			
Pilot-scale Galvalume roofs	Austin, Texas. Several rain events in 2010	<0.63 - 9.88 µg/L during first flush; <0.63 - 4.84 µg/L for later samples	Mendez, et al. (2011)
Full-scale Kynar®-coated Galvalume® roof	Austin, Texas. Several rain events in 2010	<0.02 µg/L	Mendez, et al. (2011)
New uncoated galvanized steel roof	4 mo. Field test. Pilot Scale. Harrisburg, PA	< 3µg/L	Clark, et al. (2008a)
Clay tiles, clay tiles (70%) + zinc sheets, zinc sheets, and slate	Central Paris. July 1996 and May 1997	3 - 247 µg/L (median 37 µg/L)	Gromaire-Mertz, et al. (1999)
Metal and vinyl materials panels	4 mo. Field test. Pilot Scale. Harrisburg, PA	< 25 µg/L	Clark, et al. (2008a)
New vinyl roof	14 mo. Field test. Pilot Scale. Harrisburg, PA	< 20 µg/L	Clark, et al. (2007)
Tile roof	Zurich, Switzerland. 14 rain events	400 and 50 µg/L; average 1623 µg/m^2	Zobrist, et al. (2000)
New asphalt shingles roof	4 mo. Field test. Pilot Scale. Harrisburg, PA	25 µg/L (median) 112 µg/L (75th percentile	Clark, et al. (2008a)
Tar-covered roofs	Washington	166 µg/L	Good (1993)
New cedar shakes roof	4 mo. Field test. Pilot Scale. Harrisburg, PA	from 1,500 to 27,000 µg/L	Clark, et al. (2008a)

Table 4-22. Copper Releases from Various Sources (continued)

Aged/Patinated Copper Materials			
Naturally patinated copper sheet	Brest, France. 1 year test	1.3 g/m^2/year	Sandberg, et al. (2006)
Naturally aged copper roof	Field. Suburban Stockholm, Sweden. Several rains during 2006-2008	0.74 - 1.6 g/m^2/year (median 1.0 g/m^2/year)	Wallinder, et al. (2009)
Naturally patinated copper of varying age	Field. Stockholm, Sweden	1.0 - 1.5 g/m^2/year	Karlen, et al. (2002)
Naturally patinated copper of varying age	Field. Stockholm, Sweden	900 - 9700 µg/L	Karlen, et al. (2002)
Fresh and brown prepatinated copper roofs	Stockholm, Sweden	1.1-1.6 g/m^2/year	Wallinder, et al. (2002a)
Fresh and brown prepatinated copper roofs	Singapore	5.5-5.7 g/m^2/year	Wallinder, et al. (2002a)
130 years old copper roof sheet and green prepatinated copper sheet	Singapore, Stockholm	1.6-2.3 g/m^2/year	Wallinder, et al. (2002a)
Green pre-patinated copper roof sheet	Singapore	8.4-8.8 g/m^2/year	Wallinder, et al. (2002a)
Copper Pipes			
Copper pipes		200 - 800 µg/L	Dietz, et al. (2007)
New copper drains	Zurich, Switzerland. 14 rain events	7.8 g/(m^2 y^1)	Zobrist, et al. (2000)
15 - year old drains	Zurich, Switzerland. 14 rain events	3.5 g/(m^2 y ^{1})	Zobrist, et al. (2000)
Copper facade	1 year test	10^3 – 10^4 µg/L	Boller and Steiner (2002)

The highest copper runoff rates were noted from exposed copper materials (Wallinder, et al. 2000; Sandberg, et al. 2006; Wallinder and Leygraf 1997; Leuenberger-Minger, et al. 2002; Sandberg, et al. 2006; Faller and Reiss 2005; Zobrist, et al. 2000, Boller and Steiner 2002, and Förster 1996). Copper-based paints can also be a significant source of copper in runoff (US EPA 2011). Some studies indicated relatively constant copper runoff yields with time during 5 years of exposure (Faller and Reiss 2005). However, other studies found that new copper materials had higher copper runoff yields compared to older copper materials (Zobrist, et al. 2000). Galvanized steel, vinyl, and galvalume materials had copper runoff concentrations that were less than 25 µg/L (Clark, et al. 2008a; Mendez, et al. 2011).

The major portion of the copper in the runoff at the source was in the most bioavailable form (hydrated cupric ion), but when the stormwater runoff passes through cast iron and concrete drainage systems, copper may be retained or form complexes with organic matter and change chemical speciation to less toxic or less bioavailable forms (Karlen, et al. 2002; Wallinder, et al. 2009; Bertling, et al. 2006; Boulanger and Nikolaidis 2003; and Sandberg, et al. 2006). Copper runoff yields were proportional to the chloride deposition rate on the surfaces and were also influenced by rain frequencies and amounts (Corvo, et al. 2005).

Lead

Clark, et al. (2007) studied three samples of galvanized metal: a rusted sample with no paint, bare metal with no paint and no visible degradation, and painted metal. Lead was released from all three types of galvanized steel roofing materials during the natural rain test period and was just above the method detection limit of 1µg/L. Tobiason and Logan (2000) found that zinc-galvanized metal roof was not a source of lead.

Good (1993) studied chemical concentrations and aquatic toxicity of roof runoff from different roofing materials at a sawmill on the coast of Washington. The authors found that lead was leaching from the rusty galvanized metal roof and reached 300µg/L.

Lasheen, et al. (2008) studied the effect of pH, stagnation time, pipe age, and pipe material on the concentrations of lead released from polyvinyl chloride (PVC), polypropylene (PP) and galvanized iron (GI). PVC pipes were found to be the greatest source of lead. Figures 4-27 and 4-28 show the mean lead concentrations released from PVC and galvanized iron pipes after 72 hr of exposure. The authors found that the concentrations of lead were higher after 72 hours of exposure time than after 48 hours at pH 7.5. The authors also found that as pipe age increased the lead concentrations also increased. For example, the mean lead concentrations were 95 and 120 µg/L in 2 and 20 weeks aged PVC pipes, respectively after stagnation of 72 h. For galvanized iron pipes, after 72 h of stagnation, mean lead concentrations were 53 and 64 µg/L in 2 and 20 weeks aged pipes. As pH increased (to pH=8), the concentration of lead decreased. The authors observed that increasing the ratio of Cl/SO_4 from 0.83 to 2 resulted in an increase of lead concentrations from GI pipes. The levels of lead increased in PVC pipes as the Cl/SO_4 ratio increased, however the lead concentrations were less than that in control pipes (Lasheen, et al. 2008).

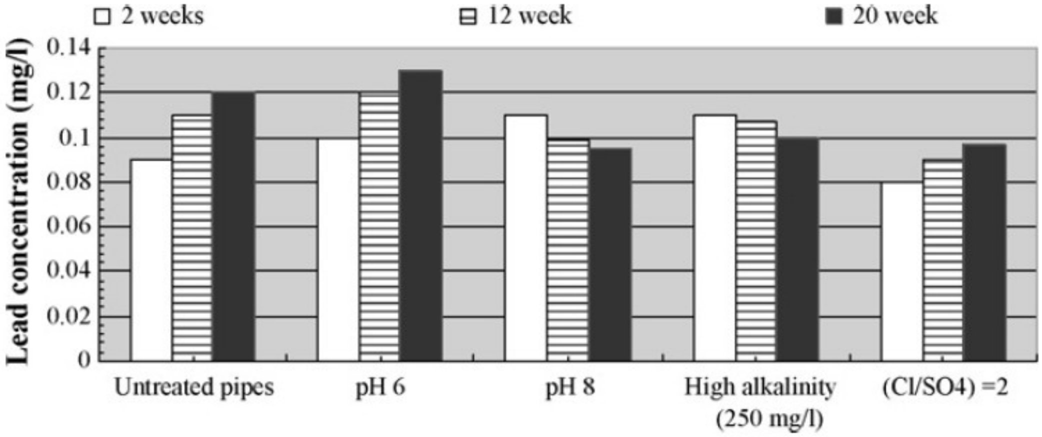


Figure 4-27. Mean lead concentrations released from PVC pipes after 72 hr. of exposure (Lasheen, et al. 2008).

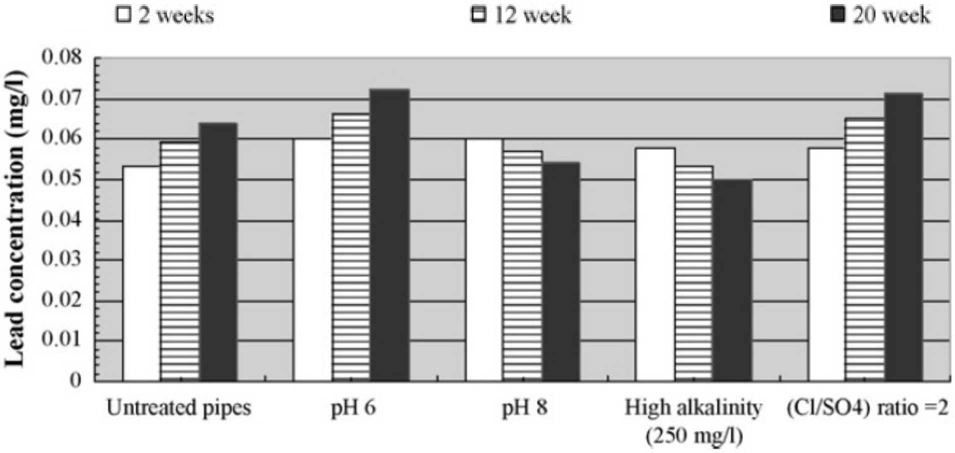


Figure 4-28. Mean lead concentrations released from galvanized iron pipes after 72 hr. of exposure (Lasheen, et al. 2008).

Al-Malack (2001) studied the migration of lead, and other metal stabilizers from unplasticized polyvinyl chloride (uPVC) pipes. The author observed an increase in lead concentrations leaching from uPVC pipes with time. After 10 h of exposure, lead concentrations migrating from the uPVC pipes into the circulated water reached a value of 430µg/L and by the end of the experiment (48 h), lead concentrations had increased to 780µg/L which was more than 50 times greater than the maximum permissible level (MCL) of 15 µg/L established by US EPA for drinking water (Al-Malack 2001). The author found that the migration of lead took place in two distinct phases. During the first phase, there was a sharp increase in diffusion rate of lead with time, in the second phase after 10 h exposure time, the diffusion rate of lead slowed with time. As pH decreased, the amount of lead leaching from the uPVC pipes increased. At pH 5, about 1000 µg/L of lead migrated from the UPVC pipe into the water after 48 h of exposure. Between pH 7 and 9, the increase in lead concentrations were insignificant, which suggests that alkaline environments do not have significant effects on lead migration from uPVC pipes.

The effect of UV-radiation (a disinfection method for the control of bacteria) on the migration of lead and other metal stabilizers from uPVC pipes was investigated at different times of exposure during static tests. Exposure to UV-radiation was found to promote the migration of lead and other metal stabilizers. After 12 h of exposure, lead concentrations reached 115 µg/L. This lead concentration is approximately eight times the MCL of lead in drinking water established by EPA. Lead concentrations of 310 and 800µg/l were detected after 5 and 14 days of exposure to UV-radiation, respectively. The latter concentration is 50 times higher than the MCL in drinking water established by EPA.

Dietz, et al. (2007) investigated lead releases from PVC, lined cast iron, unlined cast iron, and galvanized steel aged pipes (40+ years) with and without inhibitors. Water was also passed through copper pipes with embedded lead coupons to simulate residential systems. An increase in the phosphorus or SiO_2 inhibitor doses or pH elevation significantly decreased the lead concentrations. For the distribution systems with an inhibitor, the lead concentrations didn't exceed 5 µg/L, and were below the current action level of 15 µg/L for lead. For the distribution systems with the pH control, some lead concentrations reached 65 µg/L. Operation without inhibitors often resulted in lead concentrations which exceeded the action level, whereas the use of an inhibitor consistently provided compliance with the action level (Dietz, et al. 2007).

Gromaire-Mertz, et al. (1999) studied lead in roof runoff from clay tiles, zinc sheets, and slate roofing materials in Paris, France. Lead concentrations detected in the roof runoff ranged between 16 and 2,800 µg/L, with a median of about 500 µg/L. Lead concentrations in roof runoff exceeded level 2 of French water quality standards of 50 µg/L for practically all samples. Lead was bounded to particulates in nearly all samples. Schriewer, et al. (2008) studied lead in roof runoff from 14 year-old zinc roofs in Germany. Roof runoff was also affected by titanium–zinc gutters and downspouts. Five chimneys were soldered on the roof with tin-solder, which contains small amounts of lead. Samples were collected directly in the gutter. Lead was detected in only a few samples, with the maximum lead concentration observed being 31 µg/L.

Zobrist, et al. (2000) measured the concentrations of heavy metals, including Pb, in runoff from a tile roof located in suburb of Zürich, Switzerland. The average runoff lead load in tile roof runoff was 250 $\mu g/m^2$per event.

Davis and Burns (1999) examined lead release in stormwater runoff from painted structures located at the University of Maryland, College Park Campus and in surrounding commercial and residential neighborhoods in Prince George's and Montgomery Counties, Maryland and the District of Columbia. Lead concentrations were the highest from painted wood structures (geometric mean, median, Q10-Q90): 40, 49, 2.6-380 µg/L, respectively), followed by painted bricks (22, 16, 3.3-240 µg/L) and painted concrete blocks (9.7, 8.0, <2-110 µg/L). Lead concentrations were considerably affected by paint age and condition: paint age [>10 y] (77, 88, 6.9 - 590 µg/L), [5-10 y] (22, 16, <2-240 µg/L), [0-5 y] (8.4, 8.1, <2-64 µg/L). Lead releases from washes of older paints were significantly higher than from fresh paints. It was found that old surface paints have the potential to release large amounts of lead into a watershed. Simmons, et al. (2001) investigated rainwater quality harvested from residential roofs in New Zealand for beneficial uses. He also found that lead was released from the roofs that were coated with lead-based paint. The concentration ranged between 11 and 140 µg/L.

Förster (1999) examined the variability of roof runoff quality from different roofing materials, including zinc sheet in Bayreuth, Germany. Zinc and PVC rain gutters were used. The author attributed lead contamination in the roof runoff to particulate dry deposition and/or dissolution of lead components on the roofs. Total lead concentrations in roof runoff from the zinc roofs were about 10µg/L, with dissolved lead being only about 15% of the lead particulate-bound concentrations.

Heavy metal concentrations in drinking water can increase due to corrosion of distribution system and household plumbing materials; this was also noted for cistern water systems (Gumbs and Dierberg 1985; Shahmansouri, et al. 2003). Gumbs and Dierberg (1985) studied three components of 46 single-family cistern water systems having piped water delivery systems (corrugated galvanized iron roof, cistern, and distribution system) on St. Maarten Island. Lead concentrations in bulk precipitation ranged between 5.8 and 15.9 µg/L, with an average of 9.9 µg/L. They found that lead was bound with particulate matter and settled to the bottom of the cistern. The metal concentrations in the rainwater increased as it passed over the galvanized roof surface and through the gutter and downspouts connected to the cisterns. The elevated levels of lead at the final water tap compared to the cistern's lead water concentrations were attributed to corrosion of the galvanized metal parts within the distribution systems (galvanized iron pressure tanks) due to the longer residence time. The surface water concentrations for lead ranged between 0.1 and 75 µg/L with the average of 0.9 µg/L; the lead concentrations in the tap samples ranged between 0.2 amd70 µg/L with the average of 2.1 µg/L. The pipes before and after the pumps were mostly made of galvanized iron and PVC.

Mendez, et al. (2011) investigated the effects of roofing material on water quality for rainwater harvesting systems. The authors examined the quality of harvested rainwater using several pilot-scale roofs (asphalt fiberglass shingle, Galvalume® metal, concrete tile, and planted green roofs) located at the Lady Bird Johnson Wildflower Center, Austin, Texas and three full-scale roofs (two asphalt fiberglass shingle and one 7-year-old Kynar®-coated Galvalume® metal roofs). The full-scale site was located at the University of Texas at Austin Child Development Center, Comal location, Austin, Texas. Also, new and artificially aged coupons of asphalt fiberglass shingle, Galvalume® metal, and concrete tile were examined in lab-scale studies to determine the potential for changes in harvested rainwater quality influenced by aged roofing materials. Pb concentrations in the harvested rainwater from the Galvalume roofs were greater than for the Kynar®-coated Galvalume® roof. Lead concentrations in harvested rainwater from pilot-scale Galvalume roofs ranged between <0.1 and 6.4 µg/L for the first flush sample, and between <0.1 and 5.7 µg/L for later samples. The rain lead concentrations ranged between <0.1 and 0.9 µg/L. Lead concentrations in harvested rainwater from full-scale Kynar®-coated Galvalume® roof ranged between <0.01 and 0.2µg/L for the first flush sample and were <0.12µg/L for later samples. The rain lead concentrations during this test series ranged between <0.01 and 1.54 µg/L. The aging process conducted during the lab-scale studies did not significantly affect Pb concentrations from the Galvalume® metal roofing coupons (Mendez, et al. 2011).

Shahmansouri, et al. (2003) conducted a study on pilot-scale drinking water distribution systems in Zarrinshahr and Mobarakeh, Iran. The piping system materials in houses and buildings were galvanized iron, the distribution piping systems were made of asbestos, polyethylene, and occasionally iron pipes. The authors found that the samples analyzed along the distribution system show significant increases in concentrations of lead. The lead concentrations increased up to an average of 5.7 and 7.8 µg/L in Zarrinshahr and Mobarakeh respectively; the lead concentrations sometimes exceeded the MCL.

Table 4-23 summarizes lead concentrations or release rates from different materials found by various researchers.

Table 4-23. Lead Releases from Various Sources

Material tested	Test conditions	Observed lead concentrations, or runoff yields	Reference
Uncoated Galvanized Steel Roofing Materials			
Galvanized roof	Pilot scale	Just above 1 µg/L	Clark, et al. (2007)
Galvanized roof	Leaching test in the lab	0.002-0.02 g/kg/48hr	Clark, et al. (2007)
Zinc sheet, zinc and PVC gutters	Bayreuth, Germany	10µg/L	Forster (1999)
Clay tiles, flat clay tiles (70%) + zinc sheets, zinc sheets, and slate roofing materials	Field. Paris, France.	16 - 2764 µg/L (the median 493 µg/L)	Gromaire-Mertz, et al. (1999)
Cistern surface water (after galvanized iron roof)	St. Maarten Island, Netherlands	0.1 - 75.1 µg/L (avg. 0.9 µg/L).	Gumbs and Dierberg (1985)
The bottom of the cisterns (after galvanized iron roof)	St. Maarten Island, Netherlands	Avg. 19.4 µg/L	Gumbs and Dierberg (1985)
Uncoated Galvanized Aluminum Roofing Materials			
Galvalume roofs	Pilot-scale. Austin, Texas	<0.12 - 6.40 µg/L during first flush, <0.12 - 5.65 µg/L for later samples	Mendez, et al. (2011)
Coated Galvanized Aluminum Roofing Materials			
Kynar®-coated Galvalume® roof	Full-scale Austin, Texas	<0.01 - 0.21µg/L during first flush; <0.12µg/L for later samples	Mendez, et al. (2011)
Aged Galvanized Steel Roofing Materials			
Rusty galvanized metal roof	Field test during first flush. The coast of Washington	302 µg/L	Good (1993)
60 years old painted galvanized metal roof exposed in the filed	Leaching test in the lab	0.01 - 1 g/kg/48hr	Clark, et al. (2008b, 2007)
60 years old painted galvanized metal roof stored in the barn	Leaching test in the lab	0.01 - 1 g/kg/48hr	Clark, et al. (2008b, 2007)
14 year-old zinc roof, titanium–zinc gutters and the down spout	Germany	31 µg/L	Schriewer, et al. (2008)
Other Roofing Materials			
Tile roof	Zurich, Switzerland, 14 rain events	249 µg/m^2	Zobrist, et al. (2000)

Table 4-23. Lead Releases from Various Sources (continued)

Painted Materials			
Metal roof coated with aluminum paint, tar roof painted with fibrous reflective aluminum paint, anodized aluminum roof	Field test during first flush. The coast of Washington	10 - 15 µg/L	Good (1993)
Painted wood	Field test	2.6-380 µg/L (Q10[1]-Q90[2])	Davis and Burns (1999)
Painted brick	Field test	3.3-240 µg/L (Q10-Q90)	Davis and Burns (1999)
Painted block	Field test	<2-110 µg/L (Q10-Q90)	Davis and Burns (1999)
>10 year paint	Field test	6.9 - 590 µg/L (Q10-Q90)	Davis and Burns (1999)
5-10 year paint	Field test	<2-240 µg/L (Q10-Q90)	Davis and Burns (1999)
0-5 year paint	Field test	<2-64 µg/L (Q10-Q90)	Davis and Burns (1999)

Table 4-23. Lead Releases from Various Sources (continued)

Drinking Water Distribution Systems			
Galvanized iron pipe after 2 weeks of use, 72 hr of stagnation	increasing the ratio of Cl/SO_4 from 0.83 to 2	58 µg/L	Lasheen, et al. (2008)
Galvanized iron pipe after 20 weeks of use, 72 hr of stagnation	increasing the ratio of Cl/SO_4 from 0.83 to 2	70 µg/L	Lasheen, et al. (2008)
PVC pipes after 2 weeks of use, 72 hr of stagnation	pH 7.5	95 µg/L	Lasheen, et al. (2008)
PVC pipes after 20 weeks of use, 72 hr of stagnation	pH 7.5	120µg/L	Lasheen, et al. (2008)
PVC pipes after 2 weeks of use, 72 hr of stagnation	pH 6	100µg/L	Lasheen, et al. (2008)
PVC pipes after 20 weeks of use, 72 hr of stagnation	pH 6	130µg/L	Lasheen, et al. (2008)
PVC pipes after 2 weeks of use, 72 hr of stagnation	pH 8	110µg/L	Lasheen, et al. (2008)
PVC pipes after 20 weeks of use, 72 hr of stagnation	pH 8	20µg/L	Lasheen, et al. (2008)
PVC pipe after 2 weeks of use, 72 hr of stagnation	increasing the ratio of Cl/SO_4 from 0.83 to 2	80µg/L	Lasheen, et al. (2008)
PVC pipe after 20 weeks of use, 72 hr of stagnation	increasing the ratio of Cl/SO_4 from 0.83 to 2	100µg/L	Lasheen, et al. (2008)
Unplasticized PVC pipe after 10 h of exposure	-	430µg/L	Al-Malack (2001)
Unplasticized PVC pipe after 48 h of exposure	-	780µg/L	Al-Malack (2001)
Unplasticized PVC pipe after 48 h of exposure	pH 5	1000µg/L	Al-Malack (2001)
Unplasticized PVC pipe after 12 h of exposure	UV exposure	115µg/L	Al-Malack (2001)
Unplasticized PVC pipe after 5 days of exposure	UV exposure	312 µg/L	Al-Malack (2001)
Unplasticized PVC pipe after 14 days of exposure	UV exposure	799µg/L	Al-Malack (2001)
PVC, lined cast iron, unlined cast iron, and galvanized steel aged pipes (40+ years)	Phosphorus or SiO_2 inhibitor	< 5 µg/L	Dietz, et al. (2007)
PVC, lined cast iron, unlined cast iron, and galvanized steel aged pipes (40+ years)	pH control	max.65 µg/L	Dietz, et al. (2007)
Galvanized piping systems, asbestos, polyethylene, iron pipes	Pilot scale. Zarrinshahr, Iran	1.60 - 16.00 µg/L (avg. 5.7 µg/L)	Shahmansouri, et al. (2003)
Galvanized piping systems, asbestos, polyethylene, iron pipes	Pilot scale. Mobarakeh, Iran	0.60 - 18.70 µg/L (avg. 7.8 µg/L)	Shahmansouri, et al. (2003)
At the tap (after galvanized iron roof, gutter and down spout, distribution system)	St. Maarten Island, Netherlands	0.2-70.0 µg/L (average of 2.1 µg/L)	Gumbs and Dierberg (1985)

[1] and [2] 10th and 90th percentiles of data values, respectively

Galvanized steel, PVC and unplasticized PVC, (Gromaire-Mertz, et al. 1999; Schriewer, et al. 2008; Förster 1999) Galvalume (Mendez, et al. 2011), and zinc materials can be sources of lead concentration increases in water (Clark, et al. 2007; Lasheen, et al. 2008; Al-Malack 2001; Gumbs and Dierberg 1985; Shahmansouri, et al. 2003). Lead concentrations released from galvanized steel and PVC materials increase with increased exposure time, increased pipe age, and pH decreases (Lasheen, et al. 2008; Al-Malack 2001; Dietz, et al. 2007). Also, exposure to UV-radiation was determined to promote the migration of lead from unplasticized PVC pipes (Al-Malack 2001). Additionally, painted materials can be a source of lead in stormwater, with lead releases being higher from older types of paints (Davis and Burns 1999; Simmons et al 2001). The rise in the ratio of Cl/SO_4 from 0.83 to 2 resulted in an increase in lead concentrations from galvanized iron and PVC pipe exposure (Lasheen, et al. 2008).

Cadmium

Al-Malack (2001) investigated the effect of water quality parameters and direct exposure to UV-radiation on the migration of metal stabilizers, including cadmium, from unplasticized polyvinyl chloride (uPVC) pipes. As exposure time increased, cadmium concentrations in the runoff also increased. Cadmium concentrations increased from below detection limit level (<50 µg/L) to 88 µg/L after 48 hrs of exposure. It was observed that exposure to UV-radiation promoted the migration of metal stabilizers and that this increased the Cd concentrations with time. As water pH decreased, the cadmium concentrations released from the uPVC pipes increased. A pH change from pH 9 to pH 6 caused cadmium concentrations increase from 53 to 89 µg/L. The water temperature reached 35^oC after 24 h of exposure to the UV radiation, and remained at that level till the end of the study.

Gromaire-Mertz, et al. (1999) examined runoff from different roofing materials and gutters in Paris, France, between July 1996 and May 1997. Roofing materials included clay tiles, zinc sheets, and slate. Cadmium concentrations in roof runoff (1 to 5 µg/L) were below the level 2 water quality criteria (1,000 µg/L) with the exception of runoff from the zinc sheet roof runoff samples. Cadmium concentrations were extremely high in roof runoff from the zinc roofs. Leaching of cadmium is explained by the erosion of the zinc roofing material, in which cadmium is a minor constituent. Förster (1996) found that for cadmium, the association with dissolved and particulate fractions varied, however, it was noted that generally, the dissolved fraction of cadmium was greater than the particulate fraction for the roof runoff.

Schriewer, et al. (2008) studied runoff from 14 year-old zinc roofs in Germany during a period of 1 year. Roof runoff flowed into titanium–zinc gutters and downspouts. Five chimneys were also soldered on the roof with tin-solder, which contains fractions of other metals. Samples were collected directly in the gutter. Cadmium concentrations (0.5 - 0.8 µg/L) were detected only in a few samples.

Zobrist, et al. (2000) measured the concentrations of heavy metals including Cd in runoff from tile, polyester, and gravel roofs located in a suburb of Zürich, Switzerland. The roof drainage system for the clay tile roof was made of 15-year old copper; for polyester roof out of new copper; and for gravel roof out of PVC material. Average runoff total cadmium losses from tile roof were2.5 µg/m^{2}per event. Cd was chiefly associated with the dissolved fraction.

Tar felt roofing was found to be a source of cadmium in roof runoff monitored by Förster (1999) in Bayreuth, Germany. Roofing materials examined included concrete tiles, clay pantiles, fibrous cement, tar felt, and zinc sheet. Zinc and PVC gutters were used. The dissolved cadmium concentrations were about ten times the particulate-bound cadmium concentrations in the runoff.

Gumbs and Dierberg (1985) investigated 46 single-family water cistern systems having piped delivery systems (roof, cistern, and distribution system) on St. Maarten Island. The roof catchment surface for the cisterns was made of corrugated galvanized iron sheets. Most of the cistern systems had galvanized iron pressure tanks. The pipes before and after the pumps were mainly made out of galvanized iron and PVC pipes. The authors found that cadmium concentrations in bulk precipitation were between 0.5 and1.1 µg/L with the average of0.8 µg/L. The elevated levels of cadmium at the tap (<0.02 to 30 µg/L with the average of 0.1 µg/L) compared to the cistern surface water concentrations (< 0.02-0.4 µg/L with the average of 0.03 µg/L) were attributed to the corrosion of the galvanized metal parts within the distribution systems (mostly the galvanized pressure tanks) due to the extended residence times in the tanks. Average concentrations of cadmium at the bottom of the cisterns (mixture of water and sediment) were significantly higher than in the surface and tap water samples (Gumbs and Dierberg 1985).

Shahmansouri, et al. (2003) conducted a study on drinking water distribution systems in Zarrinshahr and Mobarakeh, Iran. The piping system materials in houses and buildings were galvanized, the distribution piping systems were made of asbestos, polyethylene, and iron pipes. The researchers found that the samples analyzed before and after the distribution system indicated significant increases in cadmium concentrations of up to 0.1 and 0.8 µg/L in Zarrinshahr and Mobarakeh respectively.

Gromaire, et al. (2002) examined cadmium concentrations in stormwater runoff from zinc roofing in Paris. Annually, runoff from Parisian zinc roofs generated approximately 15 to 25 kg of cadmium.

Table 4-24 summarizes cadmium concentrations and release rates from different materials found by various researchers.

Table 4-24. Cadmium Releases from Various Sources

Materials tested	Test conditions	Observed cadmium concentrations or runoff yields	Reference
Uncoated Galvanized Roofing Materials			
Parisian zinc roofs	Paris, France	15 - 25 kg/year for the city	Gromaire, et al. (2002)
Cistern surface water (after galvanized iron roof)	St. Maarten Island, Netherlands	< 0.02-0.40 µg/L (avg. 0.03 µg/L)	Gumbs and Dierberg (1985)
The bottom of the cisterns (after galvanized iron roof)	St. Maarten Island, Netherlands	Avg. 0.99 µg/L	Gumbs and Dierberg (1985)
clay tiles, flat clay tiles (70%) + zinc sheets, zinc sheets, and slate	Paris, France. July 1996 and May 1997	0.1-32 µg/L (median of 1.3 µg/L)	Gromaire-Mertz, et al. (1999)
Aged Galvanized Steel Roofing Materials			
14 year-old zinc roof runoff	Germany, 1 year test	0.5 µg/L (DL) – 0.8µg/L	Schriewer, et al. (2008)
Other Roofing Materials			
Clay tile roof with 15-year old copper gutter	Filed test. Tuffenwies, Switzerland	2.5 µg/m^2 per event	Zobrist, et al. (2000)
Tar felt roof	Bayreuth, Germany	0.5µg/L	Forster (1999)
Drinking Water Distribution Systems (DWDS)			
Unplasticized PVC pipe after 48 hrs of exposure	-	88 µg/L	Al-Malack (2001)
Unplasticized PVC pipe after 14 days of exposure	Change from pH 9 to pH 6	increase from 53 to 89 µg/L	Al-Malack (2001)
Unplasticized PVC pipe after 48 hrs of exposure	Exposure to UV-radiation	800 µg/L	Al-Malack (2001)
At the tap (after galvanized iron roof, gutter and down spout, distribution system)	St. Maarten Island, Netherlands	<0.02-30.2 µg/L (average 0.12 µg/L)	Gumbs and Dierberg (1985)
Drinking Water Distribution System (asbestos, polyethylene, and iron pipes), after min of 6 hrs.	Zarrinshahr, Iran	Before DWDS 0.08 µg/L, after DWDS 0.11 µg/L	Shahmansouri, et al. (2003)
Drinking Water Distribution System (asbestos, polyethylene, and iron pipes), after min of 6 hrs.	Mobarakeh, Iran	Before DWDS 0.06 µg/L, after DWDS 0.8 µg/L	Shahmansouri, et al. (2003)

PVC, zinc, tile, tar felt, and galvanized iron materials can all be sources of cadmium in runoff (Al-Malack 2001; Gromaire-Mertz, et al. 1999; Zobrist, et al. 2000; Förster 1999; Schriewer, et al. 2008; Gumbs and Dierberg 1985; Shahmansouri, et al. 2003; Gromaire, et al. 2002). Exposure to UV-radiation promoted the migration of cadmium stabilizers from unplasticized PVC pipes. A decrease in the pH of the water was also found to increase the cadmium concentrations released from the uPVC pipes (Al-Malack 2001).

Chromium

Zobrist, et al. (2000) examined the concentrations of heavy metals, including Cr, in runoff from various roofing materials that were installed in a suburb of Zürich, Switzerland. The drainage system for the monitored clay tile roof was made of 15-year old copper. Tile roof was a source of chromium. Average runoff total chromium losses from tile roof were10 µg/m^2 per event. Cr was chiefly associated with the dissolved fraction.

Faller and Reiss (2005) investigated the exposure of different metallic materials to the open atmosphere in Dubendorf, Switzerland. The roof runoff concentrations of chromium were less than the detection limit (10µg/L) from aluminum, stainless steel and titanium test roofs. However, a study on the release rates of chromium from stainless steel roofs determined runoff rates in the range of 200 to 700µg/m^2/year (Wallinder, et al. 2002b).

Gumbs and Dierberg (1985) examined three components of 46 single-family cisterns with a piped water delivery system (roof, cistern, and distribution system) on St. Maarten Island. The roof catchment surface was made of corrugated galvanized iron sheets. The majority of the cisterns systems had galvanized iron pressure tanks. The pipes before and after the pumps were mostly made out of galvanized iron and PVC pipes. Chromium was not a significant constituent of the galvanized materials and there was no increase of chromium noted in the delivered tap water (Gumbs and Dierberg 1985).

Table 4-25 summarizes chromium concentrations and release rates from different materials found by various researchers.

Table 4-25. Chromium Releases from Various Sources

Material tested	Test method	Observed chromium concentrations or runoff yields	Reference
Tile roof with 15-year old copper drainage system	Zurich, Switzerland. 14 rain events	Avg. runoff load 10 µg/m^2 per event	Zobrist, et al. (2000)
Aluminum, stainless steel and titanium roofs	Stockholm, Sweden. 2 year test	< DL (10µg/L)	Faller and Reiss (2005)
Stainless steel	-	200 - 700µg/m^2/year	Wallinder, et al. 2002b)
Cistern surface water (after galvanized iron roof)	St. Maarten Island, Netherlands	< 0.04 - 13.4 µg/L (avg. 0.4 µg/L)	Gumbs and Dierberg (1985)

Tile and stainless steel materials can be sources of chromium in runoff (Wallinder, et al. 2002b; Zobrist, et al. 2000).

Iron

Lasheen, et al. (2008) investigated the effect of water quality parameters, holding time, pipe age, and pipe material on heavy metal concentrations of iron (and other metals) released from different types of water pipe materials, including polyvinyl chloride (PVC), polypropylene (PP) and galvanized iron (GI) pipes. The authors found that the concentrations of iron were higher after 72 hours holding time than for 48 hours at pH

7.5. The authors also analyzed iron concentrations as a function of pipe material and pipe age at pH 7.5. The galvanized pipes released the highest concentrations of iron when compared to PVC or polypropylene pipes, as expected. The lowest concentrations of iron were released from the PP pipes. The concentrations of iron were not different for the PVC and PP pipes, but for galvanized iron pipes, the concentrations were different from both plastic pipes. The experiments conducted by Lasheen, et al. (2008) showed that as pipes age, the iron concentrations also increase. For example, for PVC pipes, after 72 h of contact time, the mean iron concentrations were 58 and 70 µg/L in 2 and 20 weeks aged pipes, respectively. For PP pipes, the mean iron concentrations were 60 and 70 µg/L in2 and 20 weeks aged pipes for 72 h stagnation time. The galvanized pipes released the highest concentrations of iron, with the mean concentrations of 700 and 1440µg/L in 2 and 20 weeks aged pipes after 72 hours of contact. The authors also found that at low pH conditions (pH = 6), the concentrations of iron increased. The greatest increase in iron concentrations at pH 6 was observed in GI and PP pipes, while the lowest increase was noted in PVC pipes. For PVC pipes, the mean iron concentrations were found to be 68 and 80 µg/L for 2 and 20 weeks after 72 hr of stagnation. In PP pipes, the mean iron release was 73 and 83 µg/L and in GI pipes 990 and 1,650 µg/L for 2 and 20 weeks after 72 hr stagnation. As the pH increased (pH = 8), the concentrations of iron decreased. The mean iron concentrations dropped from approximately 70 to 60 µg/L for PVC pipes and from about 69 to 60 µg/L for PP pipes for 20 weeks aged pipes. The reduction of iron release was 14 and 13% for PVC and PP pipes, respectively when compared to the control pipes. For GI pipes, the concentration of iron decreased by 9.7 % compared to control pipes and the mean iron concentration dropped from 1,440 to 1,300 µg/L for 20 weeks aged pipes. Also, the authors found that high Cl^-/SO_4^{2-} ratios increased iron concentrations in all pipes. Dietz, et al. (2007) examined iron releases from PVC, lined cast iron, unlined cast iron, and galvanized steel aged pipes (40+ years) with and without inhibitors. Water was also passed through copper pipes with embedded lead coupons to simulate residential systems, as the use of lead solder with copper pipes is common (US EPA, 1993). Four inhibitors were examined at three doses each: blended ortho/poly phosphate (BOP), ortho-phosphate (OP), zinc ortho-phosphate (ZOP), and silicate (SI). Dietz, et al. (2007) observed a modest decrease of iron releases associated with addition of inhibitor, or elevation of the pH. For example, increasing the dose of silicate inhibitor also increased alkalinity due to the high pH of that inhibitor. The elevated alkalinity decreased iron concentrations (Dietz, et al. 2007).

Zobrist, et al. (2000) examined the concentrations of heavy metals including Fe in runoff from tile and polyester roofs located in a suburb of Zürich, Switzerland. The drainage systems for the clay tile roof was 15-year old copper and for the polyester roof, new copper. Average iron runoff loads from the tile roof were 2,050 µg/m^2 per event. Fe in tile and polyester roof runoff samples were mainly associated with the particulate fraction. During another study, runoff rates of iron from stainless steel roofs were found to be between 10 and 200 mg m^2/year Fe (Wallinder, et al. 2002b).

Mendez, et al. (2011) investigated the quality of harvested rainwater from five pilot-scale roofs (which included Galvalume® metal) and three full-scale roofs (which included one

7-year-old Kynar®-coated Galvalume® metal located in Austin, Texas). The Kynar®-coated Galvalume® roof released lower iron concentrations compared to the uncoated Galvalume roof. Iron concentrations in harvested rainwater from pilot-scale Galvalume roofs ranged between 18 and 1,700 µg/L for the first flush sample, and between 8.9 and 560 µg/L for later samples. The rain had iron concentrations between 12 and 1,100 µg/L. Fe concentrations in harvested rainwater from full-scale Kynar®-coated Galvalume® roof ranged between 6.2 and 24µg/L for the first flush sample and between 4.1 and 7.9µg/L for later samples. During these tests, the rain had iron concentrations ranging between 12 and 42 µg/L.

Shahmansouri, et al. (2003) conducted a pilot-scale drinking study of water distribution systems in Zarrinshahr and Mobarakeh, Iran. The piping system materials in the houses and buildings were galvanized iron, while the distribution piping systems were made of asbestos, polyethylene, and occasionally iron pipes. The authors found that samples collected along the distribution system showed significant increases in iron concentrations, which sometimes exceeded the recommended levels. For Zarrinshahr, the iron concentrations before the distribution systems were 0.08 µg/L and after distribution systems 0.71 µg/L. For Mobarakeh, the iron concentrations before the distribution systems were 0.05 µg/L and after distribution systems 0.85 µg/L.
Sarin, et al. (2004) investigated the effects of dissolved oxygen (DO) on iron releases from old corroded iron pipes. They found that corrosion scales from 70-year-old galvanized iron pipe were characterized as porous deposits and were made of Fe (III) phases (goethite (a-FeOOH), magnetite (Fe_3O_4), and maghemite (a-Fe_2O_3)) with a shell-like, dense layer near the top of the scales and high concentrations of readily soluble Fe (II) content which was present inside the scales. Small amounts of siderite ($FeCO_3$) were also found as a component phase. It was determined that corrosion scales can alter the behavior of metal pipes such that they behave differently compared to non-corroded metal. The authors examined iron releases from the corroded pipes under flow and stagnant water conditions. Iron released from corroded iron pipes were mainly in the ferrous form (Fe^{2+}).

Sarin, et al. (2004) observed that when oxidants were present in water, greater iron releases was found during water storage in comparison to flowing water conditions. After 24 hours of the experiment, the amount of iron released from iron pipes under stagnation conditions (initial DO = 1.0 and 6.2 mg/L) reached 150µg/m of pipe length and under flow conditions (initial DO = 2.74 mg/L) iron release was75 µg/m of pipe length. Also, it was determined that increasing DO concentrations in water from 6.2 mg/L to 16 mg/L under stagnant conditions decreased the amount of iron released from approximately 360 µg/m of pipe length to 225 µg/m of pipe length. They concluded that increasing the concentrations of oxidants in the water and maintaining flowing conditions can lower the amount of iron released from corroded iron pipes. The authors suggested that iron is released from corroded iron pipes by dissolution of corrosion scales, and that the microstructure and composition of the corrosion scales are important factors that can affect the amount of iron leaching from the system. The rate of depletion of oxidants (e.g. DO) in water was faster during flowing conditions than during stagnation conditions. The oxidants present in water were chiefly consumed in oxidizing the Fe (II) inside the scales or the Fe (II) present in the water. Also, oxidants are likely to be consumed in later pipe metal corrosion.

Corrosion scales can have a negative effect on water quality during water distribution, which includes ‘‘red water’’ or ‘‘colored water’’ when iron is released from corrosion scales, high demand for chlorine and dissolved oxygen (DO), biofilm growth, and adsorption and accumulation of substances such as arsenic, and radium, which can be released during changes in the water quality. Colored water is formed when iron is released into the bulk water as ferric particles, or as Fe (II) that then oxidizes and then forms ferric particles (Sarin, et al. 2004).

In the absence of any corrosion scales, corrosion of iron is the primary cause of iron release. When metal surfaces are covered with corrosion scales, iron may be released by the corrosion of iron metal, the dissolution of ferrous components of the scales, and hydraulic scouring of particles from the scales (Sarin, et al. 2004). The corrosion rate of clean iron surfaces typically increases with the increase of the oxidant (such as oxygen) concentrations. When scale layers are formed during the corrosion process, they can influence the rate of diffusion of oxygen to the metal, and slow down corrosion. The environment inside the corrosion scales present in water distribution pipes is characterized with highly reducing conditions and high concentrations of Fe (II). They found that for metal pipes with oxide scales less than one year old, the rate of dissolved oxygen decrease could not be used as a measure of the corrosion rate. It was suggested that oxygen was primarily consumed in oxidizing Fe (II) within the iron oxide layers, and not in the corrosion reaction at the metal/electrolyte interface (Sarin, et al. 2004). Sarin, et al. (2004) also noted that iron releases increased with stagnation time, while the DO concentration diminished. For initial DO concentration of 6.2 mg/L and pH of 8.9, iron releases from the iron pipe wereapproximatelly100 µg/m of pipe length after 20 hours of stagnation, and reached 375 µg/m of pipe length after 120 hours of stagnation.

Corvo, et al. (2005) examined changes in the atmospheric corrosion rate caused by chloride ions based on rain conditions. Test materials included plain carbon steel that were exposed in two atmospheric test stations in Havana, Cuba and Medellin, Colombia. The samples were subjected to accelerated outdoor tests by intermittent spraying of a salt solution. The acceleration of corrosion caused by chloride ions was notably higher at Havana for steel during the 1 year of exposure. Iron mass losses were lower at Medellin (1280 g/m^2 mass loss after 1 year) in comparison with Havana (samples were completely destroyed by corrosion after six months of exposure) due to higher frequencies and amounts of rainfall at Medellin. The authors found that metal mass loss was proportional to the chloride deposition rate and that rain amount and frequency have a great influence on the acceleration rate caused by chloride ions on atmospheric corrosion of steel due to rain’s washing effect. The authors found that large amounts and durations of rain correspond to a lower corrosion rate for a given chloride deposition rate. Additionally, rain diminishes chloride surface concentrations; the corrosion acceleration rate caused by chloride ions is likely to lessen with an increase in rain amounts at constant exposure time. The addition of salt spray at Havana increased the corrosion rate of iron materials when compared to the samples at the same location but under natural conditions. The formation of green rust in the presence of chloride ions involves an incorporation of the chloride ions from solution into the inter-layers of green rust and an oxidation of Fe (II) to Fe (III) without any structural changes. Table 4-26 summarizes iron concentrations and runoff yields from different materials found by various researchers.

Table 4-26. Iron Releases from Various Sources

Materials tested	Test conditions	Observed iron concentrations or runoff yields	Reference
Uncoated Galvanized Aluminum Roofing Materials			
Galvalume roofs	Pilot-scale. Austin, Texas	18 - 1690 μg/L during first flush, and 8.94 - 563.00 μg/L for later samples	Mendez, et al. (2011)
Coated Galvanized Aluminum Roofing Materials			
7-year-old Kynar®-coated Galvalume® roof	Full-scale. Austin, Texas	6.23 - 23.8 μg/L during first flush; 4.10 - 7.88 μg/L for later samples	Mendez, et al. (2011)
Other Roofing Materials			
Stainless steel	1 year field exposure. Stockholm, Sweden	10 - 200 mg/ m^2/year	Wallinder, et al. (2002b)
Carbon steel	(salt spray) Medellin, Colombia. 1 year test	1280 g/m^2/year mass loss	Corvo, et al. (2005)
Carbon steel	(salt spray) Havana, Cuba. 1 year test	Samples (2mm x100 mm x150 mm) completely destroyed by corrosion after 6 months of exposure	Corvo, et al. (2005)
Carbon steel	(natural conditions) Havana, Cuba. 1 year test	280 g/m^2/year mass loss	Corvo, et al. (2005)
Clay tile roof with 15-year old copper	Field test. Tuffenwies, Switzerland	Average 2.05 mg/m^2 per event	Zobrist, et al. (2000)

Table 4-26. Iron Releases from Various Sources (continued)

Drinking Water Distribution Systems (DWDS)			
2 weeks aged galvanized iron pipes after 72 h of contact time	Lab test	Avg. 0.7 mg/L	Lasheen, et al. (2008)
20 weeks aged galvanized iron pipes after 72 h of contact time	Lab test	Avg. 1.44 mg/L	Lasheen, et al. (2008)
2 weeks aged galvanized iron pipes after 72 h of contact time	pH = 6	Avg. 0.99 mg/L	Lasheen, et al. (2008)
20 weeks aged galvanized iron pipes after 72 h of contact time	pH = 6	Avg. 1.65 mg/L	Lasheen, et al. (2008)
2 weeks aged galvanized iron pipes after 72 h of contact time	pH = 8	Avg. 1.44 mg/L	Lasheen, et al. (2008)
20 weeks aged galvanized iron pipes after 72 h of contact time	pH = 8	Avg. 1.3 mg/L	Lasheen, et al. (2008)
Drinking Water Distribution System (asbestos, polyethylene, and iron pipes), after min of 6 hrs.	Zarrinshahr, Iran	Before DWDS 0.08 µg/L, after DWDS 0.71 µg/L	Shahmansouri, et al. (2003)
Drinking Water Distribution System (asbestos, polyethylene, and iron pipes), after min of 6 hrs.	Mobarakeh, Iran	Before DWDS 0.05 µg/L, after DWDS 0.85 µg/L	Shahmansouri, et al. (2003)
2 weeks aged PVC pipes after 72 h of contact time	Lab test	Avg. 0.058 mg/L	Lasheen, et al. (2008)
20 weeks aged PVC pipes after 72 h of contact time	Lab test	Avg. 0.07 mg/L	Lasheen, et al. (2008)
2 weeks aged PVC pipes after 72 h of contact time	pH = 6	Avg. 0.068 mg/L	Lasheen, et al. (2008)
20 weeks aged PVC pipes after 72 h of contact time	pH = 6	Avg. 0.08 mg/L	Lasheen, et al. (2008)
2 weeks aged PVC pipes after 72 h of contact time	pH = 8	Avg. 0.07 mg/L	Lasheen, et al. (2008)
20 weeks aged PVC pipes after 72 h of contact time	pH = 8	Avg. 0.06 mg/L	Lasheen, et al. (2008)
2 weeks aged polypropylene pipes after 72 h of contact time	Lab test	Avg. 0.06 mg/L	Lasheen, et al. (2008)
20 weeks aged polypropylene pipes after 72 h of contact time	Lab test	Avg. 0.07 mg/L	Lasheen, et al. (2008)
2 weeks aged polypropylene pipes after 72 h of contact time	pH = 6	Avg. 0.073 mg/L	Lasheen, et al. (2008)
20 weeks aged polypropylene pipes after 72 h of contact time	pH = 6	Avg. 0.083 mg/L	Lasheen, et al. (2008)
2 weeks aged polypropylene pipes after 72 h of contact time	pH = 8	Avg. 0.069 mg/L	Lasheen, et al. (2008)
20 weeks aged polypropylene pipes after 72 h of contact time	pH = 8	Avg. 0.06 mg/L	Lasheen, et al. (2008)

PVC, polypropylene, galvanized iron, clay tile, polyester, stainless steel, galvanized iron, and Galvalume® metal materials were found to release iron to the runoff water (Lasheen, et al. 2008; Shahmansouri, et al. 2003; Zobrist, et al. 2000; Wallinder, et al. 2002b; Mendez, et al. 2011). Exposure time had an effect on iron released from PVC, polypropylene, and galvanized iron materials (Lasheen, et al. 2008). Greater iron runoff concentrations were observed for aged PVC, polypropylene, and galvanized iron pipes compared to new materials (Lasheen, et al. 2008). As pH decreased, iron concentrations leaching from PVC, polypropylene, and galvanized iron, cast iron, and galvanized steel materials increased (Lasheen, et al. 2008; Dietz, et al. 2007). High Cl^-/SO_4^{2-} ratios increased iron concentrations from PVC, polypropylene, and galvanized iron pipes. In iron pipes, in the presence of oxidants, greater releases of iron were observed under stagnant conditions compared to flowing conditions (Sarin, et al. 2004). The amount of iron released in water under stagnant conditions was decreased when the DO concentrations increased. The level of iron from corroded iron pipes was lowered when the water was flowing and the concentration of oxidants were raised. Compared to stagnant conditions, the depletion rate of oxidants in water was more rapid than during flowing conditions. When the oxidant concentrations increase, there is usually an increase in the corrosion rate of clean iron surfaces. Corrosion can be retarded and the rate of diffusion of oxygen to the metal can be influenced when scale layers are formed. The mass loss of carbon steel is influenced by the frequency and the amount of rain and is proportional to the chloride deposition rate (Corvo, et al. 2005). For a given chloride deposition rate, a lower corrosion rate occurs during heavy, long duration rains.

Aluminum

Mendez, et al. (2011) studied the effects of roofing material on water quality for rainwater harvesting systems. The authors examined the quality of harvested rainwater using five pilot-scale roofs (asphalt fiberglass shingle, Galvalume® metal, concrete tile, cool, and green) and three full-scale roofs (two asphalt fiberglass shingle and one 7-year-old Kynar®-coated Galvalume® metal) in Austin, Texas. The authors found that aluminum concentrations released by full-scale 7 year old Kynar®-coated Galvalume® roof were substantially lower than from the pilot-scale Galvalume® roof. Aluminum concentrations in harvested rainwater from pilot-scale Galvalume roofs ranged between 20 and 2,000 µg/L for the first flush sample, and between 14 and 550 µg/L for later samples. The aluminum concentrations in the rain ranged between 4.1 and 560 µg/L. Aluminum concentations in harvested rainwater from full-scale Kynar®-coated Galvalume® roof ranged between 0.06 and 12 µg/L for the first flush sample, and between 0.06 and 6.7µg/L for later samples. The aluminum concentrations in the rain water during these tests ranged between 12 and 55 µg/L. Table 4-27 summarizes aluminum concentrations from different materials.

Table 4-27. Aluminum Releases from Various Sources

Materials tested	Test conditions	Observed aluminum concentrations	Reference
Pilot-scale Galvalume roofs	Austin, Texas. Several rain events in 2010	20 to2050 µg/L during first flush; 14 to555 µg/L for later samples	Mendez, et al. (2011)
Full-scale Kynar®-coated Galvalume® roof	Austin, Texas. Several rain events in 2010	0.06 to 12µg/L during first flush sample; 0.06 to6.7µg/L for later samples	Mendez, et al. (2011)

Galvalume materials have been found to be a source of aluminum with concentrations in the 10's of µg/L (Mendez, et al. 2011).

pH

Pitt, et al. (2004) evaluated runoff characteristics during wet weather conditions for different source areas and found that pH varied widely in urban areas. pH values of roof runoff were more acidic than other runoff sources and ranged between 4.4 and 8.4, with a mean value of 6.9. The highest pH was observed for storage areas at a concrete batch plant with the range between 6.5 and 12, and a mean of 8.5. Different pH conditions can have a great effect on the speciation and toxicities of the metals (Pitt, et al. 2004).

Rainwater pH influences the degradation of roofing and gutter materials. An acidic environment dissolves the $CaCO_3$ content of concrete and metal ions from metal roofing materials. This results in corrosion and damage of the roofing and piping materials and the change of the roof runoff pH. In the case of concrete and metal materials, the pH of the roof runoff is usually higher than that of rainwater, attributed to the $CaCO_3$ and metal ions (Horvath 2011).

Clark, et al. (2007 and 2008b) investigated pollutant release from commonly used roofing materials including galvanized metals: the rusted portion with no paint, the bare metal with no paint and no visible degradation, and the painted metal. The test site was located on the campus of Penn State Harrisburg. The authors found that pH values of the runoff were below neutral, ranging between 5 and 6.5. Clark, et al. (2008a) further investigated runoff water quality from different roofing materials during the first four months of their exposures to rain. Figure 4-29, from Clark, et al. (2008a), shows the pH of the roof runoff from different roofing materials. The roof runoff from all the materials was slightly acidic (25th and 75th percentile values for galvanized steel were between pH 6 and 7, except for green roofs which were close to neutral, and cedar shakes that further decreased roof runoff pH).

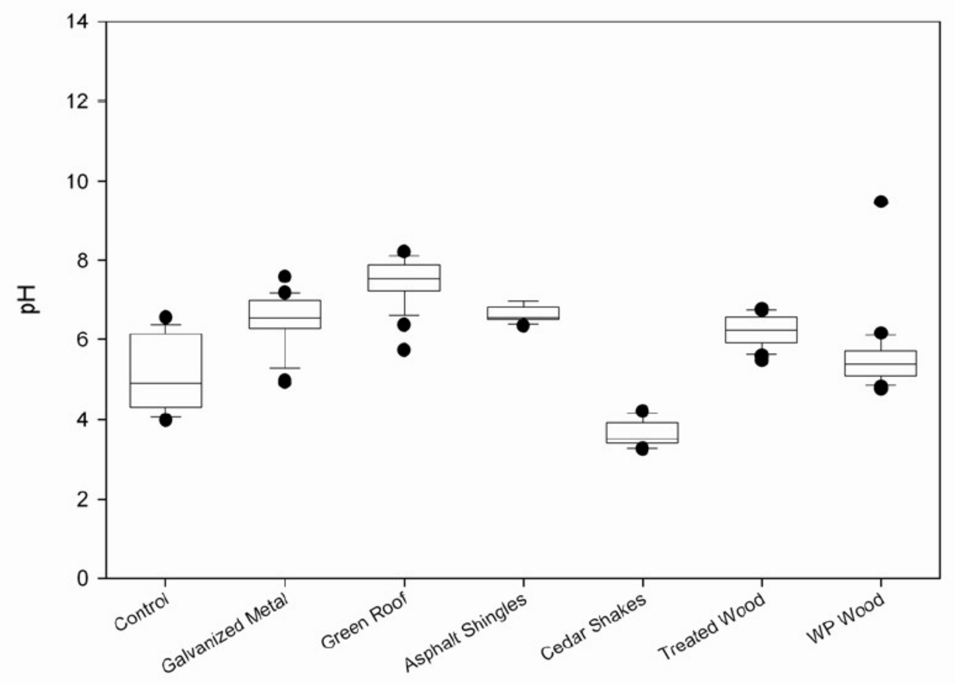


Figure 4-29. Runoff pH from roofing materials and control (Rainfall pH ranged between 3.9 and 6) (Clark, et al. 2008a)

Tobiason (2004) investigated unpainted Galvalume metal roof runoff quality at Seattle Tacoma International Airport (STIA) and found the runoff pH to be slightly acidic. Tobiason and Logan (2000) studied pollutant concentrations in roof runoff from four areas at the Seattle-Tacoma International Airport. The pH of the uncoated galvanized steel roof runoff ranged from 6.1 to 8, with the average value of 6.9.

Veleva, et al. (2010) studied zinc concentrations leaching from hot dip galvanized (HDG) steel. Samples of galvanized steel were exposed to the Gulf of Mexico environment for two years. pH values of the runoff collected after the first flushes of rain were in the range 5.5–7.0, while pH values of the rainwater were between 4.7 and 6.10. Schriewer, et al. (2008) studied roof runoff from 14 year-old zinc roofs in Germany for a period of 1 year. Roof runoff was directed to titanium–zinc gutters and the downspouts. The pH of the roof runoff ranged between 5.8 and 8.4, with a median value of 6.7. Förster (1999) studied roof runoff from different roofing materials (concrete tiles, clay pantiles, fibrous cement, tar felt and zinc sheet) in Bayreuth, Germany, followed by zinc and PVC gutters. The runoff pH from the zinc roofs was between 6.2 and 6.5, and between 7.1 and 7.5 from fibrous cement.

Zobrist, et al. (2000) measured the concentrations of heavy metals in runoff from tile, polyester, and gravel roofs located in the suburb of Zürich, Switzerland. The drainage system for the clay tile roof was 15-year old copper, new copper for the polyester roof, and PVC material for the gravel roof. pH values of the roof runoff were between 6.5 and 7.5 and those in rain events ranged mainly from 5.3 to 6.2.

Table 4-28 summarizes pH values from different materials found by various researchers.

Table 4-28. pH Values from Various Sources

Material tested	Test conditions	Observed pH values	Reference
Uncoated Galvanized Steel Roofing Materials			
14-year old zinc roof	Field study. Germany	5.8-8.4 (avg. 6.7)	Schriewer, et al. (2008)
Zinc roof with zinc and PVC gutters	Field study. Bayreuth, Germany	6.2-6.5	Forster (1999)
New uncoated galvanized steel roof	4 mo field test. Pilot Scale	4.5-7	Clark, et al. (2008a)
Uncoated galvanized steel roof	Field study. Seattle	6.1-8 (avg. 6.9)	Tobiason and Logan (2000)
Galvanized steel	Filed study. Mexico	5.5-7.0	Veleva, et al. (2010)
Uncoated Galvanized Aluminum Roofing Materials			
New galvanized corrugated aluminum roof	2 year field test. Pilot Scale	5 - 6.5	Clark, et al. (2008b)
Other Roofing Materials			
Cement roof with zinc and PVC gutters	Field study. Bayreuth, Germany	7.1-7.5	Forster (1999)
New corrugated polyvinyl chloride roof	2 year field test. Pilot Scale	5 - 6.5	Clark, et al. (2008b)
Tile, polyester, and gravel roofs	Filed study	6.5 – 7.5	Zobrist, et al. (2000)
Other Materials			
Storage areas at a concrete batch plant	Field study.	6.5-12 (avg. 8.5)	Pitt, et al. (2004)

The pH of rainwater can range between approximately 3.9 and 6.10 depending on the region (Horvath 2011; Clark, et al. 2007; Veleva, et al. 2010; Zobrist, et al. 2000). When rainwater comes in contact with concrete, plastic, metals, and other materials, its pH usually increases to close to neutral conditions. The pH of stormwater runoff varied widely for different source areas (Pitt, et al. 2004). The pH values of roof and gutter runoff usually ranges between 4.4 and 8.4, with a mean value of 6.9 (Pitt, et al. 2004; Clark, et al. 2007 and 2008b; Veleva, et al. 2010; Tobiason 2004; Tobiason and Logan 2000; Veleva, et al. 2010; Schriewer, et al. 2008; Zobrist, et al. 2000). The runoff pH from cement materials is usually higher than from metallic materials (Förster 1999; Pitt, et al. 2004). The speciation of metals can be greatly affected by changing pH conditions (Pitt, et al. 2004).

Nutrients

Clark, et al. (2007, 2008a, b) studied runoff water quality from different roofing materials during exposure to rain. Figures 4-30 and 4-31 represent nitrate and phosphorus concentrations released from several types of roofing materials. They observed that the nutrient concentrations (ammonia, nitrates, total nitrogen, and phosphate) from uncoated galvanized steel and vinyl roofing materials were closer to the background levels, but with intermittent elevated concentrations. Plastic/vinyl materials didn't release any noticeable concentrations of COD. Cedar shakes and asphalt shingles were a significant source of nitrates; asphalt shingles were also the most significant source of total phosphorous. They also concluded that certain growth media and substrate components of green roofs can be a significant source of nutrients.

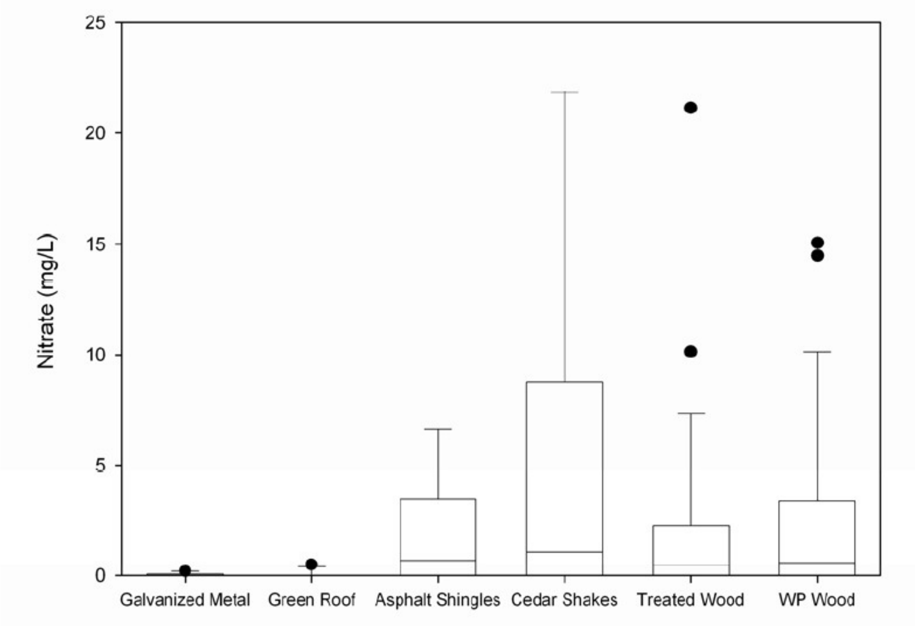


Figure 4-30. Runoff nitrate concentration from roofing materials, background corrected (Clark, et al. 2008a).

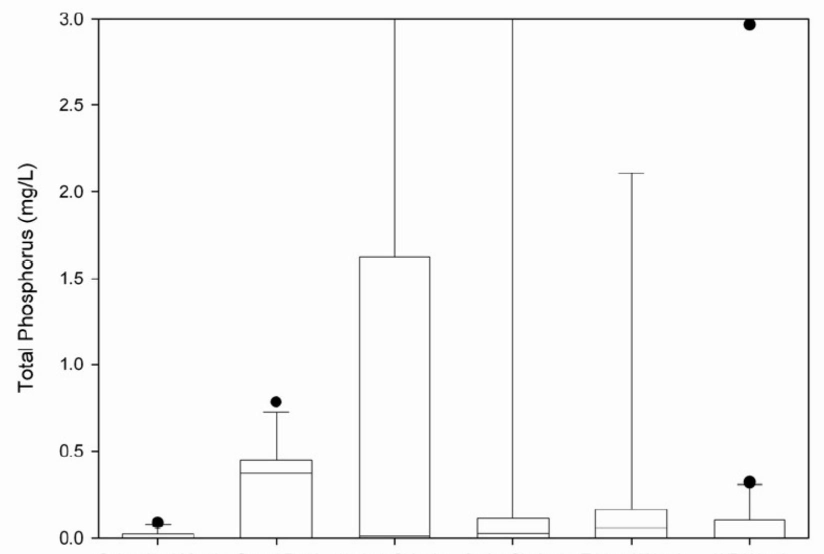


Figure 4-31. Runoff phosphorus concentration from roofing materials, Background corrected (Clark, et al. 2008a).

Clark, et al. (2008b) studied the leaching of metals and nutrients from two sixty year old painted galvanized metal roofing panels during laboratory studies. They also studied leaching of nutrients from several materials including galvanized corrugated aluminum, prepainted 55% aluminum-zinc alloy coated steel (Galvalume), and corrugated polyvinyl chloride panel during pilot-scale testing for 2 years. The nutrient concentrations for metal and vinyl roofs were closer to the background levels with periodic spikes in the runoff, compared to the other materials. For example, for galvanized aluminum, there was a nitrate spike of 35 mg/L at Day 50. Similar trends were noted for total nitrogen, ammonia, and total phosphorus. It was noted that the potential for nutrient release exists in the galvanized metal probably as a result of phosphate washes and binders used in the material's preparation and in wood products due to natural degradation (Clark, et al. 2008b).

Table 4-29 and 4-30 summarize nutrient concentrations from different materials found by various researchers.

Table 4-29. Nitrate Releases from Various Sources

Material tested	Test conditions	Time Frame	Observed nitrate concentrations or runoff yields	References
New uncoated galvanized steel roof	Field. Pilot Scale	4 mo.	< 1 mg/L	Clark, et al. (2008a)
New coated galvanized metal roof	Field. Pilot Scale	4 mo.	< 1 mg/L	Clark, et al. (2008a)
60 years old painted galvanized metal roof exposed	Leaching test in the lab	-	60 mg/kg/48hr	Clark, et al. (2008b)
60 years old painted galvanized metal roof, stored in the barn	Leaching test in the lab	-	60 mg/kg/48hr	Clark, et al. (2008b)
New galvanized aluminum roof	Field. Pilot Scale	14 mo.	35 mg/L at day 50	Clark, et al. (2007)
New planted green roofs	Field. Pilot Scale	4 mo.	< 1 mg/L	Clark, et al. (2008a)
New asphalt shingles roof	Field. Pilot Scale	4 mo.	0.9 mg/L (median) 3.5 mg/L (75th percentile)	Clark, et al. (2008a)
New cedar shakes roof	Field. Pilot Scale	4 mo.	1.3 mg/L (median) 8.5 mg/L (75th percentile)	Clark, et al. (2008a)

Table 4-30. Phosphorus Releases from Various Sources

Material tested	Test conditions	Time Frame	Observed phosphorus concentrations or release rates	References
New uncoated galvanized steel roof	Field. Pilot Scale	4 mo.	< 1 mg/L	Clark, et al. (2008a)
New coated galvanized metal roof	Field. Pilot Scale	4 mo.	< 1 mg/L	Clark, et al. (2008a)
60 years old painted galvanized metal roof. exposed	Leaching test in the lab	-	31 - 55 mg/kg/48hr	Clark, et al. (2008b)
60 years old painted galvanized metal roof stored in the barn	Leaching test in the lab	-	31 - 55 mg/kg/48hr	Clark, et al. (2008b)
New asphalt shingles roof	Field. Pilot Scale	4 mo.	0.02 mg/L (median) 1.6 mg/L (75th percentile)	Clark, et al. (2008a)
New planted green roofs roof	Field. Pilot Scale	4 mo.	< 1 mg/L	Clark, et al. (2008a)

Galvanized steel, galvalume, and vinyl roofing materials had nutrient concentrations (ammonia, nitrates, total nitrogen, and phosphate) close to background levels, but with periodic elevated concentrations (Clark, et al. 2007, 2008a and b). The most significant sources of total phosphorus were asphalt shingles. It has also been noted that certain green roofs can be a substantial source of nutrients (Clark, et al. 2007, 2008a and b).

Toxicity

Good (1993) studied metal concentrations and aquatic toxicity of roof runoff from different roofing materials at a sawmill on the coast of Washington. The roofing materials included a rusty galvanized metal roof, weathered metal roof that may have been coated with aluminum paint many years ago, roof coated with tar, tar roof sealed with aluminum paint, and a relatively new aluminum roof. Zinc leached out of each type of roofing materials, with especially high zinc releases observed from galvanized roofing materials. Copper leached out of tar-covered roofs. Lead leached out of plastic rain gutters. Lead, zinc, and copper concentrations in roof runoff samples surpassed the water quality criteria for the corresponding constituents. Though the concentrations of copper and zinc were lower three hours after the beginning of the storm event but still during the rain, high dissolved metal concentrations remained higher than water quality criteria and the roof runoff was still highly toxic to rainbow trout.

Tobiason and Logan (2000) studied the whole effluent toxicity (WET) of stormwater samples from four outfalls at Seattle-Tacoma International Airport. For the WET tests, water fleas and fathead minnows were used. It was found that the source of the toxicity was the 10-year old unpainted galvanized metal roofs. They determined that zinc-galvanized metal roofs were a source of the zinc that ranged from 66 to 92% dissolved. Samples with low pH adjusted to pH values within acceptable ranges produced little to no toxicity reductions (Tobiason and Logan 2000). Mason, et al. (1999) also found that the leaching of metals from galvanized metal roofing materials can cause aquatic toxicity. Tobiason (2004) also observed that such commonly used galvanized products as fencing, guardrails, light poles and unpainted Galvalume metal roofing leach substantial concentrations of dissolved zinc in stormwater runoff causing toxicity. Bailey, et al. (1999) studied toxicity of stormwater runoff samples from three sawmills on Vancouver Island, British Columbia. Zinc in runoff from the galvanized roofs from the sawmills was found to be the major source of toxicity, based on rainbow trout toxicity tests. All except 1 of 27 samples were found to be toxic. In 24 of the samples, the toxicity was linked to divalent cations, especially zinc.

Zinc toxicity is commonly linked to water hardness (Leland and Kuwabara 1985; Bradley and Sprague 1985). The toxicity is high with low hardness in the majority of the samples. For values of hardness ranging from 9 to 100 mg/L, the LC_{50} (as dissolved zinc) was between 72 and 272 µg/L tested with juvenile rainbow trout (Bailey, et al. 1999).

The zinc contaminants in the roof runoff originate from dissolution of the roofing and gutter materials rather than from atmospheric deposition. Zinc in the roof runoff was predominantly in ionic form (Zn^{2+}), which is the most bio-available form (Heijerick, et al. 2002; Schriewer, et al. 2008).

Heijerick, et al. (2002) studied the bioavailability of zinc in runoff from 15 different zinc-based roofing materials in Stockholm, Sweden. The authors found that most zinc (94.3-99.9%) was present as the free Zn ion, which is the most bioavailable speciation form. Biosensor tests (Biomet™) that use genetically modified bacterium (the bacterial biosensor emits light in the presence of bioavailable zinc) also confirmed the findings that all zinc was bioavailable. Analysis of the ecotoxicity (conducted using the internationally recommended 72 h algal toxicity test with *R. subcapitata*) data also suggested that the toxic effects were due to the presence of Zn^{2+} ions.

Shokes and Moller (1999) and Cantrell, et al. (1995) have indicated that a significant decrease of copper levels have been noted over a short period of time when the water is in contact with iron surfaces, likely due to co-precipitation. Sundberg (1998) also noted that concrete can reduce copper from roof runoff. Michels, et al. (2003) found that the toxicity of stormwater runoff decreased as it passed through cast iron and concrete drainage systems. Michels, et al. (2002) suggested passing roof runoff through filters that contain iron filings to reduce copper release into the environment.

Veleva, et al. (2010) studied zinc leaching from hot dip galvanized (HDG) steel in humid tropical climates. Samples of galvanized steel were exposed in the state of Tabasco, along the Gulf of Mexico, for two years. High zinc concentrations released from zinc sheet roofing were observed and compared with different criteria (aquatic toxicity, sewage sludge, soil). The results showed that the zinc concentrations exceeded the threshold values by up to three orders of magnitude.

Wallinder, et al. (2001) investigated zinc in runoff from 15 different zinc panels or zinc coatings, which included new and naturally aged sheets, all being commercial zinc-based construction materials. Almost all of the zinc (greater than 95%) found in the runoff was in the form of hydrated Zn^{2+} ions, which is the most bioavailable form (Wallinder, et al. 2000; He, et al. 2001). The toxicity effect was studied using the alga R. Subcapitata. The toxicity effects were highly correlated with zinc concentrations. The authors concluded that most zinc found in the runoff was in the form of Zn^{2+} and bioavailable for algae.

Sandberg, et al. (2006) examined corrosion-induced copper runoff from copper sheeting, naturally patinated copper, and pre-patinated copper in a chloride-rich marine environment during one year of tests. The bioavailable concentrations (the portion that is available for uptake by an organism) of released copper comprised a low fraction (14–54%) of the total copper concentration due to complexation towards organic matter in impinging seawater aerosols (Sandberg, et al. 2006). The authors concluded that released copper is complexed with other ligands which reduce the copper bioavailability. Factors that influence the bioavailability of copper include alkalinity, hardness, pH and dissolved organic matter.

Wallinder et al (2009) studied the copper released from a naturally aged copper roof (installed 48 years) on a shopping center building in Farsta, Stockholm and the interaction of copper with the internal drainage system and storm drains made of cast iron and concrete.

Wallinder, et al. 2009 observed that the major part of the copper released from the roof was already retained during transport through the internal cast iron and concrete drainage system of the building. The laboratory and field studies showed that the concrete pipes and concrete-based pavement materials have a high capacity to retain copper released from roofs by forming corrosion product malachite, $Cu_3(CO_3)_2(OH)_6$ (Bahar, et al. 2008a,b; Sundberg 1998; Boulanger and Nikolaidis 2003; Wallinder, et al. 2009). The interaction of roof runoff water and the drainage system also changes the chemical speciation of non-retained copper. Most copper that was not retained by cast iron and concrete surfaces was strongly complexed with organic matter, which significantly reduced the bioavailable fraction. Bertling, et al. (2006) and Boulanger and Nikolaidis (2003) studied the copper runoff process and its environmental fate and also found that released copper as a result of atmospheric corrosion is retained by different solid surfaces located in the close proximity of its source.

Förster (1999) investigated the variability roof runoff from different roofing materials (concrete tiles, clay pantiles, fibrous cement, tar felt, and zinc sheet) in Bayreuth, Germany. Drainage systems were made of zinc and PVC gutters. Zinc concentrations (from zinc roofs and ordinary roofs with zinc gutters) were compared to aquatic toxicity, sewage sludge, soil, etc. criteria and were found to exceed those standards up to three orders of magnitude and advised to connect roofs having metal surfaces to infiltration facilities. Förster (1999) also found very high copper concentrations in the runoff from copper sheets as fittings around roof windows and chimney bases. The dissolved to particulate copper concentration ratio was on the order of 1.4. Copper concentrations were compared to aquatic toxicity criteria and were also found to exceed those standards by up to three orders of magnitude.

Karlen, et al. (2002) sampled roof runoff directly after the release from the naturally patinated roofs of varying age (0 and 30 years) in Sweden and found that the roof runoff containing 60-100% free hydrated cupric ion, $Cu(H_2O)_6^{2+}$, $Cu(OH)^+$ and $Cu_2(OH)_2^{2+}$ ions which caused significant reduction in growth rate of green algae during the 72-hr growth inhibition test.

Effect of pH on toxicity

Jennings, et al. 2001 studied the inhibition of light emitted by the bioluminescent bacterium, Vibrio fischeri by various chemicals at eight concentrations using reagents from three commercial assay systems (ToxAlert 101, Microtox1 and LUMIStox1). They noted an apparent relation of the toxicity of many chemicals to their pH in solution and at high chemical concentrations, and to osmotic imbalances. In highly acidic or alkaline solutions, pH can be the primary cause of toxicity (Jennings, et al. 2001; Chou and Hee 1993; Carlson- Ekvall and Morrison 1995; Ho, et al. 1999; Sinclair, et al. 1999). Chou and Hee (1993) and Ho, et al. (1999) found that the toxicity of chemicals in bioluminescent assays depend on the pH of the solution. This effect was also observed by Jennings, et al. (2001) for potassium dichromate the toxicity was high when the pH of the stock solution was outside of acceptable range for the assay (pH 6.0-8.5), however, when the pH was adjusted to 7.0, the toxicity was substantially decreased For some relatively non-toxic chemicals, very high concentrations were used to give a full dose/ response and in these cases, an increase in osmolarity may be been the main cause of toxicity. In addition to these differences, it has also been suggested that different batches of luminescent bacterial media and reagents from the same manufacturer can contribute to some of the observed variation. The author noted that antagonistic and synergistic interactions with other compounds are complicating factors that can significantly influence toxic responses of test organisms.

Ho, et al. (1999) found that metals have pH dependent toxicity. The scientists determined that alteration of pH can change the toxicity of Cu, Cd, Ni, Pb, and Zn to Mysidopsis Bahia (mysid), Ampelisca abdita (amphipod) and Vibrio fischeri (Microtox solid phase test (MSP)). For the MSP assay, the authors observed, as the pH decreased, the toxicity for Pb, Ni, Cd, and Zn also decreased and the toxicity of for Cu increased. Studies were conducted at three pH values of 6, 7, and 8 for the MSP. Metal toxicity is often dependent upon pH in freshwater and soils.

Ho, et al. (1999) noted that changes in toxicity with changing pH are metal and marine test organism specific. For the MSP assay, Cu was the most toxic metal, followed by Pb and Zn, Ni the least toxic. For the MSP assay, as pH decreased, toxicity for Pb, Ni, Cd, and Zn also decreased, however the toxicity for Cu increased. Based upon these tests on the three marine species, Cu toxicity was the most dependent on pH. The authors found that IC50 values vary with changing pH and noted that their IC50 values for metals with M. bahia were higher than the literature values, however Ho's metals IC50 values for A. abdita generally agreed with the values for Cd and Cu previously obtained by another authors, but were two orders of magnitude higher for PB- This discrepancy was explained by different exposure conditions (p 237).

Ho, et al. (1999) reviewed studies conducted by different researchers and noted that change in toxicity is frequently metal and test species dependent, indicating that at lower pH values, the toxicity of Cd, Cu, and Zn generally decreased, however at lower pHs the toxicity of Pb generally increased. It was shown that the toxicity of Cu and Zn for Ceriodaphnia dubia increased as pH decreased. Another study examined *C.* dubia, Pimphales promelas, and Hyalella azteca and concluded that the toxicity of Zn, Cd, and Ni decreased at lower pH conditions, while the toxicity of Pb and Cu increased at lower pH conditions. In his study, Ho, et al. (1999) noted that for three marine organisms, pH generally caused a change in metal toxicity, and this change was different for different organisms and metals. The authors concluded that it is reasonable to expect that different metals have different modes of action and that different species would evolve different approaches to compensate for metal toxicity. It was found that the toxicity of metals depend on the pH.

Walker, et al. (1996) noted that the increase of metal toxicity with decreasing pH can be explained by a number of factors including changes in speciation of metals in solution and increased desorption of metals from surfaces at lower pH values.

High metal concentrations of zinc, copper, and lead can leach from various roofing and pipe materials and are usually in the most bioavailable form (ions) and can cause aquatic toxicity (Good 1993; Tobiason and Logan 2000; Tobiason 2004; Mason, et al. 1999; Bailey, et al. 1999; Heijerick, et al. 2002; Schriewer, et al. 2008; Veleva, et al. 2010; Wallinder, et al. 2000; He, et al. 2001; Förster 1999; Karlen, et al. 2002). The toxicity of zinc, copper, lead, cadmium, etc. is dependent upon water hardness and is higher with lower hardness (Leland and Kuwabara 1985; Bradley and Sprague 1985; Bailey, et al. 1999). Metals can be retained by the drainage system or form complexes with organic matter, changing the chemical speciation of metals and reducing toxicity (Shokes and Moller 1999; Cantrell, et al. 1995; Sundberg 1998; Michels, et al. 2003; Sandberg, et al. 2006; Wallinder et al 2009; Bahar, et al. 2008a,b; Sundberg 1998; Boulanger and Nikolaidis 2003; Bertling, et al. 2006; and Boulanger and Nikolaidis 2003). pH can be the major cause of toxicity under extremely low and high pH conditions (Jennings, et al. 2001; Chou and Hee 1993; Carlson-Ekvall and Morrison 1995; Ho, et al. 1999; Sinclair, et al. 1999).

Conductivity

Schriewer, et al. (2008) studied runoff from a 14 year-old zinc roof in Germany. Roof runoff was collected into titanium–zinc gutters and the downspout. The authors found that increasing zinc concentrations in the roof runoff contribute to increases in electrical conductivity.

Horvath (2011) observed the first flush effect in conductivity values measured in the runoff from a 9 year old bituminous roof located in Budapest, Hungary. The author found that the conductivity of the roof runoff was higher than that of the rainwater by one order of magnitude. This can be explained by the dissolution of dry deposition materials from the atmosphere and weathering products of the roofing materials. Reductions in conductivity during rain events were attributed to the wash off of deposited contaminants. Consequently, the roof runoff quality is dependent upon the duration of dry antecedent period (Horvath 2011); in this study, as the duration of the antecedent period increased, the conductivity of the roof runoff samples also increased (Horvath 2011).

Förster (1996) found the conductivity in the runoff from a cement roof was the highest, followed by runoff from concrete tile and zinc roofing materials. Research conducted in the US showed that the conductivity of runoff from wood shingle roofs were the highest in comparison with other roofing materials and was attributed to the accumulation of contaminants in the cracks, and subsequent dissolution during rainfall events (Chang, et al. 2004).

As the concentrations of metals in roof runoff increase, electrical conductivity also increases (Schriewer, et al. 2008; Chang, et al. 2004).

Other Constituents

Al-Malack (2001) studied the effect of water quality parameters on the migration of metal stabilizers from unplasticized polyvinyl chloride (uPVC) pipes. The author found that the metal stabilizer's concentrations (tin, Ba, Ca) leaching out of uPVC pipes increased with the duration of the study. As water pH decreased, Ca and Ba concentrations increased. Tin, barium, and calcium concentrations increased with a temperature increase from 35 to 45^{o}C by 42, 85 and 29%, respectively. The concentrations of tin increased with the increase in the concentration of TDS. Also, it was observed that exposure to UV-radiation promoted the migration of tin, and other metal stabilizers.

Veleva, et al. (2010) studied roof runoff from hot dip galvanized (HDG) steel roofs in the Gulf of Mexico environments. The carbonate ion CO_3^{2-} concentrations measured in the runoff were 1.6–1.7 times higher than those measured in rainwater, because of the dissolved zinc carbonate. Also, the authors detected several chloride containing corrosion products which were not released by the rain events.

Protective Coatings and Additives

Zinc coating are frequently applied to steel in order to prevent steel from corrosion (Degremont 1979; Veleva, et al. 2010). Zinc or aluminum is intentionally sacrificed when these metals are used for the cathodic protection of steel structures (Shreir 1976). Zinc has a negative standard redox potential of -0.76 V and therefore zinc is a very active metal and tends to corrode when it is in contact with oxygen and moisture (Veleva, et al. 2010). Zinc coatings are most commonly used to protect such materials as aluminum and iron from corrosion.

Hot-dip galvanization is a process in which steel material is immersed in a bath of zinc at 450 ^{o}C (Degremont 1979). The zinc layer is strongly bonded to the steel and its external surface is oxidized with the formation of zinc hydroxide ($Zn(OH)_2$), oxide (ZnO), or hydroxycartonate ($(Zn)_x(OH)CO_3$) depending on the temperature and alkalinity of the water. Corrugated galvanized iron sheets have lead and cadmium as typical additives in the zinc coatings (Gumbs and Dierberg 1985; Uhlig 1953). Additions of lead in small concentrations (0.04-0.2 %) improve the zinc coating uniformity and its adhesion to the steel substrate (Sere 1999).

If calcium carbonate is present in the water, it may protect galvanized steel pipe by forming a protective layer. When calcium carbonate in water exceeds the saturation concentration, and in the presence of zinc, the excess is deposited as a very thin insoluble protective hydrous-oxide coating on the surface of the galvanized steel pipe and isolates the metal from water. If damaged, this protective coat repairs itself rapidly; precipitates of calcium carbonate are formed which are insoluble scale deposit that protects the metal from corrosion (Gabriel and Moran 1998).

To protect corrugated steel and spiral rib steel pipes from aggressive drainage waters and soils, pipes are coated with zinc, aluminum, asphalt, asphalt with aramid fiber (derived from nylon), thermosetting epoxy, PVC, ethylene acrylic acid, and polyethylene layer. Concrete lining can also be used (Gabriel and Moran 1998).

When aluminum is exposed to the atmosphere, a very thin natural coating of aluminum oxide forms and securely adherers to the metal surface, thus enhancing its resistance to corrosion. If a fresh surface is exposed by abrasion or cutting, a new film is quickly formed in the presence of air or water. With some exceptions, the protective oxide film that is created is soluble in alkaline solutions and in strong acids, however it is stable in the middle range of pH values between 4 and 9. Under soft water conditions, the resistance to pitting is high. Pitting corrosion is more likely to take place in waters containing ions of copper, chloride, sulfate, and oxygen. Such heavy metal ions as copper and iron increase the possibility of electrochemical corrosion by forming stray electrical currents and galvanic couples. Combinations of low resistivity with low pH values tend to increase the average metal loss (Gabriel and Moran 1998). A Florida study of aluminum pipe observed failure of coatings and advance pitting corrosion in a coastal area where the soil became saturated with chlorides as a result of tidal effects when the pH was between 6.5 and7.0 (Gabriel and Moran 1998).

In order to prevent the polymer from decomposing and disintegrating, heat stabilizers are used. Stabilizers improve the resistance of the polymer or composite to various degradation-promoting factors during processing, storage, and service (Al-Malack 2001). For unplasticized PVC pipe, mixtures of lead, cadmium, barium, and organotin compounds are used as heat stabilizers (Al-Malack, et al. 2000). In Australia, Asia and Europe, lead-based stabilizers have traditionally been used during the unplasticized PVC pipe manufacturing process. In the United States tin-based stabilizers are commonly used (Al-Malack 2001).

In construction and other extended-life applications, lead and other heavy metal stabilizers such as cadmium and zinc are added to PVC materials. Stabilizers, plasticizers, colorants, and other additives are mixed with pure PVC to produce a usable plastic with desired properties. In its pure form, PVC is rigid and brittle, and it gradually catalyzes its own decomposition when exposed to ultraviolet light. Additives are mixed with the PVC polymer to make it flexible, moldable, and long lasting. Studies have shown that lead can leach into water carried in PVC pipes that contain lead stabilizers (Thornton 2002).

Roof paints used to prolong the lifespan of a roofing material or for aesthetic reasons can include metallic compounds which supply another source of metal (Gumbs and Dierberg 1985). Davis and Burns (1999) examined lead release in stormwater runoff from painted structures in an urban area. The author observed lead concentrations which ranged from 10's to 100's of µg/L. It was found that old surface paints have the potential to release large amounts of lead.

First flush of runoff from exposed roofing materials

The first flush effect is the initial period of runoff from a roof having elevated concentrations of contaminants compared to concentrations during the later stages of the rain event (Gupta and Saul 1996). Zinder, et al. (1988) pointed out that the first flush effect is caused by one or a combination of three processes: (1) matter deposited on the roofing material during antecedent dry period which is washed off by the initial period of rain; (2) the initial rain washes off weathering and corrosion products of the roofing material and drainage system; and (3) the increasing in total rainfall depth causes concentrations in the falling rain itself to diminish due to scavenging of gases, particles, and aerosols by rain drops(Zinder, et al. 1988). For each contaminant, the comparative importance of the potential sources and the physical – chemical properties of respective contaminant affect the contributions of processes mentioned above to concentrations found in roof runoff. Zobrist, et al. (2000) found that heavy metal concentrations were influenced by the first and ultimately second process. It was observed that, for heavy metals, the washout effect in the atmosphere was significantly less important than the other processes.

He, et al. (2001a) noted that the magnitude of the first flush is determined by a combination of several parameters including dry deposition, length of dry and wet periods, and characteristics of the corrosion layer prior to a precipitation event. A sufficient rain volume is needed in order to transport soluble corrosion products from the surface. The rain intensity governs the contact time during which the stormwater is in contact with the surface and therefore determines the rate at which the easily soluble corrosion products are washed off and consequently determines the magnitude of the first flush (He, et al. 2001a;Schriever 2008).

Dry atmospheric deposition and the degradation of the roofing material affect the suspended solid concentration of roof runoff. As the duration of the dry period between rainfall events increases, the concentration of suspended solids also increases (Quek and Förster 1993; Horvath 2011). Van Metre and Mahler (2003) noted that most of the particulates which can be easily mobilized are washed off during the first 2.6 mm (0.1 in) of rain. Transport and dissolution processes during washoff are correlated with runoff volume (Förster 1999).Faller and Reiss (2005) also found that the total copper and zinc concentrations in the rain runoff for copper and titanium-zinc materials were a function of the total rain depth of the event. The concentrations in smaller rains were found to be higher than those in larger rains. In the beginning of a rain event, water-soluble compounds like sulfates, nitrates and chlorides are washed from exposed surfaces (Faller and Reiss 2005).

Veleva, et al. (2007) observed that zinc runoff concentrations are higher after dry periods of when the rain events are scarce and more time is available for the formation of new corrosion products on the surface of zinc during the time of wetness, without the loss of corrosion products during runoff.

Gromaire-Mertz, et al. (1999) studied runoff from zinc roofs and gutters in Paris between July 1996 and May 1997. Mean metal concentrations in the roof runoff varied greatly and were mainly correlated with the antecedent dry period. Zobrist, et al. (2000) also observed the first flush effect with very high concentrations that declined rapidly to lower constant levels for the inclined tile and polyester roofs.

Roof runoff first flushes were observed during 93% of runoff events in the research conducted by Schriewer, et al. (2008). Zinc concentrations were higher at the beginning of the runoff events and averaged 13.4 mg/L in the first sample bottles and decreased to comparatively constant concentrations of approximately 5 mg/L. pH of the roof runoff ranged between 5.8 and 8.4 with median values of 6.7. High variations of zinc concentrations during runoff events were observed.

Horvath (2011) studied roof runoff from bituminous roofs in Budapest, Hungary. They observed the first flush effect in the following roof runoff water constituents: conductivity, turbidity, suspended solids, and dry and organic matter concentration. This effect is explained by the dissolution of deposited aerosols and weathering products on roofing materials. Consequently, the roof runoff quality was found to be dependent upon the duration of the dry antecedent period. Horvath (2011) also observed that the suspended solids concentrations of the first roof runoff samples ranged between 86 and 155 mg/L and were several times higher than that of in rainwater (ranging between 14 and 54 mg/L). The variability in the conductivity of roof runoff during three rainfall events was explained by the different durations of antecedent dry periods. In this study, as the duration of the antecedent period increased, the conductivity of the roof runoff samples also increased.

Good (1993) studied metal concentrations and aquatic toxicity of roof runoff from different roofing materials at a sawmill on the coast of Washington. They observed first flushes in samples that were collected after more than a week of dry weather. They sampled roof runoff from aluminum painted metal roofs at the beginning of the storm and approximately three hours later. He found that the concentrations of many parameters (including copper and zinc) were lower in the samples collected after three hours (especially zinc).

Other researchers have also noted roof runoff first flushes (He 2002; Gumbs and Dierberg 1985; Yaziz, et al. 1989; He, et al. 2001a). Faller and Reiss (2005) observed some rain events, which did not show a first flush effect, which could have been explained by the different length of dry periods and different degrees of dry deposition before the rain event.

Veleva, et al. (2010) studied zinc concentrations leaching from hot dip galvanized steel exposed in the Gulf of Mexico. The first flush (rain event which occurs after a long dry period) was one of the most important factors explaining zinc releases during runoff events. During first flushes, weakly acidic rain dissolves the zinc carbonate corrosion product, hydroxycarbonate [$Zn_5(OH)_6(CO_3)_2$]–hydrozincite, and releases carbonate ions $CO^{2-}{}_3$ from zinc galvanized steel surfaces. The amount of dissolved carbonate ions is a function of the rain pH, its periodicity and intensity. The authors note that during the dry period, neutral zinc salts such as $ZnSO_4$ or $Zn(NO_3)_2$ are often formed, they have high solubility and are readily dissolved during the first flush, and less soluble zinc salts are formed, including zinc hydrosulphates and hydroxychlorosulphates. During steady state runoff, further dissolution is controlled by the solubility properties of the latter salts (Veleva, et al. 2010).

Förster (1999) investigated the variability roof runoff from different roofing materials in Bayreuth, Germany. They observed that first flushes from roofs were frequently heavily contaminated and therefore should be treated.

Laboratory Tests and Model Fitting to Predict Metal Releases from Material Exposures

Appendix D contains the basic measurements concerning the laboratory tests to measure the releases of heavy metals from different materials immersed in different test waters. The data are presented as time series plots indicating the accumulative total losses on an area basis. Linear regression analyses were then conducted on the time series plots of log-transformed metal releases per pipe surface area vs. log time for different pipe and gutter materials under controlled and natural pH conditions, after supporting statistical analyses were used to identify groupings of the data. The majority of the scatterplots revealed that first order polynomials can be fitted to the log of metal releases vs. log of time.

Time Series Plots of Metal Concentrations with Exposure Time

The time series of lead releases from steel gutters at pH 5 and of steel pipes at pH 8 were not fitted with linear equations due to initial lag periods before releases were observed. In the container with steel gutters at pH 5, no lead was detected until after 1 month exposure: after 1 month exposure, the lead release reached 0.97 mg/m^2 (0.02 mg/L) and after 2 months exposure, the lead release exceeded 1 mg/m2 (0.028 to

0.037 mg/L). There were only three detected lead concentrations in the data series. In the containers with steel pipe at pH 8, lead releases were detected after 2 months exposure and exceeded 29 mg/m^2 (0.71 mg/L). Two concentration values above the detection limits were available.

Time series for copper releases from copper gutters under pH 5 conditions showed an apparent increase in the copper concentrations after 0.5 h exposure, and, after 27 h exposure, reached 970 mg/m^2 (6.8 mg/L). However, after 27 h exposure, copper concentrations leveled off. The linear regression equation fitted to this data was not significant (p-value for regression equation is greater than 0.05 and is highlited in red in Table 4.3).These copper data were therefore fitted using first order polynomial and 2 segment liner equations due to the obvious change in release rate after 27 hrs. The numbers of data points in these time series were limited and the high concentration observed after 27 h exposure could have been an unusually high value. On the other hand, cupric ions could have been combined with the orthophosphate from the solution and thereby reducing copper solubility. Edwards (2002) observed that higher doses of orthophosphate tend to decrease solubility of copper.

Modeling the Effects of Material Type, Exposure Time, pH, and Salinity on Metal Releases and Toxicity

A model was developed to evaluate the effects of different materials available for various applications (roofing components, drainage pipes, culverts, and rainwater storage tanks) on runoff water quality for a range of field conditions, such pH, conductivity, and time of contact. To build an empirical model, Spearman correlation, Cluster, Principal Component and Factorial analyses were used to identify the significant water quality, material and exposure time factors, and their interactions that influence pollutant releases and toxicity.

Spearman correlation analysis was performed to determine the association between constituents and the degree of that association, while cluster analyses were conducted to identify more complex relationships between the parameters. Principle component analyses were conducted to identify groupings of parameters having similar characteristics. The significant factors determined from the factorial analyses were used to combine the data into groups. The final model can be used to determine which materials can be safely used for short contact times such as for gutters and pipes, and for longer term storage, such as for tanks.

The Spearman correlation matrices were constructed using the statistical software Sigma Plot 11.0 (Systat Software, Inc). The cluster analyses were conducted using the statistical software Minitab 16 (Minitab, Inc). Principle component analyses were also conducted using Minitab 16 (Mintab, Inc).

Full 2^3 Factorial Analyses

Full 2^3 factorial analyses were performed on Cu, Zn, Pb constituents (using the release rates of mg per m^{2}of surface area of exposed materials) and toxicities in percent light reductions at 15 and 45 min of Microtox bacteria exposure times. These analyses therefore examined the effects of time, pH, and material and their interactions for the first testing series data and the effects of time, conductivity, and material and their interactions during for the second testing series data. Table 4-31 shows the levels for the different factors defining how the data were sorted. The data from the first and the second testing stages were not combined into a single 2^3factorial analysis because of the lack of data having pH 5 with low conductivity conditions. As described earlier, Kruskal-Wallis tests were performed for each constituent to determine if the data for 1, 2, and 3 months of pipe and gutter exposure could be combined as replicates representing long term exposure times. The tests indicated that there were no statistically significant differences (at 0.05 significance level) between these data so they were combined into one data category. Kruskal–Wallis tests were also conducted for each constituent on the data after 0.5 and 1h of exposure to indicate if they could be combined to represent short exposure periods. These tests similarly showed that these data could be combined into one category for short term exposure times.

Table 4-31. 2^3 Factorial Experiment. Factors and levels.

Constituent	Factors and levels		
	Time	pH or Conductivity	Material
Cu (mg/m^2)	short (0.5h, 1h) (-) vs. long (1mo, 2mo,3mo) (+)	pH 5 (-) vs. pH8 (+)	copper (-) vs. the rest of the materials (+)
Cu (mg/m^2)	short (1h) (-) vs. long (1mo, 2mo,3mo) (+)	high cond. (-) vs. low cond. (+)	copper (-) vs. the rest of the materials (+)
Zn (mg/m^2)	short (0.5h, 1h) (-) vs. long (1mo, 2mo,3mo) (+)	pH 5 (-) vs. pH8 (+)	galv. steel (-) vs. the rest of the materials (+)
Zn (mg/m^2)	short (1h) (-) vs. long (1mo, 2mo,3mo) (+)	high cond. (-) vs. low cond. (+)	galv. steel (-) vs. the rest of the materials (+)
Pb (mg/m^2)	short (0.5h, 1h) (-) vs. long (1mo, 2mo,3mo) (+)	pH 5 (-) vs. pH8 (+)	galv. steel (-) vs. the rest of the materials (+)
Pb (mg/m^2)	short (1h) (-) vs. long (1mo, 2mo,3mo) (+)	high cond. (-) vs. low cond. (+)	galv. steel (-) vs. the rest of the materials (+)
Tox @15 min (%)	short (0.5h, 1h) (-) vs. long (1mo, 2mo,3mo) (+)	pH 5 (-) vs. pH8 (+)	metal (-) vs. non-metal (+)
Tox @15 min (%)	short (0.5h, 1h) (-) vs. long (1mo, 2mo,3mo) (+)	pH 5 (-) vs. pH8 (+)	copper and galv. steel (-) vs. the rest of the materials (+)
Tox @15 min (%)	short (1h) (-) vs. long (1mo, 2mo,3mo) (+)	high cond. (-) vs. low cond. (+)	copper and galv. steel (-) vs. the rest of the materials (+)
Tox @45 min (%)	short (0.5h, 1h) (-) vs. long (1mo, 2mo,3mo) (+)	pH 5 (-) vs. pH8 (+)	metal (-) vs. non-metal (+)
Tox @45 min (%)	short (0.5h, 1h) (-) vs. long (1mo, 2mo,3mo) (+)	pH 5 (-) vs. pH8 (+)	copper and galv. steel (-) vs. the rest of the materials (+)
Tox @45 min (%)	short (1h) (-) vs. long (1mo, 2mo,3mo) (+)	high cond. (-) vs. low cond. (+)	copper and galv. steel (-) vs. the rest of the materials (+)

The results of the 2^3 factorial analyses are shown in Appendix D. Appendix D shows normal probability plots of the effects and their interactions. The factorial effect/pooled standard error ratio of the factorial analysis (shown in Tables 4-32 and 4-33) were used to determine whether or not the data could be combined into groups for each constituent based on the effect (or absence of effect) of the factors and their interactions. The ratios of Effect/SE that were greater than three are highlighted in red, and those that are greater than five are highlighted in bold red, indicating likely significant factors and interactions. For each constituent, effects and their interactions were sorted into significant, marginally significant, and not significant groups, according to the absolute values of their effects (Tables 4-34 and 4-35).

Table 4-32. 2^3Factorial effect/standard error of the effect ratio (Controlled pH tests).

		Effect/Pooled Standard Error of the Effect						
Constituent	**2^3 Factorial**	**pH**	**Material**	**Time**	**pH x Material**	**pH x Time**	**Material x Time**	**pH x Material x Time**
Cu	pH: 5 vs. 8 M: Cop vs. the rest[1] T: Short vs. Long[4]	**-49.79**	**-108.74**	**82.24**	**49.61**	**-24.12**	**-81.10**	**24.01**
Zn	pH: 5 vs. 8 M: Galv. vs. the rest[2] T: Short vs. Long	3.44	**-6.64**	**6.04**	-3.42	4.03	**-6.01**	-4.02
Pb	pH: 5 vs. 8 M: Galv. vs. the rest[2] T: Short vs. Long	1.91	**-5.21**	**5.30**	-1.91	1.91	**-5.33**	-1.91
Tox. at 15 min	pH: 5 vs. 8 M: Cop, Galv. vs. the rest[3] T: Short vs. Long	**-26.77**	-2.36	-1.72	-3.34	**6.29**	0.25	-1.99
Tox. at 45 min	pH: 5 vs. 8 M: Cop, Galv. vs. the rest[3] T: Short vs. Long	**-25.78**	-2.41	-1.74	-3.23	4.46	-0.82	-1.86

[1] The rest = all the materials excluding copper: concrete, PVC, HDPE, and galv. steel pipes, and vinyl, aluminum, and galv. steel gutters.

[2] The rest = = all the materials excluding galvanized steel: concrete, PVC, HDPE pipes, and vinyl, aluminum, and copper gutters.

[3] The rest = all the materials excluding copper and galvanized steel: concrete, PVC, HDPE pipes, and vinyl and aluminum gutters.

[4] Short, long exposure times

The ratios of Effect/SE of the effect that were greater than three are highlighted in red, and those that are greater than five are highlighted in bold red, indicating the likely significant factors and interactions.

Table 4-33. 2^3 Factorial effect/pooled standard error of the effect ratio (Natural pH tests).

		Effect/Standard Error of the Effect						
Constituent	**2^3 Factorial**	**Cond.**	**Material**	**Time**	**Cond. x Material**	**Cond. x Time**	**Material x Time**	**Cond. x Material x Time**
Cu	Cond.: High vs. Low M: Cop vs. the rest[1] T: Short vs. Long[4]	**-6.59**	**-9.15**	**8.94**	**6.59**	**-6.45**	**-8.94**	**6.45**
Zn	Cond.: High vs. Low M: Galv. vs. the rest[2] T: Short vs. Long	2.29	**-5.41**	**5.28**	-2.29	2.32	**-5.27**	-2.32
Pb	Cond.: High vs. Low M: Galv. vs. the rest[2] T: Short vs. Long	2.00	-2.34	2.24	-2.00	3.01	-2.41	-3.01
Tox. at 15 min	Cond.: High vs. Low M: Cop.& Galv. vs. the rest[3] T: Short vs. Long	2.04	**-24.72**	**17.31**	**5.08**	-2.27	**-13.94**	-0.42
Tox. at 45 min	Cond.: High vs. Low M: Cop.& Galv. vs. the rest[3] T: Short vs. Long	3.04	**-41.68**	**20.99**	**8.79**	1.32	**-17.19**	-2.56

[1] The rest = all the materials excluding copper: concrete, PVC, HDPE, and galv. steel pipes, and vinyl, aluminum, and galv. steel gutters.

[2] The rest = all the materials excluding galvanized steel: concrete, PVC, HDPE pipes, and vinyl, aluminum, and copper gutters.

[3] The rest = all the materials excluding copper and galvanized steel: concrete, PVC, HDPE pipes, and vinyl and aluminum gutters.

[4] Short, long exposure times

The ratios of Effect/SE of the effect that were greater than three are highlighted in red, and those that are greater than five are highlighted in bold red, indicating likely significant factors and interactions.

Table 4-34. 2^3 Factorial significant effects and their interactions (Buffered pH Tests).

Constituent	**2^3 Factorial**	Effect		
		Significant	Marginally Significant	Not Significant
Cu	pH: 5 vs. 8 M: Cop vs. the rest T: Short vs. Long	pH, material, time, pH x material, pH x time, material x time, pH x material x time.		
Zn	pH: 5 vs. 8 M: Galv. vs. the rest T: Short vs. Long	material, time, material x time	pH, pH x material, pH x time, pH x material x time.	
Pb	pH: 5 vs. 8 M: Galv. vs. the rest T: Short vs. Long	material, time, material x time,		pH, pH x material, pH x time, pH x material x time.
Tox. at 15 min	pH: 5 vs. 8 M: Cop, Galv. vs. the rest T: Short vs. Long	pH, pH x time,	pH x material,	material, time, material x time, pH x material x time.
Tox. at 45 min	pH: 5 vs. 8 M: Cop, Galv. vs. the rest T: Short vs. Long	pH,	pH x material, pH x time,	material, time, material x time, pH x material x time.

Table 4-35. 2^3 Factorial significant effects and their interactions (Natural pH Tests).

Constituent	**2^3 Factorial**	Effect		
		Significant	Marginally Significant	Not Significant
Cu	Cond.: High vs. Low M: Cop vs. the rest T: Short vs. Long	cond., material, time, cond. x material, cond. x time, material x time, cond. x material x time.		
Zn	Cond.: High vs. Low M: Galv. vs. the rest T: Short vs. Long	material, time, material x time,		cond., cond. x material, cond. x time, cond. x material x time.
Pb	Cond.: High vs. Low M: Galv. vs. the rest T: Short vs. Long		cond. x time, cond. x material x time.	Cond., material, time, cond. x material, material x time,
Tox. at 15 min	Cond.: High vs. Low M: Cop.& Galv. vs. the rest T: Short vs. Long	material, time, cond. x material, material x time,		cond., cond. x time, cond. x material x time.
Tox. at 45 min	Cond.: High vs. Low M: Cop.& Galv. vs. the rest T: Short vs. Long	material, time, cond. x material, material x time,	cond.,	cond. x time, cond. x material x time.

Combined Data Group Analyses

Figures 4-32 through 4-44 show metal releases and toxicities at 15 and 45 min for the combined data groups, based on the prior analyses. The significant factors and their interactions from 2^3 factorial analyses were used for grouping the samples and conditions. The box plots were constructed only for the groups that were found to be significant. Group box plots were plotted for these constituents to illustrate the variations and differences between each group. Figure 4-32 is a group box plot of copper releases comparing the copper material samples with the all of the other samples for pH 5 and 8 conditions during both short and long exposure times. Full 2^3 factorial analyses showed that the three-way interaction of pH x material x time was significant, therefore the main effects should not be interpreted (Navidi 2006).The data was combined into the groups according to the interaction of pH, material, and time. Copper materials were the most significant source of copper, as expected. Lower pH conditions increased the copper releases from the copper materials. The copper releases in the sample groups of all materials increased with exposure time. The combination of conditions, such as copper materials under pH 5 water conditions during short exposure time, significantly increased copper releases. Similarly, copper releases increased dramatically for copper materials immersed into pH 5 water for long exposure periods, as well as for copper materials immersed into pH 8 waters for long exposure periods. Figure 4-33 shows the groups combining the rest of the materials for pH 5 and pH 8 conditions during short exposure time into one group; also, the rest of the materials for pH 5 and pH 8 conditions during long exposure time into one group.

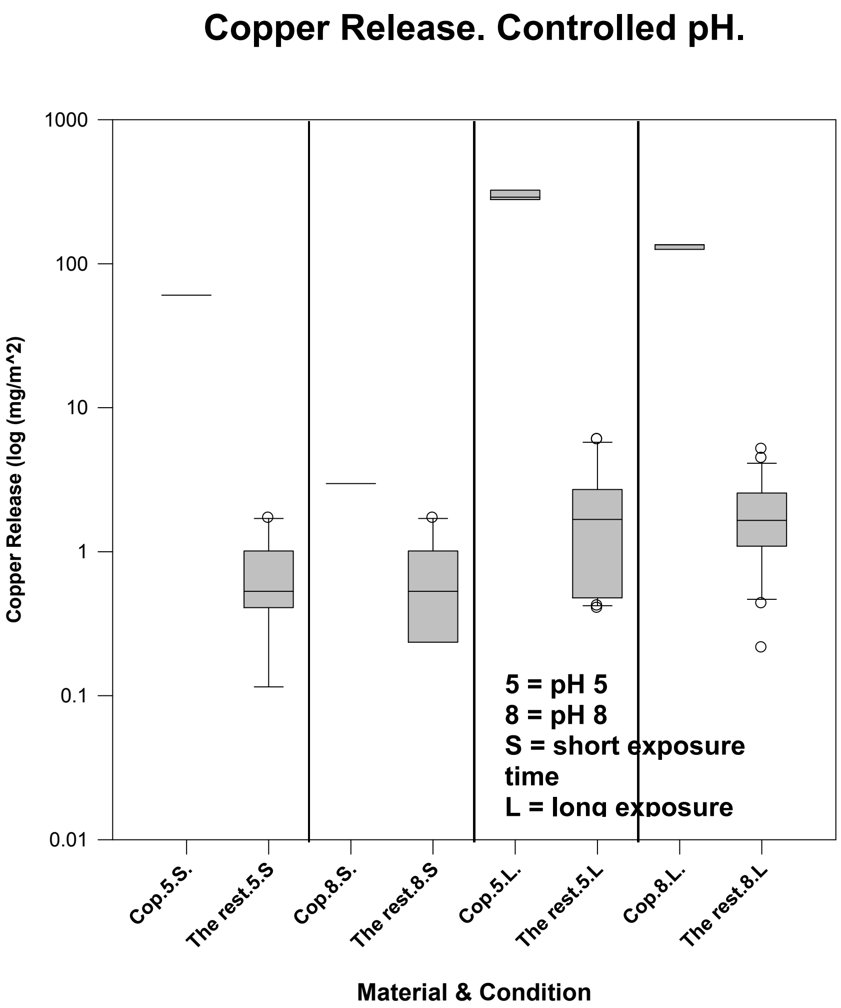


Figure 4-32. Group box plot for copper release in mg/m^2 for materials immersed in pH 5 and pH 8 waters.

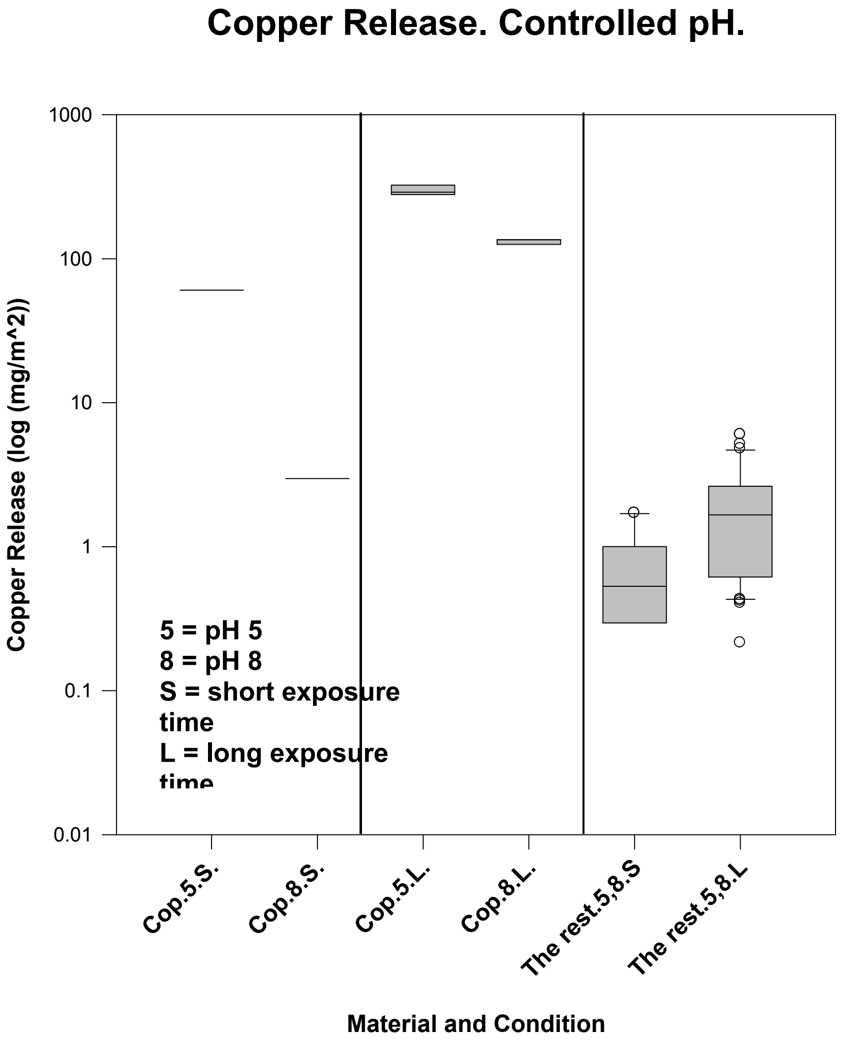


Figure 4-33. Group box plot for copper release in mg/m^2 for materials immersed in pH 5 and pH 8 waters.

Figure 4-34 shows copper releases in the pipe and gutter samples immersed in bay and river waters. Copper releases were detected during both short and long exposures for controlled pH conditions and for both the natural bay and river water tests. Copper concentrations were greater for bay water exposure tests compared to river water exposure tests. Exposure time also increased copper releases in the samples with copper gutter materials. The combination of copper materials, high conductivity, and long exposure periods, as well as copper materials, low conductivity, and long exposure periods, significantly increased copper releases.

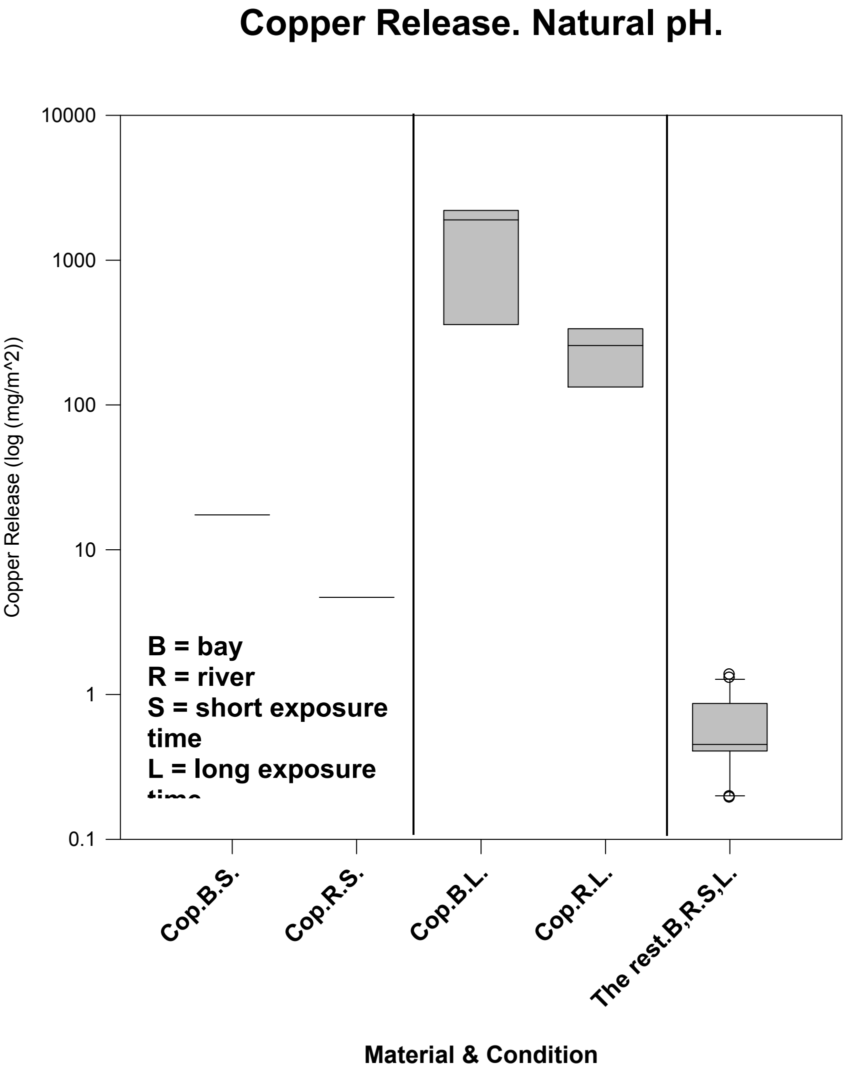


Figure 4-34. Group box plot for copper release in mg/m^2 for materials immersed in bay and river waters.

Figure 4-35 is a group box plot of zinc releases for the galvanized steel samples compared to the rest of the material samples for pH 5 and8 conditions during short and long exposure periods. Galvanized steel materials were the greatest source of zinc. During short exposure times, low pH conditions increased zinc releases in the samples with galvanized materials, however during long exposure times, zinc releases were greater under controlled pH 8 conditions compared to controlled pH 5 conditions. Exposure time increased zinc releases in the samples with galvanized materials. The combination of such factors as galvanized materials, pH 5, and short exposure periods, resulted in significant increases in zinc releases. Similarly, zinc releases were much higher for galvanized materials immersed into pH 5 waters for long exposure periods, and for galvanized materials immersed into pH 8 waters for long exposure periods. Figure 4-36 shows “the rest” of the materials at pH 5 and pH 8 conditions during short and long exposure periods combined into one group.

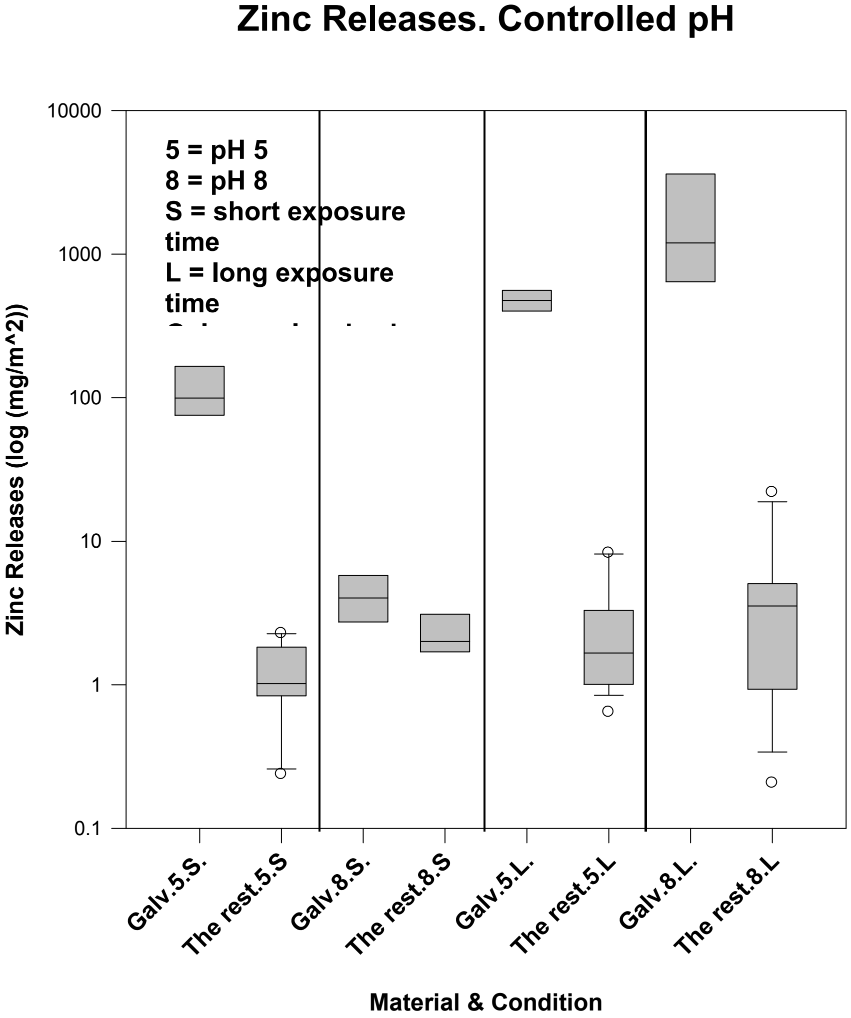


Figure 4-35. Group box plot for zinc release in mg/m^2 for materials immersed in pH 5 and pH 8 waters.

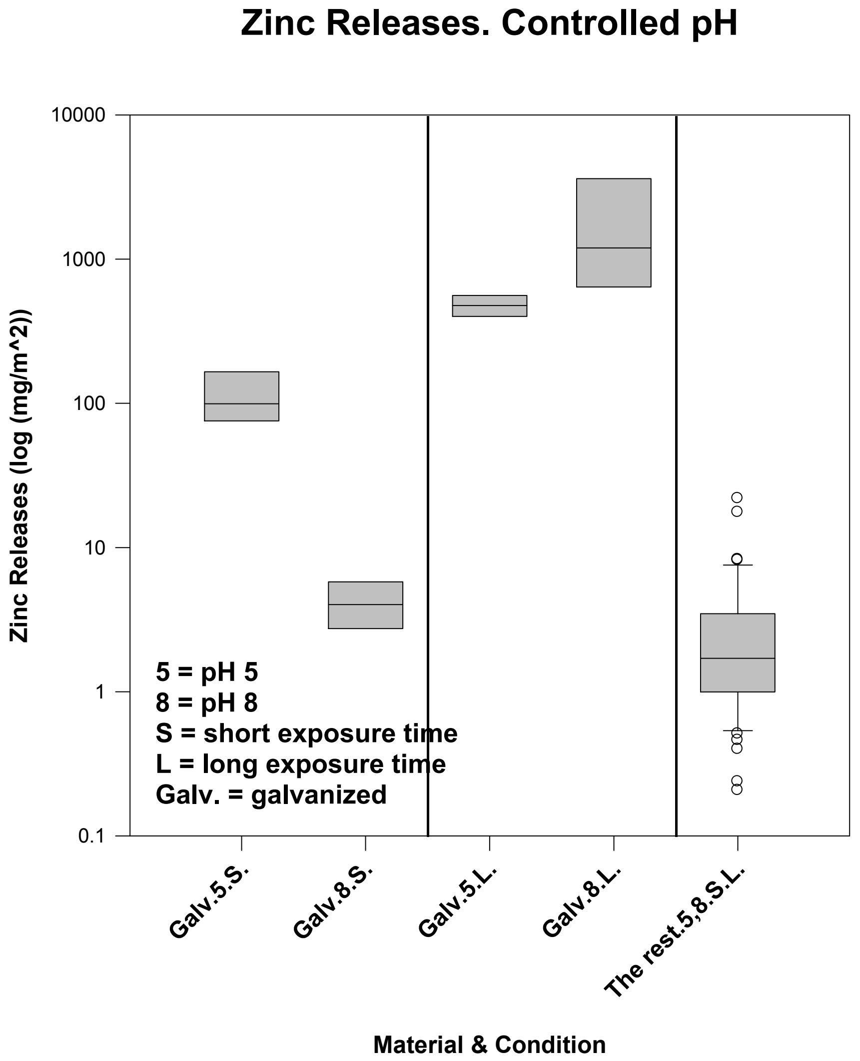


Figure 4-36. Group box plot for zinc release in mg/m^2 for materials immersed in pH 5 and pH 8 waters.

Zinc releases also increased with exposure time for galvanized steel pipes and gutters immersed in bay and river waters (Figure 4-37). In this example, the interaction of material and exposure time was significant. Galvanized materials exposed to natural pH waters during short periods resulted in elevated zinc releases. The combination of galvanized materials exposed to natural pH waters for long periods further increased zinc releases.

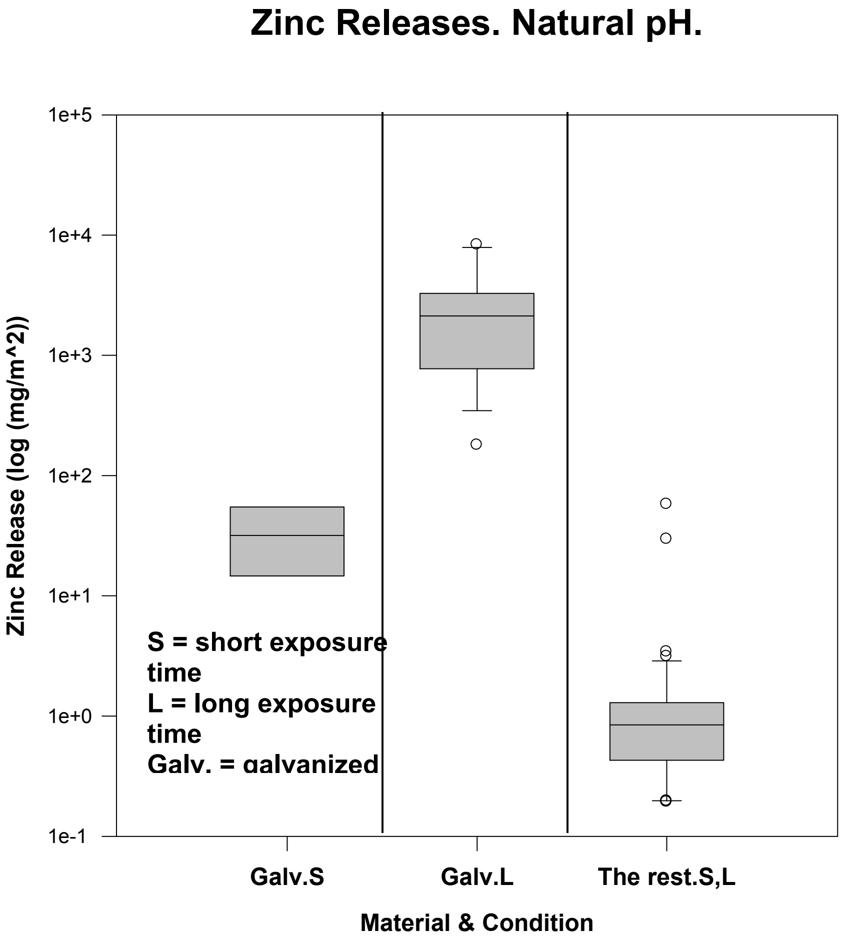


Figure 4-37. Group box plot for zinc release in mg/m^2 for materials immersed in bay and river waters.

Galvanized steel materials were the only source of lead releases. For lead releases under controlled pH conditions (Figure 4-38), there was a difference between the groups of galvanized materials during long exposure times and the group of galvanized materials during short exposure times and the rest of the materials during both short and long exposure times. Under controlled pH conditions, lead releases significantly increased for galvanized materials and long exposure periods.

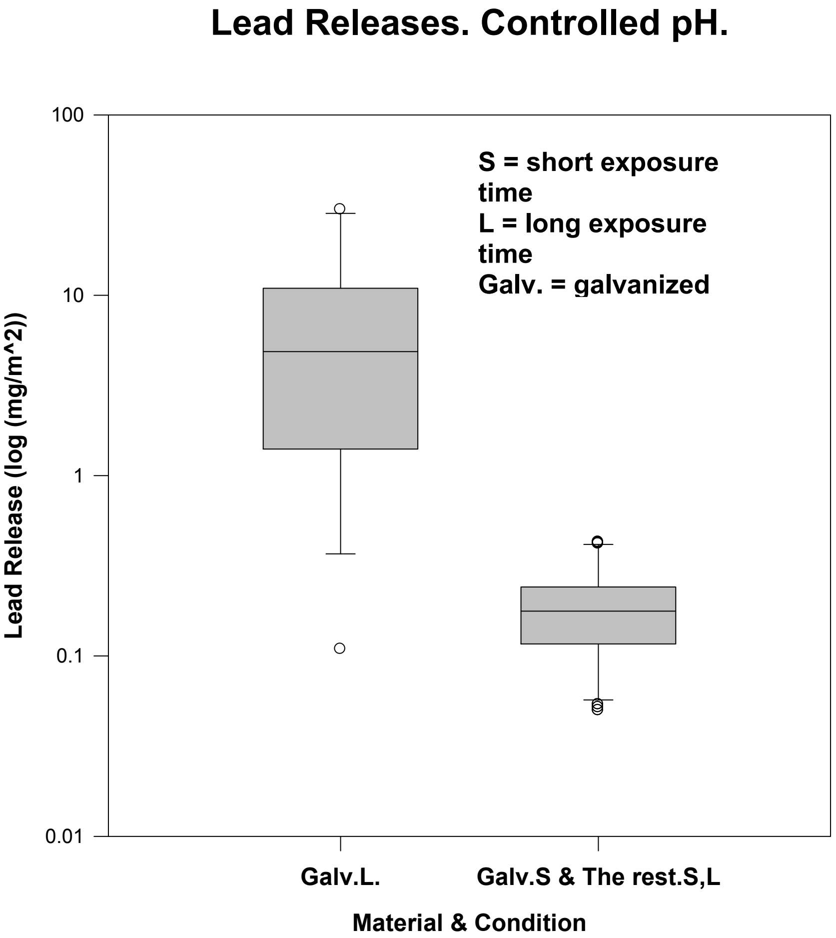


Figure 4-38. Group box plot for lead release in mg/m^2 for materials immersed in pH 5 and pH 8 waters.

Long exposure times increased lead releases in the samples with galvanized materials immersed into river water (Figure 4-39), however this tendency was not observed for galvanized steel materials immersed in bay water and can be explained by the metal releases being close to detection limit. Figure 4-40 shows that lead releases were combined in two groups.

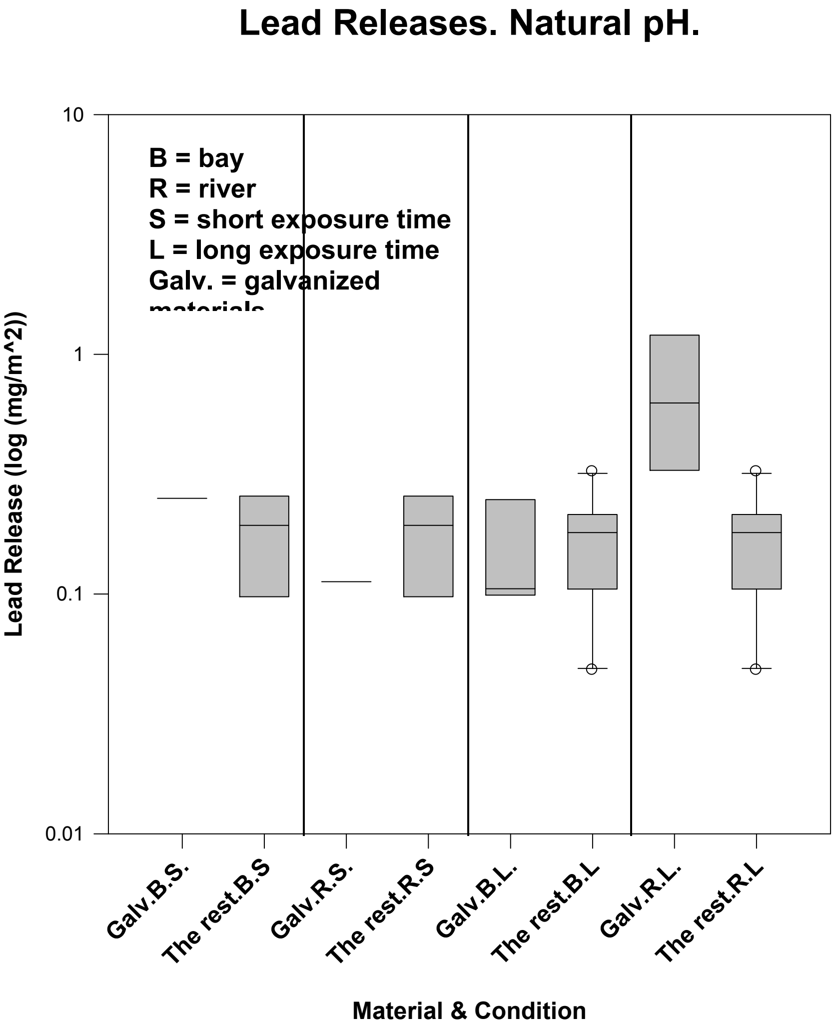


Figure 4-39. Group box plot for lead release in mg/m^2 for materials immersed in bay and river waters.

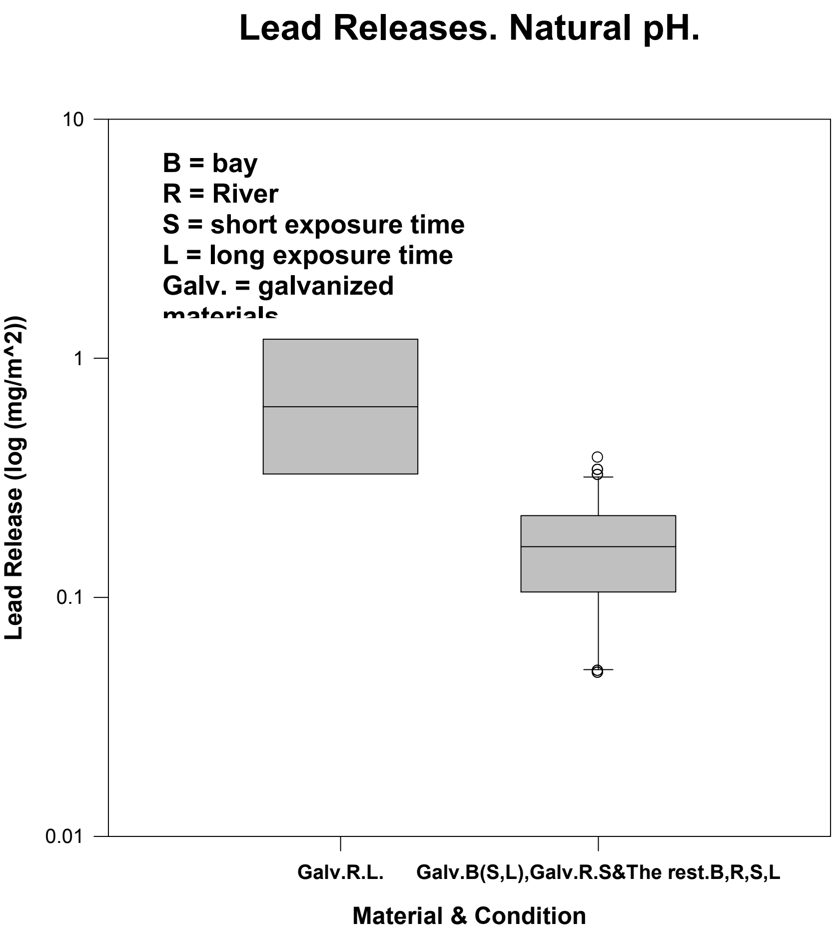
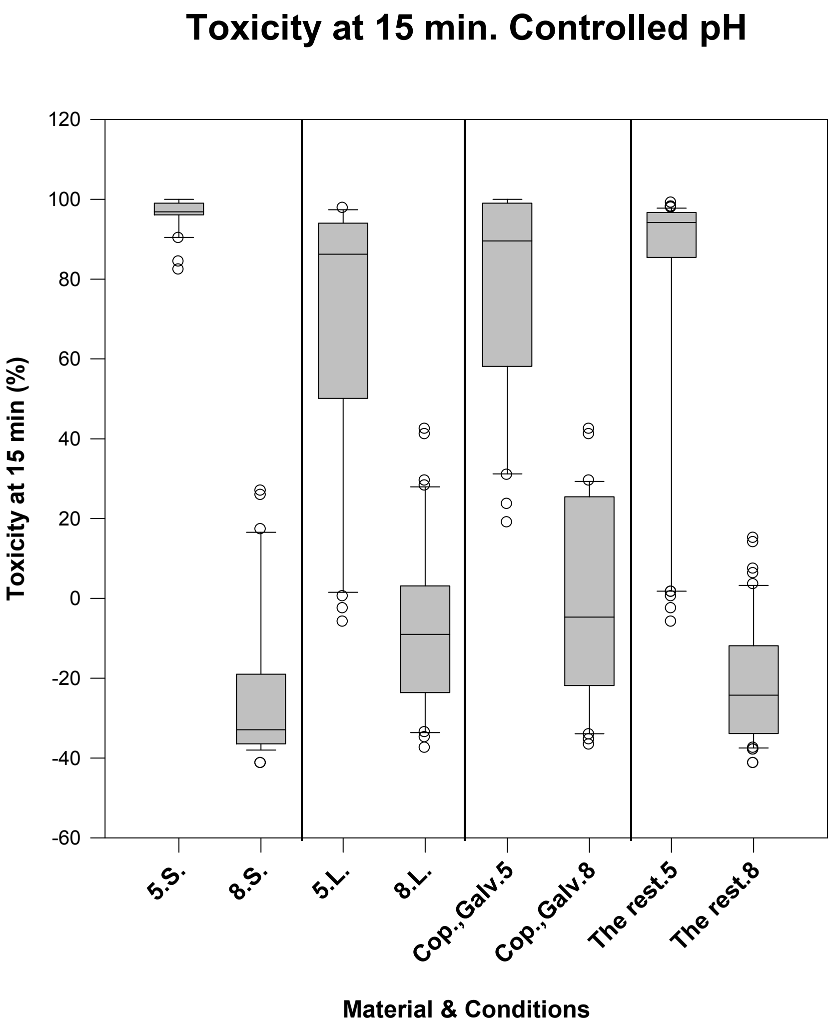


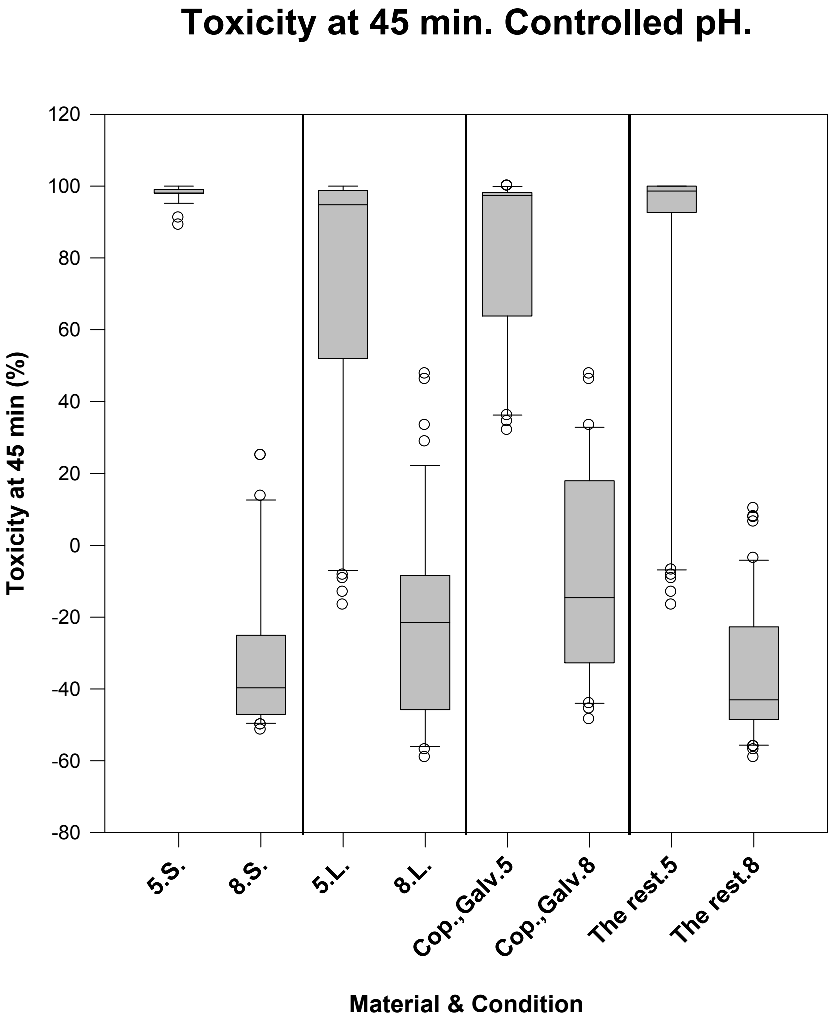
Figure 4-40. Group box plot for lead release in mg/m^2 for materials immersed in bay and river waters.

Figure 4-41 is a group box plot of toxicities at 15 min of bacteria exposure in the samples with galvanized steel, copper, and the rest of the materials under pH 5 and pH 8 conditions during both short and long exposure periods. Low pH conditions increased the toxicity effect for all pipe and gutter materials. The toxicity of the galvanized materials samples under low pH conditions decreased with material exposure time and was likely due to the increase in pH in the containers as the pH value approached the optimum pH range for the bacteria. The interactions of pH and material, and pH and exposure period, were significant. Low pH and short and long exposure periods resulted in toxicity values approaching 100%.The combination of concrete, plastic, and aluminum materials and controlled pH 8 water conditions produced conditions that were the least toxic for the Microtox test bacteria. Similar trends were observed for toxicity response at 45 min for the materials under controlled pH conditions (Figure 4-42).



Footnote: 5 = pH 5; 8 = pH 8; S = short exposure time; L = long exposure time; Cop. = copper material; Galv. = galvanized material.

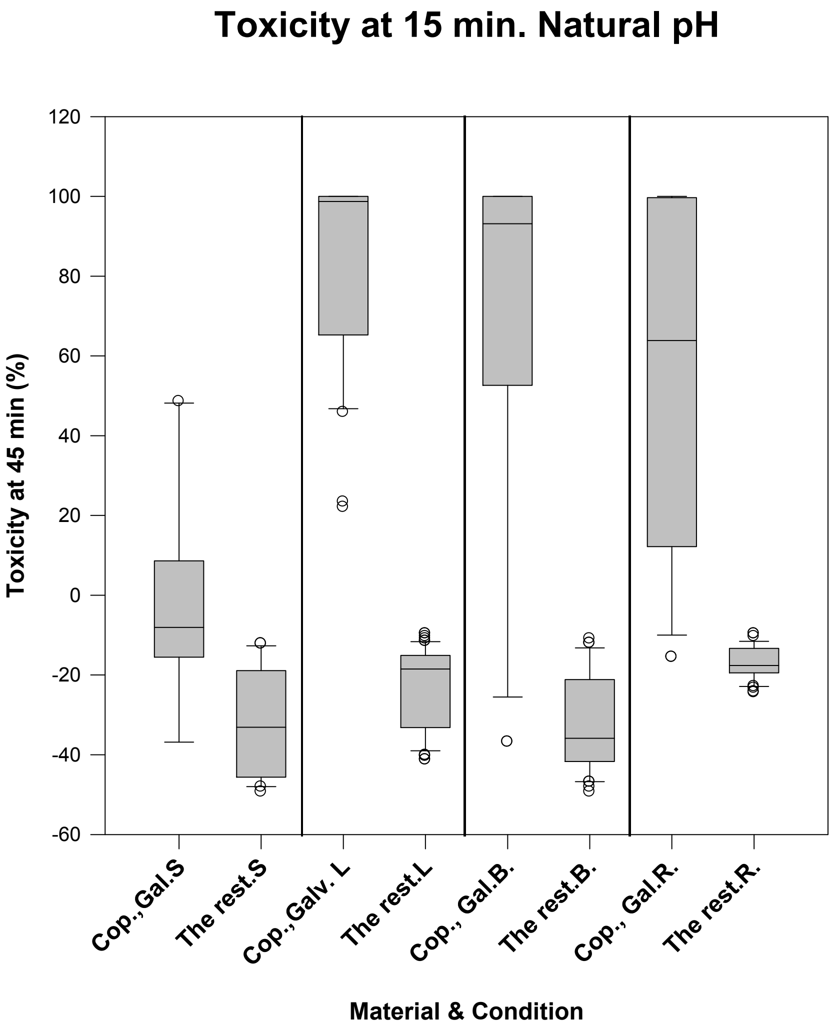
Figure 4-41. Group box plot for toxicity (%) at 15 min of bacteria exposure. Materials immersed in pH 5 and pH 8 waters.



Footnote: 5 = pH 5; 8 = pH 8; S = short exposure time; L = long exposure time; Cop. = copper material; Galv. = galvanized material.

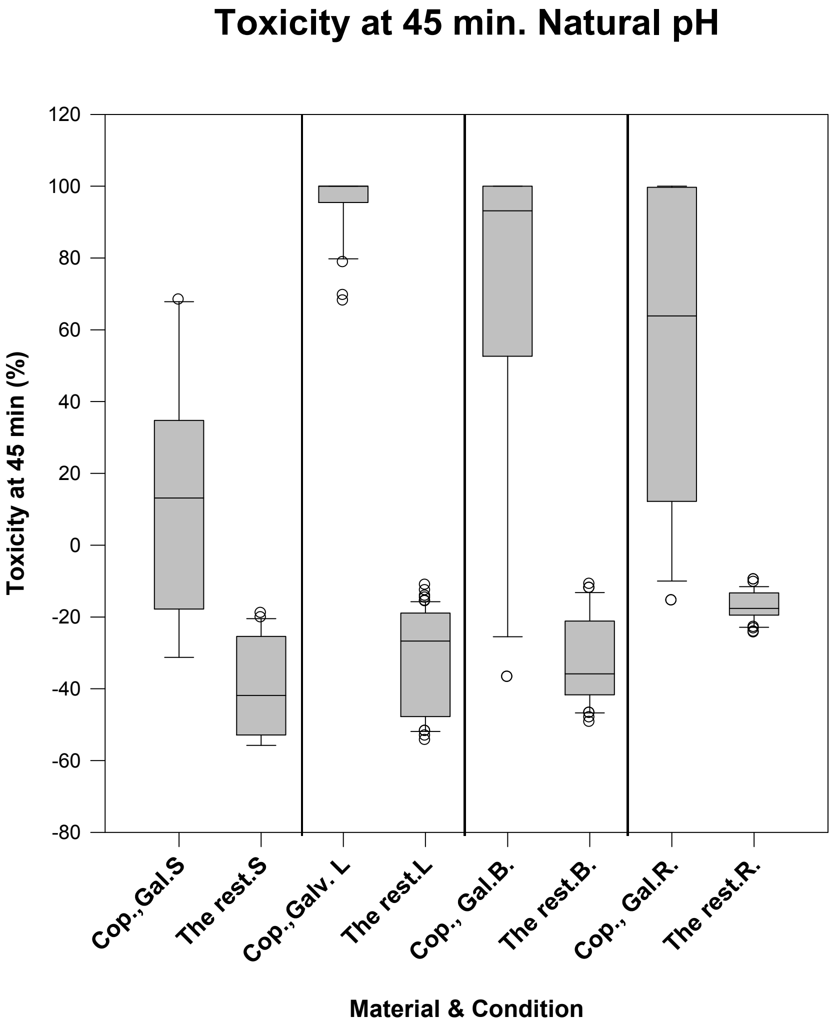
Figure 4-42. Group box plot for toxicity (%) at 45 min of bacteria exposure. Materials immersed in pH 5 and pH 8 waters.

Figure 4-43 is a group box plot of toxicities at 15 min of bacterial exposure in the samples with gutter and pipe materials immersed into bay and river water. There were no statistically significant differences between the toxicity effect in containers with copper and galvanized steel materials immersed in bay and river waters (P value of Mann-Whitney test = 0.38). The toxicity in the containers with galvanized steel and copper materials increased with time and can be explained by the increase in metal concentrations and the increase in pH values with time which exceeded the optimum pH range for the Microtox test bacteria. The interactions of conductivity and material, and material and exposure period were significant. The combination of copper and galvanized materials exposed during long exposure periods resulted in significant toxicity increases. Concrete, plastic, and aluminum materials and bay waters resulted in the least toxic conditions for all exposure periods. Similar trends were noted for toxicity at 45 min of Microtox test bacteria exposures (Figure 4-44).



Footnote: B = bay; R = River; S = short exposure time; L = long exposure time; Cop. = copper material; Galv. = galvanized material.

Figure 4-43. Group box plot for toxicity (%) at 15 min of bacteria exposure. Materials immersed in bay and river waters.



Footnote: B = bay; R = River; S = short exposure time; L = long exposure time; Cop. = copper material; Galv. = galvanized material.

Figure 4-44. Group box plot for toxicity (%) at 45 min of bacteria exposure. Materials immersed in bay and river waters.

Group box plots illustrated critical combinations of samples and conditions that resulted in elevated metal releases and resulting toxicities.

Predictive Models of Metal Releases from Different Pipe and Gutter Materials

The results from the full factorial experiments were used to build empirical models in order to determine which materials can safely be used for long term storage of water and for short term exposures such as for roof gutters and drainage pipes.

Tables 4-36 through 4-52 represent simple models that quantify the expected contaminant releases for different material selections for different application uses (drainage system vs., storage tanks) and water types (low and high pHs and saline and non-saline waters). It was found that copper materials are not advised for drainage system applications, especially when acidic rain conditions are expected, due to high copper releases and associated high toxicity. Galvanized materials should also be avoided as gutter and pipe materials as they release high zinc concentrations under all pH and exposure conditions. For stormwater drainage systems (gutters and pipes) exposed at pH 5 and pH 8 conditions, plastic and concrete materials can be used for most conditions. Galvanized steel and copper materials also should be avoided for storage tanks applications due to very high metal releases and toxicities. For stormwater storage applications, concrete, HDPE, and vinyl materials can be safely used due to their small, or non-detected, metal releases.

Table 4-36. Model based on 2^2 Factorial analyses. Concrete pipe. Controlled pH tests

Constituent	**Concrete Pipe. Controlled pH Conditions**	
Pb, mg/m^2	ND at pH 5 and 8	
Cu, mg/m^2	ND at pH 5 and 8	
Zn, mg/m^2	pH 5: Avg.= 1.68 (COV = 0.01)	pH 8: Avg.=3.07 (COV = 0.53)

Footnote: ND = non-detects

Table 4-37. Model based on 2^2 Factorial analyses. Concrete pipe. Natural pH tests

Constituent	**Concrete Pipe. Natural pH Conditions**
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	ND in bay and river waters

Table 4-38. Model based on 2^2 Factorial analyses. PVC pipe. Controlled pH tests

Constituent	**PVC Pipe. Controlled pH Conditions**
Pb, mg/m^2	ND at pH 5 and 8
Cu, mg/m^2	Cu (mg/m^2) = 0.0028*Time (hr); R^2 = 78.1%; p-value for regression = 0.00
Zn, mg/m^2	Zn (mg/m^2) = 0.0061*Time (hr); R^2 = 76.8%; p -value for regression = 0.00

Footnote: ND = non-detects.

Table 4-39. Model based on 2^2 Factorial analyses. PVC pipe. Natural pH tests

Constituent	**PVC Pipe. Natural pH Conditions**
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	Avg.= 0.17-0.9; Median = 0-0.02; Min = 0.41; Max =1.24; # of Pts above DL: 2

Footnote: ND = non-detects

Table 4-40. Model based on 2^2 Factorial analyses. HDPE pipe. Controlled pH tests

Constituent	**HDPE Pipe. Controlled pH Conditions**	
Pb, mg/m^2	ND at pH 5 and 8	
Cu, mg/m^2	Log Cu (mg/m^2) = -0.66+0.12*logTime(hr); R^2 = 48.1%; p=0.007	
Zn, mg/m^2	Zn (mg/m^2) @pH5 = 0.38 +0.00038*Time (hr); R^2 = 92.8%; p-value for regression = 0.001	Zn (mg/m^2) @pH8 = 0.0081*Time (hr); R^2 = 87.7%; p-value for regression = 0.00

Table 4-41. Model based on 2^2 Factorial analyses. HDPE pipe. Natural pH tests

Constituent	**HDPE Pipe. Natural pH Conditions**			
Pb, mg/m^2	ND in bay and river waters			
Cu, mg/m^2	ND in bay and river waters			
Zn, mg/m^2	S.B-: Avg.= 0.21 (COV = 0.02)	S.R.: Avg.= -0.21* (COV = -0.02; St. Dev. = 0.0034)	L.B-: Avg.= 0.2 (COV = 0.02)	L.R.: Avg.= 0.2 (COV = 0.02)

Footnote: S. = short exposure time; L. = long exposure time; B- = bay water; R. = river water; ND = non-detects.

* the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table 4-42. Model based on 2^2 Factorial analyses. Steel pipe. Controlled pH tests

Constituent	**Galvanized Steel Pipe. Controlled pH Conditions**
Pb, mg/m^2	Pb (mg/m^2) = 0.0092*Time (hr); R^2 = 59.2%; p-value for regression =0.00
Cu, mg/m^2	Avg.= 0.60 - 1.28; Median = 0- 0.02; Min= 0; Max= 4.785; # of Pts above DL: 3

Table 4-43. Model groups based on 2^2 Factorial analyses. Steel pipe. Natural pH tests

Constituent	**Galvanized Steel Pipe. Natural pH Conditions**			
Pb, mg/m^2	S.B-: Avg.= 0.4 (COV = 0.22)	S.R.: Avg.= 0.1 (COV = 0.02)	L.B-: Avg.= 0.1 (COV = 0.02)	L.R.: Avg.= 0.42 (COV = 0.79)
Cu, mg/m^2	ND in bay and river waters			
Zn, mg/m^2	Log Zn (mg/m^2) = 1.63 +0.51*logTime (hr); R^2 = 81.2%; p-value for regression = 0.00			

Footnote: S. = short exposure time; L. = long exposure time; B- = bay; R. = river; ND = non-detects.

Table 4-44. Model based on 2^2 Factorial analyses. Vinyl gutter. Controlled pH tests

Constituent	**Vinyl Gutter. Controlled pH Conditions**	
Pb, mg/m^2	ND at pH 5 and 8	
Cu, mg/m^2	Cu (mg/m^2) @pH5 = 1.067 +0.00082*Time (hr); R^2 = 88.9%; p-value for regression = 0.003	Cu (mg/m^2) @pH8 = 0.96 +0.00038*Time (hr); R^2 = 70.1%; p-value for regression = 0.023
Zn, mg/m^2	pH5: Avg.=1 (COV = 0.57)	pH8: Avg.= 2.7 (COV = 0.38)

Footnote: ND = non-detects.

Table 4-45. Model based on 2^2 Factorial analyses. Vinyl gutter. Natural pH tests

Constituent	**Vinyl Gutter. Natural pH Conditions**
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	Avg.= 0.43 – 1.9; Median = 0-0.02; Min= 0; Max= 3.419; # of Pts above DL: 2

Footnote: ND = non-detects.

Table 4-46. Model based on 2^2 Factorial analyses. Aluminum gutter. Controlled pH tests

Constituent	**Aluminum Gutter. Controlled pH Conditions**
Pb, mg/m^2	ND at pH 5 and 8
Cu, mg/m^2	Cu (mg/m^2) = 1.17 +0.0008*Time (hr); R^2 = 68.0%; p=0.001
Zn, mg/m^2	Avg.= 2.97 – 3.60; Median = -0.88 – 0.02; Min= 0; Max = 17.53; # of Pts above DL: 8

Footnote: ND = non-detects.

Table 4-47. Model based on 2^2 Factorial analyses. Aluminum gutter. Natural pH tests

Constituent	**Aluminum Gutter. Natural pH Conditions**
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	Avg.= 4.29 – 5.57; Median = 0 - 0.02; Min= -0.88*; Max= 57.55; # of Pts above DL: 3

Footnote: ND = non-detects.

* the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table 4-48. Model based on 2^2 Factorial analyses. Steel gutter. Controlled pH tests

Constituent	**Galvanized Steel Gutter. Controlled pH Conditions**			
Pb, mg/m^2	S. pH5: Avg.= 0.13 (COV = 0.03)	S. pH8: Avg.= 0.22 (COV = 0.7)	L. pH5: Avg.= 1.3 (COV = 0.26)	L. pH8: Avg.= 4.8 (COV = 0.05)
Cu, mg/m^2	S. pH5: Avg.= 0.52 (COV = 0.03)	S. pH8: Avg.= 0.52 (COV = 0.03)	L. pH5: Avg.= 0.47 (COV = 0.04)	L. pH8: Avg.= 1.3 (COV = 0.19)

Footnote: S. = short exposure time; L. = long exposure time; ND = non-detects.

Table 4-49. Model based on 2^2 Factorial analyses. Steel gutter. Natural pH tests

Constituent	**Galvanized Steel Gutter. Natural pH Conditions**	
Pb, mg/m^2	(Avg. = 0.41 – 0.49; Median = 0.23 - 0.24; Min= 0; Max= 2.54; # of Pts above DL: 7	
Cu, mg/m^2	ND in bay and river waters	
Zn, mg/m^2	Bay Water: Log Zn (mg/m^2) = 1.44 +0.44*logTime (hr); R^2 = 74.5%; p-value for regression = 0.017	River Water: Log Zn (mg/m^2) = 0.8 +0.85*logTime (hr); R^2 = 90.1%; p-value for regression = 0.002

Table 4-50. Model based on 2^2 Factorial analyses. Copper gutter. Controlled pH tests

Constituent	**Copper Gutter. Controlled pH Conditions**	
Pb, mg/m^2	ND at pH 5 and 8	
Cu, mg/m^2	pH5: Avg.= 250 (COV = 0.66)	pH 8: Avg.= 70.5 (COV = 0.96)
Zn, mg/m^2	pH5: Avg.= 3.2 (COV = 0.81)	pH 8: Avg.= 0.22 (COV = 1.55)

Footnote: ND = non-detects.

Table 4-51. Model based on 2^2 Factorial analyses. Copper gutter. Natural pH tests

Constituent	**Copper Gutter. Natural pH Conditions**	
Pb, mg/m^2	ND in bay and river waters	
Cu, mg/m^2	Bay Water: Log Cu (mg/m^2) = 1.25 +0.59*logTime (hr); R^2 = 91.4%; p-value for regression = 0.002	River Water: Log Cu (mg/m^2) = 0.72 +0.52*logTime (hr); R^2 = 98.0%; p-value for regression = 0.00
Zn, mg/m^2	Avg.= 3.46 - 3.79; Median = 1.27-1.62; Min= -0.67**; Max= 29.51; # of Pts above DL: 9	

Footnote: ND = non-detects.

** the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table 4-52. Model based on 2^2 Factorial analyses. Steel materials. Controlled pH tests

Constituent	**Galvanized Steel Materials (Pipe and Gutter). Controlled pH Conditions**	
Zn, mg/m^2	Log Zn (mg/m^2) @pH5 = 2.138 +0.1904*logTime (hr); R^2 = 68.2%; p-value for regression = 0.001	Log Zn (mg/m^2) @pH8 = 0.7236 +0.7643*logTime (hr); R^2 = 94.0%; p-value for regression = 0.000

The models showed that copper materials had elevated copper releases in pH 5 waters (250 mg/m^2) and in bay and river waters during short exposure times (180 and 840 mg/m^2 respectively). Long term exposure periods of copper materials under both high and low salinity conditions also resulted in high copper releases (1490 and 240 mg/m^2 respectively). Zinc concentrations released from galvanized steel materials were very high under both low and high pH conditions and during both short and long exposure times for controlled pH experiments (the average of 480 and 1860 mg/m^2 for galvanized steel materials at pH 5 and pH8 conditions respectively during long exposure time). For natural pH tests, long exposure periods resulted in high zinc concentrations released from galvanized pipes for waters with both high and low salinities (2,230 mg/m^2). Galvanized steel gutters immersed in bay and river waters had very high zinc releases during long term exposures (840 and 5,387 mg/m^2 for bay and river waters respectively). Elevated lead releases from galvanized steel materials were observed for pH 5 and 8 waters during long exposure periods, and for bay waters during short exposure periods and river waters during long exposure periods for steel pipe and for steel gutter during natural pH tests.

The residual analyses of the models indicated that the residuals were approximately normally distributed with constant variance and have zero mean (shown in Appendix A). The slight deviation from the residual requirements could be explained by small data samples available.

Scatter plots of observed vs. modeled values were used to evaluate performance of the models. Scatter plots for copper releases from copper materials and for lead releases from steel pipe under controlled pH conditions, for zinc releases from galvanized steel materials under natural pH conditions, and for metal releases from aluminum gutter under controlled and natural pH conditions showed that the models predicted values that are both higher and lower than observed for the large releases. The plots showed that models for galvanized steel gutter and PVC materials under controlled pH conditions represent metal releases reasonably well. Also, metal releases from HDPE materials under both controlled and natural pH conditions and copper releases from copper materials under natural pH conditions were modeled reasonably well.

Chemical Speciation Modeling of Heavy Metals (Medusa Water Chemistry Modeling Environment)

In stormwater, many heavy metals can sorb to inorganic and organic particulate matter that accumulate as bed sediments. Water chemistry, the suspended sediment and substrate sediment composition influence the behavior of heavy metals in natural waters. The sorption of heavy metals to particulates is affected by chemical identity, redox conditions, water pH, and complexation and precipitation chemistry (Clark and Pitt 2012). The forms of metal species present in the environment will affect toxicity and treatability of heavy metals. Comprehensive water chemistry modeling was conducted to predict the forms of the measured metals. Medusa software (Medusa, KTH, available at http://www.kemi.kth.se/medusa/) was used. Phase, Fraction, and Pourbaix diagrams show the predominant species of metals and their concentrations. For all chemical components in Medusa files, only the concentrations at and above the detection limit were used. The diagrams and summary tables were made for the zinc, copper, and lead contaminants. Phase, Fraction, and Pourbaix diagrams and the predominant species tables were constructed for time zero, one day of exposure (representing rainstorm event and applicable to gutter and pipe materials) and three months of exposure times (for tank materials) and are shown in Appendix D. The pH values of the samples are marked with a red vertical line on the Phase and Fraction diagrams. For the Pourbaix diagrams, the pH and E_{SHE} values of the samples are shown with a red cross.

For Medusa input files, an assumption was made that equilibrium was reached during the static experiments. For the buffered test, total hardness and calcium hardness, chloride, and sulfate were measured after 3 months of exposure and were assumed to be representative of conditions during the whole time of the experiment. In the buckets with copper gutter at pH 5 and with aluminum gutter at pH 8, Ca hardness was less than the detection limit of 0.02 mg/L as CaCO3. For the un-buffered test, total hardness and calcium hardness were measured at time zero and after 3 months of exposure, therefore the hardness values after one day of exposure and was assumed to be equal to those measured at time zero. Since only one form of phosphorus species can be included into a Medusa file, $H_2PO_4^-$ was used for solutions with pH 5 since at this pH, $H_2PO_4^-$ is the predominant phosphorus species, and HPO_4^{2-} for solutions with pH 8 since at pH 8, HPO_4^{2-} is a predominant phosphorus species (Golubzov 1966). Other major ions (fluoride, nitrate, total phosphorus, bromide Br^-, manganese, Boron, silicon, sodium, potassium, chloride, and sulfate) for un-buffered tests were measured in the source water were assumed to be the same for all the containers during the whole duration of the experiment.

The tables with predominant species (Appendix D) include the concentrations of the metal species in mol/L which were converted to mg/L of a compound, and then converted to the concentration of heavy metal of interest in mg/L. The cumulative percentage of a heavy metal was calculated in mg/L as a heavy metal constituent and was based on the sorted concentration of the corresponding compounds in mg/L. The predominant species tables show the predominant forms of heavy metal species that account for 99.9% of total metal concentration.

For example, Figure 4-45 is the complete phase diagram for steel pipe sample submerged into bay water after three months of exposure. In this water sample, the pH is 7 and zinc is predominantly in the free ion form (Zn^{2+}). Full phase diagrams that contain information for a wide range of pH values and contain information for large numbers of potential species in the diagram look overwhelming. Therefore, the phase diagrams for the study area were constructed that showed a smaller portion of full phase diagrams and included the pH values observed during these experiments and a few metal species of interest that had the greatest concentrations (shown in Appendix F). Figure 4-46 is the Fraction diagram of zinc shows the distribution of zinc species in this sample and also confirms that at pH 7 zinc is mainly in Zn^{2+} form. The Pourbaix diagram Figure 4-47 also shows that at pH 7 and Eh = -0.18V, free ion Zn^{2+} is the predominant species. This information is important in assessing the water toxicity which is greatly affected by the species of heavy metals in the water. Phase, Fraction, and Pourbaix diagrams for the other samples are shown in Appendix F.

$[SO_4^{2-}]_{TOT}$ = 7.02 mM
$[Cl^-]_{TOT}$ = 94.50 mM
$[Mg^{2+}]_{TOT}$ = 12.00 mM
$[Ca^{2+}]_{TOT}$ = 3.47 mM
$[Fe^{2+}]_{TOT}$ = 34.90 μM
$[Zn^{2+}]_{TOT}$ = 1.20 mM
E_H = -0.18 V

I= 0.087 M
Log P_{CO_2} = -3.50
$[K^+]_{TOT}$ = 1.72 mM
$[Na^+]_{TOT}$ = 76.60 mM
$[B(OH)_3]_{TOT}$ = 0.39 mM
$[Br^-]_{TOT}$ = 0.16 mM
$[NO_3^-]_{TOT}$ = 3.39 μM

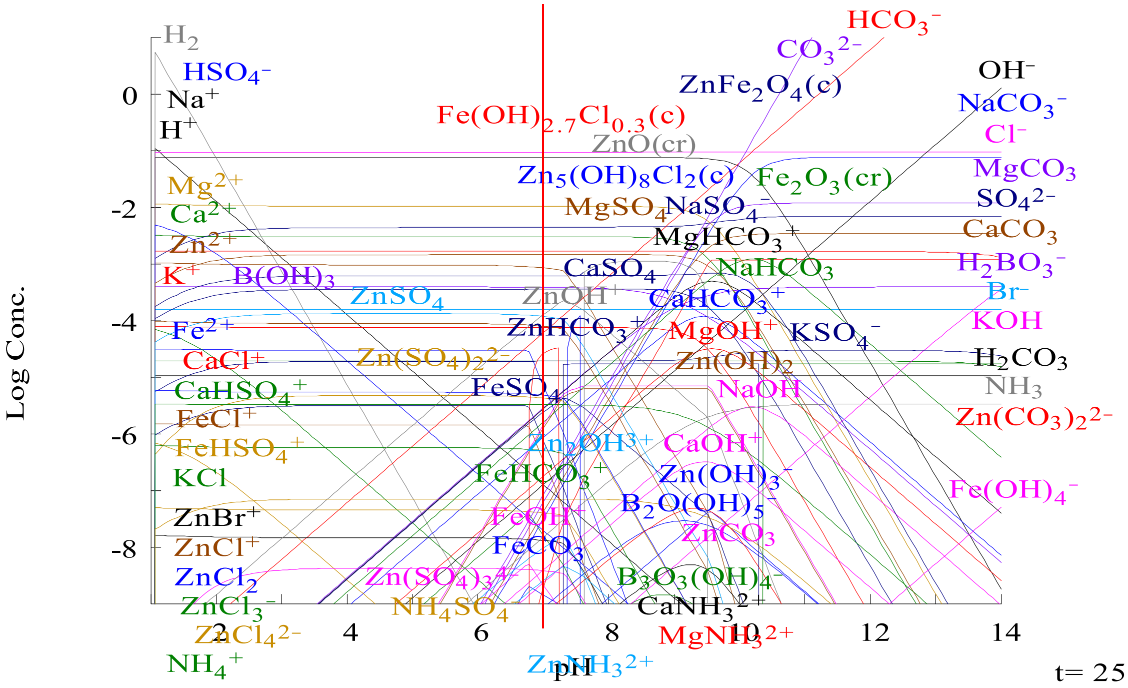


Figure 4-45. Phase diagram for steel pipe section immersed into bay water after three months of exposure.

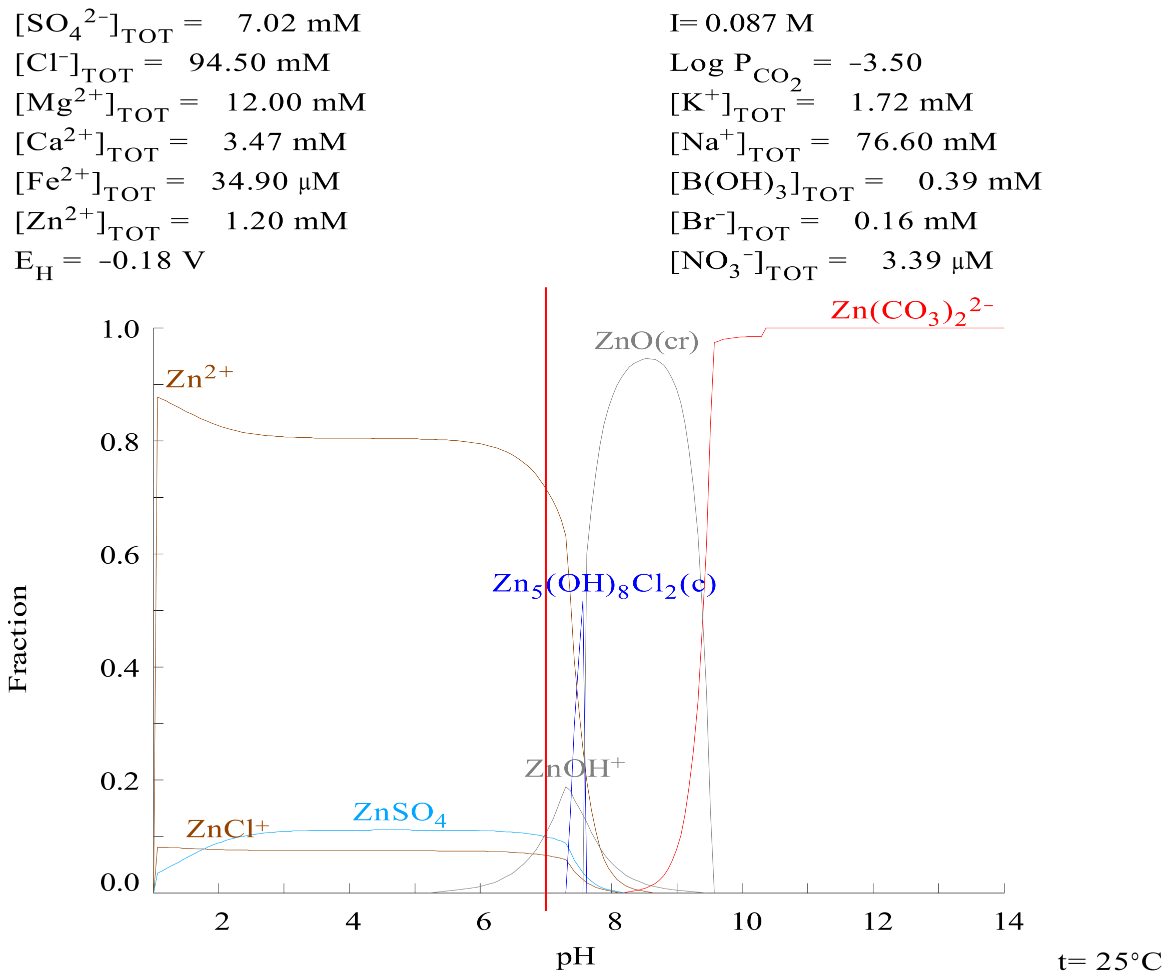


Figure 4-46. Fraction diagram of zinc for steel pipe section immersed into bay water after three months of exposure.

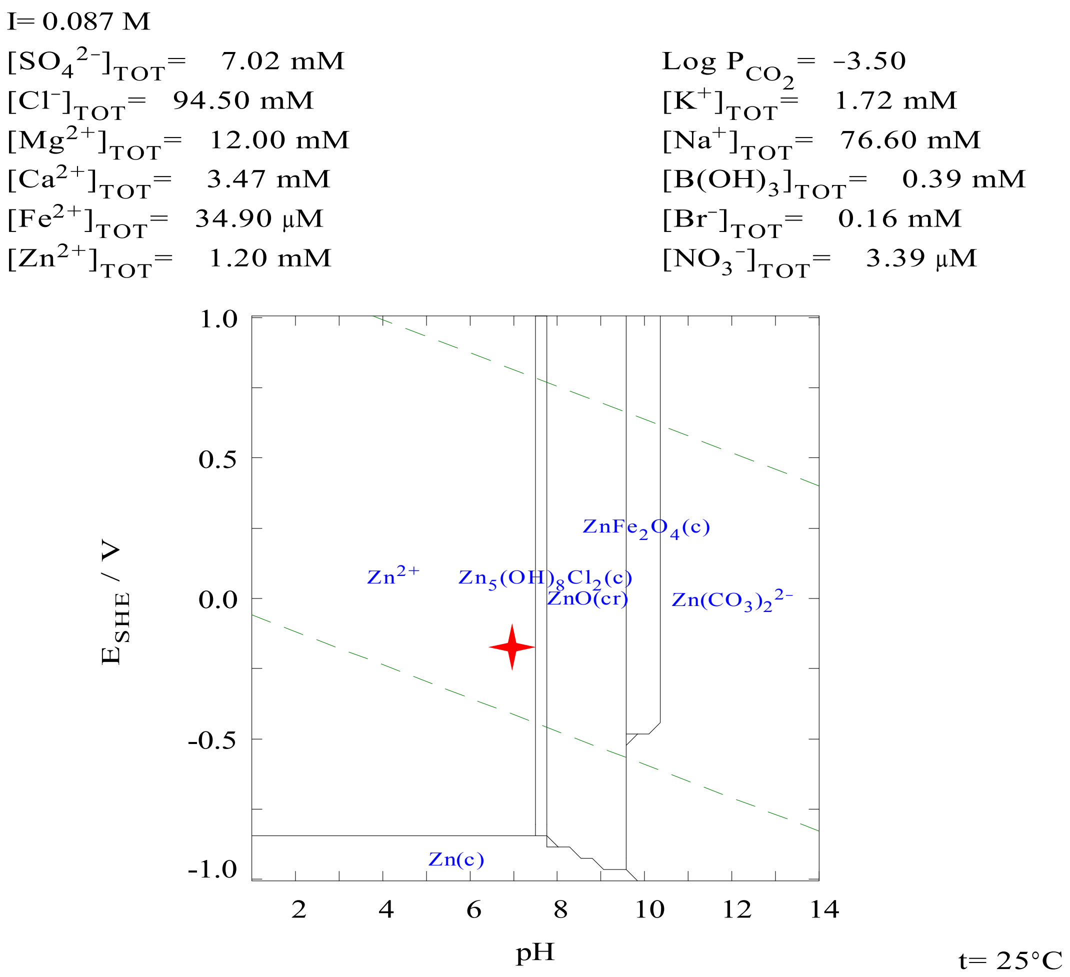


Figure 4-47. Pourbaix diagram of zinc for steel pipe section immersed into bay water after three months of exposure. Note: the symbol is located at the conditions measured during these tests

The modeled concentrations of zinc compounds in the containers were examined and compared with the theoretical maximum possible solubility of those compounds to determine if zinc would have continued to dissolve in the water if the experiment had continued for a longer time (Tables 4.5.2 through 4.5.13). The calculations were performed for the solubility of those zinc compounds which had the greatest concentrations in those containers. During these calculations, the assumption was made that those zinc compounds are dissolved in pure water (Kreshkov 1971).

The solubility of several compounds:

Solubility $CuH_2(PO_4)_2^{2-}$ = $(\text{Solubility Product}/(108\ \gamma_{Cu}{}^{2+}\ (\gamma_H{}^+)^2\ (\gamma_{PO4}{}^{2-})^2))^{1/5}$
Equation 4.5.1

Solubility $CuH_3(PO_4)_2^{-}$ = $(\text{Solubility Product}/(108\ \gamma_{Cu}{}^{2+}\ (\gamma_H{}^+)^3\ (\gamma_{PO4}{}^{2-})^2))^{1/6}$
Equation 4.5.2

Solubility $Zn_5(OH)_6(CO_3)_2$ = (Solubility Product/(0.48 $(\gamma_{Zn}{}^{2+})^5$ $(\gamma_{OH}{}^{-})^6$ $(\gamma_{CO3}{}^{2-})^2))^{1/13}$
Equation 4.5.3

The solubility of compounds with the KtAn formula (Kreshkov 1971):
Solubility $KtAn^-$ = (Solubility $Product_{KtAn}/(\gamma_{Kt}\ \gamma_{An}))^{1/2}$ Equation 4.5.4

Where,
Kt = cation
An = anion
γ = activity coefficient of cation or anion.

The solubility of compounds with the $KtAn_2$ formula (Kreshkov 1971):
Solubility $KtAn_2$ = (Solubility $Product_{KtAn2}/(4\ \gamma_{Kt}\ (\gamma_{An})^2))^{1/3}$ Equation 4.5.5

The solubility of compounds with the Kt_2An formula (Kreshkov 1971):
Solubility Kt_2An = (Solubility $Product_{Kt2An}/(4\ (\gamma_{Kt})^2\ \gamma_{An}))^{1/3}$ Equation 4.5.6

The solubility of compounds with the Kt_3An_2formula (Kreshkov 1971):
Solubility Kt_3An_2 = (Solubility $Product_{Kt3An2}/(108\ (\gamma_{Kt})^3\ (\gamma_{An})^2))^{1/5}$ Equation 4.5.7

The solubility formulas of other compounds can be found in Kreshkov 1971.

Table 4-53 shows solubility products for some reactions. The rest of the solubility products were taken from Medusa. Medusa is available from http://www.kemi.kth.se/medusa/.

Table 4-53. Solubility products

Equation	Solubility Product, K_{sp}	Reference
$Zn(OH)_2 \leftrightarrow Zn^{2+} + 2OH^-$	$1.4 *10^{-17}$	(Lurie 1989)
ZnCO3 $\leftrightarrow Zn^{2+} + CO_3^{2-}$	$1.45 *10^{-11}$	(Lurie 1989)

Medusa results showed that during the buffered pH tests, $Zn_3(PO_4)_2{:}4H_2O(c)$ precipitated in the containers with galvanized steel pipe immersed in pH 5 and pH 8 waters after three months of exposure (Table 4-54 and Table 4-56). The solubility product for $Zn_3(PO_4)_2{:}4H_2O(c)$ is very small ($K_{sp} = 9.1 *10^{-33}$ (Lurie 1989)) and $Zn_3(PO_4)_2{:}4H_2O(c)$ easily precipitates. In pure water, not taking into consideration hydrolysis of phosphoric acid and complex formation, the amount of $Zn_3(PO_4)_2{:}4H_2O$ that can dissolve in water is 5.6E-07mol/L (0.11 mg/L as Zn), however due to hydrolysis and complexation the amount of dissolved $Zn_3(PO_4)_2{:}4H_2O$ was greater that the theoretical value and reached 3.37E-05 mol/L (6.62 mg/L as Zn) in the container with galvanized steel pipe immersed into pH 5 water. Golubzov (1966) pointed out that hydrolysis increases the solubility of insoluble salts in the solution. The dissolved amount of Zn^{2+} concentrations also exceeded the theoretically calculated quantities due to the formation of complexes in the water.

Table 4-54. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Galv. steel pipe immersed in pH 5 water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
$Zn_3(PO_4)_2$:$4H_2O$(c)	3.37E-05	6.62	5.6E-07	0.11
Zn^{2+}	7.69E-05	5.03	2.32E-06	1.52E-01
$ZnOH^+$	7.80E-07	5.10E-02	9443	617653*10^3
Sum		11.7		6.2 E+08

In the containers with steel gutter immersed in pH 5 water and steel pipe immersed in bay water, there were zinc complexes and zinc compounds that have high solubility (such as ZnSO4 with solubility of 57.7 g/100g H2O at 25°C and ZnCl2 with solubility of 408 g/100g H2O at 25°C (Lide 2001)), precipitation of zinc compounds was not observed in Medusa results after three months of exposure. The comparison of concentrations of zinc compounds in the containers with the theoretical maximum possible solubility of those compounds showed that if the experiment had continued for a longer time, concentrations of zinc compounds would have continued to dissolve in the water (Table 4-55 and Table 4-56). Modeled Zn^{2+} concentrations dissolved in the water exceeded the theoretical maximum possible calculated concentrations and can be explained by complexation of Zn with other ions.

Table 4-55. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Galv. steel gutter immersed in pH 5 water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
Zn^{2+}	2.15E-04	14.06	2.32E-06	1.52E-01
$ZnOH^+$	8.92E-07	5.83E-02	9443	617653*10^3
$ZnSO_4$	1.41E-07	9.22E-03	1.5E-01	10045
Sum		14.1		6.2E+08

The amount of $Zn_3(PO_4)_2$:$4H_2O$(c) that had precipitated in the container with galvanized steel pipe immersed in pH 8 water and exceeded the theoretical maximum possible amount after three months of exposure and can be explained by hydrolysis and complexation (Table 4-56). Modeled $Zn(CO_3)_2^{2-}$ concentration in the water was smaller the calculated maximum possible concentration indicating that dissolution of that compound in the water is possible, but since protective film of $Zn_3(PO_4)_2$:$4H_2O$(c) precipitated, concentration of zinc compounds in the water will not increase. The calculated thickness of $Zn_3(PO_4)_2$:$4H_2O$(c) film was 0.5 μm, assuming that the density of that compound is equal to that of zinc.

Table 4-56. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Galv. steel pipe immersed in pH 8 water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
$Zn_3(PO_4)_2$:$4H_2O$(c)	4.19E-04	82.28	9.5E-07	0.19
$Zn(CO_3)_2^{2-}$	1.61E-05	1.06	1.3E-03	84
Sum		83.34		84.19

There was a precipitation of that $Zn_5(OH)_6(CO_3)_2$(c) and $ZnFe_2O_4$(c) compounds in the container with galvanized steel gutter immersed in pH 8 water after three months of exposure(Table 4-57), indicating that higher concentrations of zinc compounds in the water would not be expected beyond three months period. $Zn_5(CO_3)_2(OH)_6$ and $ZnCO_3$ are the most common compounds in the carbonate films. $Zn_5(CO_3)_2(OH)_6$ (hydrozincate) compound is often found in abundance in protective rust layers of zinc surfaces. This compound is comprised of a combination of $Zn(OH)_2$ and zinc carbonate: $3Zn(OH)_2+2Zn(CO_3)_2 \rightarrow Zn_5(CO_3)_2(OH)_6$(Zaki Ahmad, 2006).It was assumed that modeled $ZnFe_2O_4$(c) concentration in the water is equal to the maximum possible equilibrium concentration. Theoretically, zinc concentration that could dissolve into the water was 832,220 mg/L, but dissolved only 9.5 mg/L likely due to the protective film of $Zn_5(OH)_6(CO_3)_2$(c).

Table 4-57. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Galv. steel gutter immersed in pH 8 water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
$Zn_5(OH)_6(CO_3)_2$(c)	1.96E-05	6.42	12.72	832135
$Zn(CO_3)_2^{2-}$	4.21E-05	2.75	1.3E-03	84
$ZnFe_2O_4$(c)	2.81E-06	0.18	2.81E-06	0.18
$ZnCO_3$	1.78E-06	0.12	1.2E-05	0.8
Sum		9.5		832220

There was $CuFeO_2$(c) precipitation noted in the container with copper gutter immersed in pH 5 water (0.17 mg/L as Cu and constituted about 3 % from total copper concentration, not shown in the table), and therefore further increase in the concentration of copper compounds in the water would not have been expected. Copper concentration in the container with copper gutter immersed in pH 5 water was greater than the calculated maximum possible copper concentration (Table 4-58) due to hydrolysis of phosphate ions and complexation with phosphate ions.

Table 4-58. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Copper gutter immersed in pH 5 water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
$CuH_2PO_4^+$	2.16E-05	1.37	3.1E-11	2.0E-06
$CuHPO_4$	2.15E-05	1.37	1.4E-08	8.9E-04
$CuH_2(PO_4)_2^{2-}$	1.98E-05	1.26	4.9E-07	3.1E-02
Cu^{2+}	1.06E-05	0.67	4.19E-07	2.66E-02
Sum		4.67		0.058

For the container with the copper gutter sample immersed in pH 8 water, it was assumed that the calculated maximum possible concentrations of CuO(cr) and $CuFeO_2$(c) were equal to the modeled concentrations in the water. CuO is insoluble in water (Lide 2001). The total copper concentrations of modeled copper species exceed the calculated total maximum possible copper concentration likely due to the hydrolysis of phosphate ions and their complexation. Also, CuO(cr) and $CuFeO_2$(c) formed protective film on the metal surface (Table 4.5.7) and therefore the concentrations of copper compounds in the water would not likely to have increased after three months exposure period.

Table 4-59. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Copper gutter immersed in pH 8 water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
CuO(cr)	2.89E-05	1.84	2.89E-05	1.84
$CuFeO_2$(c)	2.69E-06	0.17	2.69E-06	0.17
$CuH_2(PO_4)_2^{2-}$	1.79E-06	0.11	7.6E-07	4.9E-02
Sum		2.12		2.06

No precipitates were formed in the container with the galvanized steel pipe immersed in bay water after three months exposure period (Table 4-60). Theoretical calculations of the maximum possible zinc concentrations showed that zinc concentration could further increase in the water after three months of exposure.

Table 4-60. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months of exposure. Galv. steel pipe immersed in bay water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
Zn^{2+}	8.64E-04	56.48	2.40E-06	0.16
$ZnOH^+$	1.22E-04	7.96	9857	$644707*10^3$
$ZnSO_4$	1.20E-04	7.86	0.17	10839
Sum		72.3		6.4E+08

For the container with galvanized steel gutter immersed in bay water, it was assumed that the calculated maximum possible concentration of ZnO and $ZnFe_2O_4$(c) was equal to the modeled concentrations in the water (Table 4-61). ZnO is insoluble in water (Lide 2001). Because protective film of ZnO and $ZnFe_2O_4$(c) were formed, further increase of zinc concentration in the water after three months exposure period would not have been likely.

Table 4-61. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Galv. steel gutter immersed in bay water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
ZnO(cr)	3.04E-04	19.92	3.04E-04	19.92
Zn^{2+}	9.93E-05	6.49	2.40E-06	0.16
$ZnOH^+$	9.67E-05	6.33	9859	$644859*10^3$
$ZnFe_2O_4$(c)	2.06E-05	1.35	2.06E-05	1.35
Sum		34.1		6.4E+08

For the container with galvanized steel pipe immersed in river water, it was assumed that the calculated maximum possible concentration of $ZnFe_2O_4$(c) was equal to the modeled concentration of $ZnFe_2O_4$(c) in the water. The theoretical maximum possible $Zn(CO3)_2^{2-}$ concentration in the water was 37 mg/L, however its solubility was restricted by the formation of protective films of $Zn_5(OH)_6(CO_3)_2$ (c) and $ZnFe_2O_4$(c) (Table 4-62). The calculations showed that theoretical maximum possible concentration of $Zn_5(OH)_6(CO_3)_2$ (c) in the protective film was 489,433 mg/L as Zn.

Table 4-62. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Galv. steel pipe immersed in river water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
$Zn_5(OH)_6(CO_3)_2$ (c)	2.0E-04	66.41	7.48	489,433
$ZnFe_2O_4$(c)	1.3E-05	0.83	1.3E-05	0.83
$Zn(CO3)_2^{2-}$	6.7E-06	0.44	5.6E-04	37
Sum		67.68		489,471

The theoretical maximum possible Zn^{2+} concentration in the container with galvanized steel gutter immersed in river water were lower than the modeled concentrations due to the complexation which increases the solubility of compounds, however the solubility of zinc in the water was restricted by the formation of protective film of $Zn_5(OH)_6(CO_3)_2$ (c) (Table 4-63).

Table 4-63. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Galv. steel gutter immersed in river water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
$Zn_5(OH)_6(CO_3)_2$(c)	3.60E-04	1.18E+02	7.74	506,515
Zn^{2+}	8.20E-04	53.6	1.89E-06	0.12
$ZnOH^+$	1.61E-04	10.5	7365	$481764*10^3$
Sum		182		4.8E+08

It was assumed that the theoretical maximum equilibrium concentrations of Cu(c) and $CuFeO_2$(c) were equal to the modeled concentrations in the water for containers with copper gutter immersed in bay and river waters (Tables 4-64 and 4-65). Because of the formation of the protective film of $CuFeO_2$(c), the copper concentration would not have been expected to increase in the water after three months of exposure period.

Table 4-64. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Copper gutter immersed in bay water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
Cu(c)	5.27E-04	33.51	5.27E-04	33.51
$CuFeO_2$(c)	3.76E-05	2.39	3.76E-05	2.39
Sum		35.9		35.9

Table 4-65. The modeled equilibrium concentrations and theoretical maximum possible solubility of zinc species after three months exposure. Copper gutter immersed in river water.

Compound	Concentration in the water as compound (mol/L)	Concentration in the water as Zn (mg/L)	Solubility of a compound (mol/L)	Amount of Zn from Solubility of a compound (mg/L)
Cu(c)	5.42E-05	3.44	5.42E-05	3.44
$CuFeO_2$(c)	3.19E-05	2.03	3.19E-05	2.03
Sum		5.47		5.47

Tables 4.5.14 through 4.5.21 show total measured metal concentrations and modeled metal species at time zero (base water alone), after one day of exposure and after three months of exposure. The total percent of compound valence doesn't always add up to 100 due to the rounding. At time zero (water without pipes and gutters), zinc and zinc compounds were predominantly in valence two state in the containers with pH 5 water, and were mostly in valence one state in the containers with pH 8 water. At time zero, copper and copper compounds in the buckets with pH 5 and 8 waters were mainly in valence two state.

After one day of exposure, zinc and zinc compounds were predominantly in valence two state in the samples with steel, copper, and plastic materials immersed in pH 5 water, and mainly in zero and one valence states in the samples with steel, copper, aluminum, and plastic materials immersed in pH 8 water. After one day of exposure, copper and copper compounds in containers with copper materials immersed into pH 5 water were approximately equally distributed between valence states of two, one, and zero, however for the buffered pH 8 waters, copper compounds in containers with copper gutters were predominantly in valence two state which can be explained by the formation of copper complexes with phosphate and other ions. Copper was generally in valence zero state in the samples with copper materials immersed in bay and river waters.

Sandberg, et al. (2006) examined corrosion-induced copper runoff from copper sheet, naturally patinated copper and pre-patinated copper in a chloride-rich marine environment during one year. The bioavailable concentration (the portion that is available for uptake by an organism) of released copper comprised a small fraction (14–54%) of the total copper concentration due to complexation towards organic matter in impinging seawater aerosols (Sandberg, et. al., 2006). The authors concluded that released copper is complexed with other ligands which reduce the bioavailability. Factors that influence the bioavailability of copper include alkalinity, hardness, pH and dissolved organic matter. Seawater contains organic matter that is primarily of biotic origin, and a significant portion of copper is most likely complexed with these ligands, which leads to reduction of the bioavailability (Sandberg, et. al., 2006). In this research, the results from Medusa modeling showed that copper released in the containers with copper gutter materials immersed into bay water was almost all in valence zero state. For containers with galvanized steel materials immersed into buffered pH 8 and bay waters, lead was mainly in valence zero after one day of exposure.

After three months of exposure, zinc and zinc compounds in the containers with galvanized steel, copper, aluminum, and plastic materials immersed into buffered pH 5 water were mainly in valence two state after; for galvanized steel, copper, aluminum, concrete, and plastic materials immersed into buffered pH 8, bay, and river waters, zinc was in one or zero valence states. For containers with copper materials immersed into pH 5 water, the valence state of copper and cooper compounds was approximately equally distributed between two, one, and zero and for copper materials submerged into buffered pH 8, bay, and river waters copper was predominantly in zero valence state after three months of exposure. Lead in containers with galvanized steel materials immersed into pH 5, pH 8, bay and river waters was mainly in zero valence state after three months of exposure. Tables 4-66 through 4-73 summarize these observations.

Table 4-66. Total measured zinc concentrations and modeled species at time zero (before material exposure, base water conditions).

Sample	**Total Measured Zn Concentration (mg/L as Zn)**	**Compound Valence, mg/L as Zn**			**Compound Valence, %**		
		Two or greater	**One**	**Zero**	**Two or greater**	**One**	**Zero**
pH 5 P. PVC	0.25	0.25 Zn^{2+} $Zn(SO_4)_2^{2-}$ Zn_2OH^{3+}	4.2E-04 $ZnOH^+$ $ZnHCO_3^+$	1.1E-03 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	99	0.17	0.45
pH 8 P. PVC	0.17	6.0E-02 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	8.2E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	2.8E-02 $ZnCO_3$ $Zn(OH)_2$ $Zn_3(PO_4)_2{:}4H_2O(c)$	35	48	17
pH 8 P. HDPE	0.03	1.0E-02 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn2OH^{3+}$	1.6E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	4.2E-03 $ZnCO_3$ $Zn(OH)_2$	34	52	14
pH 8 P. Steel	0.02	6.8E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.0E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	2.8E-03 $ZnCO_3$ $Zn(OH)_2$	34	52	14
pH 8 G. Steel	0.02	6.3E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ Zn_2OH^{3+}	1.0E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	3.3E-03 $ZnCO_3$ $Zn(OH)_2$	31	52	17
pH 8 G. Copper	0.02	6.3E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.0E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	3.3E-03 $ZnCO_3$ $Zn(OH)_2$	31	52	17
River P. HDPE	0.02	3.8E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.2E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	4.4E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	19	59	22
River G. Alum	0.02	3.8E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.2E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	4.4E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	19	59	22
River G. Steel	0.02	3.4E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.2E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	4.9E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	17	59	25
River G. Copper	0.02	3.8E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.2E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	4.3E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	19	59	22

Table 4-67. Total measured copper concentrations and modeled species after time zero.

Sample	Total Measured Cu Concentration (mg/L as Cu)	Compound Valence, mg/L as Cu			Compound Valence, %		
		Two or greater	One	Zero	Two or greater	One	Zero
pH 5 P. PVC	0.09	3.3E-02 $CuH_2(PO_4)_2^{2-}$ Cu^{2+} $CuH_3(PO_4)_2^{2-}$	3.3E-02 $CuH_2PO_4^+$ $CuH_3(PO_4)^{2-}$ Cu^+	2.4E-02 $CuHPO_4$ CuH_2PO_4 $Cu(H_2PO_4)_2$	37	36	27
pH 8 P. PVC	0.09	8.8E-02 $CuH_2(PO_4)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$ Cu^{2+}	1.2E-04 Cu^+ $Cu(OH)_2^-$ $CuOH^+$	1.8E-03 $CuHPO_4$ $CuCO_3$ $Cu(OH)_2$	98	0.14	2.0

Table 4-68. Total measured zinc concentrations and modeled species after one day.

Sample	Total Measured Zn Concentration (mg/L as Zn)	Compound Valence, mg/L as Zn			Compound Valence, %		
		Two or greater	One	Zero	Two or greater	One	Zero
pH 5 P. PVC	0.22	2.2E-01 Zn^{2+} $Zn(SO_4)_2^{2-}$	5.9E-04 $ZnOH^+$ $ZnHCO_3^+$	10E-04 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	99	0.27	0.45
pH 5 P. HDPE	0.02	2.0E-02 Zn^{2+} $Zn(SO_4)_2^{2-}$	2.6E-05 $ZnOH^+$ $ZnHCO_3^+$	1.0E-05 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.13	0.05
pH 5. P. Steel	10.20	10 Zn^{2+} $Zn(SO_4)_2^{2-}$	5.8E-02 $ZnOH^+$ $ZnHCO_3^+$	1.7E-02 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	99	0.57	0.17
pH 5. G. Steel	14.20	14 Zn^{2+} Zn_2OH^{3+}	4.4E-02 $ZnOH^+$ $ZnHCO_3^+$	9.3E-03 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.31	0.07
pH 5. G. Copper	0.04	4.0E-02 Zn^{2+} $Zn(SO_4)_2^{2-}$	7.0E-05 $ZnOH^+$ $ZnHCO_3^+$	3.5E-05 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.17	0.09
pH 8 P. PVC	0.16	0.054 Zn^{2+} $Zn(CO_3)_2^{2-}$	0.083 $ZnOH^+$ $ZnHCO_3^+$	0.023 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	34	52	14
pH 8 P. HDPE	0.02	2.0E-02 Zn^{2+} $Zn(SO_4)_2^{2-}$	3.4E-05 $ZnOH^+$ $ZnHCO_3^+$	1.6E-06 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.17	0.01

Table 4-68. Total measured zinc concentrations and modeled species after one day (continued)

pH 8. P. Steel	1.01	5.4E-02 Zn^{2+} $Zn(CO_3)_2^{2-}$	9.0E-02 $ZnOH^+$ $ZnHCO_3^+$	8.7E-01 $Zn_3(PO_4)_2{:}4H_2O(c)$ $ZnCO_3$ $Zn(OH)_2$	5.3	8.8	86
pH 8. G. Alum	0.02	6.3E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$	1.0E-02 $ZnOH^+$ $ZnHCO_3^+$	3.3E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	31	52	17
pH 8. G. Steel	2.09	5.8E-02 Zn^{2+} $Zn(CO_3)_2^{2-}$	9.9E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	1.9 $Zn_3(PO_4)_2{:}4H_2O(c)$ $ZnCO_3$ $Zn(OH)_2$	2.8	4.7	93
pH 8. G. Copper	0.02	5.9E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$	1.0E-02 $ZnOH^+$ $ZnHCO_3^+$	3.8E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	30	52	19
Bay P. Steel	8.4	0.2 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	0.42 $ZnOH^+$ $ZnCl^+$ $ZnHCO_3^+$	7.8 $Zn_5(OH)_6(CO_3)_2(c)$ $ZnFe_2O_4(c)$ $ZnCO_3$	2.3	5.0	93
Bay G. Steel	4.8	0.20 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	0.42 $ZnOH^+$ $ZnCl^+$ $ZnHCO_3^+$	4.2 $Zn_5(OH)_6(CO_3)_2(c)$ $ZnFe_2O_4(c)$ $ZnCO_3$	4.1	8.7	87
Bay G. Copper	0.05	1.4E-02 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	2.6E-02 $ZnOH^+$ $ZnCl^+$ $ZnHCO_3^+$	1.0E-02 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	28	52	20
River P. Steel	6.1	0.25 $Zn(CO_3)_2^{2-}$ Zn^{2+} $Zn(SO_4)_2^{2-}$	0.17 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	5.6 $Zn_5(OH)_6(CO_3)_2(c)$ $ZnCO_3$ $ZnFe_2O_4(c)$	4.2	2.8	93
River G. Steel	1.20	0.19 $Zn(CO_3)_2^{2-}$ Zn^{2+} $Zn(SO_4)_2^{2-}$	0.20 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	0.82 $Zn_5(OH)_6(CO_3)_2$ $ZnCO_3$ $ZnFe_2O_4(c)$	16	16	68
River G. Copper	0.02	3.2E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.1E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	5.4E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	16	57	27

Table 4-69. Total measured copper concentrations and modeled species after one day.

Sample	Total Measured Cu Concentration (mg/L as Cu)	Compound Valence, mg/L as Cu			Compound Valence, %		
		Two or greater	One	Zero	Two or greater	One	Zero
pH 5 P. PVC	0.08	3.7E-02 $CuH_2(PO_4)_2^{2-}$ Cu^{2+} $CuH_3(PO_4)_2^{2-}$	2.1E-02 $CuH_2PO_4^+$ $CuH_3(PO_4)_2^-$ Cu^+	2.3E-02 $CuHPO_4$ CuH_2PO_4 $Cu(H_2PO_4)_2$	46	26	28
pH 5 G. Copper	6.82	2.5 $CuH_2(PO_4)_2^{2-}$ Cu^{2+} $CuH_3(PO_4)_2^{2-}$	2.5 $CuH_2PO_4^+$ $CuH_3(PO_4)_2^-$ Cu^+	1.8 $CuHPO_4$ $Cu(H_2PO_4)_2$ CuH_2PO_4	37	36	27
pH 8 P. PVC	0.08	7.8E-02 $CuH_2(PO_4)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$ Cu^{2+}	1.2E-04 $Cu(OH)_2^-$ Cu^+ $CuOH^+$	1.7E-03 $CuHPO_4$ $CuCO_3$ $Cu(OH)_2$	98	0.15	2.1
pH 8 G. Copper	0.29	2.8E-01 $CuH_2(PO_4)_2^{2-}$ Cu^{2+} $CuH_3(PO_4)_2^{2-}$	2.5E-04 $Cu(OH)_2^-$ $CuOH^+$ Cu^+	6.5E-03 $CuHPO_4$ $CuCO_3$ $Cu(OH)_2$	98	8.8E-02	2.2
Bay G. Copper	2.11	1.1E-04 $CuCl_3^{2-}$ $Cu_2Cl_4^{2-}$ Cu^{2+}	3.2E-03 $CuCl_2^-$ Cu^+ $Cu(OH)_2^-$	2.1 Cu(c) $CuFeO_2$(c) $CuSO_4$	5.0E-03	0.15	100
River G. Copper	0.60	5.5E-09 $CuCl_3^{2-}$ Cu^{2+} $Cu(CO_3)_2^{2-}$	1.9E-05 $CuCl_2^-$ $Cu(OH)_2^-$ Cu^+	0.6 Cu(c) $CuFeO_2$(c) $CuCO_3$	9.2E-07	3.2E-03	100

Table 4-70. Total measured lead concentrations and modeled species after one day.

Sample	Total Measured Pb Concentration (mg/L as Pb)	Compound Valence, mg/L as Pb			Compound Valence, %		
		Two or greater	One	Zero	Two or greater	One	Zero
pH 8 G. Steel	0.008	5.9E-05 $Pb(CO_3)_2^{2-}$ Pb^{2+}	1.8E-05 $PbOH^+$ $PbHCO_3^+$	8.0E-03 $Pb_3(PO_4)_2$(c) $PbCO_3$ $PbHPO_4$	0.73	0.22	99
Bay P. Steel	0.012	1.1E-03 $Pb(CO_3)_2^{2-}$ Pb^{2+} $Pb(SO_4)_2^{2-}$	4.6E-04 $PbOH^+$ $PbCl^+$ $PbHCO_3^+$	1.1E-02 $PbCO_3$ $PbSO_4$ $Pb(OH)_2$	9.3	3.8	87
Bay G. Steel	0.005	4.7E-04 $Pb(CO_3)_2^{2-}$ Pb^{2+} $Pb(SO_4)_2^{2-}$	1.9E-04 $PbOH^+$ $PbCl^+$ $PbHCO_3^+$	4.4E-03 $PbCO_3$ $PbSO_4$ $Pb(OH)_2$	9.3	3.8	87

Table 4-71. Total measured zinc concentrations and modeled species after three months of exposure.

Sample	Total Measured Zn Concentration (mg/L as Zn)	Compound Valence, mg/L as Zn			Compound Valence, %		
		Two or greater	One	Zero	Two or greater	One	Zero
pH 5 P. Steel	11.70	5.03 Zn^{2+} $Zn(SO_4)_2^{2-}$ Zn_2OH^{3+}	0.05 $ZnOH^+$ $ZnHCO_3^+$	6.6 $Zn_3(PO_4)_2{:}4H_2O$(c) $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	43	0.44	57
pH 5 G. Steel	14.10	14.1 Zn^{2+} Zn_2OH^{3+} $Zn(SO_4)_2^{2-}$	0.06 $ZnOH^+$ $ZnHCO_3^+$	0.01 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.42	0.07
pH 8 P. Steel	84.30	1.1 $Zn(CO_3)_2^{2-}$ Zn^{2+} $Zn(OH)_4^{2-}$	0.17 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	83 $Zn_3(PO_4)_2{:}4H_2O$(c) $ZnFe_2O_4$(c) $ZnCO_3$ $Zn(OH)_2$	1.3	0.17	99
pH 8 G. Steel	9.69	2.8 $Zn(CO_3)_2^{2-}$ Zn^{2+} $Zn(OH)_4^{2-}$	10E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	6.8 $Zn_5(OH)_6(CO3)_2$ (c) $ZnFe_2O_4$(c) $ZnCO_3$ $Zn(OH)_2$	29	1.0	70
pH 5 PVC	0.44	0.44 Zn^{2+} $Zn(SO4)_2^{2-}$ $Zn2OH^{3+}$	1.2E-03 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3$-	2.0E-03 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	99	0.27	0.45
pH 8 PVC	0.68	8.4E-02 $Zn(CO_3)_2^{2-}$ Zn^{2+} $Zn(SO_4)_2^{2-}$	1.1E-01 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	0.49 $Zn_3(PO_4)_2{:}4H_2O$(c) $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	12	16	72
pH 5 HDPE	0.06	6.0E-02 Zn^{2+} $Zn(SO_4)_2^{2-}$	6.6E-05 $ZnOH^+$ $ZnHCO_3^+$	3.1E-05 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.11	5.2E-02
pH 8 HDPE	0.05	1.7E-02 $Zn(CO_3)_2^{2-}$ Zn^{2+} Zn_2OH^{3+}	2.1E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	1.2E-02 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	33	43	25
pH 5 Alum	0.02	2.0E-02 Zn^{2+} $Zn(SO_4)_2^{2-}$ Zn_2OH^{3+}	2.2E-05 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	1.2E-05 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.11	0.06
pH 8 Alum	0.21	4.9E-02 $Zn(CO_3)_2^{2-}$ Zn^{2+} Zn_2OH^{3+}	6.4E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	9.7E-02 $ZnFe_2O_4$(c) $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	23	30	46

Table 4-71. Total measured zinc concentrations and modeled species after three months of exposure (continued)

pH5 Copper	0.13	0.13 Zn^{2+} $Zn(SO_4)_2^{2-}$ Zn_2OH^{3+}	2.6E-04 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	1.1E-04 $ZnSO_4$ $ZnCO_3$ $Zn(OH)_2$	100	0.20	0.09
pH 8 Copper	0.02	1.2E-02 $Zn(CO_3)_2^{2-}$ Zn^{2+} $Zn(OH)_4^{2-}$	3.9E-03 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	4.1E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	60	19	20
pH 8 Vinyl	0.04	1.3E-02 $Zn(CO_3)_2^{2-}$ Zn^{2+} Zn_2OH^{3+}	1.7E-02 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	9.8E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	33	43	25
pH 8 Concrete	0.03	2.4E-02 $Zn(CO_3)_2^{2-}$ Zn^{2+} $Zn(OH)_4^{2-}$	2.1E-03 $ZnOH^+$ $ZnHCO_3^+$ $Zn(OH)_3^-$	3.5E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	81	7.1	12
Bay P. Steel	78.6	57 Zn^{2+} $Zn(SO_4)_2^{2-}$ $ZnCl_4^{2-}$ Zn_2OH^{3+}	13 $ZnOH^+$ $ZnCl^+$ $ZnHCO_3^+$ $ZnCl_3^-$	8.3 $ZnSO_4$ $ZnCl_2$ $ZnCO_3$ $Zn(OH)_2$	72	17	11
Bay G. Steel	36.7	6.6 Zn^{2+} $Zn(SO_4)_2^{2-}$ $Zn(CO_3)_2^{2-}$	7.1 $ZnOH^+$ $ZnCl^+$ $ZnHCO_3^+$	23 ZnO(cr) $ZnFe_2O_4$(c) $ZnSO_4$	18	19	63
River P. PVC	0.03	4.9E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.5E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	9.6E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	16	51	32
River P. HDPE	0.03	4.7E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.6E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	9.0E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	16	55	30
River P. Steel	68	0.44 $Zn(CO_3)_2^{2-}$ $Zn(SO4)_2^{2-}$ $Zn(OH)_4^{2-}$	0.13 $ZnOH^+$ Zn^{2+} $ZnHCO_3^+$	67 $Zn_5(OH)_6(CO_3)_2$ $ZnFe_2O_4$(c) $ZnCO_3$	0.65	0.18	99
River G. Alum	0.03	4.7E-03 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	1.6E-02 $ZnOH^+$ $ZnHCO_3^+$ $ZnCl^+$	9.0E-03 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	16	55	30
River G. Steel	190	54 Zn^{2+} $Zn(SO_4)_2^{2-}$ Zn_2OH^{3+}	11 $ZnOH^+$ $ZnCl^+$ $ZnHCO_3^+$	126 $Zn_5(OH)_6(CO_3)_2$(c) $ZnSO_4$ $ZnFe_2O_4$(c)	28	5.8	66
River G. Copper	0.5	7.9E-02 Zn^{2+} $Zn(CO_3)_2^{2-}$ $Zn(SO_4)_2^{2-}$	2.8E-01 $ZnOH^+$ ZnHCO3 $^+$ $ZnCl^+$	1.4E-01 $ZnCO_3$ $Zn(OH)_2$ $ZnSO_4$	16	56	29

Table 4-72.Total measured copper concentrations and modeled species after three months of exposure.

Sample	Total Measured Cu Concentration (mg/L as Cu)	Compound Valence, mg/L as Cu			Compound Valence		
		Two or greater	One	Zero	Two or greater	One	Zero
pH 8 P. Steel	0.03	7.3E-12 $Cu(CO_3)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$ Cu^{2+}	1.0E-11 $Cu(OH)_2^-$ Cu^+ $CuOH^+$ $CuHCO_3^+$ $Cu(OH)_3^-$	0.03 $CuFeO_2(c)$ $CuH_2(PO_4)_2^{2-}$ $CuCO_3$ $CuHPO_4$ $Cu(OH)_2$	2.4E-08	3.4E-08	100
pH 8 G. Steel	0.03	2.4E-10 $CuH_2(PO_4)_2^{2-}$ $Cu(CO_3)_2^{2-}$ Cu^{2+} $CuH_3(PO_4)_2^{2-}$	1.6E-11 $Cu(OH)_2^-$ $CuOH^+$ Cu^+ $Cu(OH)_3^-$ $CuHCO_3^+$	3.0E-02 $CuFeO_2(c)$ $CuCO_3$ $CuHPO_4$ $Cu(OH)_2$	8.1E-07	5.3E-08	100
pH 5 PVC	0.23	0.04 $CuH_2(PO_4)_2^{2-}$ Cu^{2+} $CuH_3(PO_4)_2^{2}$	0.02 $CuH_2PO_4^+$ $CuH_3(PO_4)_2^-$ Cu^+	0.16 $CuFeO_2(c)$ $CuHPO_4$ CuH_2PO_4 $Cu(H_2PO_4)_2$	19	11	71
pH 8 PVC	0.21	6.0E-02 $CuH_2(PO_4)_2^{2-}$ $Cu(CO_3)_2^{2-}$ $CuH_3(PO_4)_2^{2}$ Cu^{2+}	2.4E-04 $Cu(OH)_2^-$ Cu^+ $CuOH^+$	0.15 $CuFeO_2(c)$ $CuHPO_4$ $CuCO_3$ $Cu(OH)_2$	28	0.11	71
pH 5 HDPE	0.03	3.6E-06 Cu^{2+} $CuH_2(PO_4)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$	5.1E-06 $CuH_2PO_4^+$ $CuH_3(PO_4)_2^-$ Cu^+	0.03 $CuFeO_2(c)$ $CuHPO_4$ CuH_2PO_4	1.2E-02	1.7E-02	100
pH 8 HDPE	0.03	4.4E-10 $CuH_2(PO_4)_2^{2-}$ $Cu(CO_3)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$ Cu^{2+}	1.8E-12 $Cu(OH)_2^-$ Cu^+ $CuOH^+$	0.03 $CuFeO_2(c)$ $CuHPO_4$ $CuCO_3$ $Cu(OH)_2$	1.5E-06	5.9E-09	100
pH 5 Alum	0.03	2.9E-06 Cu^{2+} $CuH_2(PO_4)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$	4.8E-06 $CuH_2PO_4^+$ $CuH_3(PO_4)_2^-$ Cu^+ $Cu(H_2PO_4)_2^-$	0.03 $CuFeO_2(c)$ $CuHPO_4$ CuH_2PO_4 $Cu(H_2PO_4)_2$	1.6E-02	2.3E-02	100

Table 4-72.Total measured copper concentrations and modeled species after three months of exposure (continued)

pH 8 Alum	0.03	7.1E-10 $CuH_2(PO_4)_2^{2-}$ $Cu(CO_3)_2^{2-}$ Cu^{2+} $CuH_3(PO_4)_2^{2-}$	2.3E-12 $Cu(OH)_2^-$ $CuOH^+$ Cu^+	0.03 $CuFeO_2(c)$ $CuHPO_4$ $CuCO_3$ $Cu(OH)_2$	2.4E-06	7.7E-09	100
pH 5 Copper	5.10	1.9 $CuH_2(PO_4)_2^{2-}$ Cu^{2+} $CuH_3(PO_4)_2^{2-}$	1.6 $CuH_2PO_4^+$ $CuH_3(PO_4)_2^-$ Cu^+ $Cu(H_2PO_4)_2^-$ $CuOH^+$	1.6 $CuHPO_4$ $CuFeO_2(c)$ $Cu(H_2PO_4)_2$ CuH_2PO_4	38	32	30
pH 8 Copper	2.13	0.12 $CuH_2(PO_4)_2^{2-}$ $Cu(CO_3)_2^{2-}$ Cu^{2+}	4.3E-04 $Cu(OH)_2^-$ $CuOH^+$ $CuHCO_3^+$ $Cu+$ $Cu(OH)_3^-$ $CuH_3(PO_4)_2^-$ $CuH_2PO_4^+$	2.0 $CuO(cr)$ $CuFeO_2(c)$ $CuCO_3$ $CuHPO_4$ $Cu(OH)_2$	5.4	0.02	95
pH 5 Vinyl	0.03	4.7E-06 Cu^{2+} $CuH_2(PO_4)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$	6.8E-06 $CuH_2PO_4^+$ $CuH_3(PO_4)_2^-$ Cu^+	0.03 $CuFeO_2(c)$ $CuHPO_4$ CuH_2PO_4 $Cu(H_2PO_4)_2$	1.6E-02	2.3E-02	100
pH 8 Vinyl	0.02	4.8E-10 $CuH_2(PO_4)_2^{2-}$ $Cu(CO_3)_2^{2-}$ $CuH_3(PO_4)_2^{2-}$ Cu^{2+}	1.8E-12 $Cu(OH)_2^-$ Cu^+ $CuOH^+$	0.02 $CuFeO_2(c)$ $CuHPO_4$ $CuCO_3$	2.4E-06	8.9E-09	100
Bay G. Copper	35.90	9.4E-05 $CuCl_3^{2-}$ $Cu_2Cl_4^{2-}$ Cu^{2+}	2.8E-03 $CuCl_2^-$ Cu^+ $Cu(OH)_2^-$	36 $Cu(c)$ $CuFeO_2(c)$ $CuCl$	2.6E-04	7.8E-03	100
River G. Copper	5.47	4.4E-08 $CuCl_3^{2-}$ Cu^{2+} $Cu(CO_3)_2^{2-}$	1.4E-04 $Cu(OH)_2^-$ $CuCl_2^-$ Cu^+	5.5 $Cu(c)$ $CuFeO_2(c)$ $CuCO_3$	8.0E-07	2.5E-03	100

Table 4-73. Total measured lead concentrations and modeled species after three months of exposure.

Sample	**Total Measured Pb Concentration (mg/L as Pb)**	**Compound Valence, mg/L as Pb**			**Compound Valence**		
		Two or greater	**One**	**Zero**	**Two or greater**	**One**	**Zero**
pH 5 P. Steel	0.247	9.3E-04 Pb^{2+} $Pb(SO_4)_2^{2-}$ Pb_2OH^{3+}	7.5E-04 $PbH_2PO_4^+$ $PbOH^+$ $PbHCO_3^+$	0.24 $PbHPO_4$(c) $PbHPO_4$ $PbSO_4$	0.38	0.30	99
pH 5 G. Steel	0.037	2.2E-03 Pb^{2+} $Pb(SO_4)_2^{2-}$ Pb_2OH^{3+}	1.8E-03 $PbH_2PO_4^+$ $PbOH^+$ $PbHCO_3^+$	3.3E-02 $PbHPO_4$(c) $PbHPO_4$ $PbSO_4$ $PbCO_3$	5.8	4.9	89
pH 8 P. Steel	0.628	2.7E-03 $Pb(CO_3)_2^{2-}$ Pb^{2+}	2.6E-05 $PbOH^+$ $PbHCO_3^+$ $Pb(OH)_3^-$ $PbH_2PO_4^+$	0.63 $Pb_3(PO_4)_2$(c) $PbCO_3$ $PbHPO_4$ $Pb(OH)_2$ $PbSO_4$	0.43	4.2E-03	100
pH 8 G. Steel	0.100	1.2E-02 $Pb(CO_3)_2^{2-}$ Pb^{2+} $Pb(OH)_4^{2-}$	3.0E-05 $PbOH^+$ $PbHCO_3^+$ $Pb(OH)_3^-$	8.8E-02 $Pb_3(PO_4)_2$(c) $PbCO_3$ $PbHPO_4$ $Pb(OH)_2$	12	3.0E-02	88
River G. Steel	0.058	3.4E-02 Pb^{2+} $Pb(SO_4)_2^{2-}$ $Pb(CO_3)_2^{2-}$	7.8E-03 $PbOH^+$ $PbCl^+$ $PbHCO_3^+$	1.7E-02 $PbSO_4$ $PbCO_3$ $PbCl_2$	58	13	29

Toxicity Effects of Metal Releases

This section describes the observed toxicity of water samples that had different pipe and gutter materials exposed under different water conditions. Toxicity analyses were performed on the samples collected during controlled pH tests and during natural pH experiments. The toxicity tests were conducted using a Microtox model 500Analyzer and Microtox Omni^{TM} software to investigate how water samples that were in contact with different gutter and pipe materials may affect a biological system of receiving waters and to what degree. Methods used were taken from Microtox Acute Toxicity basic test procedures by Microbics Corporation and Manual on Microtox Model 500 Analyzer. Toxicity Effect (%) at time t was calculated using the formula:

Toxicity Effect = (Control – Sample)/Control x 100% Equation 5.1
Where,
Control = average light level of the control samples at t
Sample = light level of sample at t

Initially, tests were performed to determine the salt concentrations required to adjust water samples to optimum salinity conditions for Vibrio Fischeri osmotic pressure. Also, preliminary tests were conducted to determine $IC_{50}$and IC_{20} concentrations for the reference toxicants of $ZnSO_4$ and phenol to be used as standards to confirm the instrument performance. Three replicates of standards were used. Each water sample was analyzed in duplicate.

Controlled pH conditions

Figures 4-48 through 4-51 are plots of toxicities of the samples with different drainage materials under controlled pH conditions after 15 minutes of bacteria exposure. Similar toxicity plots for 5, 25, and 45 minute exposure times are included in Appendix D (Figures E.1.1. through E.1.16). The toxicities of the water from the roof and pipe materials were much greater for lower pH conditions than for higher pH conditions. During the controlled pH 5 tests, the highest toxicities were found for copper, aluminum, and HDPE material exposures; the samples from concrete containers were the least toxic. High toxicity of copper, alumina, and HDPE samples are explained by low pH values that are outside of optimum range for the bacteria. Concrete pipes raised the pH values in the containers from 5 to above 6 and therefore reduced the sample toxicities. For the controlled pH 8 conditions, copper materials were found to be most toxic, followed by PVC materials. Concrete pipes and vinyl roofing materials were found to be least toxic.

The toxicity of copper gutters was greater during controlled pH 5 tests compared to controlled pH 8 experiments. Similar results were obtained by Ho et al (1999) who found that for the Microtox solid phasetest, as the pH decreased, the toxicity for Cu increased. The toxicity of galvanized steel pipes and gutters, which released the greatest concentrations of zinc and lead, was also higher at pH 5 conditions than at pH 8 conditions, however Ho et al (1999) observed the toxicity of Pb and Zn decreased as pH decreased. The increase in toxicity of galvanized materials at low pH values can be explained bythe test pH values beingbelow the optimum pH range for Vibrio Fischeri bacteria; minimal pH effect on Vibrio Fischeri bacteria is observed in the range from 6 to 8 (Microbics Corporation, 1995. ACUTE User's Manual. Microtox Acute Toxicity. Basic Test Procedures).

Under controlled pH 5 conditions, generally for all pipe and gutter materials, toxicity decreased with time. The toxicity of copper materials at pH 5 gradually decreased with time, however for galvanized steel materials at pH 5, the decrese of toxicity with time was more abrupt. The decrease of toxicity with time corresponds to the slow increase in pH of the buffered solutions from pH 5 to pH 6. There was a general tendency in the toxicity increase for copper and galvanized steel materials for samples buffered at pH 8 during the first series of tests**.** The toxicity increase can be explained by the slow increase in pH values of the containers from pH 8 to pH 9, with pH 9 being out of the natural habitat value. The toxicity values of less than zero may be explained by the presence organic matter that may provide a second food source for the bacteria (Burton and Pitt 2002).

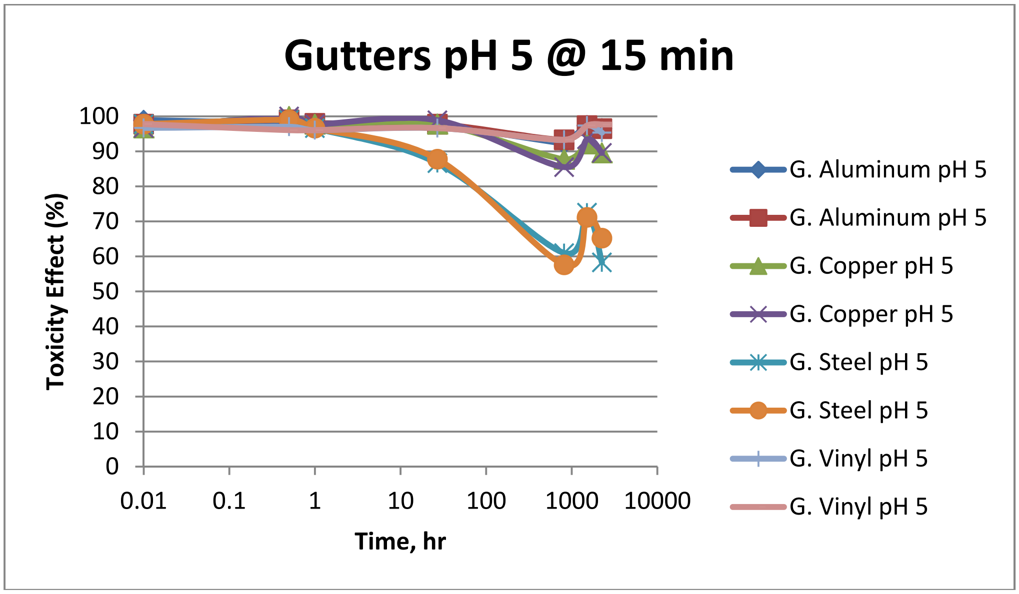


Figure 4-48. Toxicity effect in samples with gutter materials under pH 5 conditions at 15 min Microtox exposure time.

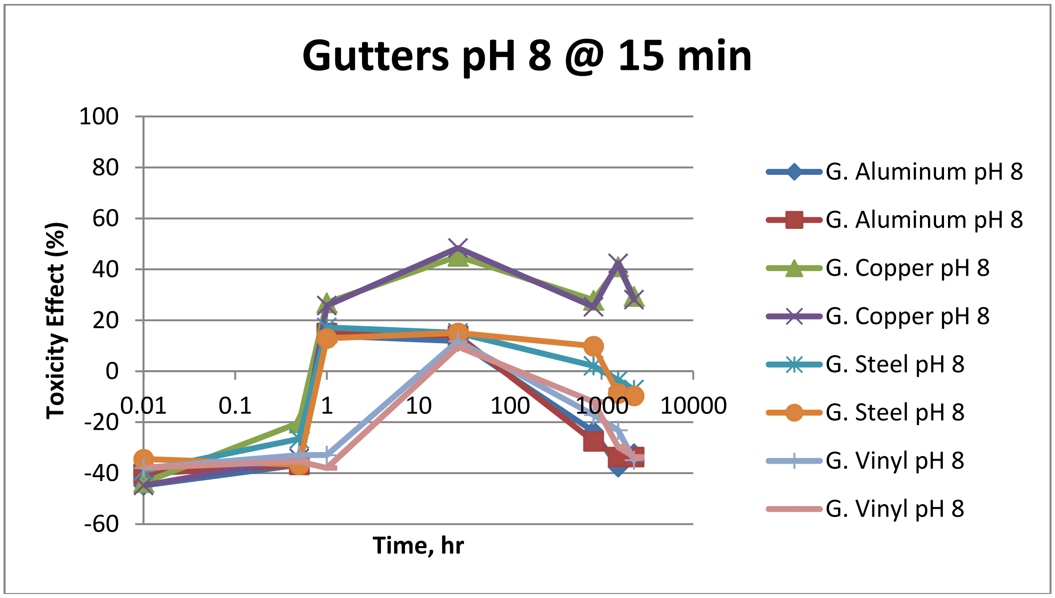


Figure 4-49. Toxicity effect in samples with gutter materials under pH 8 conditions at 15 min Microtox exposure time.

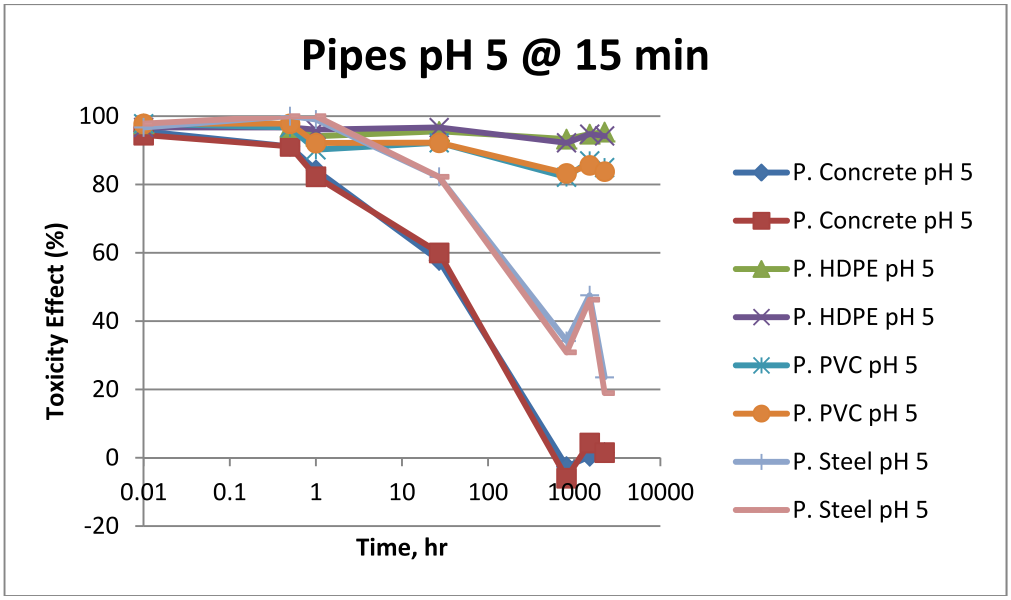


Figure 4-50. Toxicity effect in samples with pipe materials under pH 5 conditions at 15 min Microtox exposure time.

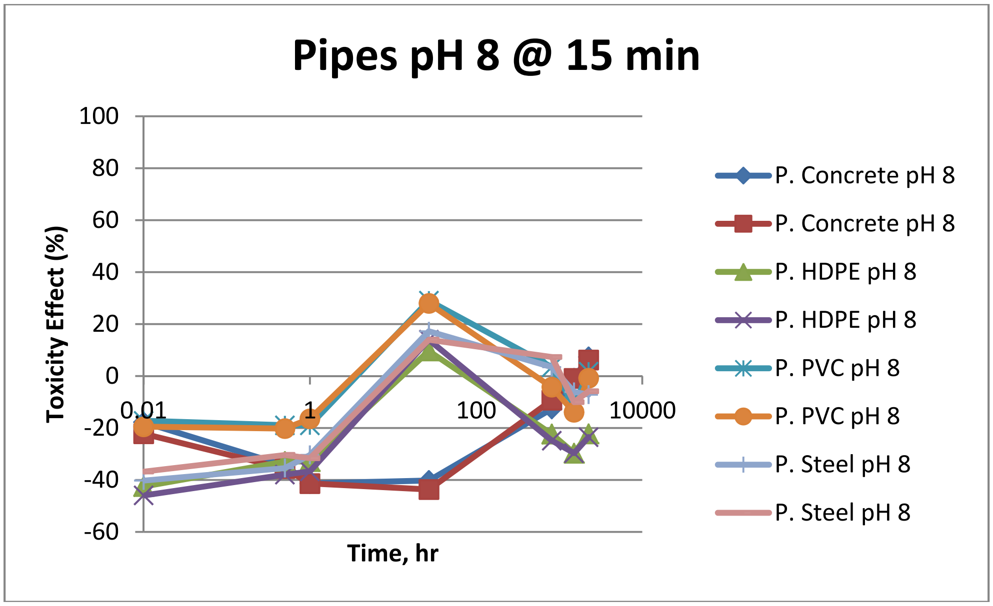


Figure 4-51. Toxicity effect in samples with pipe materials under pH 8 conditions at 15 min Microtox exposure time.

Metal Toxicity during Natural pH Tests

Figures 4-52 through 4-55 show toxicities of the samples with different drainage materials under natural pH conditions after 15 minutes of bacteria exposure to the samples. The toxicities after 5, 25, and 45 minutes of exposure are shown in Appendix D. Aluminum and vinyl gutters and concrete, PVC, and HDPE pipes were not a source of toxicity, as the heavy metal concentrations were very low, barely detected, or below the detection limits. In containers with bay and river waters, copper materials had the highest toxicity values, followed by galvanized steel materials. The toxicity of the samples with copper and galvanized steel materials increased with exposure time and was likely due to the increase in metal concentrations and increases in pH values that were outside of the optimum pH range for bacteria. For copper gutters and galvanized steel pipes, the increase in toxicity with exposure time was greater and faster for bay water than for river water (Figures 4-56 through 4-59) and can be explained by greater metal concentrations for bay waters than for river waters. For example, for galvanized steel pipe immersed in bay water, total zinc concentration after 3 months of exposure was 78 mg/L with 72% being of valence 2 state. However for galvanized steel pipe immersed in river water, total zinc concentration after 3 months of exposure was 67 mg/L with 99% of valence 0. For galvanized steel gutters, after about 2 months of exposure, the toxicity in river water samples were higher than in bay water samples and can be explained by 34% being valence of 1 and greater and the pH values outside of optimum pH range for toxicity.

For the copper and galvanized steel materials, the measured Microtox toxicity was greater when measured at 45 min compared to 15 min, as expected when heavy metals are the likely source of the toxicity. As an example, Figure 4-60 shows the Microtox toxicity values for the steel gutter sample immersed in bay water for different Microtox test periods. The longer sample exposure periods (27 hr, 34 days, and 64 days) all had increasing toxicity indications with longer Microtox exposure times. The 94 day sample reached maximum toxicity after 5 min of Microtox exposure period due to the very high zinc concentrations (37 mg/L). The short sample exposure time samples (0.01 and 1 hour) were never toxic, due to their much lower metal concentrations (< 0.02 and 0.48 mg/L for 0.01 and 1 hour respectively).

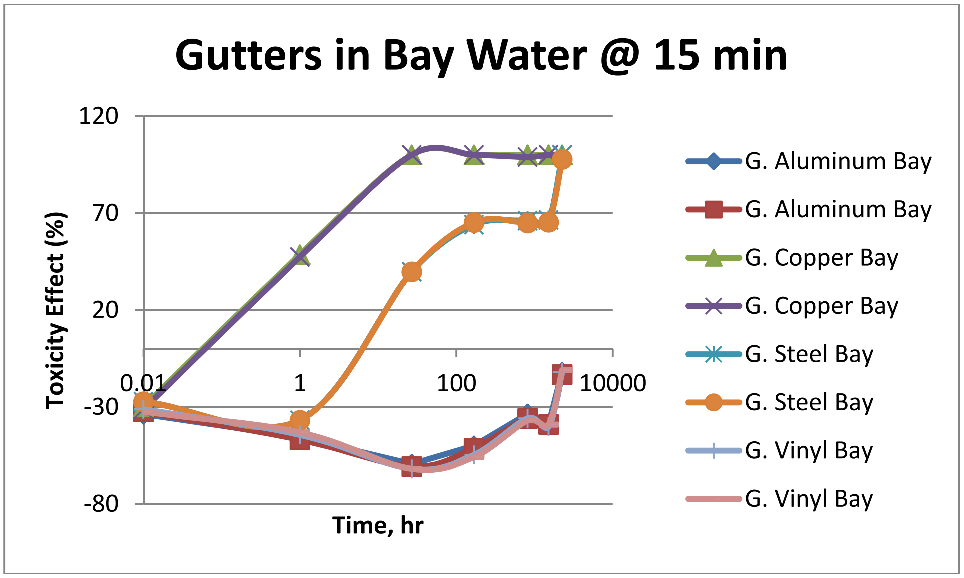


Figure 4-52. Toxicity effect in samples with gutter materials. Bay water at 15 min Microtox exposure time.

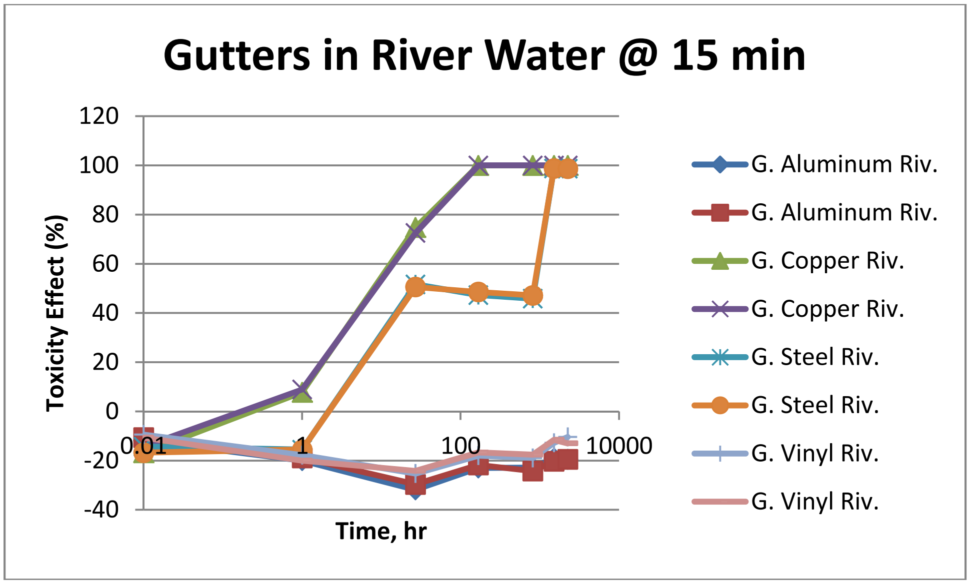


Figure 4-53. Toxicity effect in samples with gutter materials. River water at 15 min Microtox exposure time.

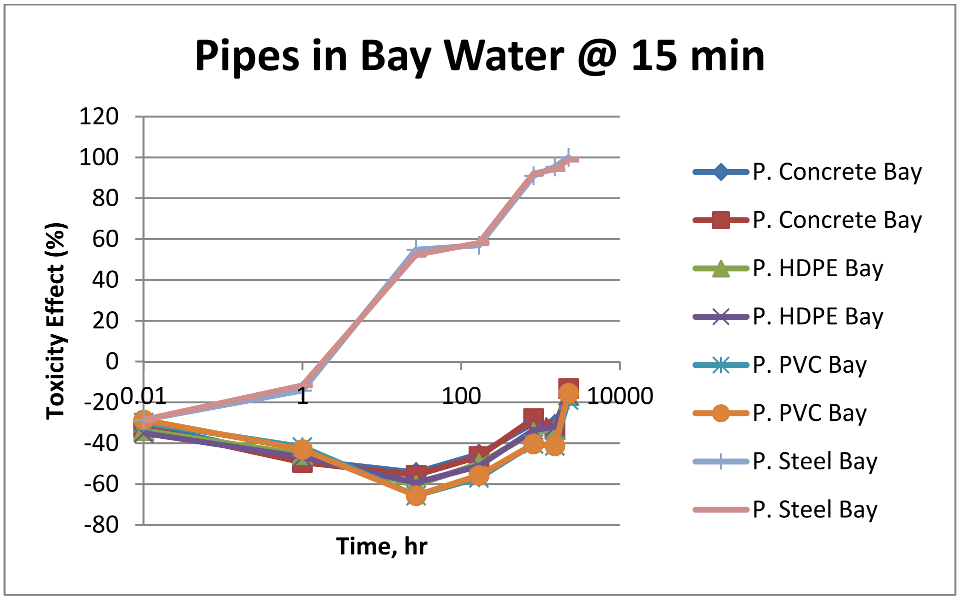


Figure 4-54. Toxicity effect in samples with pipe materials. Bay water at 15 min Microtox exposure time.

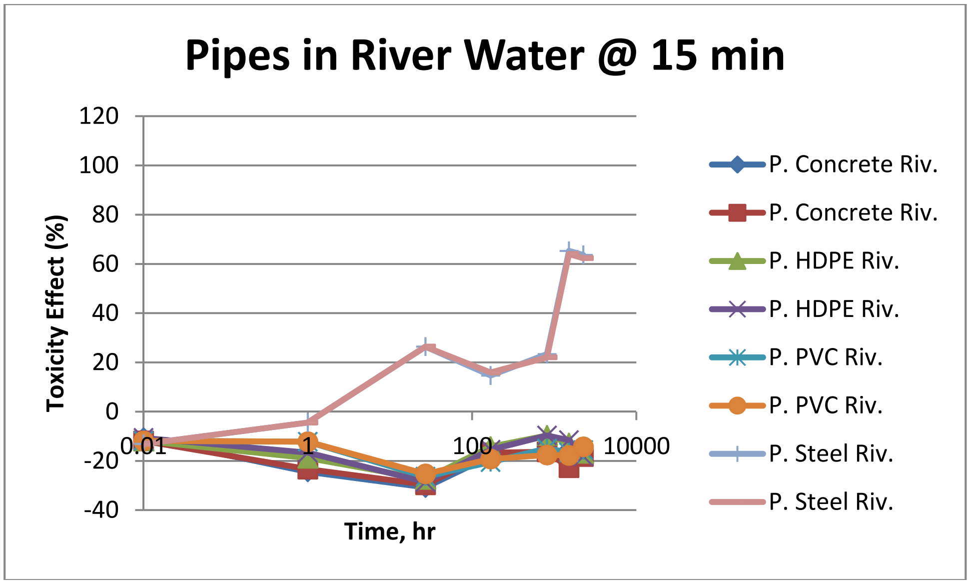


Figure 4-55. Toxicity effect in samples with pipe materials. River water at 15 min Microtox exposure time.

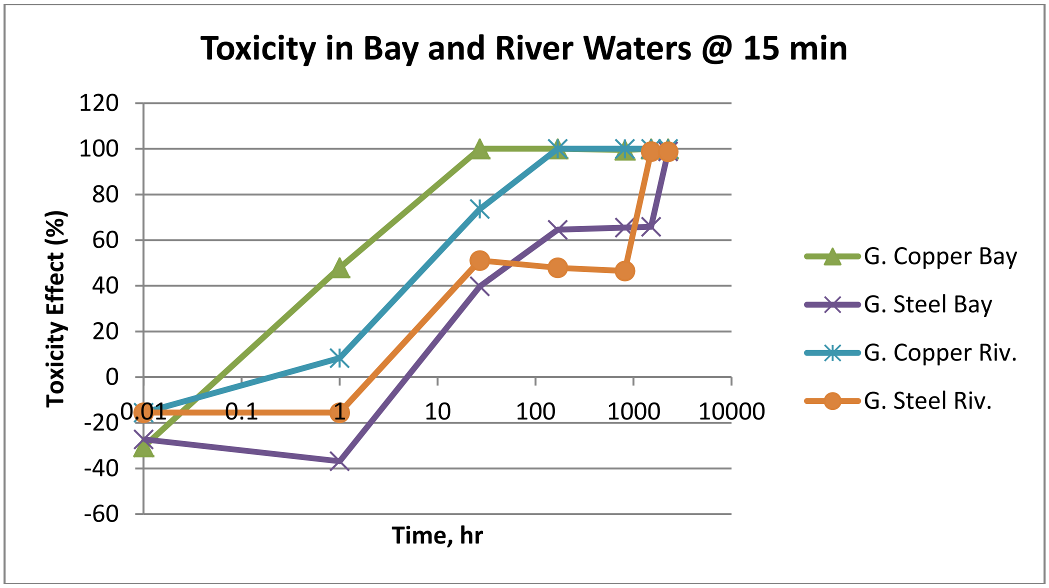


Figure 4-56. Toxicity effect in samples with copper and galvanized steel gutters immersed in bay and river water at 15 min Microtox exposure time (Each point is an average of 2 replicates).

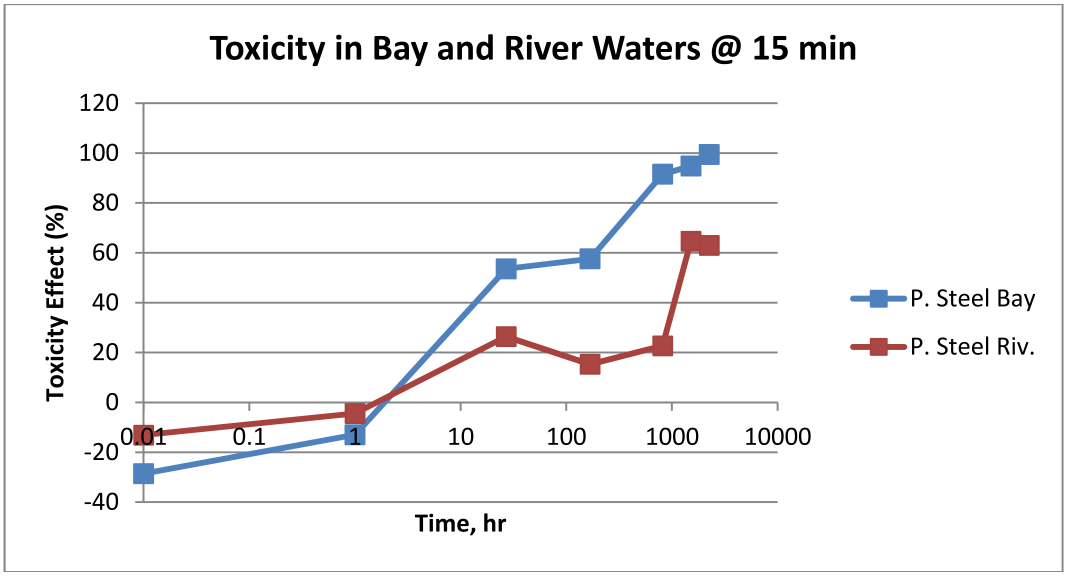


Figure 4-57. Toxicity effect in samples with galvanized steel pipes immersed in bay and river water at 15 min Microtox exposure time (Each point is an average of 2 replicates).

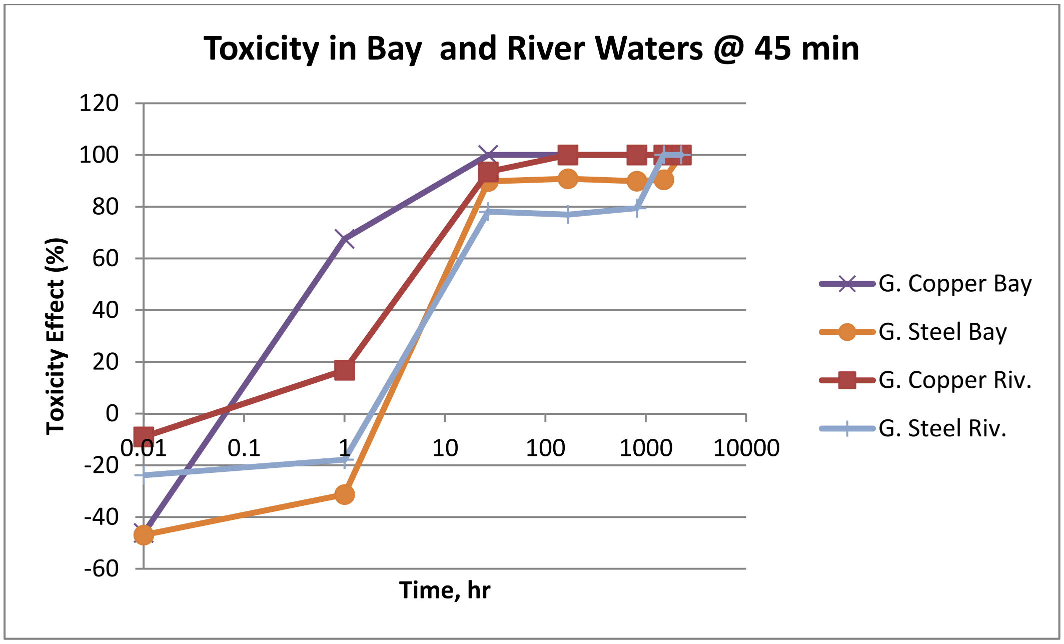


Figure 4-58. Toxicity effect in samples with copper and galvanized steel gutters immersed in bay and river water at 45 min Microtox exposure time (Each point is an average of 2 replicates).

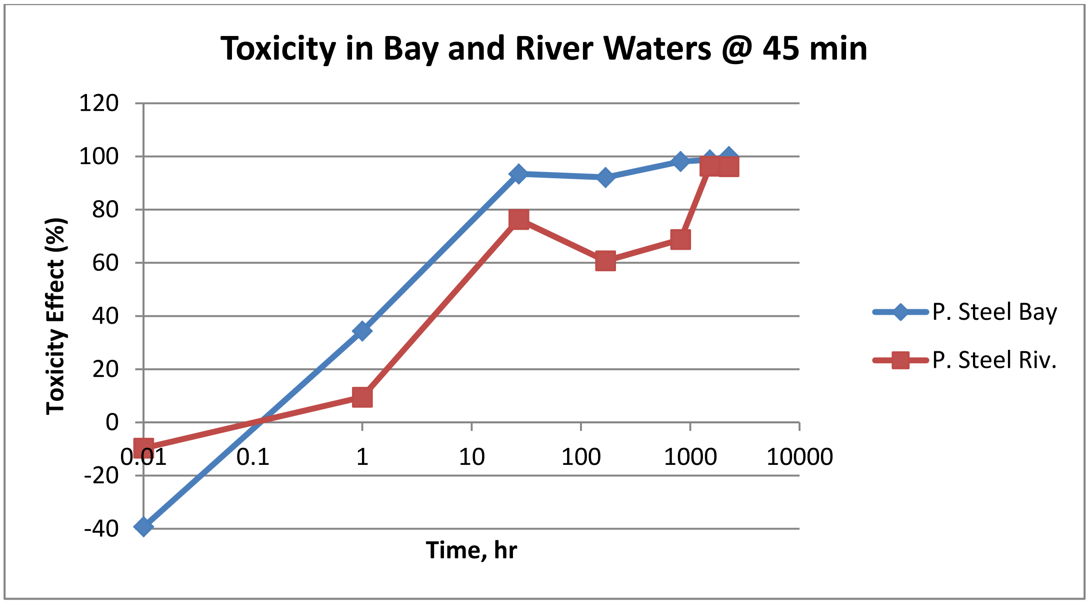


Figure 4-59. Toxicity effect in samples with galvanized steel pipes immersed in bay and river water at 45 min Microtox exposure time (Each point is an average of 2 replicates).

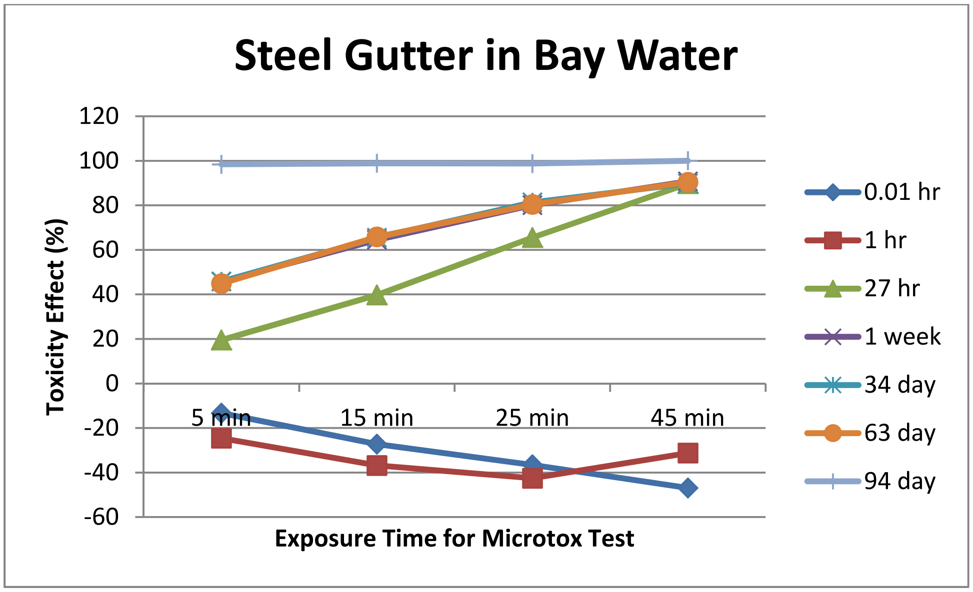


Figure 4-60. Toxicity effect in samples with galvanized steel gutter immersed in bay water for different Microtox exposure times (Each point is an average of 2 replicates).

Indicator Microorganism Die-off and Re-Growth on Urban Surfaces

Because of historic difficulties in the measurement of sewage borne pathogens, the microbiological quality of stormwater runoff is often characterized on the basis of bacterial indicator species. These species are assumed to derive from a common (sewage) source with pathogens of interest, and to arrive in, survive in, and move through watershed environments in numbers that correlate with the health risk from those pathogens. Commonly used indicator species (especially *E. coli,* and *Enterococcus* spp. or Enterococci), however, may derive from sources other than sewage, and survive in the (non-enteric) environment at rates divergent from those of the pathogens they are presumed to indicate (National Research Council, 2004).

Field and Samadpour (2007) provide a critical review of both the “indicator paradigm” (our current reliance on fecal indicator bacteria, FIBs) and an alternative monitoring regimen utilizing fecal source tracking (FST) methods. While noting the inadequate state of the art for direct measurements of pathogens, the authors find deficiencies in the correlations of FIBs to specific pathogens, and of FIBs to epidemiological measures of human health. They ascribe the deficiencies in the indicator paradigm to its inability to identify the source hosts of environmental FIBs. Landscape survival of FIBs and the ratio of FIBs to human pathogens deposited on the landscape are dependent on the source of the feces. More specifically, though zoonotic infections from non-human sources occur, correlation between human health threat and FIB presence suffers when major fecal sources other than sewage are present. They found that current-state FST methods alone were also deficient. They therefore proposed a multi-level combination of expanded source and epidemiological surveys, and pathogen, FIB and FST testing, while noting the expense and laboratory-retooling that would be required for such an approach.

Continued reliance on the use of FIBs to manage microbiological risk of environmental waters would be better informed by knowledge of the non-human contributions of FIBs to stormwater. The following subsection describes the laboratory tests conducted to develop a model for the environmentally relevant survival of indicator species (*E. coli* and Enterococci) on impervious environmental surfaces. These were conducted in an on-going effort to model background (i.e. of non-sewage origin) discharges of indicator species from stormwater source areas in which the presence of sewage contamination can be precluded in the Tuscaloosa, Alabama area.

A full 2^3 factorial study (examining temperature, moisture, and UV-B exposure and their interactions) of the indicator-species' environmental survival factors was performed for enterococci and *E. coli*. Pet feces slurries (1 mL) were applied to salt-passivated paving blocks and incubated in controlled environmental chambers. The test chambers were freezerless refrigerators fitted with BOD-controllers/heaters for temperature control, dehumidifiers or humidifiers for moisture control, and UV-B enhanced fluorescents with Lexan panels to split the chambers into UV-exposed and UV-shielded regions. These represent conditions likely to be found in Tuscaloosa, AL. Active control of temperature (40 and 90 degrees F, representing cool and warm conditions) held the temperatures steady (+/- 2 degrees) over the study period. Relative humidity (25% and 80%, representing dry and wet conditions) varied over about +/- 4%. UV exposure was treated as present or absent (UV or dark conditions).

Environmental Factors for Bacteria Survival Tests

Each taxon (*E. coli* and Enterococci) was subjected to traditional (pooled variance) factorial analysis to rank the importance of the environmental factors (temperature, humidity, and UV exposure, coded as 1 = shaded and 0 = exposed, plus their interactions) to the abscissa of each breakpoint and to the slope (k) of each intervening segment. tBPs, their associated uncertainties, and the k of each segment were derived directly from the breakpoint analysis above. Variance of each k was determined from log (MPN / initial MPN) / t = k for each non zero t in the segment.

This was problematic by the fact that different treatments (even within a taxon) differed in the number of tBPs revealed, from R = 1 (one segment with no BP) to R = 3 (three segments with two BPs). Orthogonality of the contrasts was achieved by the generation of artificial BPs within segments without breakpoints but for which tBPs were revealed in corresponding segments of other treatments. Transparency of the artificial points to the factorial analysis was achieved by assigning to them abscissae equal to the weighted average of revealed tBPs, and by assigning them zero variance. The k values of the new segments (on each side of the artificial BP) generated by this action were held to be equal, but the number of observation points (n) and the variance associated with those points were distributed (n-weighted) between the new segments.

Environmental factor effects on tBP or k values were deemed important if their standard errors (SE) led to conclusions of at least 90% confidence (reasonable, considering the small sample sets) that the effects were not zero, although confidence in the importance of effects was much higher (and noted) in some cases. Conclusions that effects were not zero were reached when the calculated confidence interval (CI) was smaller than the calculated effect:

CI = SE * t(a)

where:

t(a) = Student’s t-table return for the appropriate degrees of freedom and
(a) = the p-value resulting in the reported confidence level (i.e. alpha).

Model Construction

The important environmental effects (main effects and interactions) on k and tBP values, derived above, were used to model those parameters as a function of environmental factors:

Model Parameter = Mean (Parameter) +
Sum of (Effects of Environmental Factors)

where:

Parameter = treatment k or BP (artificial or not) entered into the tables of contrast for the factorial analyses,

Mean (Parameter) = treatment weighted mean for that parameter, and
Effects of Environmental

Factors (EEF) = adjustments to Mean (Parameter) attributable to each important environmental factor.

For a 2-level factorial setup, effects are of the form:

EEF = [Product(EF-MEF) * (1/2 environmental effect)] / Product(REF)
where:

EF = value of that environmental factor for an observation point,

MEF = mean of that environmental factor amongst observation points, and

REF = range (high value to low value) of an environmental factor amongst observation points.

Test Results of Indicator Bacteria Survival on Impervious Surfaces

E. coli

Results from breakpoint analyses of the *E. coli* dataset (Figure 4-61) are complex. One treatment (warm/wet/dark) showed no significant tBP (not even a lag), and also exhibited an absence of any initial accelerated decline. Two treatments (warm/dry/UV and warm/wet/UV) showed two tBPs each, with an initial decline, a rebound of growth, and a subsequent second decline. Cool treatments were nearly indistinguishable from each other, and resulted in more rapid declines than warm/shade treatments. All treatments exhibiting BPs showed slower declines later in the study period than in the initial die-off.

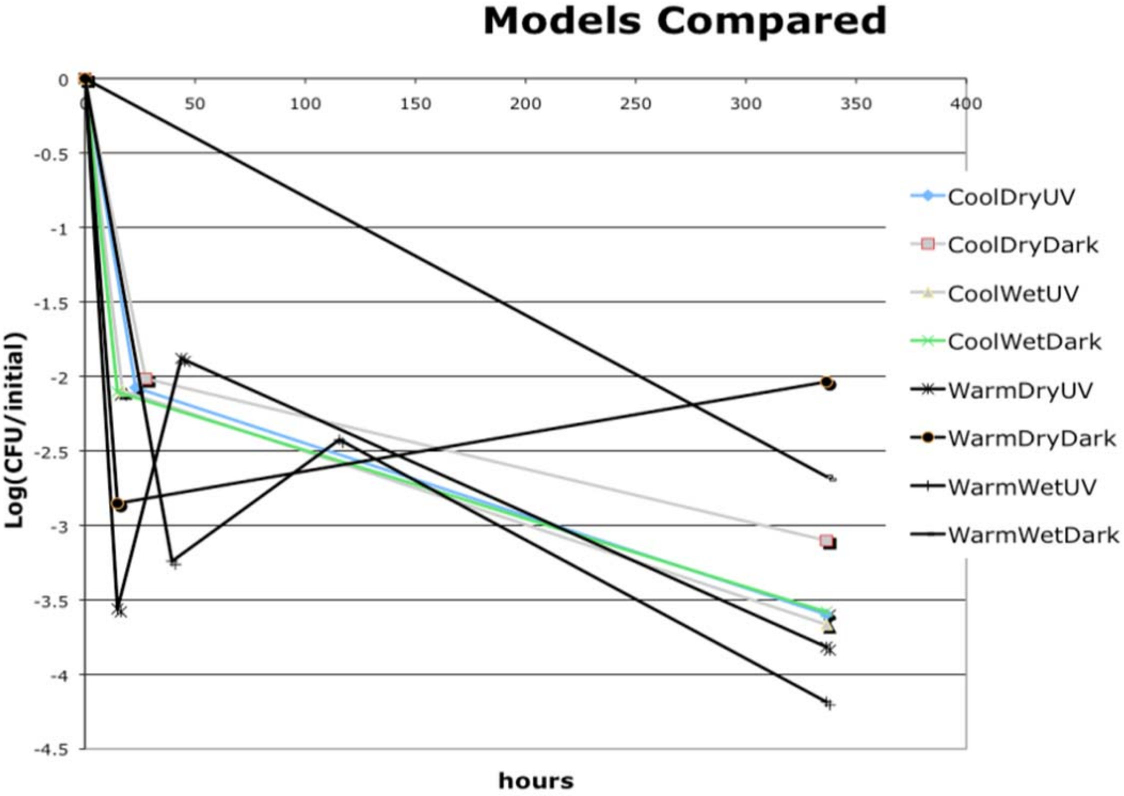


Figure 4-61. *E. coli* BP models. CFU determined by MPN (IDEXX) methods

Warm conditions in general, and warm/wet/dark in particular, most closely match the primary habitat (gut of warm blooded animals) of our enteric bacteria, and would likely impose the least stringent adaptation requirements. The fact that only warm/UV treatments elicit regrowth and three phase behavior suggests an interaction. While UVB (the primary bactericidal band in sunlight) is not strictly ionizing radiation, it is of sufficiently high frequency to rearrange bonds in complex biomolecules. Most importantly, UVB causes dimerization of adjacent thymine units (and other photoproducts) within bacterial genomes that inhibit the progression of (both RNA and DNA) polymerases. An unrepaired lesion within a gene prevents transcription of that gene. Each unrepaired legion also stops replication of the entire genome during fission (Wulff and Rupert 1962).

The factorial analysis results (Table 4-74) are likewise complex, especially in terms of the timing of the breakpoints. Such complexity should not be unexpected considering that even the number of breakpoints is treatment specific. The fact that only k1 shows any significant evidence of influence by environmental factors may imply adaptation (either at cellular or population levels) for later segments.

Table 4-74. Important *E. coli* Factorial Factors Affecting Survival or Regrowth (alpha, (a) ≤0.01)

E. coli	**k1**				
Main Effects	**Effects**	**SE(Effect)**	**t(a)**	**CI(effect**	**df=17**
Humidity	0.061	0.00055	2.6	0.060	(a)=0.01
Interactions					
TempHumid	0.11	0.024	2.9	0.070	(a)=0.01

E. coli	**BP1**				
Main Effects	**Effects**	**SE(Effect)**	**t(a)**	**CI(effect**	**df=224**
Temperature	2.1	0.33	2.6	0.87	(a)=.005
Humidity	3.2	0.33	2.6	0.87	(a)=.005
ShadeCode	-3.9	0.33	2.6	0.87	(a)=.005
Interactions					
TempHumid	12.6	0.33	2.6	0.87	(a)=.005
TempShade	-5.0	0.33	2.6	0.87	(a)=.005
HumidShade	-6.2	0.33	2.6	0.87	(a)=.005
TmpHumShd	-2.8	0.33	2.6	0.87	(a)=.005

E. coli	**BP2**				
Main Effects	**Effects**	**SE(Effect)**	**t(a)**	**CI(effect**	**df=37**
Temperature	-9.2	1.05	2.8	2.9	(a)=.005
Humidity	17.9	0.80	2.8	2.2	(a)=.005
Interactions					
TempHumid	17.9	0.80	2.8	2.25	(a)=.005
HumidShade	17.9	0.80	2.8	2.2	(a)=.005
TmpHumShd	17.9	0.80	2.8	2.2	(a)=.005

The resulting model for *E. coli* survival is therefore, for times t ≤ tBP1:

log(MPN / initial MPN) = k1 * t

where:

k1 = –0.108 + (H – 52.5) * 0.000551 + (T – 65) * (H – 52.5) * 0.0000203

where:

T = temperature (ºF)

H = %relative humidity, and

tBP1(hours) = 21.6 + (T – 65) * 0.0209 +

$$\begin{aligned}
&(H - 52.5) * 0.0293 - \\
&(S - 0.5) * 1.95 + (T - 65) * (H - 52.5) * 0.00229 - \\
&(T - 65) * (S - 0.5) * 0.0503 - \\
&(H - 52.5) * (S - 0.5) * 0.0560 - (T - 65) * (H - 52.5) * (S - 0.5) * 0.000506
\end{aligned}$$

where:

S = shade code (1 = shade, 0 = exposed)

Our model for *E. coli* survival is, for times $t > tBP1$ and $t \le tBP2$:

$$\log(MPN / \text{initial } MPN) = k1 * tBP1 + 0.002214 * (t - tBP1)$$

where:

$$\begin{aligned}
tBP2 = 80.71 - (T - 65) * 0.0924 &+ \\
&(H - 52.5) * 0.163 + \\
&(T - 65) * (H - 52.5) * 0.00326 - \\
&(H - 52.5) * (S - 0.5) * 0.163 - \\
&(T - 65) * (H - 52.5) * (S - 0.5) * 0.00326
\end{aligned}$$

Our model for E. coli survival is, for times $t > tBP2$:

$$\log(MPN / \text{initial } MPN) = k1 * tBP1 + 0.00221 * (tBP2) - (0.00501) * (t - tBP2)$$

The model presented does not fully account for all of the variability in the observations (R^2 is only 0.42, and see Figure 4-62) of the full *E. coli* dataset. It does, however, offer improved correlations with, and better balance between, under-and over-predictions than would be provided by a simple linear regression of the same dataset (compare Figures 4-63 and 4-64). Residuals of the model show little evidence of any trend over time, providing some comfort in the pooled variance methods used here (Figure 4-65).

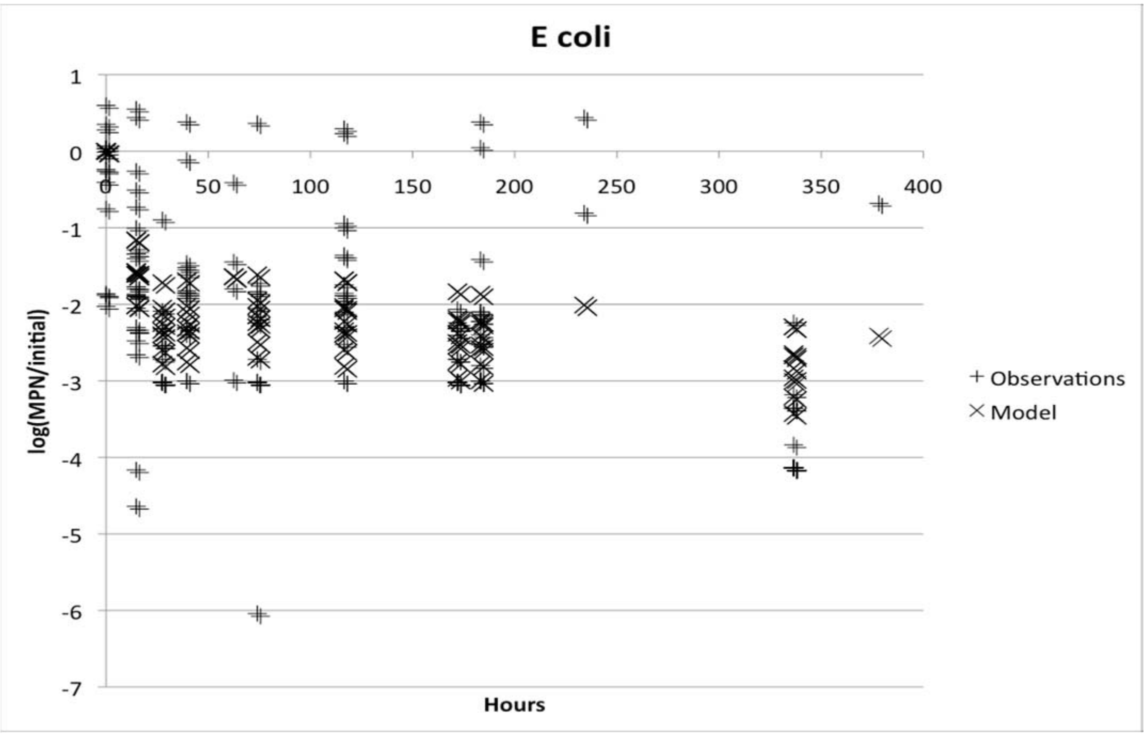


Figure 4-62. Overlay of model predictions on observations, all treatments combined.

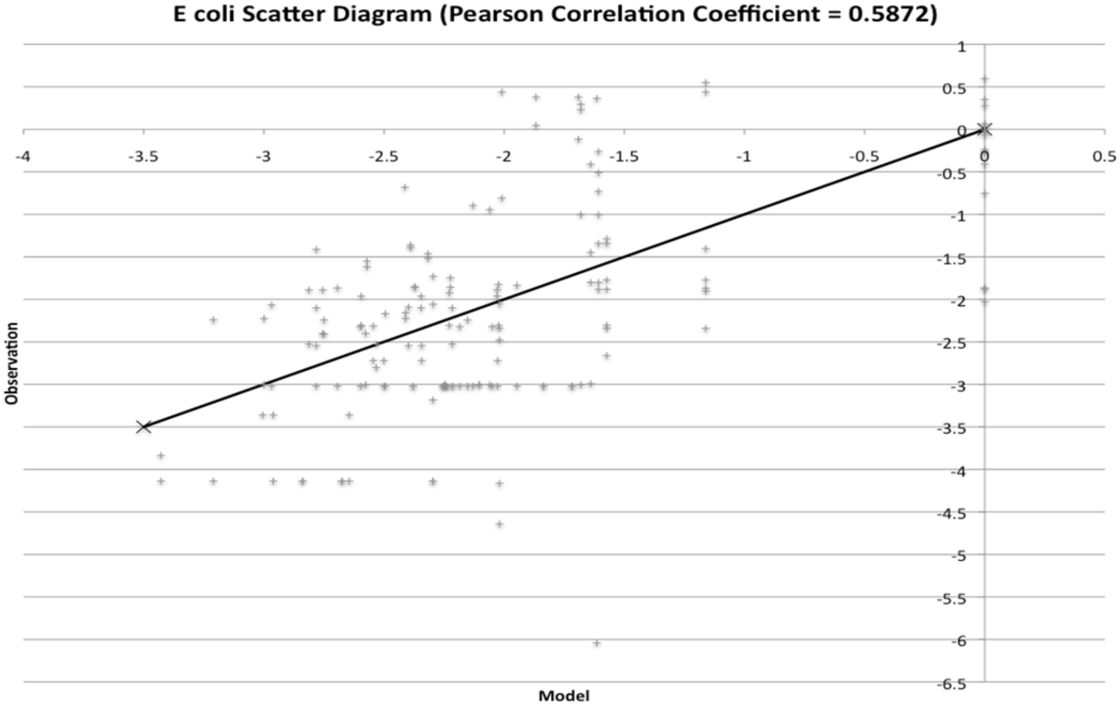


Figure 4-63. Observations vs. model; line is observation = model prediction.

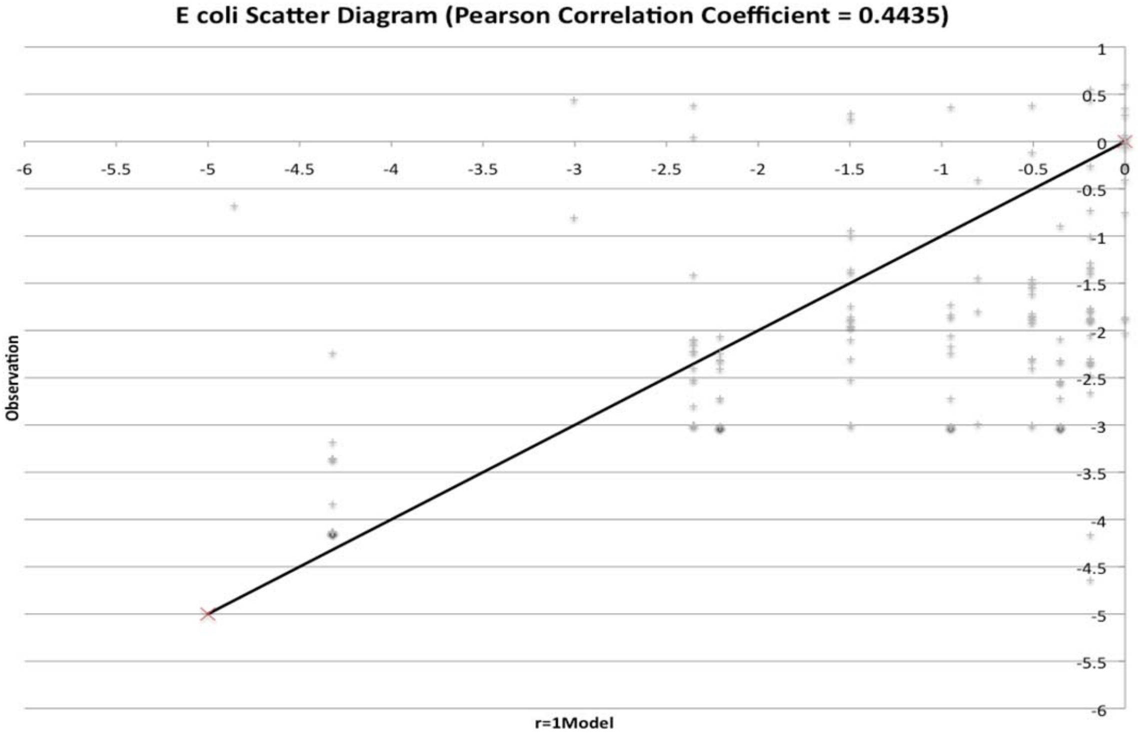


Figure 4-64. Observations vs. predictions of linear regression without environmental factorial.

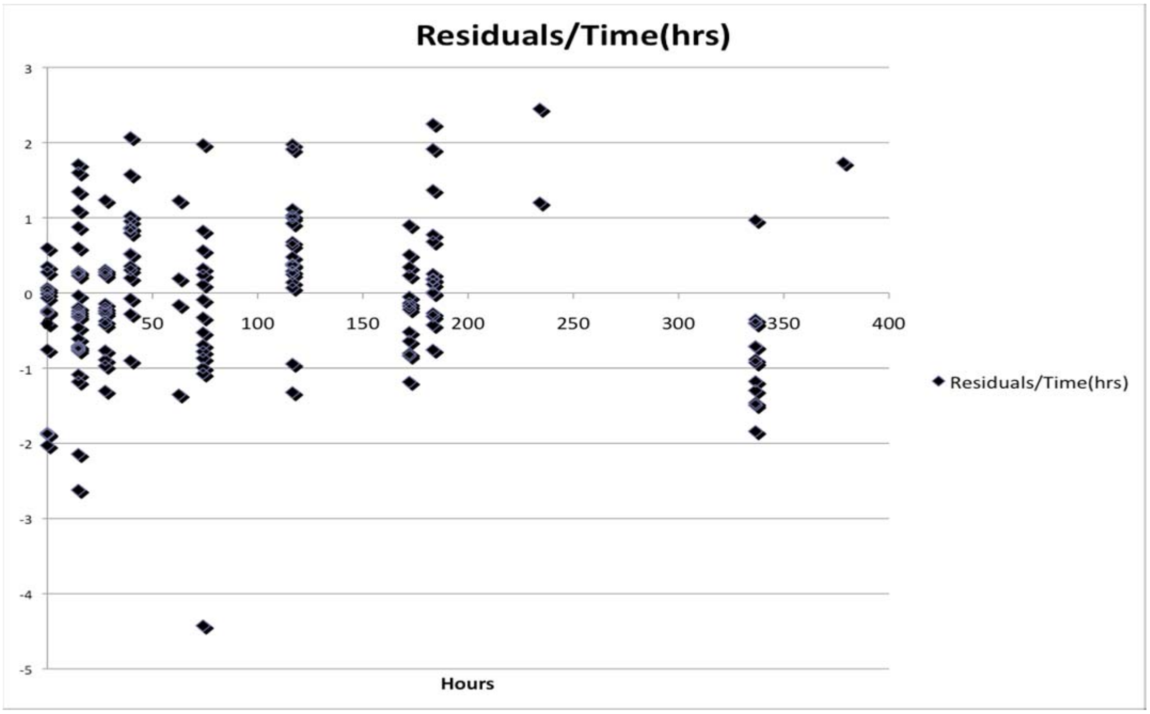


Figure 4-65. Residuals vs. time for the presented *E. coli* model.

The model derived parameters applied to our experimental conditions are presented in Table 4-75. All treatments exhibit an initial lag or die-off, the rate of which depends on the temperature and humidity. Notably, the warm/wet conditions (those most like the enteric habitat, and exerting the least pressure for adaptation) show the lowest initial rate (k1) of decline, but all inoculants had declined from two to three orders of magnitude within a day or so. The duration of the decline appears to be quite variable (19 h to 27 h), but should be interpreted with caution. Recall that the BP analysis resulted in several tBPs that coincided with the first (earliest) observation point. Though the values listed in the table represent the best estimates for predictive purposes, they must be viewed mechanistically as the latest likely time for the change. The true BP1 may have occurred before the first observation. The insensitivities of k2 and k3 to environmental factors imply that all adaptive mechanisms available to the inoculant population had been implemented prior to (and caused) the first breakpoint. The two phase behavior subsequent to BP1 could be attributed to waste buildup in these batch systems or to accumulation of UV generated thymine dimers (and review of the warm treatment behaviors in the original BP analysis, Figure X.4 above, suggests that both factors are involved).

Table 4-75. *E. coli* modeled parameters, applied to experimental conditions.

	k1 (1/hours)	BP1 (hours)	k2 (1/hours)	BP2 (hours)	k3 (1/hours)
CoolDryUV	-0.109	21.6	0.00221	76.8	-0.00501
CoolDryDark	-0.109	22.1	0.00221	79.0	-0.00501
CoolWetUV	-0.107	21.3	0.00221	83.5	-0.00501
CoolWetDark	-0.107	19.4	0.00221	81.2	-0.00501
WarmDryUV	-0.137	20.4	0.00221	71.0	-0.00501
WarmDryDark	-0.137	19.1	0.00221	77.8	-0.00501
WarmWetUV	-0.0787	27.1	0.00221	91.2	-0.00501
WarmWetDark	-0.0787	22.0	0.00221	84.5	-0.00501

Enterococci

Treatment analyses of the breakpoints were less complex for Enterococci than for *E. coli* (see Figure 4-66), although some disparity as to number and tBP values per treatment appears here as well. The warm/wet/dark treatment shows no evidence of a breakpoint (even a lag). It also displays a slope statistically indistinguishable from zero. The clear trend of greater net survival in warm treatments seen in the *E. coli* analysis is not evident here, and the timing of breakpoints in treatments (where they occur) is less varied than occurred for *E. coli*. Our assay in this case is sensitive to metabolic signals for an entire genus rather than a single species. One is tempted to argue that the greater genetic diversity of the higher taxon provides an overall greater potentiality of adaptive capacity (natural selection affecting differently distinct species or strains in different conditions) and a greater likelihood of genes for UVB damage repair mechanisms within the initial inoculant. Remarkably, when regrowth phases are recognized, none of the treatments show a net decline of more than about one order of magnitude over a two week period. It also should be noted that no population is in decline at the end of the study period.

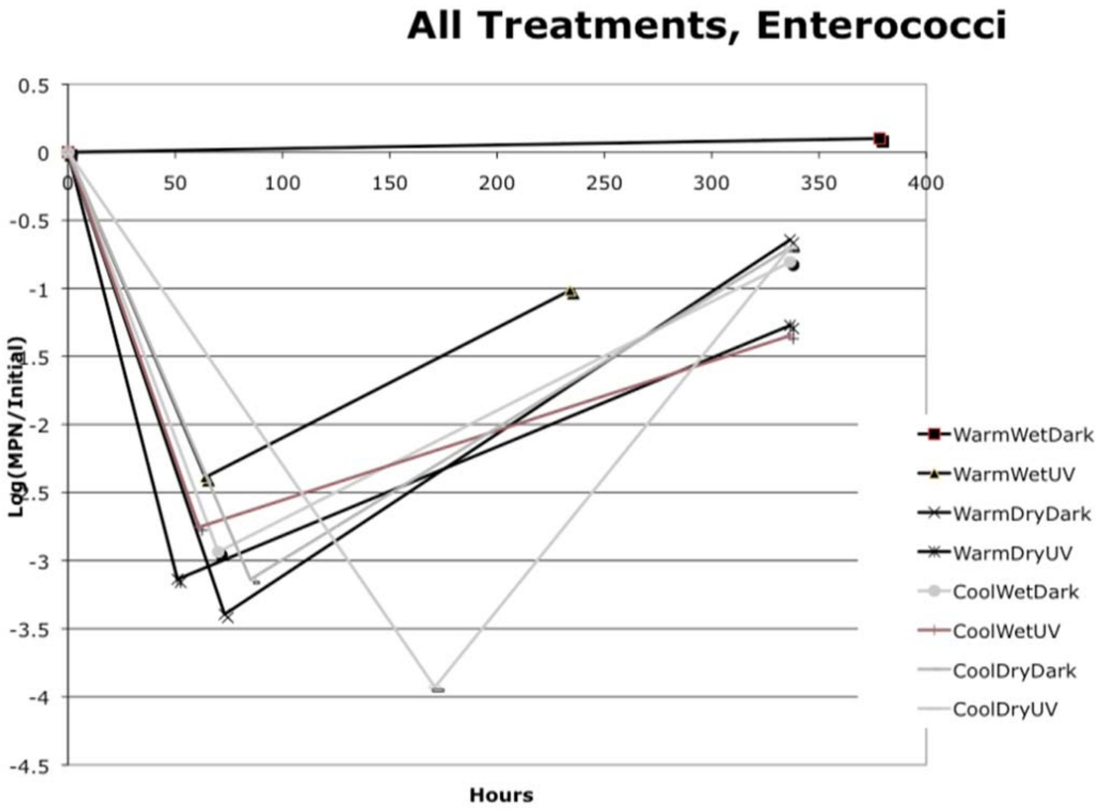


Figure 4-66. Enterococci BP models.

Factorial analyses (Table 4-76) for Enterococci were also simpler than for *E. coli*, but again showing greater complexity for tBP values than for intervening segments. As for the *E. coli* analyses, k values become insensitive to environmental factors subsequent to the tBP, implying capacity for adaptation to the secondary (non-enteric) habitat.

Table 4-76. Important factors per Enterococci factorial analysis

Enterococci	**k1**				
Main Effects	**Effects**	**SE (Effect)**	**t(a)**	**CI(effect)**	**df=56**
Humidity	0.015	0.011	1.3	0.014	(a)=0.1
ShadeCode	0.015	0.11	0.010		(a)=0.1
<u>Interactions</u>					
TempHumid	0.020	0.011	1.7	0.019	(a)=0.05
TempShade	-0.077	0.011	2.7	0.030	(a)=0.005

Enterococci	**BP**				
Main Effects	**Effects**	**SE (Effect)**	**t(a)**	**CI(effect)**	**df=233**
Temperature	-8.8	0.31	2.7	0.84	(a)=0.005
Humidity	-5.3	0.32	2.7	0.84	(a)=0.005
ShadeCode	11.2	0.31	2.7	-0.84	(a)=0.005
Interactions					
TempHumid	8.7	0.31	2.7	0.84	(a)=0.005
TempShade	1.2	0.32	2.7	0.85	(a)=0.005
HumidShade	-5.3	0.32	2.7	0.84	(a)=0.005
TmpHumShd	-4.3	0.32	2.7	0.85	(a)=0.005

The resulting model for Enterococci survival is therefore:

$$\log(\text{MPN} / \text{initial MPN}) = k1 * t \text{ for } t \le tBP$$

where:

$$\begin{aligned} k1 = {} & -0.0356 + (H - 52.5) * 0.000137 + \\ & (S - 0.5) * 0.00727 + \\ & (T - 65) * (H - 52.5) * 0.00000372 - \\ & (T - 65) * (S - 0.5) * 0.00771 \end{aligned}$$

and

$$\begin{aligned} tBP = {} & 68.74 - (T - 65) * 0.881 - \\ & (H - 52.5) * 0.0483 + \\ & (S - 0.5) * 5.59 + \\ & (T - 65) * (H - 52.5) * 0.00158 + \\ & (T - 65) * (S - 0.5) * 0.0119 - \\ & (H - 52.5) * (S - 0.5) * 0.0483 - \\ & (T - 65) * (H - 52.5) * (S - 0.5) * 0.000784 \end{aligned}$$

and for $t > tBP$:

$$\log(\text{MPN} / \text{initial MPN}) = k1 * tBP + 0.00652 * (t - tBP)$$

Comparison of the model with observations (Figure 4-67) makes it apparent that there are other sources of variability than the environmental factors analyzed here (and R^2 is only 0.59). However, the model again provides closer (and more balanced) agreement with the data than does a simple regression (Figures 4-68 and 4-69). The residual plot, again, provides no evidence of increase or decrease over time (Figure 4-70).

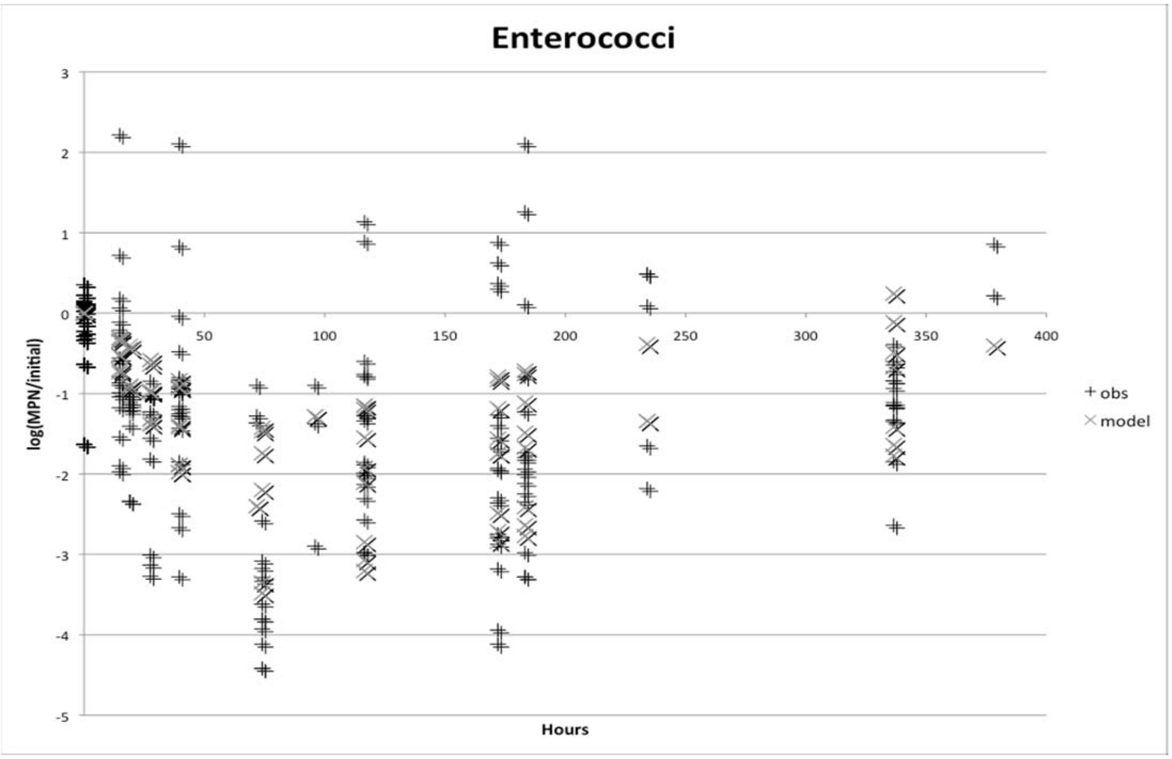


Figure 4-67. Enterococci, Observations vs Model comparison.

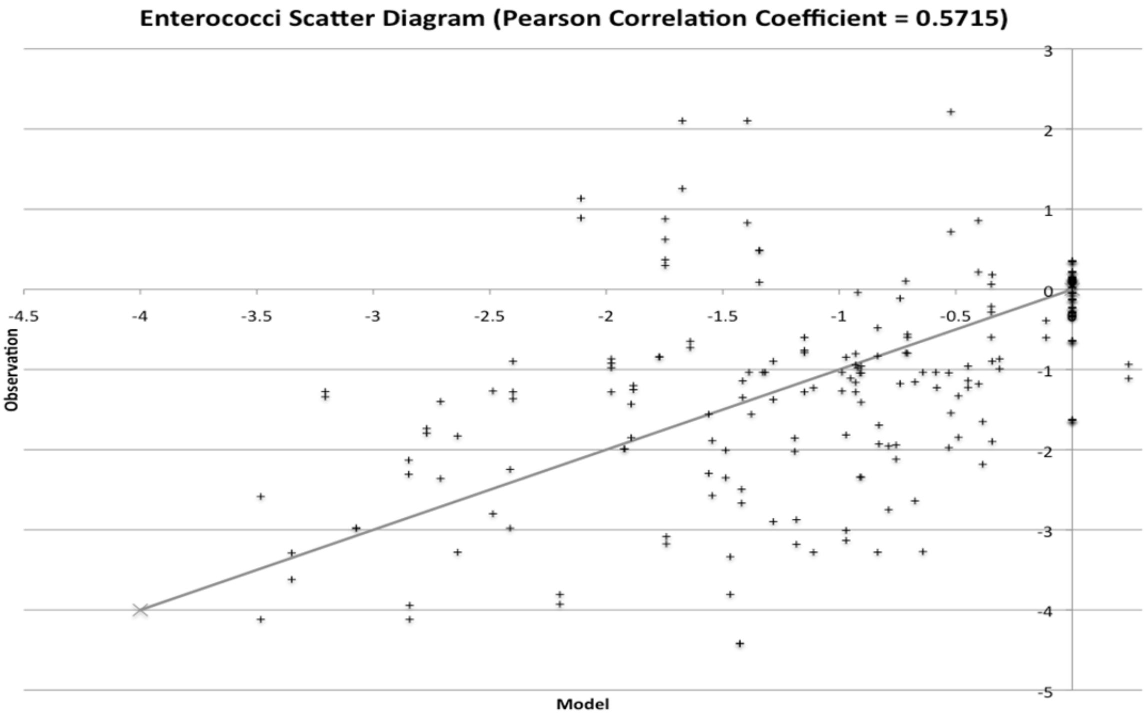


Figure 4-68. Model Predictions vs. Observations. Line shows Observation=Prediction.

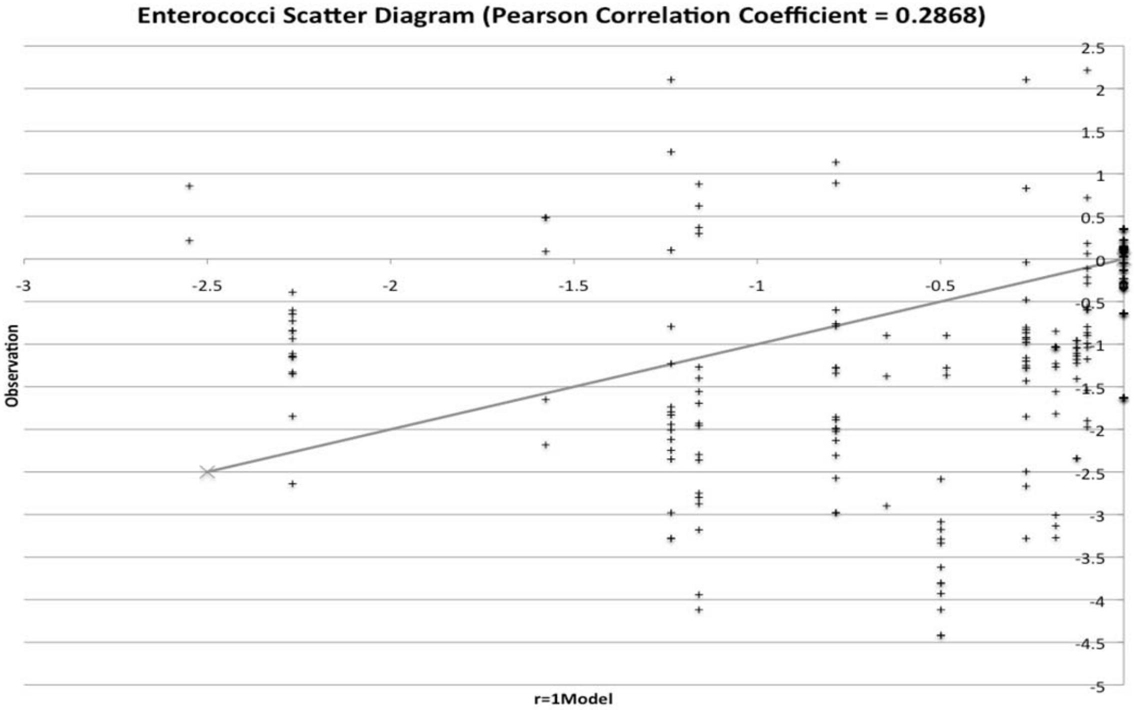


Figure 4-69. Paired Observations vs. predictions from a simple linear regression. Line displays Observation=Prediction.

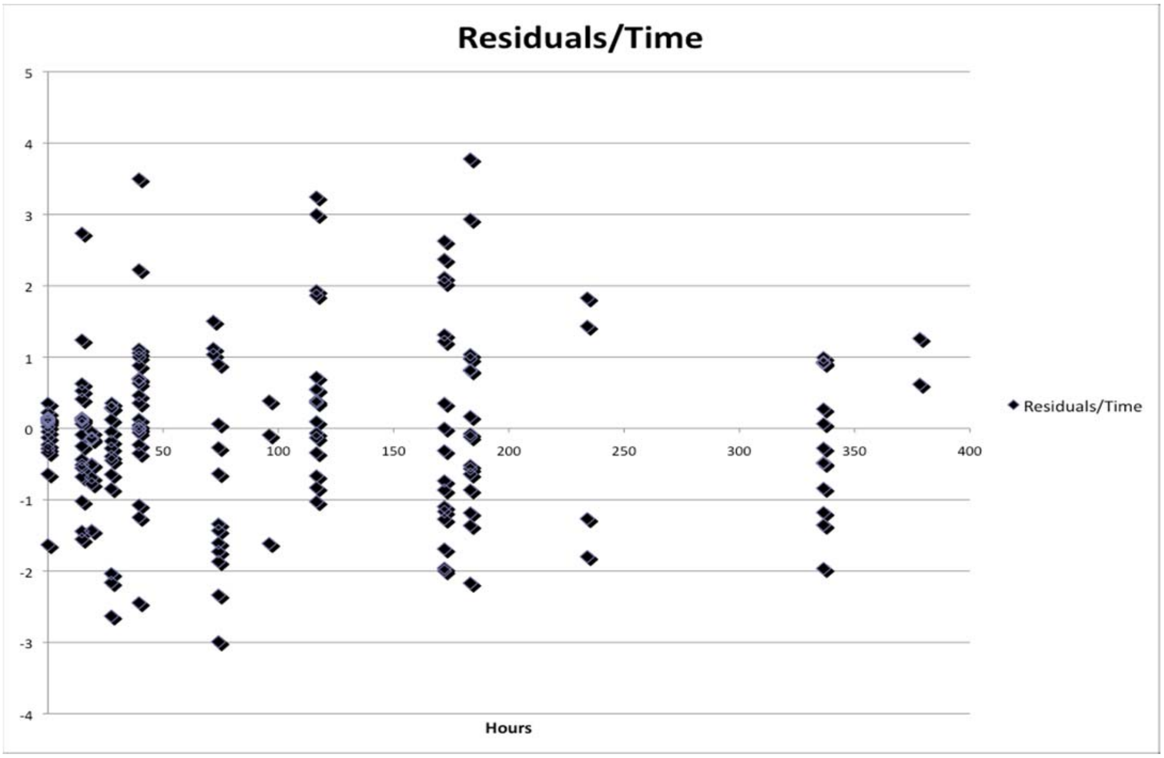


Figure 4-70. Residuals, over time, of the proposed model.

The model derived parameters applied to our experimental conditions are presented in Table 4-77. All treatments, again, exhibit an initial decline, with all three environmental factors (temperature, humidity, and UV exposure) contributing (either as main effects or within interactions). The rates of decline, however, are only about half of those shown by *E. coli*. None of the BPs for these populations coincided with initial observations, and the adaptation phase of these inoculants lasted about three days. Even with the slower rates of decline, most inoculants had been reduced by two or three orders of magnitude in the initial period. The insensitivity of k2 to environmental effects, and the fact that it is positive (indicating net growth) implies that these organisms adapt to impervious environmental surfaces quite well. By the end of the study period (about two weeks) all inoculants had rebounded to within about 10% of their original populations.

Table 4-77. Enterococci modeled parameters, applied to experimental conditions.

	k1 (1/hours)	BP (hours)	k2 (1/hours)
CoolDryUV	-0.0501	70.0	0.00652
CoolDryDark	-0.0235	76.7	0.00652
CoolWetUV	-0.0477	66.5	0.00652
CoolWetDark	-0.0211	70.5	0.00652
WarmDryUV	-0.0359	63.2	0.00652
WarmDryDark	-0.0479	70.4	0.00652
WarmWetUV	-0.0233	64.0	0.00652
WarmWetDark	-0.0353	68.6	0.00652

Preliminary Results for Bacteria Survival Tests in Soil Media

A study into the survival of fecal-indicator bacteria (FIBs) on pervious environmental surfaces was designed as a 2^5 factorial experiment (Temperature, Humidity, pH, and presence/absence of UVB exposure and added bioavailable organics). Parallel studies were performed for two taxons (*E. coli*, and *Enterococcus spp.* or Enterococci). These tests were a continuation of the previously reported investigations of the bacteria survival on impervious surfaces. However, the statistical analyses for these tests were not completed by the time this report was prepared. Basic data plots are included some general comments follow.

Slurries of dog feces (obtained from a local veterinarian) were prepared with distilled water in a lab blender, applied to simulated soil samples of varying acidity/organic content, and then incubated in controlled environmental chambers for over two weeks. Most Probable Numbers (MPN) of Colony Forming Units (CFU) of viable FIBs obtained from periodic samples were compared to MPNs obtained from similarly inoculated samples prepared before incubation ("Day 0"). MPNs were determined by IDEXX methods (Colilert and Enterolert), a selective-media system which can (fluorometrically) return meaningful data over a 3-order range (1CFU to 2400 CFU with no further dilution) for samples incubated over 24 hours.

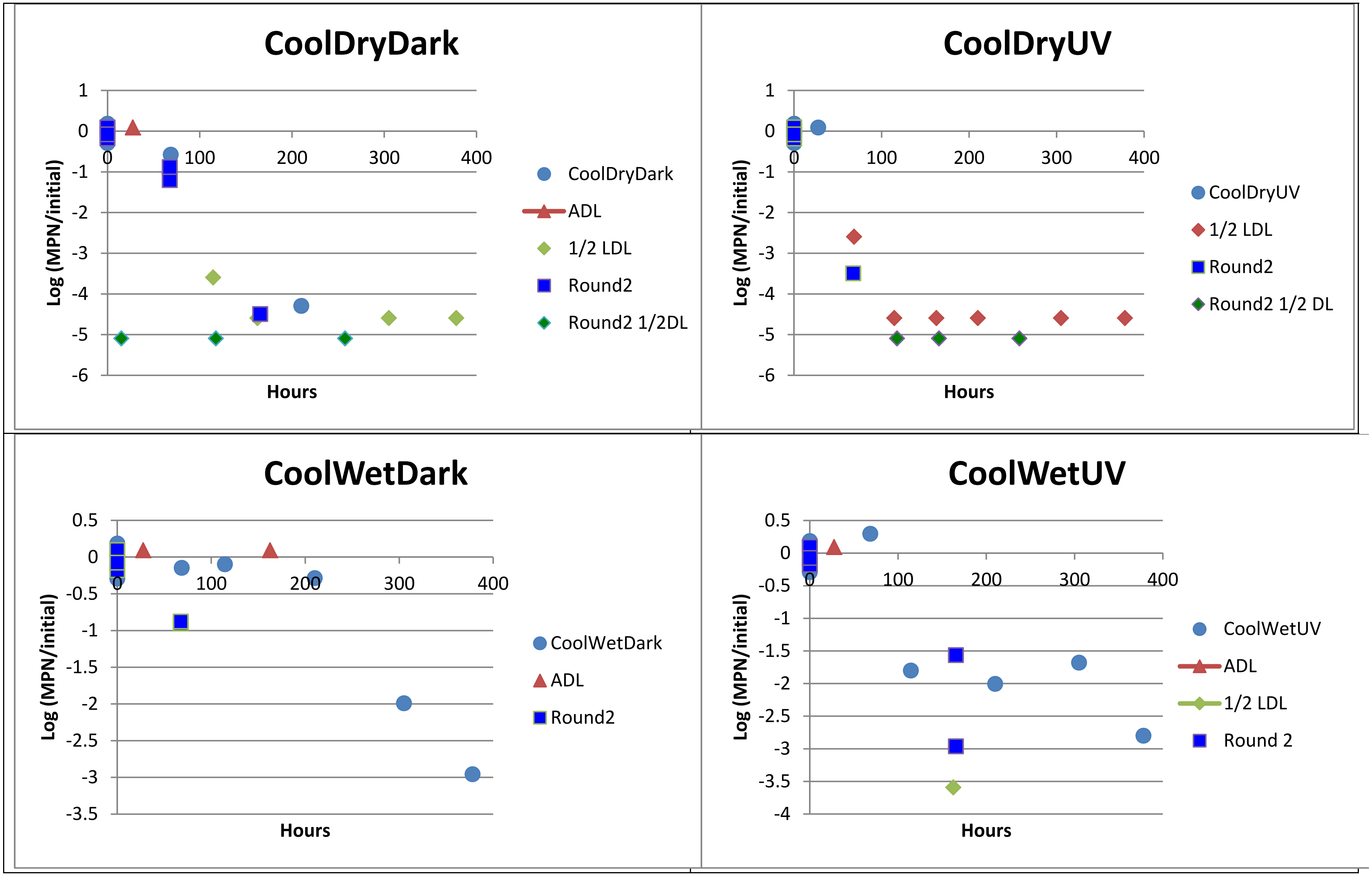
The test media was locally obtained creek sediment that was sand also with considerable clay/smaller particle content, but with no visual evidence (darkening) of significant organics. The creek sand was sterilized (350^{o}F in a kitchen oven for 2 hours in a Pyrex baking dish, with frequent stirring and hand-pulverized). One tablespoon of the media was per small aluminum weighing dish for the tests. Each media sample was "wetted" prior to inoculation; equal volumes of distilled water (to achieve neutral/no added organics), dilute vinegar (to achieve pH 6/no added organics), dilute molasses (to achieve pH 6/1% total sugars by weight), and dilute molasses and baking soda (to achieve neutral/1% total sugars by weight). While *E. coli* is capable of metabolizing the acetate (vinegar) as another "organic," it is an energetically unfavored reaction (and requires subsidy from others).

The environmental test chambers were the same freezerless refrigerators used for the impervious tests, fitted with BOD controllers (for "warm" temperatures ~93^{o}F) or included controls (~35^{o}F), humidifiers (~90% RH) or chemical desiccants (~30%), and UVB-enhanced fluorescent fixtures. The refrigerators were split into UV-exposed and UV-shaded areas by Lexan panels.

Statistical analysis of the combined (several dilution) studies is still ongoing. The curve fitting is based on Tobit Type I (censored) regression of tentative segments for input into Bai and Perron multiple-breakpoint analysis for each treatment. Analysis of each (taxon-based) survival model will be by ordinary factorial analysis.

Comparisons with previous studies that investigated these same bacteria on pavement sections are instructive. In a 2^3 study (same environmental conditions, but only neutral/no added organics) of *E.coli* survival on impervious surfaces, nearly all treatments exhibited a marked initial rapid die-off within 24 hours of inoculation to the surface, followed by a regrowth phase and then a secondary period of reductions. Warm treatments resulted in greater survival rates than cooler ones, and warm/wet tests showed a sensitivity to UV exposure (with UV light hindering survival of the bacteria). All treatments resulted in a loss of 2-4 orders of magnitude (99 to 99.99%) of the original inoculant by 300 hours of exposure (Figure 4-61). Comparison to the current pervious media survival results (Figure 4-71a) for the neutral/no added organics condition (by inspection) shows a similar long-term behavior for all treatments but an apparent absence of the initial (first day) rapid die-off. Cool/dry conditions are still antagonistic to survival, but UV appears less interactive with the other environmental conditions. Overall, the *E. coli* populations in the soil had less rapid changes with time as on the impervious surfaces.

The Enterococci survival study on the soil media exhibited less sensitivity to environmental conditions than did *E. coli*. Some treatments actually showed growth to MPNs greater that the variability range of the original inoculant (Figure 4-71b). These pervious tests for neutral pH/no added organics condition includes some samples indicating over 10-fold growth during the extended test period.


CoolDryDark
Log (MPN/initial)
1
0
-1
-2
-3
-4
-5
-6
0
100
200
300
400
Hours
CoolDryDark
ADL
1/2 LDL
Round2
Round2 1/2DL
CoolDryUV
Log (MPN/initial)
1
0
-1
-2
-3
-4
-5
-6
0
100
200
300
400
Hours
CoolDryUV
1/2 LDL
Round2
Round2 1/2 DL
CoolWetDark
Log (MPN/initial)
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
0
100
200
300
400
Hours
CoolWetDark
ADL
Round2
CoolWetUV
Log (MPN/initial)
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
0
100
200
300
400
Hours
CoolWetUV
ADL
1/2 LDL
Round 2

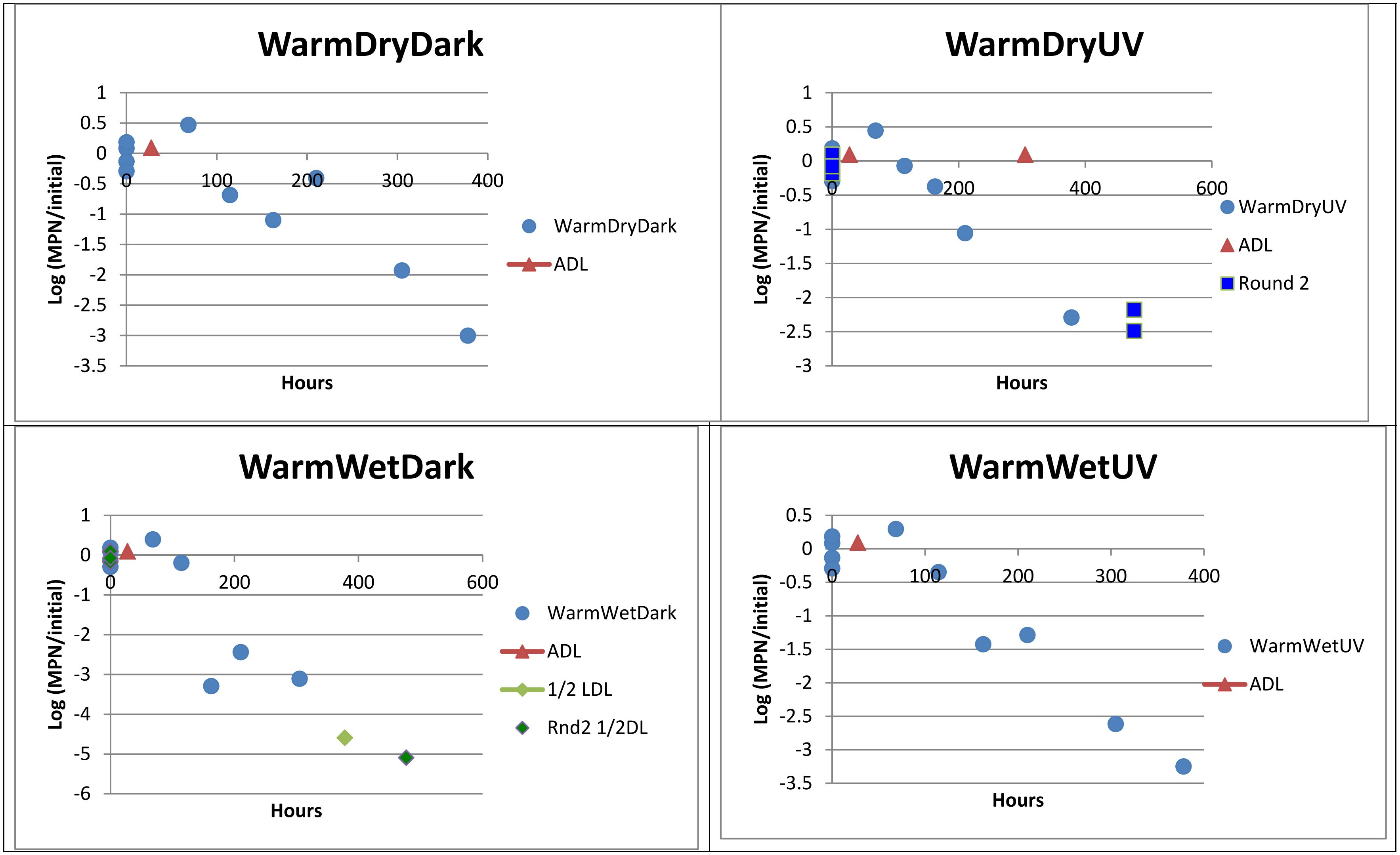
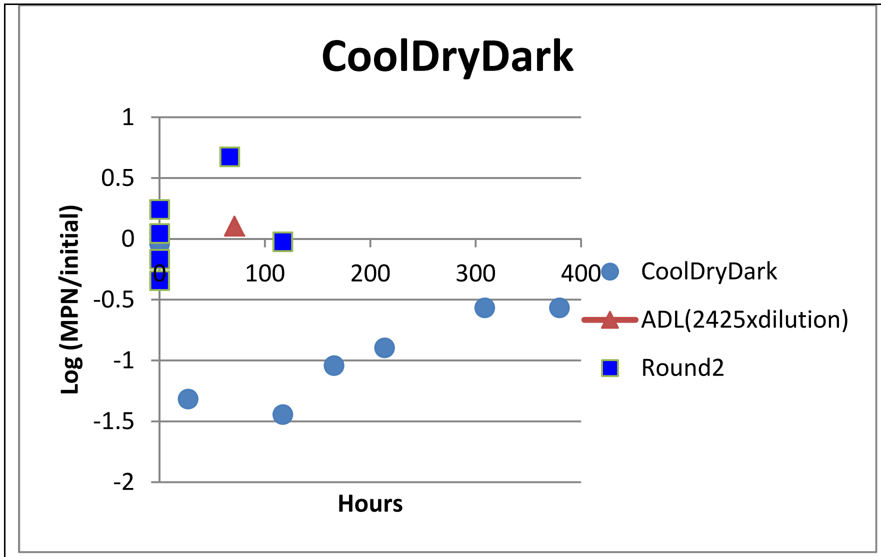
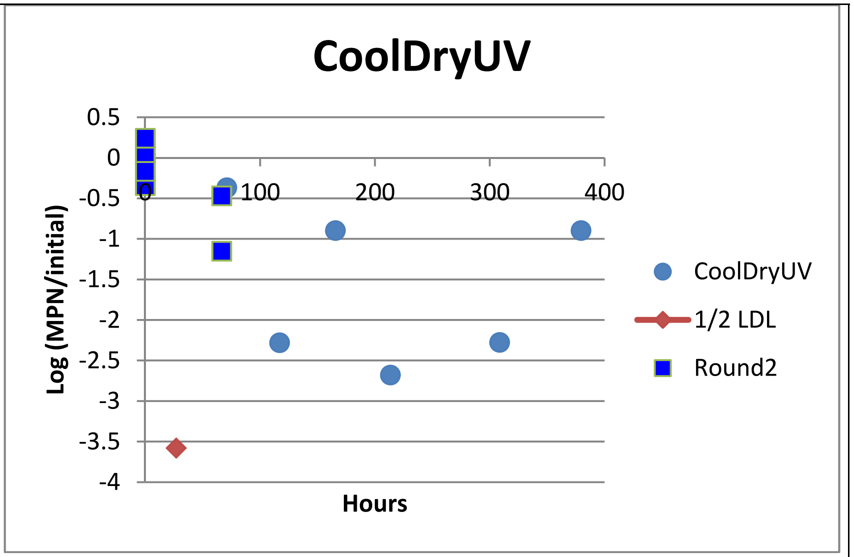
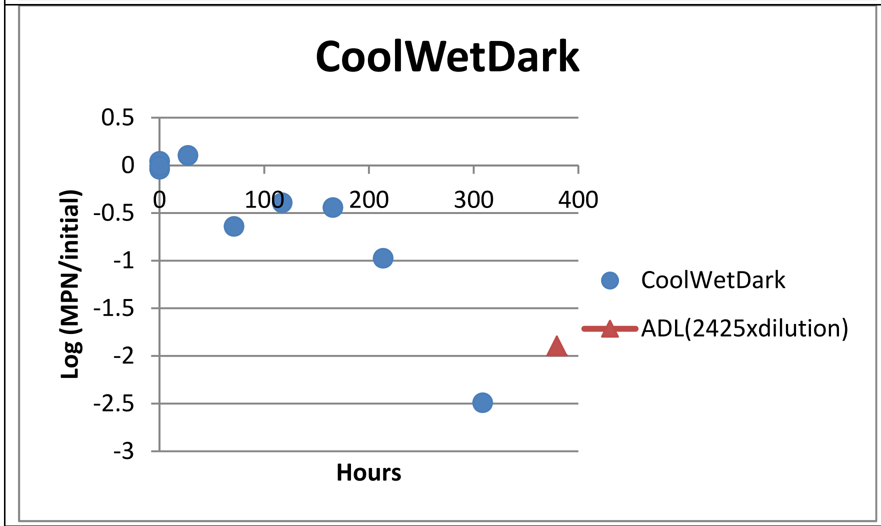
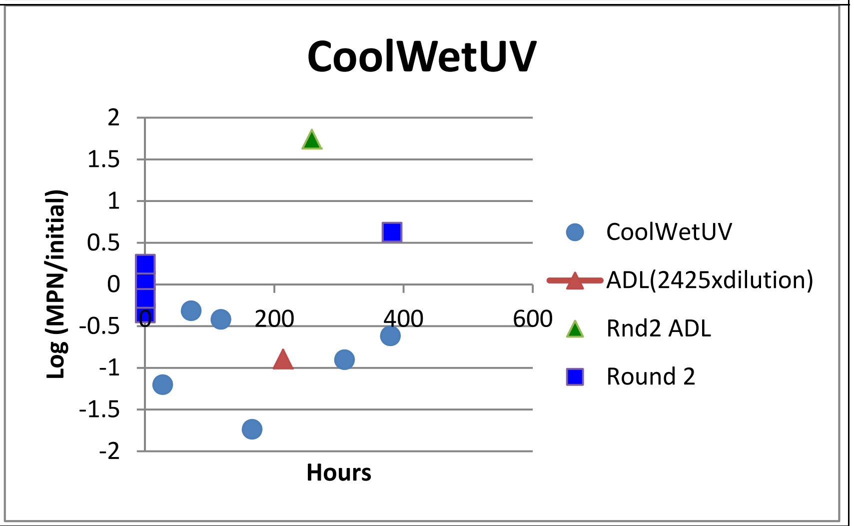


Figure 4-71a. *E. Coli* survival on soil growth media under different test conditions (neutral pH no organics added).


CoolDryDark


CoolDryUV


CoolWetDark


CoolWetUV

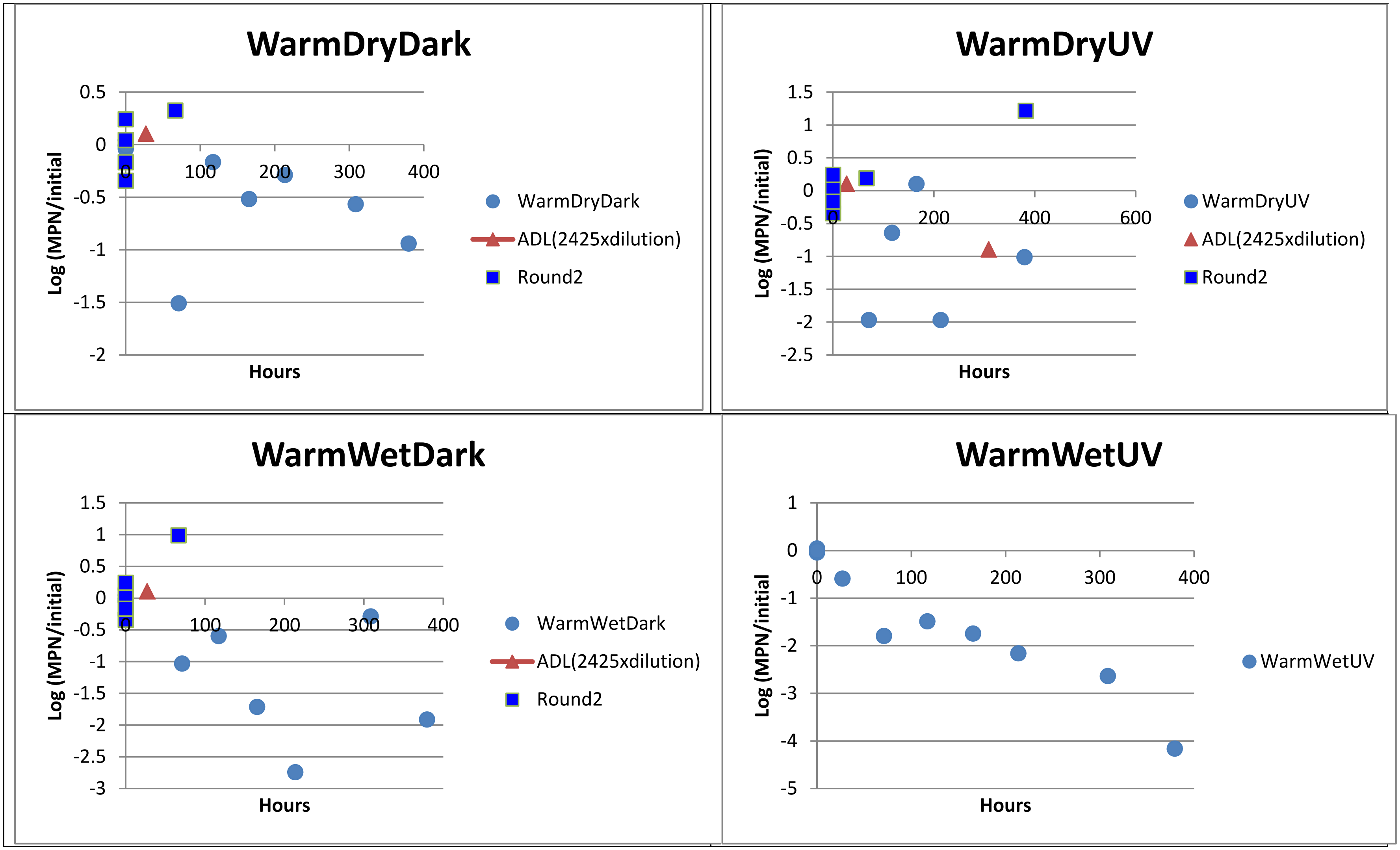


Figure 4-71b. Enterococci survival on soil growth media under different test conditions (neutral pH no organics added).

Influent Mass Loads of Pharmaceuticals and PAHs to Tuscaloosa Wastewater Treatment Plant

In summary, Table 4-87 shows the significant slope terms for the analyzed pharmaceuticals, reflecting the increasing concentrations as the daily average wastewater treatment plant flow increased during different sized rains. These slope terms were used to calculate approximate influent concentrations for these increasing flows, and the loads, expressed as mg/km^2 for each rain category.

Table 4-78. Calculated Influent Mass Loadings for Pharmaceuticals during Different Sized Rain Events

Pharmaceutical compound	Slope term (µg/L/MGD)	Conc. (µg/L) during 0 to 0.5 inch rain (18 MGD; 1.5 hr duration)	Mass per event (mg/km^2)*	Conc. (µg/L) during 0.6 to 1.5 inch rain (23 MGD; 4 hr duration)	Mass per event (mg/km^2)*	Conc. (µg/L) during 1.6 to 2.5 inch rain (34 MGD; 12 hr duration)	Mass per event (mg /km^2)*
Gemfibrozil	2.81	51	1.1	65	4.9	96	32
Ibuprofen	1.85	33	0.74	43	3.2	63	21
Triclosan	1.86	34	0.74	43	3.2	63	21
Fluoxetine	2.44	44	0.97	56	4.2	83	28
Sulfamethoxazole	2.51	45	1.00	58	4.4	85	29
Trimethoprim	0.66	12	0.26	15	1.2	22	7.5

* 74 mi^2 (192 km^2) service area

Tables 4-79 and 4-80 summarize some of the reported influent pharmaceutical and PAH concentrations at wastewater treatment plants as reported in the literature compared to the concentrations observed at the influent at the Tuscaloosa wastewater treatment plant during this study. The gemfibrozil and ibuprofen values are within the range previously reported, but the triclosan, sulfamethoxazole, and trimethoprim observed concentrations seem larger than typically reported (ay about one order of magnitude). However, the laboratory QA/QC results, including frequent testing of standards and extraction efficiencies, indicated that the results are acceptable. Most of the methods used during the reported studies were advanced procedures that had very low detection limits, while our methods were more basic HPLC units, and we used specially developed solid-phase extraction methods for enhanced recoveries. The detection limits were suitable, but relatively close to the observed values. Appendix B contains the chromatographs for the analyses, indicating the relatively low signal to noise ratios. Therefore, the pharmaceutical concentrations reported during this project may have greater uncertainly than many of the reported sources. However, the analyses of the treatment results reported in the next section show consistent results and expected behavior, with similar values for the influent and after primary treatment, and most of the removals occurring during the secondary treatment phase, resulting in much lower effluent concentrations. Some compounds did not show any significant removals, so the repeated results helped establish the analytical performance.

Table 4-79. Observed Influent Pharmaceutical Concentrations Compared to Reported Concentrations

Pharmaceutical compound	**Concentrations reported for influents at wastewater treatment plants (µg/L)**	**Influent concentrations observed during this study (average µg/L)**
Gemfibrozil	0.1 to 36	59
Ibuprofen	4 to 84	28
Triclosan	0.9 to 4	28
Sulfamethoxazole	0.05 to 1.5	38
Trimethoprim	0.05 to 1.5	9

Table 4-80. Calculated Influent Mass Loadings for PAHs during Different Sized Rain Events

PAH compound	Slope term (µg/L/MGD)	Conc. (µg/L) during 0 to 0.5 inch rain (18 MGD)	Mass per event (mg/km^2)*	Conc. (µg/L) during 0.6 to 1.5 inch rain (23 MGD)	Mass per event (mg/km^2)*	Conc. (µg/L) during 1.6 to 2.5 inch rain (34 MGD)	Mass per event (mg/mi^2 and mg/km^2)*
Naphthalene	0.5	9.0	0.20	11.5	0.87	17.0	5.7
Acenaphthene	0.31	5.6	0.12	7.1	0.54	10.5	3.5
Fluorene	0.057	1.0	0.02	1.3	0.10	1.9	0.65
Fluoranthene	0.047	0.8	0.02	1.1	0.08	1.6	0.54
Phenanthrene	0.11	2.0	0.04	2.5	0.19	3.7	1.3
Anthracene	0.055	1.0	0.02	1.3	0.10	1.9	0.63
Pyrene	0.059	1.1	0.02	1.4	0.10	2.0	0.67

* 74 mi^2 (192 km^2) service area

Table 4-81compares the observed influent PAH concentrations during this study with some reported PAH values from the literature. The concentrations reported in the wastewater literature are again much lower than observed during this research. During our prior PAH studies in wet weather flows (Pitt, et al. 1999, for example). We have commonly seen even higher PAH concentrations. We suspect the main differences are associated with the extraction methods. The use of solid-phase extraction methods for PAHs in the presence of particulates results in very low recoveries, requiring multiple extractions using separation funnels instead. Most of the PAHs are strongly associated with particulates which are difficult to extract by some methods. For groundwater samples, where little of the PAHs are associated with particulates and the particulate content in the samples is very low, solid phase extraction can work well; for surface water samples (and wastewater samples), the particulate matter significantly interferes with PAH extractions using solid-phase extraction methods.

Table 4-81. Observed Influent PAH Concentrations Compared to Reported Concentrations

PAH compound	Concentrations reported for influents at wastewater treatment plants (range µg/L)	Influent concentrations observed during this study (average µg/L)
Naphthalene	0.1 to 7	11
Acenaphthene	0.02 to 0.4	11
Fluorene	0.04 to 0.7	5
Fluoranthene	0.1 to 0.2	5
Phenanthrene	0.3 to 2	3
Anthracene	0.03 to 0.1	75
Pyrene	0.1 to 0.5	5

Pharmaceuticals, Pesticides, PAHs, Heavy Metals and Indicator Microorganisms Observed in Tuscaloosa Area Stormwater Sheetflows

The following discussion summarizes the sheetflow characteristics associated with the source area sampling conducted during wet weather. Appendix G contains the complete set of information, and Appendix H also includes the chromatographs associated with the organic analyses of these samples. This section is divided into separate discussions of the pharmaceuticals and personal care products (PPCE) (Table 4-82 and Figures 4–72 and 4-73), the polycyclic aromatic hydrocarbon (PAHs) (Table 4-83 and Figure 4-74), heavy metals (Table 4-84 and 4-85; Figure 4-75 through 4-78), bacteria (Table 4-86 and Figure 4-79), toxicity screening (Table 4-87 and Figure 4-80), solids (Table 4-88 and Figures 4-81 through 4-84) and pesticide and selected other semi-volatile organic results (Tables 4-89 and 4-90).

Pharmaceuticals and Personal Care Products in Stormwater Sheetflows

Samples were analyzed for selected PPCP concentrations, including trimethoprim, sulfamethoxazole, carbamazepine, fluoxetine, ibuprofen, gemfibrozil, and triclosan. Triclosan was not detected in any of the samples, while ibuprofen was only detected in 15% of the samples, and trimethoprim was only detected in 23% of the samples. The nonparametric Kurskal-Wallis one-way analysis of variance on ranks test was applied on these data using SigmaPlot version 11 (SYSTAT Software Inc.) to detect the presence of any significant differences in land use or source area grouping. For the PPCPs, only carbamazepine (detected in 95% of the sheetflow samples) was found to have at least one source area statistically significantly different from the other source area categories. None were found to have any significant differences by land use, for the number of samples available.

Grouped box and whisker plots (using SigmaPlot version 11) were also prepared for all of the PPCPs showing differences by source area and land use. Probability plots (Minitab version 16) were also prepared for the constituents having sufficient data (sulfamethoxazole, bacteriostatic antibiotic, often used with trimethoprim; carbamazepine, an anticonvulsant; fluoxetine, and antidepressant such as Prozac; and gemfibrozil, used to lower lipid levels).

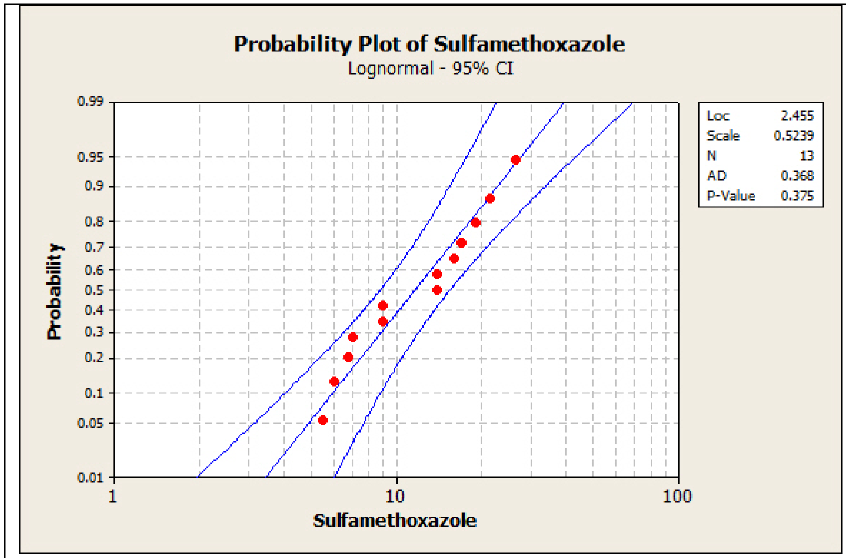
The probability plots were prepared showing each source area separately for carbamazepine to also help distinguish the source areas that were likely different from the others. The probability plots indicate good fits of the data to log-normal statistical distributions, with some very large values and some low values observed, as generally seen for most stormwater constituents.

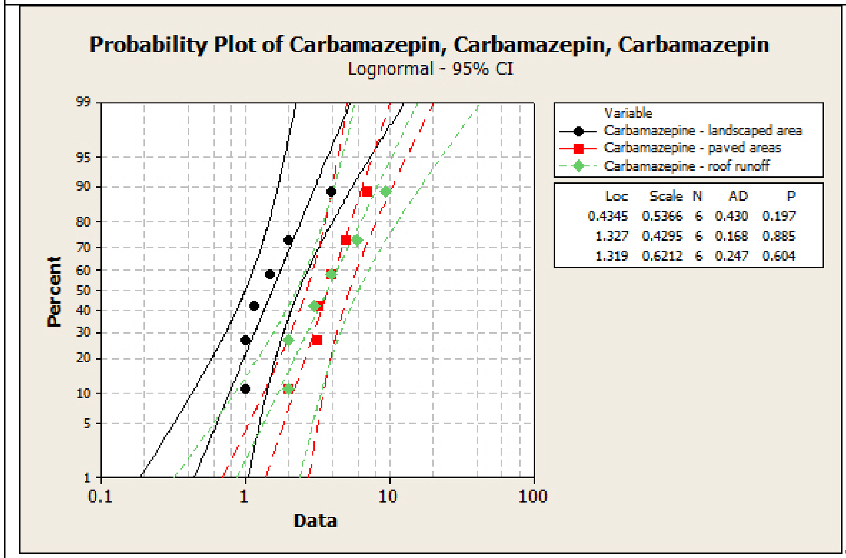
These analyses clearly show that landscaped areas had low average concentrations of carbamazepine (about 1 µg/L), while the other source areas (paved areas and roof runoff) had average concentrations at about 4 µg/L. The reasons for these concentration relationships are not clear.

Table 4-82. Significant Groupings of Pharmaceuticals and Personal Care Products in Stormwater Sheetflows*

	Trimethoprim	Sulfamethoxazole	Carbamazepine	Fluoxetine	Ibuprofen	Gemfibrozil
% detected	23	59	95	41	15	100
categories	overall	overall	by source area (p = 0.026)	overall	overall	overall
summary statistics for observed values:						
overall						
average	7.3	13.2	3.5	6.5	38	76
median	6.1	14	3.3	7	38	34
min	5.5	5.5	1	2	13	23
max	10	26.5	9.5	12	62	327
COV	0.3	0.5	0.6	0.5	0.9	1.4
landscaped						
average			1.5			
median			1.2			
min			1			
max			4			
COV			0.8			
paved						
average			4.1			
median			3.6			
min			2.0			
max			7.0			
COV			0.4			
roofs						
average			4.4			
median			3.5			
min			2.0			
max			9.5			
COV			0.7			

*Insufficient data (all not detected) for triclosan; trimethoprim and ibuprofen have too few data to plot





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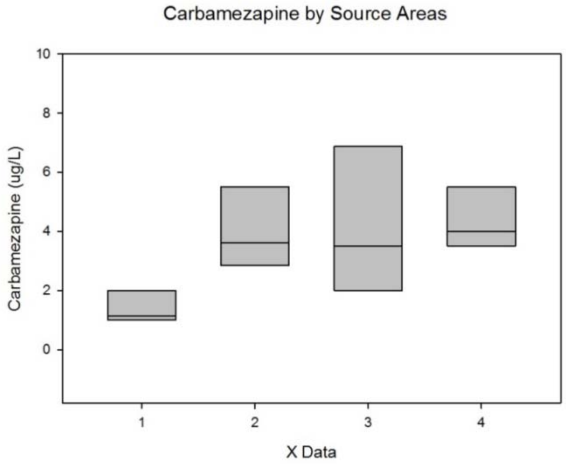


Carbamazepine by source area (1: landscaped areas, 2: paved areas; 3: roof runoff; 4 institutional combined flow)

Figure 4-72. Significant groupings of sulfamethoxazole and carbamazepine in stormwater sheetflows.

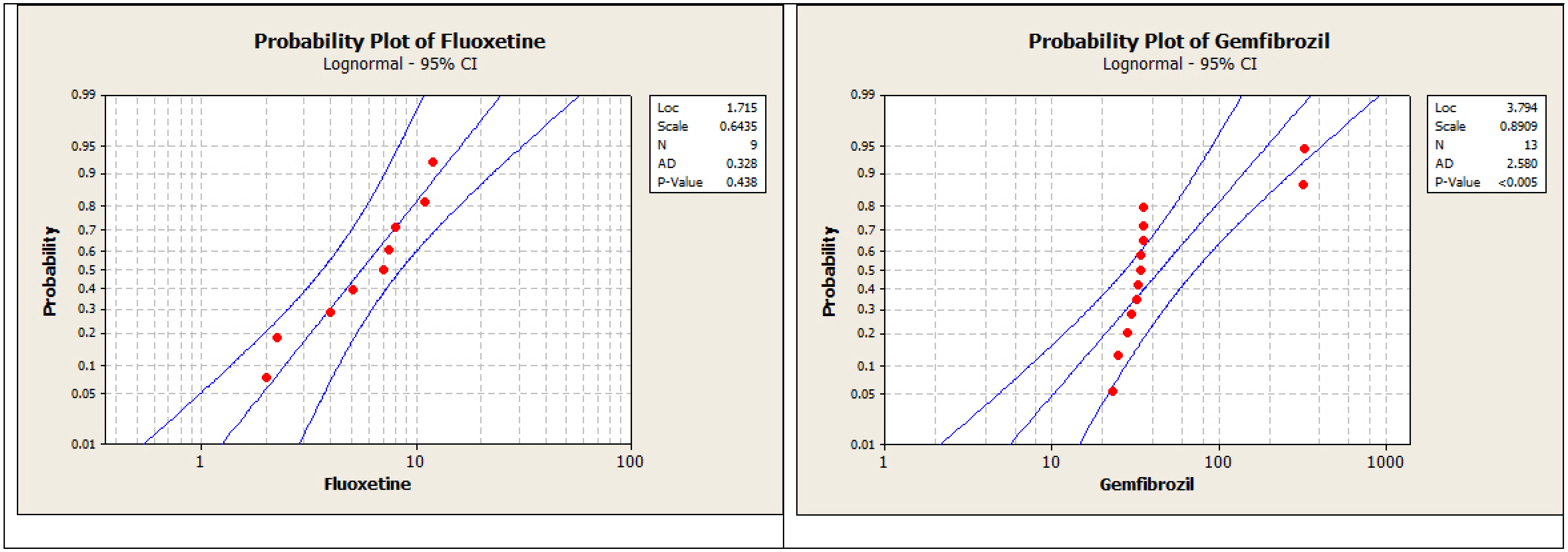


Figure 4-73. Significant groupings of fluoxetine and gemfibrozil in stormwater sheetflows.

Polycyclic Aromatic Hydrocarbons (PAHs) in Stormwater Sheetflows

Table 4-83 and Figure 4-74 show the summary of the PAH data, as contained in Appendix G. Summaries and plots are shown for naphthalene (detected in 64% of the sheetflow samples), phenanthrene (detected in 29% of the sheetflow samples), and indeno(1,2,3-cd)anthracene (detected in 21% of the sheetflow samples). Anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(a,h)anthracene, and benzo(ghi)perylene were also included in the GC/MSD analyses for the PAHs, but were detected in less than 20% of the samples. The Kurskal-Wallis nonparametric ANOVA test did not identify any significant groupings by source area or land use, for the number of observed data available, for any of the PAHs. Naphthalene had the highest concentrations observed, with about half greater than 2 µg/L (maximum of about 9 µg/L), while phenanthrene and indeno(1,2,3-cd)anthracene were much lower (medians of about 0.3 µg/L and maximums of about 1 µg/L). These are generally low PAH concentrations compared to prior research findings (such as Pitt, *et al.* 1999) that have indicated typical values in the range of 1 to 10 µg/L for a longer list of PAH constituents. The probability plots (and associated Anderson-Darling test statistics) also indicated general agreement with log-normal statistical distributions of the observed PAH concentrations (phenanthrene was more irregular than the other two).

Table 4-83. Significant Groupings of Polycyclic Aromatic Hydrocarbons (PAHs) in Stormwater Sheetflows*

	Naphthalene	Phenanthrene	Indeno(1,2,3-cd)anthracene
% detected	64	29	21
categories	overall	overall	overall
summary statistics for observed values:			
overall			
average	2.4	0.5	0.4
median	1.7	0.3	0.3
min	0.2	0.3	0.2
max	8.7	1.1	1.0
COV	1.0	0.7	0.7

*Insufficient data (<20% detected) for anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(a,h)anthracene, and benzo(ghi)perylene

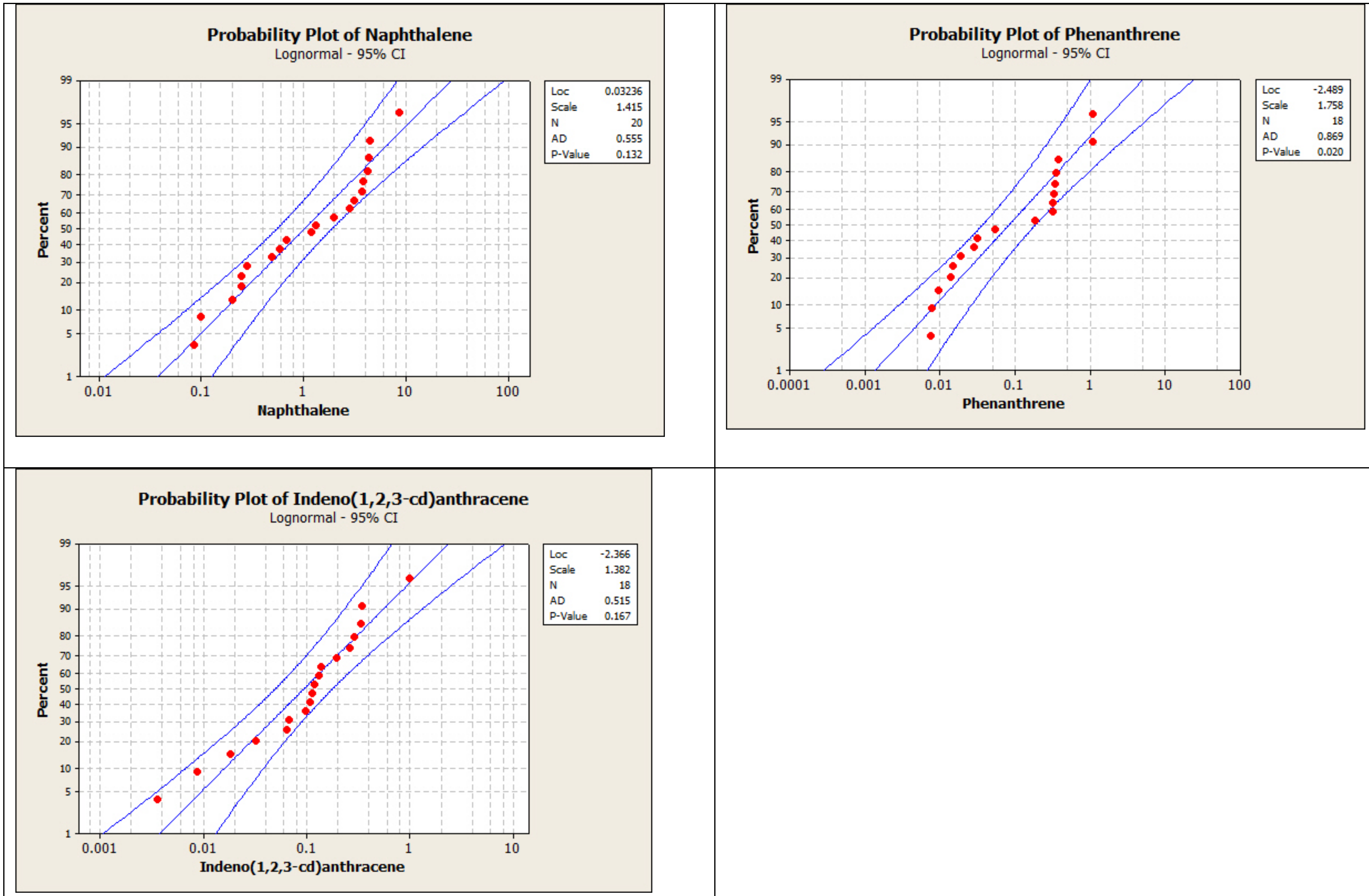


Figure 4-74. Significant groupings of naphthalene, phenanthrene, and indeno(1,2,3-cd)anthracene in stormwater sheetflows.

Heavy Metals in Stormwater Sheetflows

Tables 4-84 and 4-85, along with Figures 4-75 through 4-78 summarize the data presented in Appendix G for heavy metals observed in stormwater sheetflows. Table 4-84 lists all of the metals that were analyzed for the approximately 30 samples, showing the detection limits (5 µg/L for all metals except for iron which was 10 µg/L, using a graphite furnace atomic adsorption spectrophotometer at Stillbrook Environmental Laboratory), the percent of the samples greater than the detection limit, the average and maximum observed concentrations, and the coefficient of variation (the ratio of the standard deviation to the average). No samples had detected cadmium (total or filtered), filtered chromium, and filtered lead, while less than 20 percent of the samples had detected total chromium, total lead, and total and filtered nickel. The filtered copper concentrations were generally equal to, or greater, than the reported total copper concentrations. Therefore, the values shown on the table for total copper are the reported larger filtered values (usually considered to be more reliable in this type of situation as filtering the samples removes possible interfering constituents). It is assumed that the percentage filtered copper was therefore 100% of the copper observed. The average filtered percentages of the observed metals were:

Chromium: 0% filtered (few samples had chromium detected)
Lead: 0 % filtered (few samples had lead detected)
Copper: 100% filtered
Zinc: 57% filtered
Aluminum: 52% filtered
Iron: 75% filtered

Table 4-84. Summary of All Monitored Metals in Stormwater Sheetflows

	Detection limit (µg/L)	No. of samples	Percent greater than detection limit	Average (µg/L)	Maximum (µg/L)	COV
Filtered Cadmium	5	28	0	0	0	n/a
Total Cadmium	5	29	0	0	0	n/a
Filtered Chromium	5	28	0	0	0	n/a
Total Chromium	5	29	14	1	18	3.0
Filtered Lead	5	28	0	0	0	n/a
Total Lead	5	29	17	4	48	2.7
Filtered Copper	5	28	68	10	54	1.3
Total Copper	5	29	34	5	43	1.9
Filtered Nickel	5	28	7	1	11	3.9
Total Nickel	5	29	10	1	7	3.0
Filtered Zinc	5	28	79	21	185	1.8
Total Zinc	5	29	90	46	350	1.6
Filtered Aluminum	5	28	100	100	1180	2.2
Total Aluminum	5	29	100	804	4380	1.6
Filtered Iron	10	28	89	145	670	1.1
Total Iron	10	29	83	739	5320	1.9

Table 4-85 shows the values for total and filtered concentrations for the metals having sufficient samples for statistical analyses, along with the particulate strengths (the particulate form of the metal: total minus filtered concentration/TSS concentration). The Kurskal-Wallis non-parametric ANOVA tests indicated the following metal forms that had significant groupings by either source area or land use:

Total aluminum ($p<0.001$) for source areas
Total zinc ($p = 0.012$) for land uses
Filtered zinc ($p = 0.007$) for land uses
Total iron ($p = <0.001$) for source areas
Filtered iron ($p = 0.013$) for source areas

Figures 4-75 show the plots showing the groupings for total aluminum, indicating the highest concentrations for landscaped area runoff (median of about 2,100 µg/L), and the lowest concentrations in the roof runoff (median concentrations of about 15 µg/L), with intermediate concentrations with the paved area and the combined flows from the institutional area (median concentrations of about 210 µg/L). The probability plot for the total aluminum source areas also shows these separations, with little overlap. Almost all of these distributions fit a log-normal statistical distribution.

Figure 4-76 is the probability plot for total copper, which did not indicate any significant groupings by source area or land use. The distribution is also seen to fit a log-normal statistical distribution, with a median concentration of about 12 µg/L.

Figure 4-77 are plots for iron, indicating the groupings for both total and filtered iron for different source areas. It appears that the total and filtered iron concentrations in the roof runoff (median concentrations of about 40 µg/L) is significantly less than in the similar landscaped area (1,100 and 175 µg/L) and paved area (120 and 90 µg/L) categories. The probability distributions also fit log-normal statistical distributions.

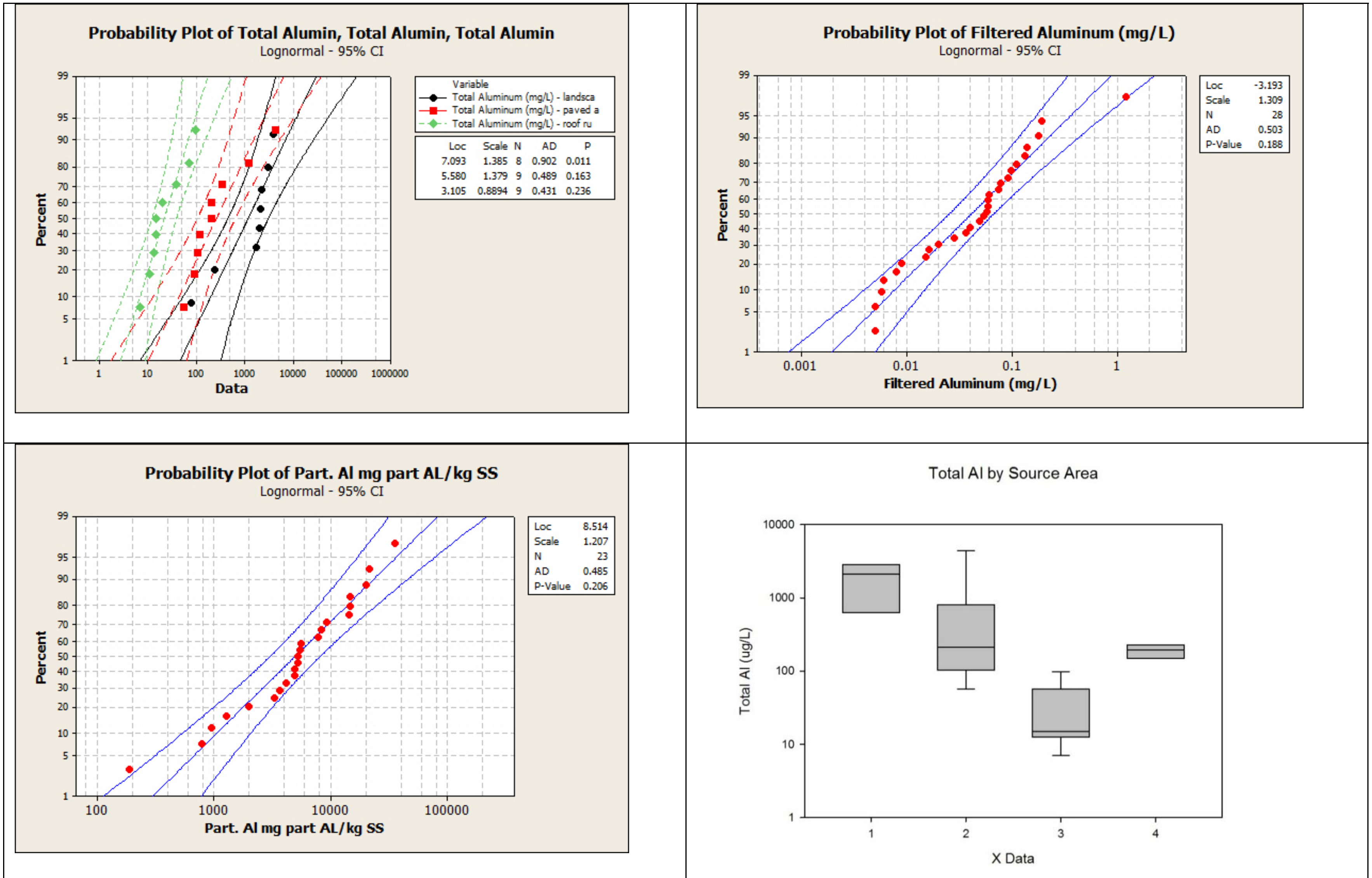
Figure 4-78 shows the land use groupings for total and filtered zinc. The commercial areas are shown to have significantly higher concentrations (140 and 41 µg/L for total and filtered zinc) compared to the institutional (20 and 12 µg/L) and residential (19 and 9 µg/L) areas, apparently reflecting the greater use of galvanized metals in the commercial land use areas. The probability distributions also fit log-normal statistical distributions.

Table 4-85. Significant Groupings of Metals in Stormwater Sheetflows

	Total Aluminum (mg/L)	Filtered Aluminum (mg/L)	mg part AL/kg SS	Total Copper (mg/L) (all filtered Cu, no particulate Cu)	Total Zinc (mg/L)	Filtered Zinc (mg/L)	mg part Zn/kg SS	Total Iron (mg/L)	Filtered Iron (mg/L)	mg part Fe/kg SS
% detected	100	97	86	66	93	76	83	90	86	79
categories	source areas (p < 0.001)	overall	overall	overall	land use (p=0.012)	land use (p = 0.007)	overall	source areas (p < 0.001)	source areas (p = 0.013)	overall
summary statistics for observed values:										
overall										
average	806	96	7,770	17	51	27	1,387	838	163	4,418
median	148	53	5,246	12	19	14	109	145	90	543
min	7	0	0	5	7	5	0	20	20	0
max	4,380	1,180	35,600	54	350	185	11,600	5,320	670	20,000
COV	1.6	2.2	1.1	0.8	1.5	1.5	2.2	1.7	1.0	1.5
landscaped										
average	1,965							1,668	241	
median	2,090							1,120	175	
min	79							80	30	
max	4,080							4,030	670	
COV	0.7							0.9	0.9	
paved										
average	755							849	164	
median	211							120	90	
min	57							40	40	
max	4,380							5,320	400	
COV	1.9							2.0	0.7	
roofs										
average	33							45	50	
median	15							40	40	
min	7							20	20	
max	98							100	100	
COV	1.0							0.7	0.6	

Table 4-85. Significant Groupings of Metals in Stormwater Sheetflows (continued)

	Total Aluminum (mg/L)	Filtered Aluminum (mg/L)	mg part AL/kg SS	Total Copper (mg/L) (all filtered Cu, no particulate Cu)	Total Zinc (mg/L)	Filtered Zinc (mg/L)	mg part Zn/kg SS	Total Iron (mg/L)	Filtered Iron (mg/L)	mg part Fe/kg SS
summary statistics for observed values:										
commercial										
average					148	64				
median					140	41				
min					16	14				
max					350	185				
COV					0.8	1.0				
institutional										
average					27	14				
median					20	12				
min					7	6				
max					77	31				
COV					0.9	0.6				
residential										
average					17	10				
median					19	9				
min					7	5				
max					34	17				
COV					0.5	0.4				



Total aluminum by source area (1: landscaped areas, 2: paved areas; 3: roof runoff; 4 institutional combined flow)

Figure 4-75. Significant groupings of aluminum in stormwater sheetflows.

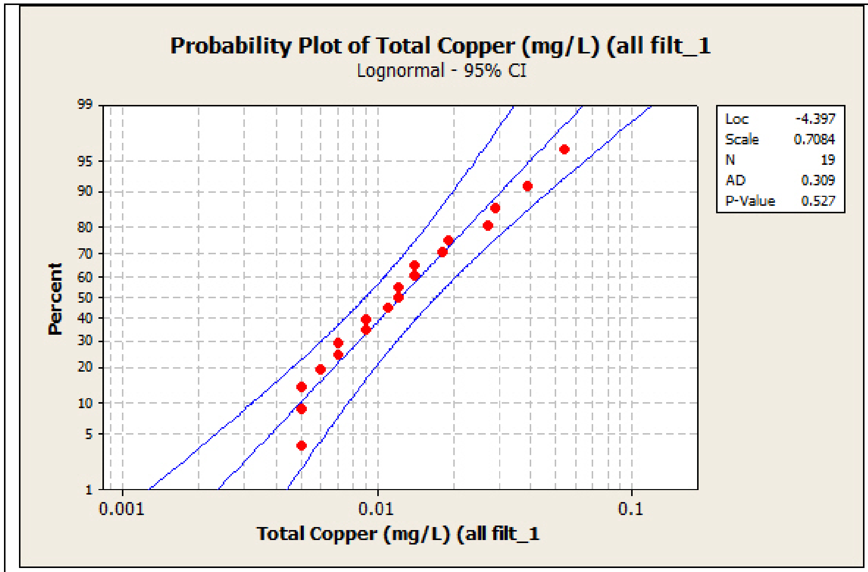
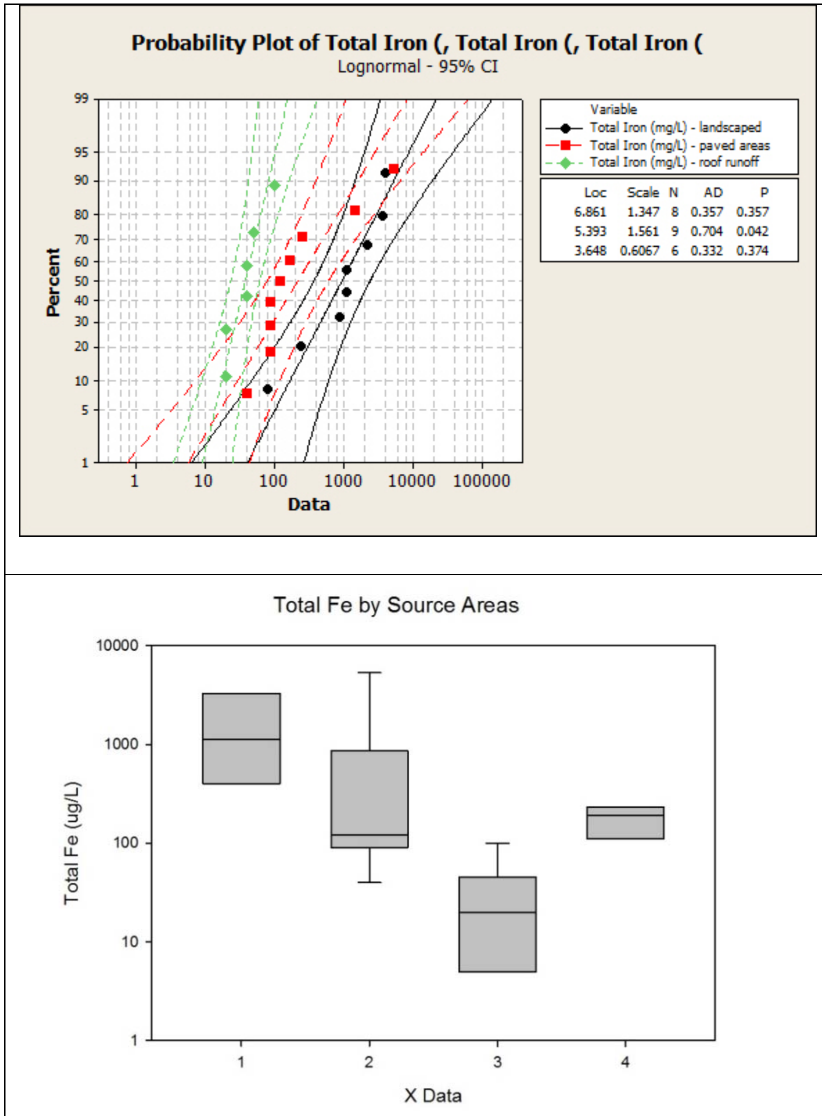
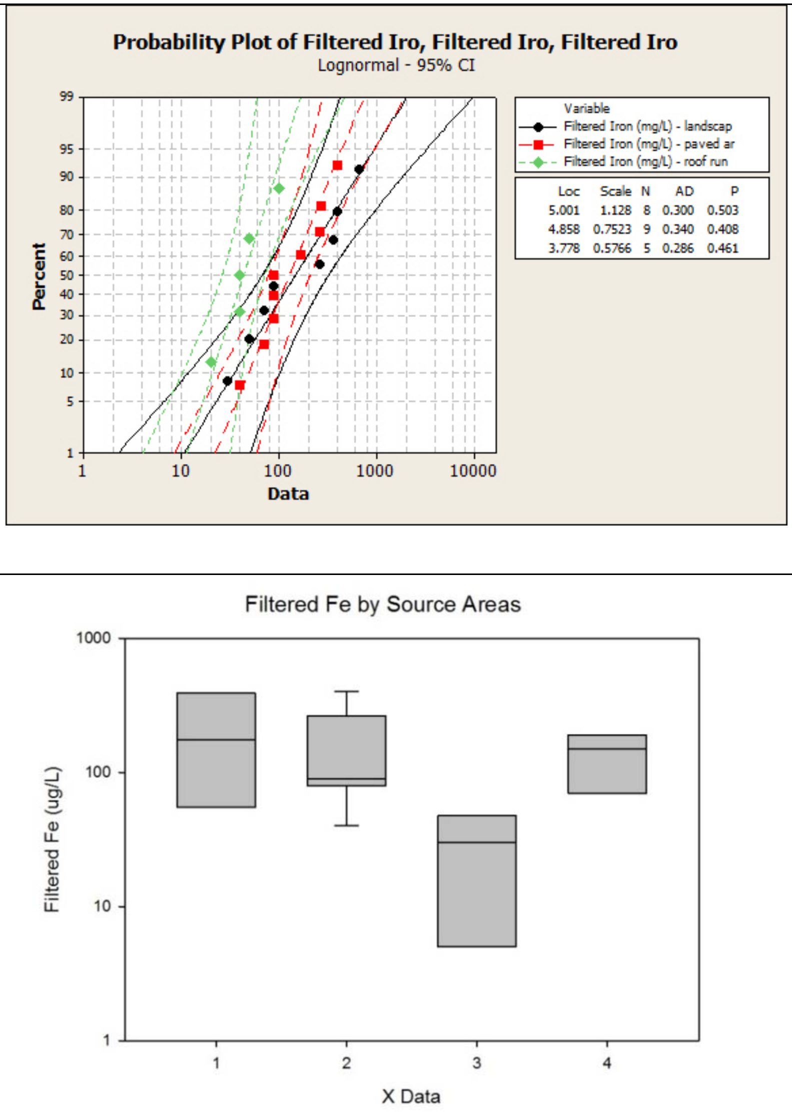


Figure 4-76. Significant groupings of copper in stormwater sheetflows.



Total iron by source area (1: landscaped areas, 2: paved areas; 3: roof runoff; 4 institutional combined flow)



Filtered iron by source area (1: landscaped areas, 2: paved areas; 3: roof runoff; 4 institutional combined flow)

Figure 4-77. Significant groupings of iron in stormwater sheetflows.

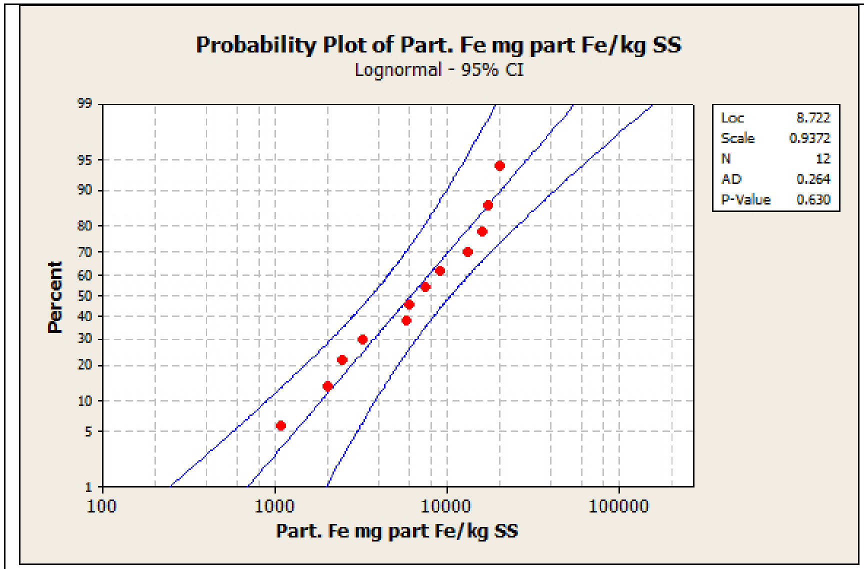
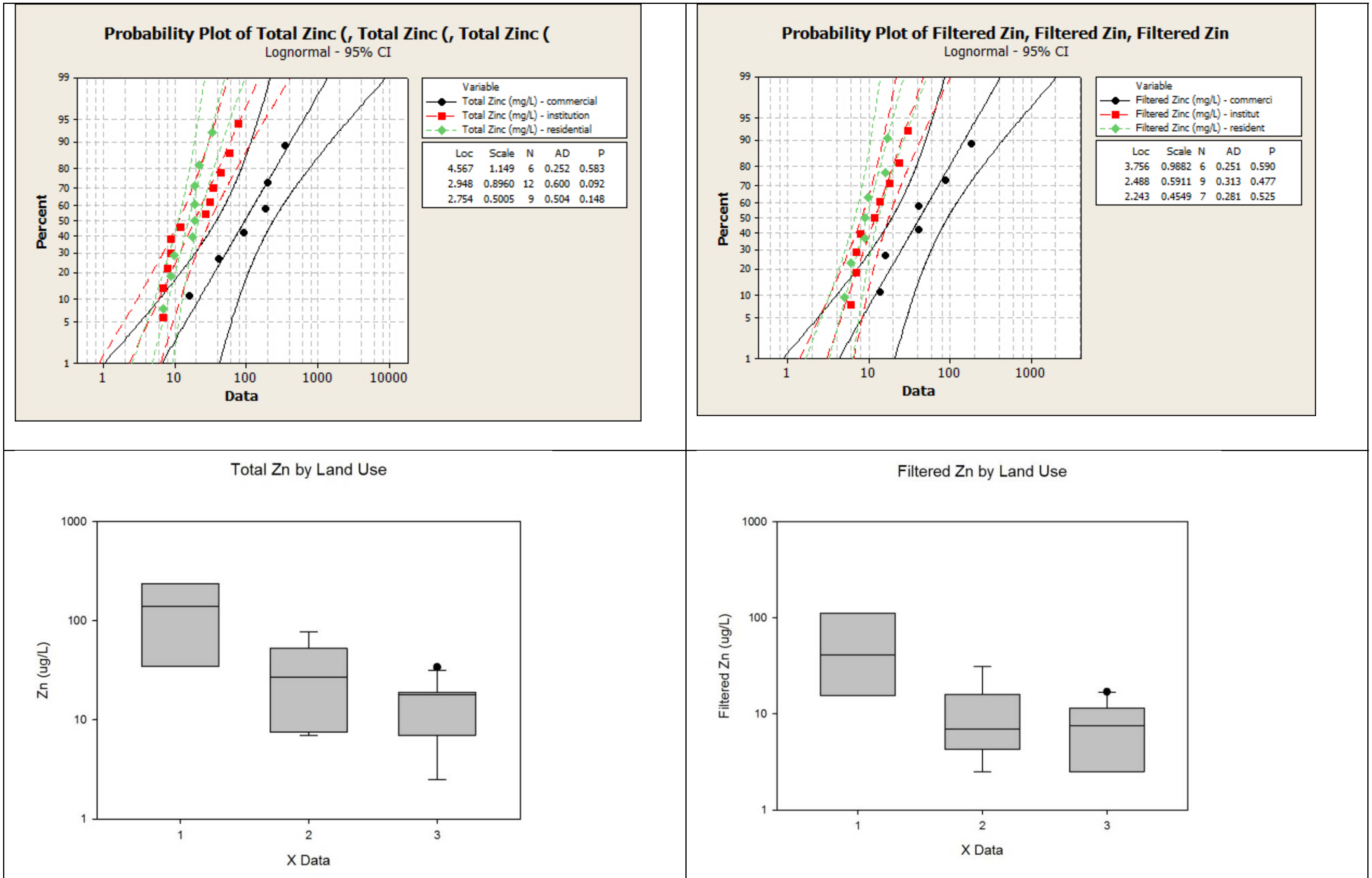


Figure 4-77. Significant groupings of iron in stormwater sheetflows (continued).



Loc	Scale	N	AD	P
4.567	1.149	6	0.252	0.583
2.948	0.8960	12	0.600	0.092
2.754	0.5005	9	0.504	0.148

Loc	Scale	N	AD	P
3.756	0.9882	6	0.251	0.590
2.488	0.5911	9	0.313	0.477
2.243	0.4549	7	0.281	0.525

Total zinc by land use (1: commercial, 2: institutional; 3: residential)

Filtered zinc by land use (1: commercial, 2: institutional; 3: residential)

Figure 4-78. Significant groupings of zinc in stormwater sheetflows.

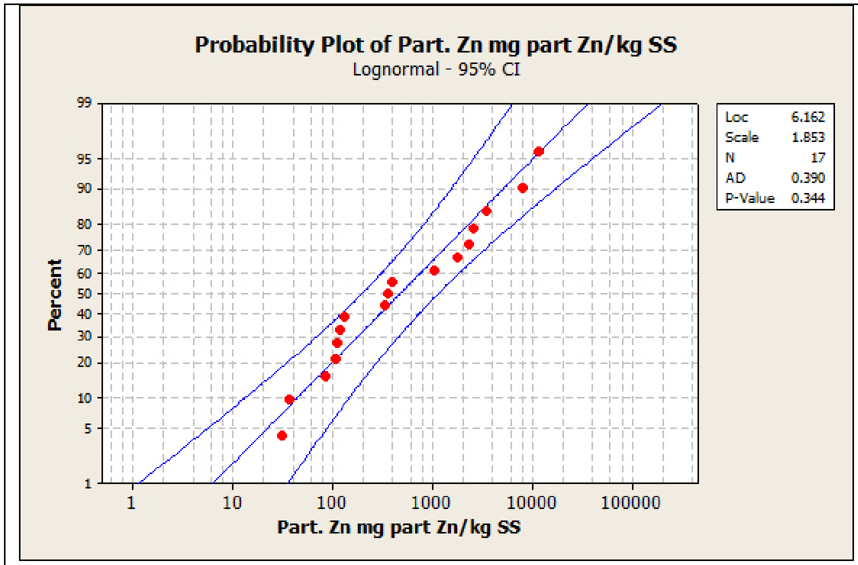


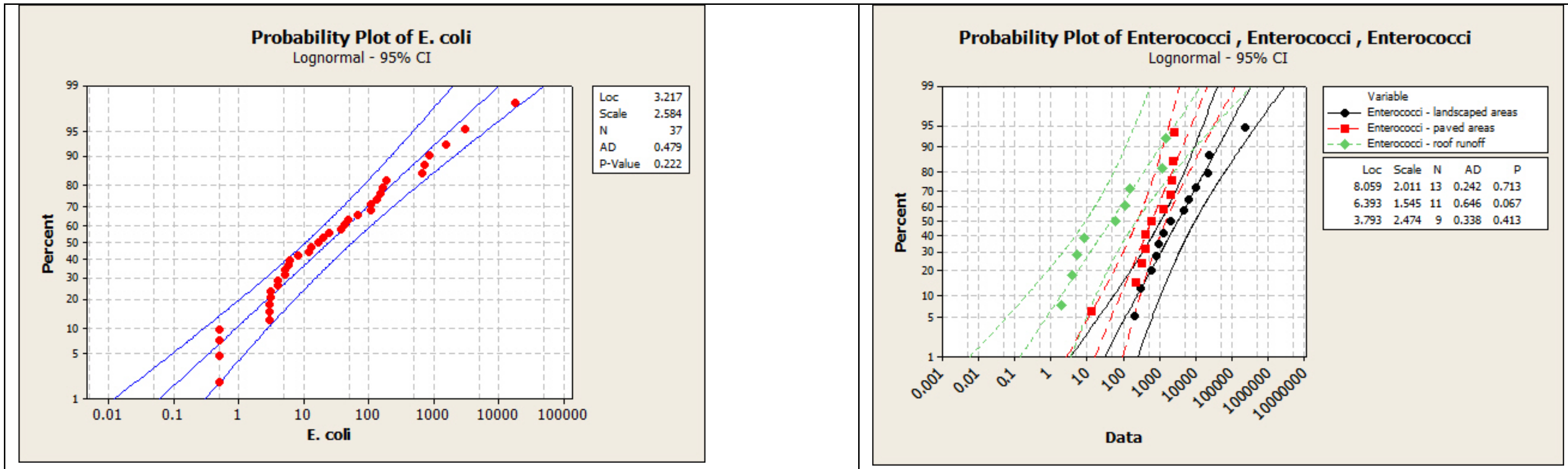
Figure 4-78. Significant groupings of zinc in stormwater sheetflows (continued).

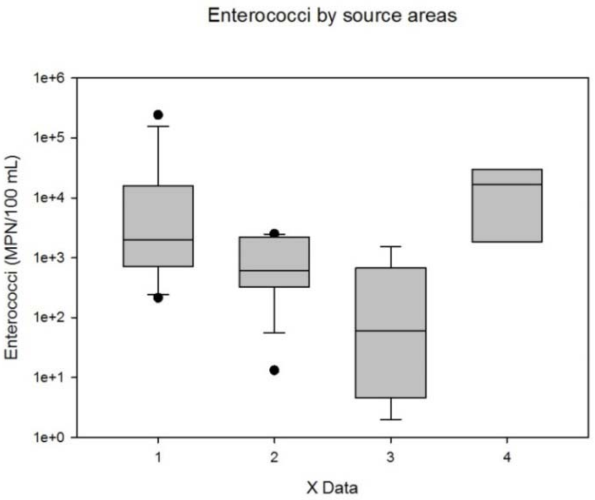
Bacteria in Stormwater Sheetflows

Figure 4-79 shows the probability distribution plots for the bacteria analyses. Enterococci results are shown to have at least one significantly different source area compared to the others. The roof runoff (median 60 MPN/100 mL) samples appear to have significantly lower counts compared to the highest levels from the landscaped area (median of about 2,000 MPN/100 mL) samples, while the paved area (median of about 600 MPN/100 mL) samples had intermediate levels (but close to the landscaped area samples). The probability distributions also fit log-normal statistical distributions. The *E. coli* sheetflow values are much lower than typically observed for stormwater, with a median of only 17 MPN/100 mL, but with an observed maximum of about 18,000 MPN/100 mL).

Table 4-86. Significant Groupings of Bacteria in Stormwater Sheetflows

	E. coli	Enterococci
% detected	100	100
categories	overall	source areas (p = 0.001)
summary statistics for observed values:		
overall		
average	715	10,690
median	17	1,046
min	1	2
max	18,350	241,960
COV	4.2	3.7
landscaped		
average		24,255
median		1,986
min		214
max		241,960
COV		2.7
paved		
average		1,128
median		613
min		13
max		2,500
COV		0.9
roofs		
average		343
median		60
min		2
max		1,533
COV		1.7





Enterococci by source area (1: landscaped areas, 2: paved areas; 3: roof runoff; 4 institutional combined flow)

Figure 4-79. Significant groupings of bacteria in stormwater sheetflows.

Toxicity Screening in Stormwater Sheetflow Samples

Toxicity tests were conducted on the sheetflow samples using a Microtox analyzer that measures the fluorescence of the sample containing a phosfluorescent bacteria test organism. Most of these samples actually had an increase in fluorescent activity with exposure to the sample, with only a very few indicating barely moderate toxicity (up to 30 to 33% light decrease).

Table 4-87. Significant Groupings of Toxicity Screening in Stormwater Sheetflows

	15 minutes exposure	25 minutes exposure	45 minutes exposure
% detected	100%	100%	100%
categories	overall	overall	overall
summary statistics for observed values:			
overall			
average	-8.4	-10.4	-8.3
median	-7.1	-13.5	-10.2
min	-32.4	-27.7	-36.4
max	30.6	33.1	33.1
COV	-1.6	-1.5	-2.4

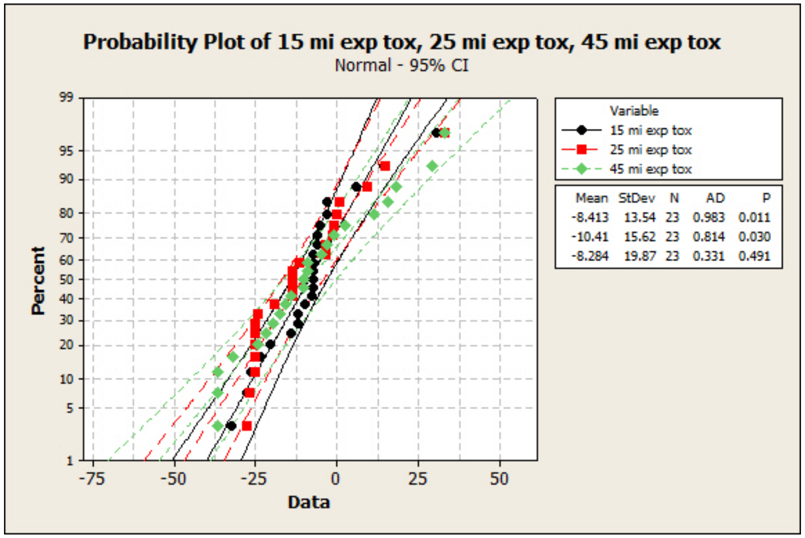


Figure 4-80. Significant groupings of toxicity indicators in stormwater sheetflows.

Particulates in Stormwater Sheetflows

Table 4-88 and Figures 4-81 through 4-84 summarize the particulate analytical results that are shown in Appendix G. The Kurskal-Wallis nonparametric ANOVA tests indicated that at least one source area subgroup was significantly different from the others for total solids, TSS, and SSC. TDS did not indicate any differences between the source area groups for the number of samples available. From the box and whisker and probability distribution plots, it is apparent that the landscaped areas generate much more sediment than the paved areas or roof runoff. The median TSS concentration in the landscaped runoff was about 300 mg/L, while the paved area median TSS was about 18 mg/L and the roof runoff median TSS was about 3 mg/L. The SSC concentrations were slightly higher than the TSS values and showed the same pattern, as did the total solids values. The TDS were not separated statistically by source area and had a median value of about 23 mg/L.

Table 4-88. Significant Groupings of Particulates in Stormwater Sheetflows

	TDS	TS	SSC	TSS (0.45 - 250)
% detected	100%	100%	100%	100%
categories	overall	source area (p = 0.036)	source area (p = 0.002)	source area (p = 0.028)
summary statistics for observed values:				
overall				
average	58	271	214	108
median	23	136	41	18
min	3	3	3	2
max	312	1,125	813	568
COV	1.3	1.2	1.4	1.6
landscaped				
average		532	442	286
median		619	512	309
min		120	50	46
max		1,125	813	568
COV		0.7	0.7	0.8
paved				
average		121	121	55
median		20	20	18
min		3	3	2
max		757	757	296
COV		2.1	2.1	1.8
roofs				
average		137	118	7
median		33	5	3
min		3	3	3
max		489	489	32
COV		1.5	1.7	1.4

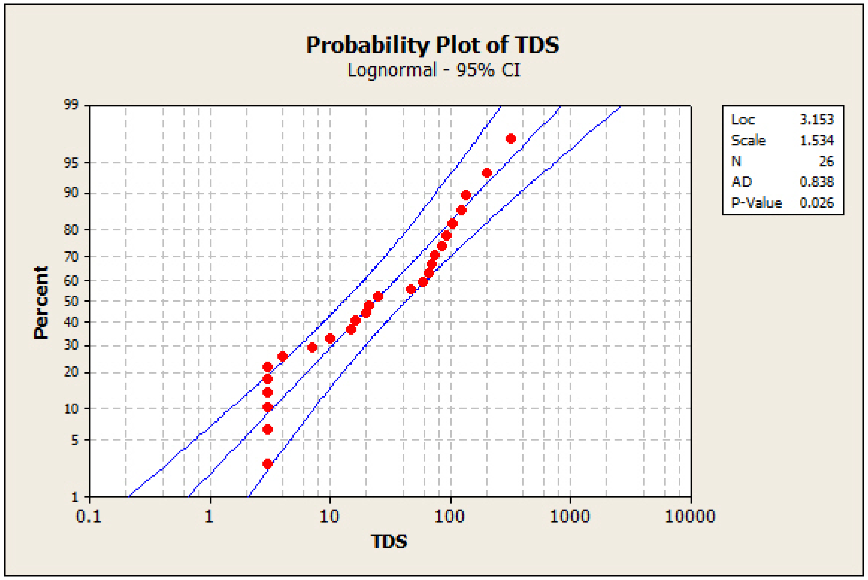
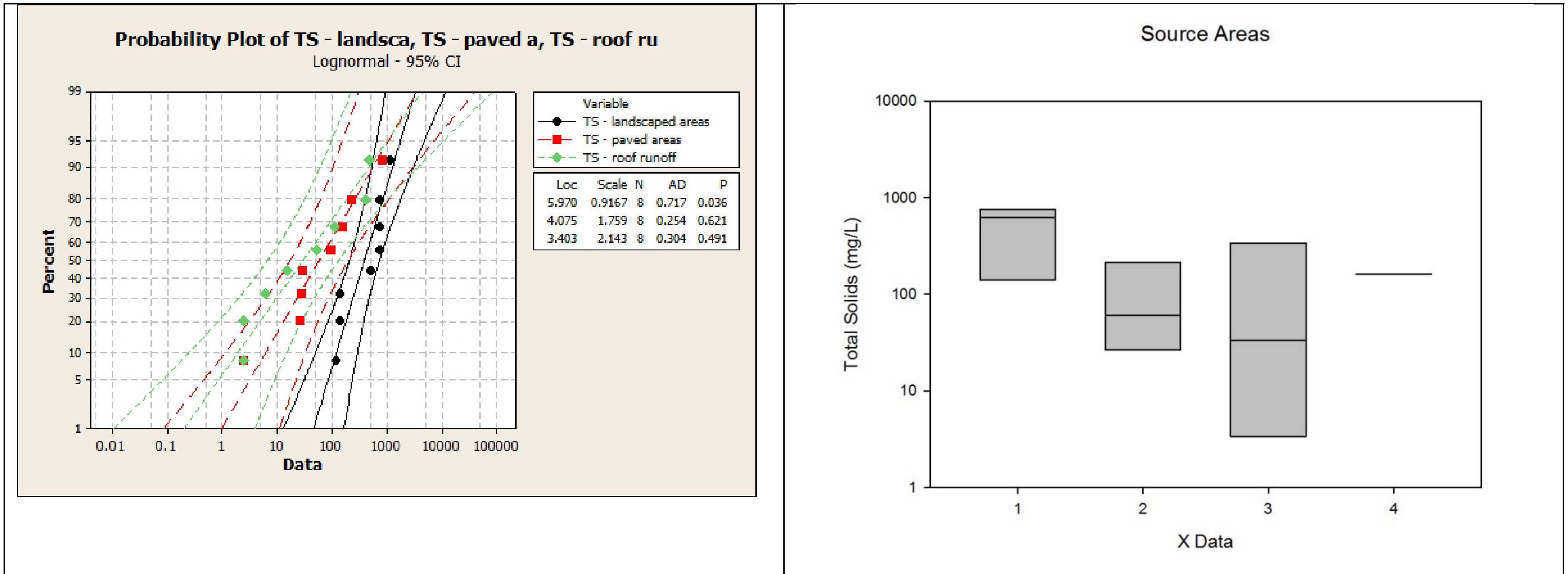
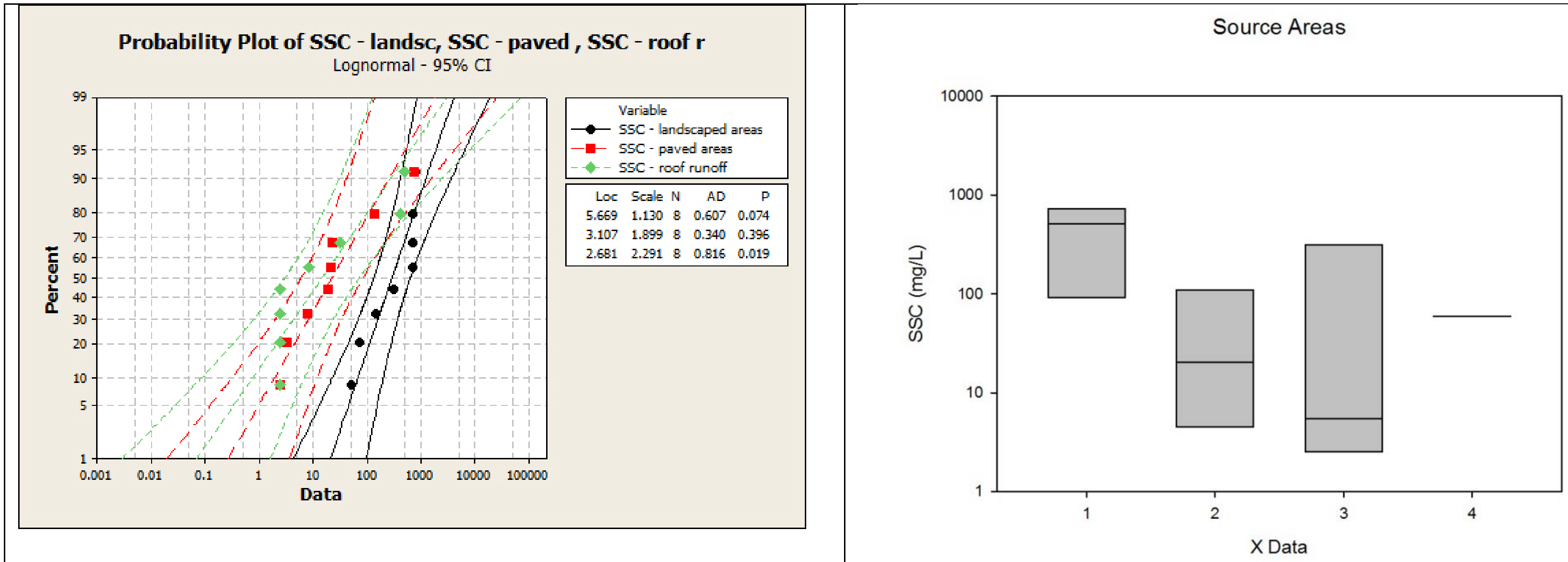


Figure 4-81. Significant groupings of total dissolved solids (TDS) in stormwater sheetflows.



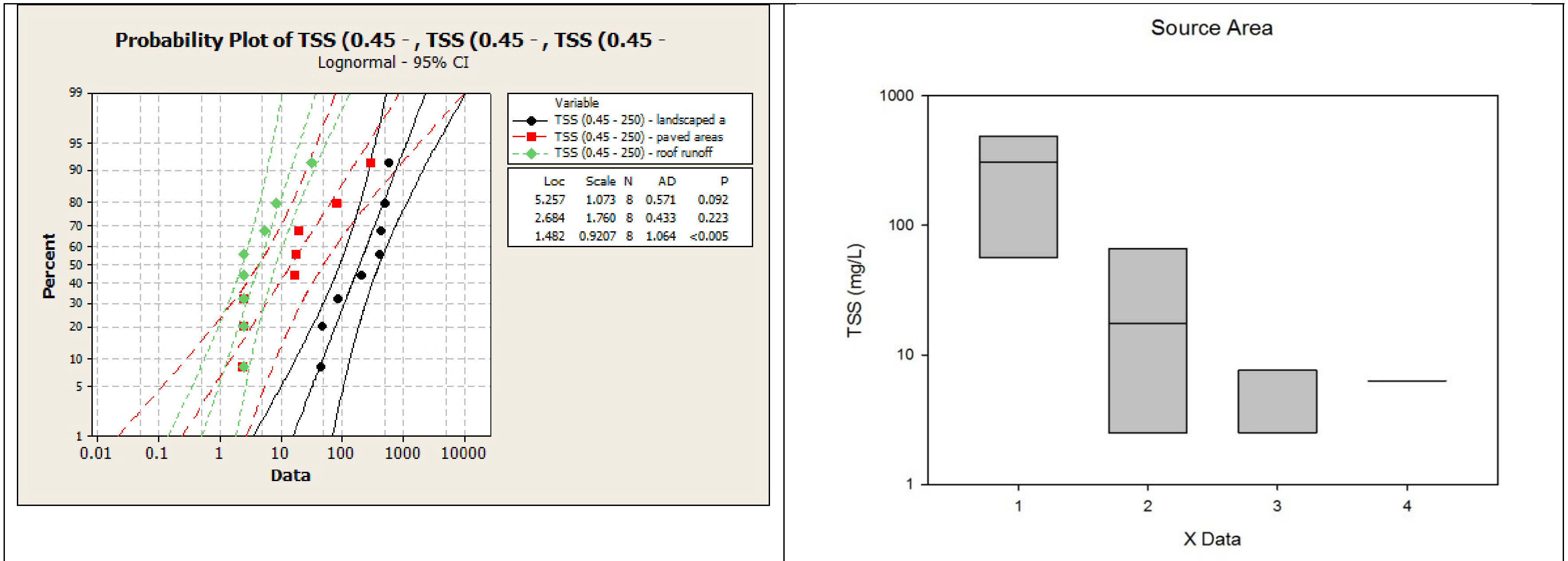
Total solids by source area (1: landscaped areas, 2: paved areas; 3: roof runoff; 4 institutional combined flow)

Figure 4-82. Significant groupings of total solids in stormwater sheetflows.



Suspended solids concentration (SSC) by source area (1: landscaped areas, 2: paved areas; 3: roof runoff; 4 institutional combined flow)

Figure 4-83. Significant groupings of suspended solids concentrations (SSC) in stormwater sheetflows.



Loc	Scale	N	AD	P
5.257	1.073	8	0.571	0.092
2.684	1.760	8	0.433	0.223
1.482	0.9207	8	1.064	<0.005

Total suspended solids (TSS) by source area (1: landscaped areas, 2: paved areas; 3: roof runoff; 4 institutional combined flow)

Figure 4-84. Significant groupings of total suspended solids (TSS) in stormwater sheetflows.

Pesticides and Other Semi-Volatile Organics in Stormwater Sheetflows

EPA Method 525 was used to analyze samples for pesticides and other semi-volatile compounds (ALS Environmental, Middletown, PA). Table 4-89 lists the compounds investigated with this method, showing the pesticides, selected PAHs and various other semi-volatile compounds (mainly plasticizers). The detection limits for the pesticides were mostly 0.5 or 1.0 µg/L, which is relatively high. As shown on Table 4-90, most of the detections were for the other semi-volatiles related to phthalates, a very common plasticizer found in many materials (including roofing compounds and membranes). Some of the street and other pavement runoff samples had detected PAHs in addition to the phthalates, all at concentrations <15 µg/L. The roof runoff samples only had phthalate related compounds detected. The outfall samples with detected compounds were also mostly phthalate compounds, along with one PAH at a very low concentration (phenanthrene). Only one sample (a commercial pavement runoff sample) had detectable pesticides.

Table 4-89. Pesticides and Other Semi-Volatile Compounds Analyzed in Sheetflows and Detection Limits

	Detection Limit (µg/L)
Pesticides:	
4,4'-DDE	1.0
Acetochlor	1.0
Aldrin	1.0
Atrazine	1.0
Butachlor	1.0
Dibenzofuran	0.5
Dieldrin	1.0
Endrin	1.0
EPTC	1.0
gamma-BHC	0.5
Heptachlor Epoxide	0.5
Heptachlor	0.5
Hexachlorocyclopentadiene	1.0
Methoxychlor	1.0
Metolachlor	1.0
Metribuzin	1.0
Molinate	1.0
Propachlor	1.0
Simazine	1.0
Terbacil	2.5

Table 4-89. Pesticides and Other Semi-Volatile Compounds Analyzed in Sheetflows and Detection Limits (continued)

PAHs:	
2-Methylnaphthalene	1.0
2,4,5-Trichlorobiphenyl	0.5
Acenaphthene	0.5
Acenaphthylene	0.5
Anthracene	0.5
Benzo(a)anthracene	0.5
Benzo(a)pyrene	0.5
Benzo(b)fluoranthene	0.5
Benzo(g,h,i)perylene	0.5
Benzo(k)fluoranthene	0.5
Chrysene	0.5
Dibenzo(a,h)anthracene	0.5
Fluoranthene	0.5
Fluorene	0.5
Hexachlorobenzene	0.5
Indeno(1,2,3-cd)pyrene	0.5
Naphthalene	1.0
Phenanthrene	0.5
Pyrene	0.5
Other semivolatile compounds:	
2,4-Dinitrotoluene	2.5
2,6-Dinitrotoluene	2.5
bis(2-Ethylhexyl)phthalate	5.0
Butylbenzylphthalate	2.5
Di(2-Ethylhexyl)adipate	2.5
Diethylphthalate	5.0
Dimethylphthalate	2.5
Di-n-Butylphthalate	2.5

Table 4-90. Significant Groupings of Pesticides and Other Semi-Volatile Organics in Stormwater Sheetflows*

Landscaped Areas	**Date**	**Analytical results (µg/L)**
Resid landscape	11/16/2010	all ND
Galleria grass	6/28/2011	all ND
BamaBelle landscaped	1/26/2012	Butylbenzophthalate 4.9
Galleria landscaped	3/22/2012	Di-n-butylphthalate 6.2
Academy Dr. landscaped	10/14/2012	Di-n-butylphthalate 4.9
Academy Dr. grass	9/20/2011	Di-n-butylphthalate 3.6
Streets and Pavement	**Date**	**Analytical results (µg/L)**
Resid. Street	11/16/2010	all ND
Galleria pavement	6/22/2011	Anthracene 1.7 Atrazine 1.1 Benzo(a)pyrene 2.4 Benzo(b)fluoranthene 4.5 Benzo(g,h,i)perylene 2.1 Benzo(k)fluoranthene 1.2 Chrysene 2.7 bis(2-Ethylhexyl)phthalate 11.1 Fluoranthene 4.4 Indeno(1,2,3-cd)pyrene 2.4 Indeno(1,2,3-cd)pyrene 2.4 Pyrene 3.7
BamaBelle pavement	6/28/2011	all ND
Academy Drive	6/28/2011	all ND
BamaBelle pavement	1/26/2012	Di-n-butylphthalate 6.2 Di(2-Ethyxl)adipate 3.7
Academy Dr. pavement	9/20/2011	Butylbenzophthalate 6.8 Di-n-butylphthalate 13.7 Di(2-Ethyxl)adipate 10.9 Phenanthrene 0.68
Galleria paved	3/22/2012	Di-n-butylphthalate 8.0 Fluoranthene 0.95 Phenanthrene 0.79 Pyrene 1.3
Academy Dr. paved	9/30/2012	Butylbenzophthalate 7.7

Table 4-90. Significant Groupings of Pesticides and Other Semi-Volatile Organics in Stormwater Sheetflows* (continued)

Roof Runoff	**Date**	**Analytical results (µg/L)**
Resid. Roof	11/16/2010	all ND
Galleria Roof	6/22/2011	all ND
BamaBelle roof	6/28/2011	all ND
Academy Dr. roof	6/28/2011	all ND
BamaBelle roof	1/26/2012	Di-n-butylphthalate 3.6 Di(2-Ethyxl)adipate 2.9
Academy Dr. roof	9/20/2011	Butylbenzophthalate 2.9 Di-n-butylphthalate 5.7 Di(2-Ethyxl)adipate 4.9
Galleria roof	3/22/2012	Butylbenzophthalate 3.0
BamaBelle roof	8/17/2012	Butylbenzophthalate 11.5
Academy Dr. roof	9/30/2012	Di-n-butylphthalate 3.1
Outfall Samples	**Date**	**Analytical results (µg/L)**
BamaBelle outfall	6/28/2011	all ND
BamaBelle outfall	1/26/2012	all ND
BamaBelle	9/5/2011	Butylbenzophthalate 4.9 Di-n-butylphthalate 10.4 Di(2-Ethyxl)adipate 8.1 Bis(2-Ethylhexyl)phthalate 6.3
BamaBelle outfall	8/17/2012	Butylbenzophthalate 5.3 Di-n-butylphthalate 12.2 Di(2-Ethyxl)adipate 8.1 Phenanthrene 0.51

* all of the surrogate recoveries of the internal standards (1,3-Dimethyl-2-Nirtobenzene; Perylene-d12; Triphenylphosphate; and Pyrene-d10) had recoveries within the acceptable range of 70 – 130%. These internal standards were analyzed for each sample.

Summary of Occurrences and Characteristics of Emerging Contaminants in Wet Weather Flows

This report section contains information concerning characteristics (mainly concentrations and frequency of observations) of emerging contaminants examined in wet weather flows during this research. Literature information supplements the new data. The major subsections address pharmaceuticals and personal care products (PPCP), PAHs, pesticides, trace heavy metals, and indicator bacteria features of special interest in wet weather flows. The information in these two sections was supplemented by outcomes from parallel research projects (mainly supported by Alabama NSF – EPSCoR) which focused on characterization and treatment of toxicants associated with natural disasters, along with sources and fates of these materials.

Pharmaceuticals and Personal Care Products, Pesticides, and PAHs in Wet Weather Flows

Many of the publications during the last two decades have reported the occurrences of pharmaceuticals and personal care products in a wide variety of waters. Most of these included municipal wastewater treatment influents and effluents, rivers, other surface waters, and drinking waters. However, very little information is available addressing these compounds in wet weather flows. Stormwater I&I can have a significant effect on wastewater treatment flows (and pollutant concentrations) and may in turn potentially affect treatment of wastewater pollutants. As an example, PAHs are more likely associated with stormwater in urban areas than in separate sanitary wastewater. Increases of PAHs in wastewater influent during wet weather suggest stormwater is entering the sewer system. Pesticides are also of interest for this study and are known pollutants associated with stormwater. Some pharmaceuticals have dual roles in both human and veterinary medicine. While many would enter the sanitary sewage system from human wastes, pet pharmaceuticals could enter the system through stormwater contaminated by fecal matter from treated animals.

Samples were collected during a range of flow and rain conditions to understand whether stormwater contributes ECs to the treatment plant. I&I are not likely significant until the daily rain depth is greater than about one-half inch, when the treatment plant flow can increase to greater than about 20 MGD. During the largest rain depth observed (2.67 inches), the treatment plant flow was also the largest observed (42.2 MGD). Mass loads were calculated based on the measured daily flow rates and the influent concentrations. The mass loads for the dry weather days were compared to the wet weather day mass loads. The differences were then related to the rain depth observed for the day to determine if stormwater contribute to the EC discharges to the treatment plant. Eight dry weather samples were taken in addition to nine wet weather samples at four locations at the treatment facility. Some of the constituents did not have values for some of the sample dates and in a few instances, insufficient sample volumes were available to complete the full suite of analyses.

There are few obvious sources of PPCPs in wet weather flows (beyond some associated with veterinarian drugs). However, regression analyses of influent concentrations vs. treatment plant flow rate indicated significant slope terms for all of the pharmaceutical compounds (increasing concentrations with increasing flow rates at the treatment facility, except for carbamazepine. Table 4-91 summarizes the observed concentrations during both low and high flow conditions, along with the overall observed range. In general, the average concentrations for peak flows were about double the dry weather period concentrations, although there was substantial variability.

Table 4-91. Dry and Wet Weather Pharmaceutical Concentrations at Tuscaloosa Wastewater Treatment Plant

	Average dry weather concentrations (at about 18 MGD at treatment plant)	Average wet weather concentrations (at about 40 MGD at treatment plant)
Gemfibrozil, µg/L	55	110
Ibuprofen, µg/L	35	60
Triclosan, µg/L	35	60
Carbamazepine, µg/L	8	15
Fluoxetine, µg/L	45	100
Sulfamethoxazole, µg/L	50	100
Trimethoprim, µg/L	12	25

The samples obtained at the influent at the Tuscaloosa Wastewater Treatment Plant were also analyzed for selected PAHs (Table 4-92). The PAH concentrations all had statistically significant increasing concentrations with increasing daily average flow rates (except for acenapthtylene), although there were generally wide variations in concentrations during dry weather. In general, the average concentrations for peak flows were also about double the dry weather period concentrations, although there was also substantial variability for the PAHs.

Table 4-92. Dry and Wet Weather PAH Concentrations at Tuscaloosa Wastewater Treatment Plant

	Average dry weather concentrations (at about 18 MGD at treatment plant)	Average wet weather concentrations (at about 40 MGD at treatment plant)
Naphthalene, µg/L	10	20
Acenaphthene, µg/L	6	12
Fluorene, µg/L	1	2
Fluoranthene, µg/L	0.8	2
Phenanthrene, µg/L	2	4
Anthracene, µg/L	1	2
Pyrene, µg/L	1	2

In summary, Table 4-93 shows the significant slope terms for the analyzed pharmaceuticals and PAHs, reflecting the increasing concentrations as the daily average wastewater treatment plant flow increased during different sized rains. These slope terms were used to calculate approximate influent concentrations for these increasing flows, and the loads, expressed as mg/km^2 for each rain category.

Table 4-93. Calculated Influent Mass Loadings for Pharmaceuticals during Different Sized Rain Events

Pharmaceutical compound	Slope term (µg/L/MGD)	Conc. (µg/L) during 0 to 0.5 inch rain (18 MGD; 1.5 hr duration)	Mass per event (mg/km^2)*	Conc. (µg/L) during 0.6 to 1.5 inch rain (23 MGD; 4 hr duration)	Mass per event (mg/km^2)*	Conc. (µg/L) during 1.6 to 2.5 inch rain (34 MGD; 12 hr duration)	Mass per event (mg /km^2)*
Gemfibrozil	2.81	51	1.1	65	4.9	96	32
Ibuprofen	1.85	33	0.74	43	3.2	63	21
Triclosan	1.86	34	0.74	43	3.2	63	21
Fluoxetine	2.44	44	0.97	56	4.2	83	28
Sulfamethoxazole	2.51	45	1.00	58	4.4	85	29
Trimethoprim	0.66	12	0.26	15	1.2	22	7.5

* 74 mi^2 (192 km^2) service area

Tables 4-94 and 4-95 summarize some of the reported influent pharmaceutical concentrations at wastewater treatment plants as reported in the literature compared to the concentrations observed at the influent at the Tuscaloosa wastewater treatment plant during this study. The gemfibrozil and ibuprofen values are within the range previously reported, but the triclosan, sulfamethoxazole, and trimethoprim observed concentrations seem larger than typically reported (ay about one order of magnitude). However, the laboratory QA/QC results, including frequent testing of standards and extraction efficiencies, indicated that the results are acceptable. Most of the methods used during the reported studies were advanced procedures that had very low detection limits, while our methods were more basic HPLC units, and we used specially developed solid-phase extraction methods for enhanced recoveries. Our detection limits were suitable, but relatively close to the observed values. Therefore, the pharmaceutical concentrations reported during this project may have greater uncertainly than many of the reported sources. However, the analyses of the treatment results reported in the next section show consistent results and expected behavior, with similar values for the influent and after primary treatment, and most of the removals occurring during the secondary treatment phase, resulting in much lower effluent concentrations. Some compounds did not show any significant removals, so the repeated results helped establish the analytical performance.

Table 4-94. Observed Influent Pharmaceutical Concentrations Compared to Reported Concentrations

Pharmaceutical compound	**Concentrations reported for influents at wastewater treatment plants (µg/L)**	**Influent concentrations observed during this study (average µg/L)**
Gemfibrozil	0.1 to 36	59
Ibuprofen	4 to 84	28
Triclosan	0.9 to 4	28
Sulfamethoxazole	0.05 to 1.5	38
Trimethoprim	0.05 to 1.5	9

The following table is a similar calculation of influent mass loadings for PAHs.

Table 4-95. Calculated Influent Mass Loadings for PAHs during Different Sized Rain Events

PAH compound	Slope term (µg/L/MGD)	Conc. (µg/L) during 0 to 0.5 inch rain (18 MGD)	Mass per event (mg/km^2)*	Conc. (µg/L) during 0.6 to 1.5 inch rain (23 MGD)	Mass per event (mg/km^2)*	Conc. (µg/L) during 1.6 to 2.5 inch rain (34 MGD)	Mass per event (mg/mi^2 and mg/km^2)*
Naphthalene	0.5	9.0	0.20	11.5	0.87	17.0	5.7
Acenaphthene	0.31	5.6	0.12	7.1	0.54	10.5	3.5
Fluorene	0.057	1.0	0.02	1.3	0.10	1.9	0.65
Fluoranthene	0.047	0.8	0.02	1.1	0.08	1.6	0.54
Phenanthrene	0.11	2.0	0.04	2.5	0.19	3.7	1.3
Anthracene	0.055	1.0	0.02	1.3	0.10	1.9	0.63
Pyrene	0.059	1.1	0.02	1.4	0.10	2.0	0.67

* 74 mi^2 (192 km^2) service area

Table 4-96 compares the observed influent PAH concentrations during this study with some reported PAH values from the literature. The concentrations reported in the wastewater literature are again much lower than observed during this research. During our prior PAH studies in wet weather flows (Pitt, et al. 1999, for example). We have commonly seen even higher PAH concentrations in separate stormwater. We suspect the main differences are associated with the extraction methods. The use of solid-phase extraction methods for PAHs in the presence of particulates results in very low recoveries, requiring multiple extractions using separation funnels instead. Most of the PAHs are strongly associated with particulates which are difficult to extract by some methods. For groundwater samples, where little of the PAHs are associated with particulates and the particulate content in the samples is very low, solid phase extraction can work well; for surface water samples (and wastewater samples), the particulate matter significantly interferes with PAH extractions using solid-phase extraction methods.

Table 4-96. Observed Influent PAH Concentrations Compared to Concentrations Reported in the Literature

PAH compound	**Concentrations reported for influents at wastewater treatment plants (range µg/L)**	**Influent concentrations observed during this study (average µg/L)**
Naphthalene	0.1 to 7	11
Acenaphthene	0.02 to 0.4	11
Fluorene	0.04 to 0.7	5
Fluoranthene	0.1 to 0.2	5
Phenanthrene	0.3 to 2	3
Anthracene	0.03 to 0.1	75
Pyrene	0.1 to 0.5	5

Trace Heavy Metal Sources in Wet Weather Flows

Stormwater runoff from roofs and pipes can be contaminated with high heavy metal concentrations. The dissolution of roofing and pipe material is affected by rainwater pH, and other factors. Acidic rainwater can dissolve the $CaCO_3$ content of cement roofs and drainage system, and metal ions from metal and plastic materials. These processes lead to weathering and degradation of the roofing and piping materials. Factors that affect material deterioration include the chemical composition of water and the time of contact with it. Many studies identified that the type of material influences heavy metal concentrations leaching into the water. Metal ions released from roofs are chiefly in the most bioavailable form, and therefore roof runoff can be a significant source of toxicity.

The greatest zinc concentrations were observed from exposure of zinc and galvanized materials (Förster 1999; Heijerick, et al. 2002; Clark, et al. 2008a, b, and 2007; Burton and Pitt 2002; Bannerman, et al. 1983; Pitt, et al. 1995; Good 1993; Tobiason and Logan 2000; Tobiason 2004; Veleva, et al. 2007, 2010; Gromaire-Mertz, et al. 1999; Schriewer, et al. 2008; Wallinder, et al. 2001, 2000; Gromaire, et al. 2002). Coated galvanized steel materials released lower zinc concentrations compared to un-coated galvanized metals (Clark, et al. 2008a; Wallinder, et al. 2001, 2000; Mendez, et al. 2011). When exposed to the atmosphere, zinc material forms a protective layer (zinc oxides/hydroxides/carbonates), which serves as a physical barrier between the metal surface and the atmosphere (Legault and Pearson 1978; Zhang 1996). Clark, et al. (2008a, b, and 2007) noted that there can be elevated zinc concentrations form zinc and galvanized metal materials throughout their useful life. Clark, et al. (2008a), Good (1993), and Gromaire-Mertz, et al. (1999) found that zinc concentrations in stormwater frequently exceed the criterion for aquatic toxicity. Heijerick, et al. (2002), Clark, et al. (2008a), and Wallinder, et al. (2001) also determined that as the age of metal panels increased, zinc concentrations increased also.

Copper materials released high copper concentrations (Wallinder, et al. 2009, 2002a; Sandberg, et al. 2006; Zobrist, et al. 2000; Karlen, et al. 2002; Boller and Steiner 2002). Fresh copper sheets released greater copper concentrations compared to naturally patinated copper sheet (Sandberg, et al. 2006). The copper concentrations from galvanized metals and vinyl materials didn’t exceed 25 µg/L (Clark, et al. 2008a, b; Mendez, et al. 2011). Copper-based paints are important sources of copper at marina basins (US EPA 2011). Corvo, et al. (2005) observed that the metal mass loss was proportional to chloride deposition rate. However Sandberg, et al. (2006) found that copper runoff rates were significantly lower at the marine site compared to data acquired in an urban environment even despite substantially higher chloride deposition rates at the marine site. Copper concentrations may continue to leach out in an acid rain environment during the material’s useful life (Clark, et al. 2008b).

Galvanized steel and galvalume roofing materials were not major sources of lead (Tobiason and Logan 2000; Gromaire-Mertz, et al. 1999; Förster 1999; Gumbs and Dierberg 1985; Shahmansouri, et al. 2003; Mendez, et al. 2011). Clark, et al. (2007) determined that old galvanized metals released lead. It was found that lead was leaching out of PVC rain gutters and that lead concentrations in roof runoff samples surpassed the water quality criteria for the corresponding constituents (Good 1993). Davis and Burns (1999) found that lead can be released in stormwater runoff from painted structures. Lead concentrations were significantly affected by paint age and condition. Lead releases from washes of older paints were significantly higher than from fresh paints. It was found that old surface paints have the potential to release high masses of lead into a watershed. Such factors as stagnation time, pH of the water, pipe age, and the Cl/SO_4 ratio influence lead release from PVC, polypropylene, and galvanized iron pipes (Lasheen, et al. 2008). Al-Malack (2001) also found that pH of water, time of contact, UV-radiation affected the migration of lead and other metal stabilizers from unplasticized polyvinyl chloride (uPVC) pipes. The author observed the increase of lead concentrations leaching out of uPVC pipes with the time. Gromaire-Mertz, et al. (1999) found that lead concentrations in roof runoff exceeded level 2 of French water quality standards of 50 µg/L for practically all samples.

Galvanized iron and PVC can leach iron concentrations, with galvanized iron materials releasing higher concentrations compared to PVC materials (Lasheen, et al. 2008; Shahmansouri, et al. 2003; Wallinder, et al. 2002b). Lasheen, et al. (2008) found that water quality parameters (pH, Cl^-/SO_4^{2-} ratio), stagnation time, pipe age, and pipe material affect heavy metal concentrations. Stagnation time and pipe age increase iron concentrations. At low pH (pH = 6) the concentrations of iron increased. High Cl^-/SO_4^{2-} ratio increased iron concentrations in all pipes. Sarin, et al. (2004) observed that when oxidants were present in water, greater iron release was noted during stagnation in comparison to flowing water conditions. Corvo, et al. (2005) found that metal mass loss was proportional to chloride deposition rate.

Rainwater pH influences the degradation of roofing and gutter material. The acidic environment of the rainwater dissolves $CaCO_3$ content of cement roofs and drainage system, and metal ions from metal roofing materials. This results in corrosion and damage of the roofing and piping materials and the change of the roof runoff pH. In case of concrete and metal materials, pH of the roof runoff is usually higher than that of rainwater and attributed to the $CaCO_3$ and metal ions, but below neutral (Horvath 2011; Pitt, et al. 2004; Clark, et al. 2007; Clark, et al. 2008 a, b; Tobiason 2004; Tobiason and Logan 2000).

Periodic spikes in nutrients were noted from galvanized roofing materials (Clark, et al. 2007; Clark, et al. 2008 a, b). It was found that roof runoff can be highly toxic (Good 1993; Tobiason and Logan 2000; Bailey, et al. 1999; Heijerick, et al. 2002).
First flush was observed for heavy metals in the stormwater runoff and was dependent on the antecedent dry period and the rain intensity (Zobrist, et al. 2000; He, et al. 2001a; Schriever 2008; Gromaire-Mertz, et al. 1999; Horvath 2011).

Factors that affect runoff concentrations include time of exposure, runoff water composition (pH, Cl-, etc.), meteorological factors (climate, humidity etc.), and material characteristics such as composition of the metal itself, its age, condition (Faller and

Reiss 2005; Schriewer, et al. 2008; He, et al. 2001a; He 2002; Cramer et al 2002; Veleva, et al. 2010, 2007; Sarin, et al. 2004; Lasheen, et al. 2008; Horvath 2011). The form of the metals affects their behavior and toxicity in natural waters. Ionic forms of metal are the most bioavailable forms.

This research examined metal releases from different stormwater drainage and tank materials under various water conditions. It was found that galvanized steel materials released the largest amounts of lead, zinc, and iron, while copper materials were the most significant sources of copper. Zinc and lead releases from galvanized steel materials were observed during both short and long exposure times. During controlled pH tests, zinc releases in the samples with galvanized steel materials exceeded those at higher pH values during long exposure times. During short exposure times, zinc releases from galvanized materials were lower in river water samples compared to the bay water samples; however, during long time exposures, zinc concentrations in the river water samples were greater than in the bay water samples. Plastic and concrete materials were the least sources of zinc. Galvanized pipes and gutters were found to be the only source of lead releases. During short exposure times, copper releases were noted only for copper materials at both low and high pH for controlled pH conditions and for bay and river water during un-controlled pH tests. During the first series of tests, copper releases from copper gutters increased as pH decreased. During the second test series copper losses were greater in containers with bay water compared to containers with river water. The smallest copper release was noted from HDPE and galvanized materials. The highest aluminum concentrations were released from aluminum materials.

Medusa chemical modeling software was used to perform water chemistry modeling with the test data. Eh-pH and log Concentration-pH diagrams were constructed and metal forms present were determined. The results showed that metal releases range in form from being strongly charged (valence state +2 and -2) to zero valence. In some of the containers zinc (copper) compounds precipitated and formed protective film, therefore zinc (copper) concentration in those waters would not be expected to increase since there would be equilibrium between ions dissolved in the water and the precipitated compounds. Langelier Index calculated for the containers with concrete pipes immersed in pH 5 and pH 8 waters indicated that the waters were undersaturated with respect to $CaCO_{3(s)}$ and the waters would have a tendency to dissolve $CaCO_{3(s)}$ from the concrete. The samples with concrete pipes immersed in bay and river waters were oversaturated with respect to $CaCO_{3(s)}$ indicating that waters in these samples had a tendency to precipitate $CaCO_{3(s)}$ from the solution and there was no degradation of the concrete pipe after 3 months of exposure.

Under the controlled pH 8 conditions, samples with pipes and roofing materials were found to be less toxic compared to the same materials at controlled pH 5 conditions during the buffered experiments. Copper materials were the most toxic. The concrete pipes were least toxic under both high and low pH conditions during buffered and natural pH tests.

At pH 5, samples with copper, aluminum, vinyl, and HDPE materials resulted in the highest toxicities and were attributed to low pH values. Under buffered pH 8 conditions copper, materials were the most toxic. PVC and galvanized steel materials were slightly toxic. Under natural pH conditions, only the samples with copper and galvanized steel materials were a source of toxicity. Copper and galvanized steel materials caused high toxicity during all tests with buffered and natural conditions.

Based on the toxicity analyses, copper materials should be avoided, and the use of galvanized materials should be limited. Concrete pipes can be used with a wide range of water pH values. In natural water environments with pH values from 7 to 8 and with low and high salinity values, PVC, HDPE, vinyl, aluminum materials also can be used with minimal toxicity issues.

High concentrations of heavy metals leaching out of pipe and gutter materials are toxic to the bacteria. However, the pH of the test water may also interfere with the tests. The pH of stormwater can change as it comes in contact with different drainage and roofing materials and may affect the water toxicity. In the next chapter, correlation matrices, Cluster and Principal analyses will examine simple and complex correlations between toxicity and other water chemistry parameters and full Factorial analyses will evaluate the effect of the water pH, time of contact, material, and interactions of those factors during the first test series; and the effect of water conductivity, time of contact, material, and interactions of those factors during the second test series.

The Spearman Correlation Analyses indicated that pH values and metal releases influence the water toxicity during these tests. Under natural pH conditions, the toxicity in the samples with galvanized steel materials was strongly associated with zinc losses, and the toxicity in the samples with copper materials was strongly associated with copper releases. Cluster analyses also confirmed that toxicities were affected by both metal releases and pH values, and the metal losses were influenced by pH, conductivity, and time of exposure.

Principal Component Analyses showed that the first four principal components explained about 78% of total variance. Toxicity and pH have high loadings on the first principal component. The second principal component has high loadings of time, Pb, and Zn. Copper has a large loading on the third principal component. Conductivity, pH, and material type were the highest loadings on the fourth principal component. Principal component analysis showed groupings of samples with similar characteristic. Samples with concrete, plastic, and aluminum materials immersed in controlled pH 8 waters had low lead and zinc releases and low toxicities. The samples with controlled pH 5 waters were associated with high toxicities.

Full 2^3 Factorial Analyses showed that for the controlled pH conditions, three-way interactions of pH, material, and time of exposure all had significant effects on copper and zinc releases; the two-way interactions of material and time were important for lead releases. The two-way interactions of pH and material and pH and time had significant effects on toxicity. During the natural pH tests, the three-way interaction of conductivity, material, and time had a significant effect on copper and lead releases. For zinc releases, the two-way interaction of material and exposure period was significant. The two-way interactions of conductivity and material, and material and time, both had significant effects of toxicity during the natural pH test series.

Full 2^2 Factorial Analyses that examined the type of material indicated that for copper materials under controlled pH conditions, pH had a significant effect on copper releases; under natural pH condition, time and conductivity had significant effects on copper concentrations. For zinc releases from galvanized steel materials under controlled pH conditions, the interaction of time and pH was significant. For zinc releases from galvanized materials under natural pH conditions, time had a significant effect on zinc releases. For lead releases from galvanized steel pipe, exposure time was significant, and for galvanized steel gutter materials, the interaction of pH and time was significant. The interaction of exposure time and conductivity had an effect of lead releases from steel pipe under during natural pH tests.

The results from the factorial analyses were used to build an empirical model to identify the significant factors, materials, exposure times, and their combinations that influence pollutant releases. Copper and galvanized steel roof gutters and pipes should not be used when acidic water conditions are expected due to high copper (for copper materials) and high zinc (for galvanized steel materials) releases and high toxicity. For stormwater drainage systems (gutters and pipes) exposed to pH 5 and 8 conditions, concrete and plastic materials can be employed. Galvanized steel and copper materials are not advised for use in storage tanks applications due to very high metal releases and associated toxicity. For stormwater storage applications, concrete, HDPE, and vinyl materials can be used due to their little or non-detected metal losses.

Indicator Microorganism Die-off and Re-growth on Urban Surfaces

A full 2^3 factorial study (examining temperature, moisture, and UV-B exposure and their interactions) of the indicator-species' environmental survival factors was performed for enterococci and *E. coli*. Pet feces slurries (1 mL) were applied to salt-passivated paving blocks and incubated in controlled environmental chambers. The test chambers were freezerless refrigerators fitted with BOD-controllers/heaters for temperature control, dehumidifiers or humidifiers for moisture control, and UV-B enhanced fluorescents with Lexan panels to split the chambers into UV-exposed and UV-shielded regions. These represent conditions likely to be found in Tuscaloosa, AL. Active control of temperature (40 and 90 degrees F, representing cool and warm conditions) held the temperatures steady (+/- 2 degrees) over the study period. Relative humidity (25% and 80%, representing dry and wet conditions) varied over about +/- 4%. UV exposure was treated as present or absent (UV or dark conditions).

All treatments exhibit an initial lag or die-off for *E. coli*, as usually assumed. The rate of this die-off depends on the temperature and humidity, with the warm/wet conditions (those most like the enteric habitat, and exerting the least pressure for adaptation) showing the lowest initial rate of decline. All test conditions resulted in declines from two to three orders of magnitude within a day or so. The duration of the decline was from19 h to 27 h. After this decline, the *E. coli* populations exhibited a re-growth period lasting for several days, and then a second, but slower rate of decline.

Treatment analyses of the breakpoints were less complex for enterococci than for *E. coli*. The warm/wet/dark treatment for enterococci showed no evidence of a breakpoint. When the regrowth phases are recognized, none of the conditions show a net decline of more than about one order of magnitude over a two week period. It also should be noted that no enterococci test population was in decline at the end of the study period.

Section 5. Fate and Treatment of Emerging Contaminants

Introduction

There are many physicochemical properties known for emerging contaminants, but only some are important when estimating EC behavior in treatment systems (Maurico, et al. 2006). The main physical and chemical properties that affect EC treatment in wastewater facilities are the octanol/water coefficient, water solubility, pH, sorption coefficient, structure and the molecular weight of the compound. The biological and chemical activities of pharmaceuticals are strongly influenced by their functional groups and the pH of the solution (Nghiem, et al. 2005). Pharmaceuticals are generally polar in nature and may have a greater affinity to be soluble depending on the pollutant. PAHs and pesticides are more hydrophobic than pharmaceuticals; therefore they have a higher affinity to sorb onto particulate matter. Understanding the basic properties of contaminants in aqueous solutions gives a better understanding of how each pollutant can be removed from water.

Analyses of organic pollutants in wastewater are complex due to the variety of physicochemical and toxicological properties of compounds included in the same group (Petrovic, et al. 2006). The wastewater matrix increases the complexity of the analysis methods because of interference from other contaminants present. Each compound group requires specific analysis steps (mainly extractions and sample clean-up) using different techniques (Bolong, et al. 2009).

Research has resulted in the availability of physicochemical properties relating to emerging contaminants, such as the octanol-water coefficient (K_{ow}), solubility and molecular weight. The octanol-water coefficient is a surrogate measure of how the compound may be absorbed by organic matter. Solubility and log K_{ow} are inversely proportional. If pollutants have a higher log K_{ow} and lower solubility, they tend to sorb on organic particulate matter and can be removed in primary treatment (sedimentation). Although wastewater treatment plants are critical for the removal of emerging contaminants from sanitary wastewaters, relatively little is known about the nature, variability, transport and fate of these compounds in typical treatment facilities in the United States (Phillips, et al. 2005).

Treatment of Pharmaceuticals and Personal Care Products Summarized from the Literature

Characteristics of Pharmaceuticals Affecting Treatment

Pharmaceuticals are a growing concern because there are many being introduced into wastewater in ever-increasing amounts and variety. Many do not have discharge regulations, yet it has been shown that trace levels of some have caused adverse effects in the environment. Human and veterinary pharmaceuticals represent more than 4,000 commercially available compounds; 10,000 specialty products are made to be water soluble, biodegradable and to have short half-lives (Beausse 2004).

Pharmaceuticals have been analyzed in several studies and detected in wastewater effluent and in the environment at trace levels. Analytical techniques and equipment are now available that can detect pharmaceuticals at lower concentrations than during many past studies. Pharmaceutically active compounds (PhACs) are highly reactive and can affect receptors in the environment. Many biological, chemical, and physical properties affect PhACs in wastewater, such as their adsorption/desorption on biosolids, pH, the ionic strength of the sewage, and microbial decomposition rates (Miao, et al. 2005), as summarized in Table 5-1. Polarity, photo-stability and volatility determine the fate and transport of PhACs in the wastewater system (Miao, et al. 2005). Studies show the transformation process for specific PPCP compounds vary in a sewage treatment plant depending on the characteristics of the sewage, weather conditions and the design and operation of the treatment process (Boyd, et al. 2003).

Table 5-1. Selected Chemical Properties of Pharmaceuticals

Pharmaceutical	Log k_{ow}	Solubility (mg/L)	pKa	Toxicity (µg/L)	Chemical Group
Carbamazepine	2.45	17.7	13.9	LC_{50} D. magna >100 mg/L	Carboxide
Fluoxetine	4.05	38.4	9.5	P. subcapitata LC_{50} 24 µg/L	Amine
Gemfibrozil	4.78	5.0	4.7	D. Magna. EC_{50} 23 mg/L	Valeric Acid/Pentoic Acid
Ibuprofen	3.5-4.0	41.5	4.9	Daphnia. EC_{50} 108 mg/L	Propanoic acid
Sulfamethoxazole	0.9	600	1.7/5.7	P. subcapitata. IC_{50} 1.5 mg/L	Sulfonamide
Triclosan	4.8-5.4	2-4.6	7.8-8.1	P. subcapitata. IC_{50} 1.4 µg/L	Phenol
Trimethoprim	0.79	400	7.2	P. subcapitata. IC_{50} 80- 130 mg/L	Diamine

Pharmaceuticals are separated into three categories according to their functional groups: carboxylic, hydroxyl and amide (Nakada, et al. 2006). The biological and chemical activities of pharmaceuticals are strongly influenced by their functional groups (Nghiem, et al. 2005). The functional groups determine how the chemical compounds will react and/or degrade in water and wastewater treatment facilities. Factors such as pH, salinity, wastewater matrix and ionic content of solution affect the form of the pollutant and how it reacts in aqueous solution.

Pharmaceuticals enter the wastewater stream mainly through excretion from urine and feces as metabolites or by improper disposal (Lindqvist, et al. 2005). Some of these active conjugates and the parent compounds are discharged by the wastewater treatment plant without adequate treatment. Veterinary pharmaceuticals can also enter wastewater treatment plants through stormwater I&I and also through regular sewage by disposal from pet's fecal matter disposed in toilets. Pharmaceuticals found in the environment have acidic and basic properties. Both categories were examined during this current research. The pharmaceuticals tested include sulfamethoxazole (SMX), trimethoprim (TRM), fluoxetine (FLX), carbamazepine (CBZ), triclosan (TCL), ibuprofen (IBP) and gemfibrozil (GFB). Many of these compounds have more than one functional group that react differently in the wastewater treatment system. The structure, biodegradability rates, half-life, and toxicity of these compounds all affect their treatment in the secondary biological treatment phase. Some parent and intermediate compounds of pharmaceuticals can form hazardous byproducts during conventional chlorination (the treatment plant studied during this research uses UV disinfection). During this study, seven pharmaceuticals were examined at various stages at the wastewater treatment facility. Sulfamethoxazole, fluoxetine, triclosan, ibuprofen and gemfibrozil are acidic pharmaceuticals, while carbamazepine and trimethoprim are basic pharmaceuticals.

Sulfamethoxazole, or 4-amino-*N*-(5-methylisoxazol-3-yl)-benzenesulfonamide, is an antibiotic, generally used in conjunction with trimethoprim for bacterial infections such as urinary tract infections. Its molecular weight is 253 g/mol and it has a solubility of 600 mg/L. Sulfamethoxazole is a pharmaceutical of the sulfonamide group. They are also known as sulfanilamides because of the aniline attached to it. Amides have carbonyl groups with a nitrogen molecule. Amides are persistent and stable in nature and resist hydrolysis. They are polar compounds so they are prone to be soluble in water. Although aniline was able to degrade quickly, sulfanilamide degrades very slowly by aniline-acclimated activated sludge suggesting that biodegradation in water and soil will be slow (PubMed Molecular Biology Database). Sulfanomides are both fairly water-soluble and polar compounds, which ionize based on the pH of the medium (Accinelli, et al. 2007). Sulfamethoxazole contains two functional moieties ($-NH-S(O_2)$) at both sides of the sulfonamide linkage (Nghiem, et al. 2005). Sulfamethoxazole is shown to dissociate twice, once with the protonation of the primary amine group $-NH_2$ and then with the deprotonation of the sulfanomide (-NH) (Nghiem, et al. 2005). At pH levels above 5.7, sulfamethoxazole remains as an anionic species, remains neutral at pH values between 1.7 and 5.7, and remains positive at pH levels below 1.7 (Nghiem, et al. 2005). The pH of wastewaters generally ranges between 6 and 8, which makes it neutral under normal conditions. The log K_{ow} is low so it is believed that sulfamethoxazole will typically remain in aqueous solutions throughout the wastewater treatment system and will not sorb to particles. Sulfonamide antimicrobials are not readily biodegraded (Perez, et al. 2009). In surface waters impacted by human wastes, sulfonamides appear to resist biodegradation rather strongly, with detection of sulfamethoxazole and trimethoprim in streams with frequencies up to 27% (Hazardous Substance Database 2012). In the Reconnaissance Study by the EPA and USGS, sulfamethoxazole was categorized as a persistent antibiotic, which is possibly due to having an aromatic structure as part of the molecule (Xu, et al. 2011). Sulfamethoxazole has also been shown to be resistant to biodegradation, hydrolysis and adsorption, but photodegradation is a possible eliminating factor (Xu 2011). The biological half-life of sulfamethoxazole is 10 hours, but the biodegradation of sulfamethoxazole studied in marine water ponds indicated separate water and sediment half-lives of 47.7d and 10.1 d, respectively (DrugBank 2012; Xu, et al. 2011). Toxicity of the freshwater green alga *P. subcapitata* has an IC 50 of 1.5 mg/L (Yang, et al. 2009). Toxicities of these compounds in wastewater were found to be in the milligrams per liter range, while the literature indicates that wastewater concentrations range in the micrograms per liter and nanogram per liter range.

Trimethoprim, or 5-(3,4,5- trimethoxybenzyl) pyrimidine- 2,4- diamine, is an antimicrobial compound commonly used to treat both humans and animals (Miao, et al. 2004).. For humans, it is generally used to treat urinary tract infections and certain types of pneumonia. For animals, trimethoprim is mainly used in the treatment of livestock, such as pigs, cattle and poultry and in aquaculture for bacterial infections (Mikes and Trapp 2010). It has a molecular weight of 290.32 g/mol. At a temperature of 25°C, it has a solubility of 400 mg/L. Trimethoprim is classified as a diamine, with two amino groups attached to the molecule. The molecule also has two phenol groups and three ether groups. Ethers are stable and do not react readily unless under high temperature. Trimethoprim is a polar weak base with a pKa of 7.2, but under acidic conditions, it is completely ionized (Mikes and Trapp 2010). Under neutral conditions, it has a log K_{ow} of 0.79 but can range from -1.7 to 0.79 (acidic pH to neutral pH) (Mikes and Trapp 2010). Solubility is also contingent on the pH of the solution. Trimethoprim in wastewater under standard temperatures and neutral pH conditions theoretically remains in solution unless it is biodegraded in the activated sludge process. The biological half-life in humans for trimethoprim is 10 to 11 hours, but the half-lives of trimethoprim incorporated into sediment cores were approximately 100 and 75 days under anaerobic and aerobic conditions, respectively, suggesting that biodegradation occurs slowly in the environment (DrugBank 2012). Slow biodegradation in the environment indicates that wastewater treatment facilities may not efficiently remove the chemical.

Fluoxetine, or N-Methyl-γ-[4-(trifluoromethyl) phenoxy]benzenepropanamine, is classified as an amine with two benzene rings, one with the triflourine and one with an ether connected to a chiral group. Fluoxetine is an antidepressant used in medications such as Prozac and Sarafem. It is excreted either unchanged (20-30% unchanged) or as the metabolites glucuromide and norfluoxetine from the human body. Some of the glucuromides are reactivate in wastewater treatment plants by cleavage (Nentwig 2007). Fluoxetine has a log K_{ow} of 4.05, water solubility of 38.4 mg/L at 25˚C and vapor pressure of 8.9E-007mm Hg (Nentwig 2007). It has a high sorption rate so it should undergo some treatment in both the primary and secondary treatment processes of the treatment facility. Fluoxetine contains secondary aliphatic amines which are basic, indicating that they are predominatedly protonated at neutral pH and only partially adsorb to sludge (Bedner and MacCrehan 2006). The lethal concentration at 50% (IC 50) for *P. subcapitata* was found to be 24 µg/L (Brools, et al. 2003). The biological half-life is 1 to 3 days. The main metabolite from fluoxetine is norfluoxetine.

Carbamazepine (CBZ), or 5*H*-dibenzo[*b*,*f*]azepine-5-carboxamide, is an anti-epileptic drug with different crystalline forms, all having variable dissolutions leading to irregular and delayed adsorption (Sethia and Squillante 2004). Table 5-2 summarizes some of the properties for some of the different metabolites. Seventy-two percent of the compound is released in urine, and various metabolites are excreted from urine into the wastewater system (Zhang, et al. 2008). Carbamazepine is classified as a carboxamide and is a primary amide group. It is also known as dibenzazepine, which is a molecule with two benzene rings fused to an azepine group (DrugBank 2012). It has a log k_{ow} value of 2.45. Carbamazepine is a base with a pKa value of 2.3 and is uncharged at all conditions typical of natural water or wastewater (Nghiem, et al. 2005). Carbamazepine has a low octanol-water coefficient (K_{ow}) and a water solubility of 17.7 mg/L (25˚C) (Nakada, et al. 2006; Sethia and Squillante 2004; and Zhang, et al. 2008). Studies on removal efficiencies of carbamazepine show that carbamazepine is difficult to remove from sewage. Due to its persistent nature, carbamazepine has been proposed as a molecular marker for sewage (Nakada, et al. 2006, 3297-3303). At low concentrations, carbamazepine is resistant to biodegradation (Zhang, et al. 2008). Carbamazepine is frequently detected in groundwater up to concentrations of 610 ng/L and in other water bodies (Zhang, et al. 2008). Carbamazepine has a biological half-life of 25 to 65 hours, but was fairly persistent when tested in a field experiment using epilimnion lake water, exhibiting a half-life of 63 days (DrugBank 2012). Approximately 72% of orally administered carbamazepine is absorbed and released as metabolites in the urine, while 28% is unchanged and subsequently discharged through the feces (Zhang, et al. 2008). According to the Zhang study, carbamazepine is shown to be in many different forms in wastewater. These forms may change back into the parent carbamazepine during the treatment process, which causes it to be difficult to eliminate. The metabolites of carbamazepine may be more or less difficult to remove due to chemical altering which may give carbamazepine different chemical properties. Research shows carbamazepine increases in the effluent (Zhang, et al. 2008). Metabolites vary in their octanol water coefficient (log K_{ow}), from 0.67 to 2.67. Most of the carbamazepine is metabolized in the urine, with each of the metablites being as active as the parent compound. Zhang (2008) indicated there are limited studies on the effects of the metabolites of carbamazepine on aquatic life. The toxicity of LC 50 D. magna is >100 mg/L (Kim, et al. 2007).

Table 5-2. Log of octanol-water coefficients for carbamazepine and its metabolites

Analyte	Abbreviation	Formula/MW	Log K_{ow}
carbamazepine	CBZ	$C_{15}H_{12}N_2O$/236.10	2.25 2.67 ±0.38
10,11-dihydro-10,11-epoxycarbamazepine	CBZ-EP	$C_{15}H_{12}N_2O_2$/252.09	1.26 ± 0.54
10,11-dihydro-10,11-dihydroxycarbamazepine	CBZ-DiOH	$C_{15}H_{14}N_2O_3$/270.10	0.13 ± 0.41
2-hydroxycarbamazepine	CBZ-2OH	$C_{15}H_{12}N_2O_2$/252.09	2.25 ± 0.65
3-hydroxycarbamazepine	CBZ-3OH	$C_{15}H_{12}N_2O_2$/252.09	2.41 ± 0.73
10,11-dihydro-10-hydroxycarbamazepine	CBZ-10OH	$C_{15}H_{14}N_2O_2$/254.10	0.93 ± 0.33

Zhang 2008

Triclosan, or 5-Chloro-2-(2,4-dichlorophenoxy) phenol, is an anti-microbial compound found in many personal care products such as soaps. The U.S. Geological Survey found triclosan in 57% of 137 streams nationwide (Latch, et al. 2005). Triclosan is a chlorinated phenoxyphenol with a pka of 8.1; the pH of wastewater between 7 -9 would have a significant influence on its speciation (Singer, et al. 2002). Triclosan, a polychlorinated diphenyl ether, has similar chemical properties to hydroxlated metabolites of ortho-substituted PCBs and PBDEs (Cherednichenko, et al. 2012). PCBs are very stable in the environment and have long half-lives. Ethers are not as soluble in water as alcohol, and are not as reactive. Triclosan has a water solubility of about 2,000 to 4,600 µg/L at 25˚C and a high octanol/water partition coefficient ($\log_{10} K_{ow}$) of 4.8-5.4, indicating a significant potential for sorption to particles (singer, et al. 2002; Heidler and Halden 2007). The pKa of triclosan indicates that this compound will exist partially in anion forms in the environment. Anions generally do not adsorb as strongly to soils containing organic carbon and clay compared to their neutral counterparts (Hazardous Material substance Database 2012). Even though its dissociated form tends to degrade in sunlight, triclosan is quite resistant to hydrolysis (Singer, et al. 2002). It is converted, either by UV radiation or photohydrolysis, into 2, 8-dichlorodibenzo-p-dioxin (2, 8-DCDD, a dioxin) (Latch, et al. 2005). Methyl triclosan, a potential biotransformation product following wastewater treatment of triclosan, is more persistent, lipophilic, bio-accumulative and less sensitive towards photo-degradation in the environment than its parent compound (Chen, et al. 2011). Also, exposure of triclosan to freshwater green alga *P. subcapitata* yielded an IC 50 of 1.4 µg/L (Yang, et al. 2009). In aerobic water-sediment systems maintained in darkness at 20 ± 2°C, triclosan degraded with calculated nonlinear half-lives of 1.3 to 1.4 days in water, 54 to 60 days in sediment, and 40 to 56 days in the total system (USEPA 2008).

Ibuprofen, or α-Methyl-4-(2-methylpropyl) benzene-acetic acid, is a non-steroidal anti-inflammatory drug (NSAIDS). The classification of this compound is a propanoic acid. Propanoic acids are soluble in water and can react with many other compounds. Ibuprofen can also be classified as a phenyl acetate. Many phenyl acetates are not as soluble in water and are stable. Ibuprofen is an acidic pharmaceutical with a molecular weight of 206.28 g/mol and two dissociation constants (pKa) of 5.2 and 4.91. It is soluble in water with a solubility of 21 mg/L, and has a log K_{ow} value of 3.5. Ibuprofen has shown to be biodegradable by sewage treatment; however, analysis of activated sludge from the wastewater treatment plant at Gossau, Switzerland indicates that a residence time in excess of 6 hours is required for complete removal of ibuprofen (Hazardous Substance Database 2012). Ibuprofen has a reported half-life of 2 to 4 hours, however from an ecological study; the half-life was determined to be of 20 days using water samples from Lake Greifensee, Switzerland (Hazardous Substances Database 2012). Exposure of Daphnia to ibuprofen yielded an EC 50 of 108 mg/L (Cleuvers 2003).

Gemfibrozil or 5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanoic acid is a lipid inhibitor belonging to the group of fibrates. Gemfibrozil is classified as a pentanoic acid or a valeric acid. Pentanoic acids have carboxylic functional groups, making them soluble in water. The pH of the solution determines if the species is in ionic form or in its neutral form. It has an estimated log K_{ow} value of 4.78, so in normal conditions, it has a tendency to sorb onto particulate suspended solids. Gemfibrozil has an estimated pka of 4.5 which indicates it will exist almost entirely in the anion form at pH values of 5 to 9 (PubMed Molecular Biology Database). If it is in the anionic form, sorption is unlikely to occur and biodegradation would be the only method to eliminate it from wastewater. Gemfibrozil has a biological half-life of 1.5 hours, but has a higher half-life in the environment (DrugBank 2012). An environmental study showed gemfibrozil in open, sun-lit, lake water and reservoir water to have half-lives of 120 ± 16 days and 288 ± 61 days, respectively (Araujo, et al. 2011).

The physical and chemical characteristics are varied for all pharmaceuticals, including the analytes under study. The solubilities of some of the pharmaceuticals in wastewater make them more difficult to treat. Depending on the pH of the wastewater, many micropollutants can exist in ionized or unionized aqueous forms (Myers 2009). Dissociation constants or pKa values help predict the behavior of pharmaceuticals in the environment. For acidic pharmaceuticals, pKa values lower than the pH of the wastewater will yield an ionized compound that can easily be absorbed. For basic pharmaceuticals, pKa values higher than pH of wastewater will yield an ionized compound. If ionization of a pollutant is not significant, sorption would be a likely means of treatment. If a species is not ionized, the solubility is decreased, and sorption, biodegradation and/or oxidation could be the method of removal. If the log K_{ow} values are high (>3), sorption is a viable mechanism. The stability of the compounds is determined by their chemical structure and composition and affects their treatment in wastewater. In an activated sludge treatment system, toxicity of certain chemical compounds can inhibit the microbes that biodegrade the pollutants in wastewater.

Treatment by Unit Processes

Many reports have been published in the last two decades describing the effectiveness of different treatment methods for the removal of emerging contaminants, mostly examining municipal waste waters, as summarized on Table 5-3. The different treatment methods examined included sedimentation, flocculation, coagulation, rapid sand filtration, ozonation, adsorption, activated sludge, membrane bioreactors, nano and ultra-filtration, and UV and chlorine disinfection.

Primary sedimentation and flocculation processes at municipal treatment plants did not show large removals of the pharmaceutical compounds, with most removal rates < 40% (Thomas, et al. 2005, Carballa et al 2004). Sedimentation and ferric chloride coagulation followed by rapid sand filtration (Vieno et al 2007) was also found to be ineffective, with removal rates of about 10% for the pharmaceuticals included in the case study.

Ozonation, as described by many authors, has been shown to be a much more effective removal technique for most of the compounds. Several studies (Vieno etal 2007, Snyder et al 2006, and Jasim et al 2006) reported removal rates for most of the compounds between 60 and 99%. Increasing the ozone dosage and the addition of H_2O_2 improved the removal rates for some of the compounds (Snyder et al 2006). Reaction time, amount of ozone dosage, alkalinity of the water, and the reactivity of the ompounds towards ozone, are reported to be important factors affecting the increase of removal rates.

Conventional activated sludge was also studied (Radjenovic etal 2006, Lishman et al 2006, Nakada, et al. 2006) for the removal of emerging compounds. For most of the compounds examined, the removal rates were greater than 60%. Sorption and de-sorption from the biosolids and biodegradation was reported (Carballa, et al. 2004, Radjenovic, et al. 2006) to be the process associated with the reduction in the EC concentrations with activated sludge treatment. For a few compounds examined, the removal rates increased with an increase of SRT (sludge retention time), but the effect was not consistent for all compounds. The effect of different SRTs and temperatures were also noted to need further investigation to enhance EC treatment.

Table 5-3. Removal rates of pharmaceuticals and PCPs with respect to different treatment processes

Contaminant	Type of water	Unit processes examined	Removal (%)	Influent conc.(µg/L)	Effluent conc.(µg/L)	Reference
Carbamazepine	River water	Ferric coag+sed+ rapid sand filtration	7			Vieno et al 2007
Carbamazepine	River water	Ozonation alone after (Ferric coag+sed+ rapid sand filtration)	>99			Vieno et al 2007
Carbamazepine	Sanitary waste water	Primary+ Activated sludge	0			Castiglioni et al 2006
Carbamazepine	Sewage sludge	Anaerobic digestion	0			Carballa et al 2007
Carbamazepine	Sanitary waste water	Membrane bioreactor	0	0.24(median)	0.3(median)	Radjenovic et al 2006
Carbamazepine	Sanitary waste water	Conventional Activated Sludge	0	0.24(median)	0.25(median)	Radjenovic et al 2006
Carbamazepine	Sanitary waste water	Primary+ Activated sludge	upto 78	15-350	15-160	Nakada et al 2006
Caffeine	Sanitary waste water	Primary+ Activated Sludge+ (Alum+ Gravity Filtration+ Disinfection)	17,99.9			Thomas et al 2005
Caffeine	Distilled water	Floc/Sed+ Dual Media Filtration+ Disinfection	3.4-12.7			Bundy et al 2007
Caffeine	Distilled water	Floc/Sed+ Dual Media Filtration+GAC Disinfection	>94			Bundy et al 2007
Ibuprofen	Sanitary waste water	Activated Sludge	95	8.45(mean)	0.384(mean)	Lishman et al 2006
Ibuprofen	Sanitary waste water	primary+ biological reactor	63			Carballa et al 2004
Ibuprofen	River water	Ferric coag+sed+ rapid sand filtration	12			Vieno et al 2007

Continuation of Table 5-3

Contaminant	Type of water	Unit processes examined	Removal (%)	Influent conc.(µg/L)	Effluent conc.(µg/L)	Reference
Ibuprofen	River water	ozonation alone after (Ferric coag+sed+ rapid sand filtration)	92			Vieno et al 2007
Ibuprofen	Sanitary waste water	Primary+ Activated sludge	38[d],93[e]			Castiglioni et al 2006
Ibuprofen	Sanitary waste water	Primary+ Activated Sludge+ (Alum+ Gravity Filtration+ Disinfection)	5[a],99.8[b]			Thomas et al 2005
Ibuprofen	Sewage sludge	Anaerobic digestion	41±15			Carballa et al 2007
Ibuprofen	Sanitary waste water	Membrane bioreactor	99.8±0.386	17(median)	0(median)	Radjenovic et al 2006
Ibuprofen	Sanitary waste water	Conventional Activated Sludge	82.5±15.8	17(median)	2(median)	Radjenovic et al 2006
Ibuprofen	Sanitary waste water	Primary+ Activated Sludge	83-99	300-1200	1-110	Nakada et al 2006
Naproxen	Sanitary waste water	Activated Sludge	93	5.58(mean)	0.452(mean)	Lishman et al 2006
Naproxen	Sanitary waste water	primary + biological reactor	48			Carballa et al 2004
Naproxen	River water	Ferric coag+sed+ rapid sand filtration	10			Vieno et al 2007
Naproxen	River water	ozonation alone after (Ferric coag+sed+ rapid sand filtration)	75			Vieno et al 2007
Naproxen	Sanitary waste water	Primary+ Activated Sludge+ (Alum+ Gravity Filtration+ Disinfection)	3[a],99.8[b]			Thomas et al 2005
Naproxen	Sewage sludge	Anaerobic digestion	88±4			Carballa et al 2007

Continuation of Table 5-3

Contaminant	Type of water	Unit processes examined	Removal (%)	Influent conc.(μg/L)	Effluent conc.(μg/L)	Reference
Naproxen	Sanitary waste water	Membrane Bioreactor	99.3±1.52	11.6(median)	0(median)	Radjenovic et al 2006
Naproxen	Sanitary waste water	Conventional Activated Sludge	85.1±11.4	11.6(median)	3(median)	Radjenovic et al 2006
Naproxen	Sanitary waste water	Primary+ Activated Sludge	upto 82	30-250	11-150	Nakada et al 2006
Diazepam	Sewage sludge	Anaerobic Digestion	50±16			Carballa et al 2007
Diclofenac	River water	Ferric coag+sed+ rapid sand filtration	8			Vieno et al 2007
Diclofenac	River water	ozonation alone after (Ferric coag+sed+ rapid sand filtration)	>94			Vieno et al 2007
Diclofenac	Sanitary waste water	Primary+ Activated Sludge+ (Alum+ Gravity Filtration+ Disinfection)	14[a],89[b],100[c]			Thomas et al 2005
Diclofenac	Sewage sludge	Anaerobic Digestion	69±10			Carballa et al 2007
Diclofenac	Sanitary waste water	Membrane bioreactor	87.4±14.1	2.8(median)	0.2(median)	Radjenovic et al 2006
Diclofenac	Sanitary waste water	Conventional Activated Sludge	50.1±20.1	2.8(median)	1.2(median)	Radjenovic et al 2006
Gemfibrozil	Sanitary waste water	Activated sludge	66			Lishman et al 2006
Gemfibrozil	Sanitary waste water	Membrane bioreactor	89.6±23.3	3.8(median)	0(median)	Radjenovic et al 2006
Gemfibrozil	Sanitary waste water	Conventional Activated Sludge	38.8±16.9	3.8(median)	2.5(median)	Radjenovic et al 2006

Continuation of Table 5-3

Contaminant	Type of water	Unit processes examined	Removal (%)	Influent conc.(µg/L)	Effluent conc.(µg/L)	Reference
Acetaminophen	Sanitary waste water	Membrane bioreactor	99.6±0.299	18(median)	0(median)	Radjenovic et al 2006
Acetaminophen	Sanitary waste water	Conventional Activated Sludge	98.4±1.72	18(median)	0.1(median)	Radjenovic et al 2006
Iopromide	Sewage sludge	Anaerobic Digestion	22±11			Carballa et al 2007
Estrone	Sanitary waste water	Lagoon	86	0.0295(mean)	0.0076(mean)	Lishman et al 2006
Estrone	Sanitary waste water	Primary+ Activated sludge	0			Castiglioni et al 2006
Estrone	Sewage sludge	Anaerobic Digestion	88±6			Carballa et al 2007
Estrone	Sanitary waste water	Primary+ Activated sludge	83-90	25-200	3-110	Nakada et al 2006
Bezafibrate	River water	Ferric coag+sed+ rapid sand filtration	27			Vieno et al 2007
Bezafibrate	River water	ozonation alone after (Ferric coag+sed+ rapid sand filtration)	>77			Vieno et al 2007
Bezafibrate	Sanitary waste water	Primary+ Activated sludge	15[d],87[e]			Castiglioni et al 2006
Bezafibrate	Sanitary waste water	Membrane bioreactor	95.8±8.66	1.75(median)	0.1(median)	Radjenovic et al 2006
Bezafibrate	Sanitary waste water	Conventional Activated Sludge	48.4±33.8	1.75(median)	0.75(median)	Radjenovic et al 2006
Triclosan	Sanitary waste water	Activated Sludge	93	1.93(mean)	0.108(mean)	Lishman et al 2006

Continuation of Table 5-3

Contaminant	Type of water	Unit processes examined	Removal (%)	Influent conc.(µg/L)	Effluent conc.(µg/L)	Reference
Triclosan	Sanitary waste water	Activated sludge + filtration	95			Lishman et al 2006
Triclosan	Sanitary waste water	Primary+ Activated Sludge+ (Alum+ Gravity Filtration+ Disinfection)	26[a],98.4[b]			Thomas et al 2005
Triclosan	Sanitary waste water	Primary+ Activated Sludge	46-92	200-1000	20-200	Nakada et al 2006
Ketoprofen	Sanitary waste water	Activated sludge	44			Lishman et al 2006
Ketoprofen	Sanitary waste water	Primary+ Activated Sludge+ (Alum+ Gravity Filtration+ Disinfection)	7[a],94[b],98.9[c]			Thomas et al 2005
Ketoprofen	River water	Ferric coag+sed+ rapid sand filtration	13			Vieno et al 2007
Ketoprofen	River water	Ozonation alone after (Ferric coag+sed+ rapid sand filtration)	>62			Vieno et al 2007
Ketoprofen	Sanitary waste water	Membrane bioreactor	91.9±6.55	1.8(median)	0.2(median)	Radjenovic et al 2006
Ketoprofen	Sanitary waste water	Conventional Activated Sludge	51.5±22.9	1.8(median)	0.75(median)	Radjenovic et al 2006
Ketoprofen	Sanitary waste water	Primary+ Activated Sludge	15-68	100-400	50-200	Nakada et al 2006
Clofibric Acid	Sanitary waste water	Primary+ Activated sludge	30[d], <0.36[e]			Castiglioni et al 2006
Clofibric Acid	Sanitary waste water	Membrane bioreactor	71.8±30.9	0.11(median)	0.02(median)	Radjenovic et al 2006
Clofibric Acid	Sanitary waste water	Conventional Activated Sludge	27.7±46.9	0.11(median)	0.09(median)	Radjenovic et al 2006

Continuation of Table 5-3

Contaminant	Type of water	Unit processes examined	Removal (%)	Influent conc.(µg/L)	Effluent conc.(µg/L)	Reference
Atenolol	River water	Ferric coag+sed+ rapid sand filtration	12			Vieno et al 2007
Atenolol	River water	Ozonation alone after (Ferric coag+sed+ rapid sand filtration)	>73			Vieno et al 2007
Atenolol	Sanitary waste water	Primary+ Activated sludge	10[d],55[e]			Castiglioni et al 2006
Atenolol	Sanitary waste water	Membrane bioreactor	65.5±36.2	1.5(median)	0.5(median)	Radjenovic et al 2006
Atenolol	Sanitary waste water	Conventional Activated Sludge	<10	1.5(median)	0.9(median)	Radjenovic et al 2006
Ciprofloxacin	River water	Ferric coag+sed+ rapid sand filtration	35			Vieno et al 2007
Ciprofloxacin	River water	Ozonation alone after (Ferric coag+sed+ rapid sand filtration)	16			Vieno et al 2007
Ciprofloxacin	Sanitary waste water	Primary+ Activated sludge	60[d],63[e]			Castiglioni et al 2006
Ofloxacin	Sanitary waste water	Primary+ Activated sludge	43,57			Castiglioni et al 2006
Ofloxacin	Sanitary waste water	Membrane bioreactor	94±6.51	0.44(median)	0.04(median)	Radjenovic et al 2006
Ofloxacin	Sanitary waste water	Conventional Activated Sludge	23.8±23.5	0.44(median)	0.3(median)	Radjenovic et al 2006
Erythromycin	Sanitary waste water	Primary+ Activated sludge	0			Castiglioni et al 2006
Erythromycin	Sanitary waste water	Membrane bioreactor	67.3±16.1	0.15(median)	0.05(median)	Radjenovic et al 2006
Erythromycin	Sanitary waste water	Conventional Activated Sludge	23.8±29.2	0.15(median)	0.08(median)	Radjenovic et al 2006

Continuation of Table 5-3

Contaminant	Type of water	Unit processes examined	Removal (%)	Influent conc.(µg/L)	Effluent conc.(µg/L)	Reference
Fenoprofen	Sanitary waste water	Primary+ Activated Sludge	65-97	15-90	2--9	Nakada et al 2006
Indomethacin	Sanitary waste water	Activated sludge	23	0.23(mean)	0.19(mean)	Lishman et al 2006
Indomethacin	Sanitary waste water	Membrane bioreactor	46.6±23.2	0.11(median)	0.06(median)	Radjenovic et al 2006
Indomethacin	Sanitary waste water	Conventional Activated Sludge	23.4±22.3	0.11(median)	0.085(median)	Radjenovic et al 2006
Metoprolol	River water	Ferric coag+sed+ rapid sand filtration	11			Vieno et al 2007
Metoprolol	River water	Ozonation alone after (Ferric coag+sed+ rapid sand filtration)	>95			Vieno et al 2007
Metoprolol	Sanitary waste water	Membrane bioreactor	58.7±72.8	0.3(median)	0.1(median)	Radjenovic et al 2006
Metoprolol	Sanitary waste water	Conventional Activated Sludge	<10	0.3(median)	0.27(median)	Radjenovic et al 2006

a: mean reduction after primary treatment, b: mean reduction after secondary treatment, c: mean reduction after advanced treatment, d: median reduction rate in winter, e: median reduction rate in summer

The addition of an adsorption step (GAC, granular activated carbon, or PAC, powdered activated carbon) in most of the processes (Bundy, et al. 2007, Snyder, et al. 2007, and Vieno et al 2007) helped to increase the removal of the pharmaceuticals and PCPs, with removal rates close to 90%. The adsorption of compounds were found to increase with increases in the Kow value of the EC (hydrophobic), but ion exchange processes may also influence this removal. The addition of different dosages of powdered activated carbon, the nature of the compound and the reaction times, must be taken into consideration to achieve the best results.

The membrane processes using RO (reverse osmosis), nano and ultra filtration, proved to be very effective in the treatment of pharmaceuticals and PCPs, with removal rates greater than 90% for most of the compounds (Snyder, et al. 2007, Yoon, et al. 2007). The removal mechanism is likely due to the retention of the compounds onto the membranes due to the hydrophobic nature of the compounds.

Most of the Veterinary pharmaceuticals are similar to compounds in the general PPCP listing. Therefore, the treatability expectations discussed previously can be used as general guidance.

Removal of Pharmaceuticals and Personal Care Products in Wastewater Treatment Plants

Description of Wastewater Treatment Unit Processes

Wastewater in a conventional treatment system goes through five different unit treatment processes that incorporate sedimentation, sorption, biodegradation (or degradation), and disinfection. Depending on the chemical properties of the constituent, one or more of these processes will reduce the compound’s concentration. The five steps of the treatment systems are (1) pre-treatment; (2) grit-removal; (3) primary treatment; (4) secondary treatment; and (5) disinfection.

Pre-treatment is the removal of large particles that could potentially clog a system and cause significant damage. In toilets, large objects are flushed in the sewer lines. In sewers, items as large as animals can pass through. Sanitary sewers are not designed to treat plastic items, cans, bottles, large paper items or large organic matter. The pre-treatment screen removes coarse solids to ensure debris does not enter the treatment plant and interfere with plant operations. For emerging contaminants that cause adverse effects at low concentrations, pre-treatment provides little benefit for the direct removal of these contaminants.

Pre-treatment may include a sand or grit channel or chamber where the velocity of the incoming wastewater is adjusted to allow the settlement of sand, grit, stones, and broken glass. These particles are removed because they may damage pumps and other equipment. For emerging contaminants, grit removal may remove a small portion of the ECs that are sorbed onto the larger particles. PAHs are known to sorb onto particulate matter (especially organics). For emerging contaminants in aqueous forms, there is no treatment during the grit removal process. The sorption of these chemicals is mostly to organic solids having low specific gravities, while the grit removal units are designed more for mineral based particulates that have very rapid settling characteristics.

Primary treatment, particularly in a biological treatment facility, involves the settling of particles and suspended solids from the aqueous solution. There likely is some treatment of certain emerging contaminants in this process. PAHs tend to sorb to particles and organic material due to their hydrophobic nature. The higher the molecular weight, the more likely it will sorb on to particle material. PAHs with lower molecular weights may remain in solution. Pollutants with a log K_{ow} of 3 or more theoretically sorb to solid or organic materials. Synthetic and natural hormones and surfactants found in wastewaters tend to have high log K_{ow} values and will therefore tend to sorb to particulates. However, if these pollutants are in an oxidized or metabolic form, characteristics of the parent compound may not be applicable. If pharmaceuticals and personal care products are in acidic or basic forms, depending on the pH, they will remain in aqueous solution.

Secondary Treatment

During this research task, treatability was examined at a conventional activated sludge wastewater treatment facility. Secondary treatment uses microbial organisms for the consumption (stabilization) of organic pollutants entering the treatment facility. Organic pollutants are therefore removed primarily by biodegradation. Some PPCPs, pesticides and EDCs are only partially removed using microbial action. Removal efficiency is dependent on several factors, such as physicochemical properties, the operation and design of the treatment facility (hydraulic and sludge retention time) and weather conditions and other seasonal variations (seasonal flow patterns and temperature).

Disinfection

Disinfection is the last phase in the treatment process of wastewaters before the final discharge of the effluent from a treatment facility. Disinfection is used to reduce the amounts of pathogenic microorganisms in the effluent. There are different methods of disinfection used at wastewater treatment facilities. Chlorination is one of the most common methods used, although chlorine can react with organic matter to form harmful compounds. Ultraviolet light and ozone are other means of disinfection for wastewater treatment. UV treatment damages the genetic structure of bacteria, viruses and pathogens, making them unable to reproduce. Ozone disinfection oxidizes the organics in the wastewater, destroying microorganisms that are present, but does not have a residual effect as does chlorine. The disinfection treatment used at the Tuscaloosa wastewater treatment system is UV light. Typically, the oxidation occurring in the disinfection process can further reduce organic pollutants (such as ECs).

Wastewater Treatment of Emerging Contaminants as Reported in the Literature

The first section of this literature review focuses on the characteristics of each category of emerging contaminants. Retention time affects the treatability of the emerging contaminants and can offer an explanation to the treatability and fate of compounds under normal conditions. In this section, studies are reviewed for conventional municipal treatment systems, a membrane bioreactor (MBR) treatment system and combined sewer systems. There is very little information on treatability of ECs from stormwater entering wastewater treatment facilities, which this research is addressing.

During this research task, the treatability of each compound examined for normal climatic conditions is analyzed to gain an understanding of how rain events generally affect certain chemicals through both literature reviews and monitoring activities.

Pharmaceuticals
During the Gobel (2007) study, samples were taken from two wastewater treatment systems, Kloten-Opfikon (WWTP-K) and Altenrhein (WWTP-A), near Zurich, Switzerland. The Kloten-Opfikon plant treats wastewater from about 55,000 population equivalents (PE): the combined sewage of 25,900 residents, and of an unknown number of air traffic passengers in the catchment area (Gobel 2007). The average inflow (dry weather) is 16,500 m^3/d. The primary treatment consists of pre-treatment and a primary clarifier. Sixty-percent of the primary effluent is further treated by an activated sludge treatment system that operates at a sludge age of three days and a hydraulic retention time of 5 hours (V=2,500 m^3). The main conventional activated sludge treatment (CAS-K) includes denitrification (V=1,900 m^3) and nitrification (V=3,700 m^3) with a solid retention time of 10–12 d. The hydraulic retention time (HRT), including the secondary clarifier, is about 15 h. A membrane bioreactor pilot plant is operated in parallel to the CAS-K facility, using primary effluent at a flow rate proportional to raw water influent (HRT about 13 h). The bioreactor consists of a stirred anaerobic compartment (V=6 or 8 m^3) and a denitrification (V=4 m^3) and nitrification (V=6 m^3) cascade. The solid retention time was increased between the sampling campaigns from 16±2 to over 33±3 d (steady state operation for two to three sludge ages prior to sampling).

The Altenrhein wastewater treatment plant treats the wastewater from 80,000 population equivalents, including 52,000 inhabitants. Primary treatment consists of pretreatment and a primary clarifier. Secondary treatment is performed in two parallel operated treatment units: a conventional activated sludge (CAS-A) and a fixed-bed reactor (FBR), receiving approximately fifty percent of the primary effluent each (Gobel 2007). Both systems are designed for nitrification and denitrification. Conventional activated sludge treatment includes a denitrifying volume (anoxic, mixed) of 2,300 m^3 and nitrifying (aerobic) volume of 6,800 m^3. The solid retention time in the CAS-A system ranged between 21 d to 25 d, while no value was available for the FBR. The hydraulic retention time was approximately 31 h for the CAS-A including the secondary clarifier, whereas it ranged below 1 h for the FBR.

Gobel et al. (2007) investigated the treatment of sulfanomides, macrolides and trimethoprim in conventional activated sludge systems and in fixed bed reactor systems. Table 5-4 is a list of the reduction rates for the primary treatment process.

Table 5-4. Reduction rates of ECs by primary sedimentation treatment

Compound	Acronym	CASRN	Percentage removal (%) n=9
Sulfapyridine	SPY	144-83-2	-29 to 20
Sulfamethoxazole	SMX	723-46-6	-21 to -5
N4-acetylsulfamethoxazole	N4AcSMX SMX + N4AcSMX	21312-10-7	9 to 21 0 to 9
Trimethoprim	TRI	738-70-5	-13 to 31
Azithromycin	AZI	83905-01-5	10 to 33
Erythromycin	ERY-H2O	114-07-8	-8 to 4
Roxithromycin	ROX	80214-83-1	3 to 9

(Gobel, et al. 2007)

The Gobel study showed a high degree of variability in the removal of each of the ECs during primary treatment (Table 5-5). Sulfamethoxazole concentrations are shown to increase in all samples during primary treatment. This is perhaps caused by the simultaneous presence of compounds that have been deconjugated, substances such as human metabolites of these compounds in the influent (Gobel 2007). N4-acetylsulfamethoxazole had reductions ranging from 9% to 21% during primary treatment.

During secondary treatment, the variability increased even more compared to primary treatment. The March 2002 data demonstrates an increase in sulfapyridine and sulfamethoxazole during the secondary treatment. The metabolite of sulfamethoxazole, N4-acetylsulfamethoxazole, showed a very high removal percentage. In each of the conventional treatment sludge systems investigated, the metabolite N4-acetylsulfamethoxazole had the highest reductions. The low removal rates for this study are likely a result of conjugation and deconjugation of the targeted compounds.

Table 5-5. EC reduction rates during secondary treatment (%)

Percentage reduction	WWTP-K	WWTP-K	WWTP-K	WWTP-A	WWTP-A
N = 3 for each period	March 2002	February 2003	November 2003	September 2002	March 2003
SPY	-74 ± 66	-16 ± 45	-107 ± 8	49 ± 5	72 ± 5
SMX	-107 ± 8	9 ± 3	-79 ± 7	-138 ± 15	60 ± 3
N4AcSMX	94 ± 2	87 ± 1	90 ± 1	96 ± 2	85 ± 1
SMX + N4AcSMX	50 ± 3	53 ± 1	-1 ± 3	61 ± 3	76 ± 1
TRI	3 ± 5	-1 ± 6	14 ± 5	20 ± 11	-40 ± 20
AZI	No results	-26 ± 8	-18 ± 7	55 ± 4	22 ± 11
ERY-H2O	6 ± 4	-14 ± 4	-22 ± 4	-6 ± 8	-9 ± 8
CLA	9 ± 4	-45 ± 7	-7 ± 5	4 ± 7	20 ± 6
ROX	18 ± 4	38 ± 3	-18 ± 6	38 ± 5	5 ± 8

(Gobel 2007)

In the Castiglioni (2006) study, six different wastewater treatment plants were observed with varying flow rates and population. Table 5-6 is a summary of the influent and effluent loads of all six treatment facilities. All six of the wastewater facilities were conventional activated sludge treatment plants with standard pre-treatment and primary treatment.

Table 5-6. Characteristics of wastewater treatment plants studied by Castiglioni, et al. (2006)

STP	Population	Flow rate MGD	Type of waste treated
Cagliari	270,000	22.9	domestic
Naples	840,000	47.8	domestic
Latina	45,000	5.0	domestic
Cuneo	140,000	8.2	domestic
Varese Olona	120,000	6.1	domestic
Varese Lago	110,000	10.5	domestic and industrial

(Castiglioni, et al. 2006)

The Castiglioni research (Table 5-7) found that ibuprofen, sulfamethoxazole and carbamazepine all had relatively low to moderate removal rates. Ibuprofen and sulfamethoxazole were not associated with particulates, and showed moderate removal rates of 55 percent and 24 percent respectively. Although carbamazepine was associated with the particulate matter, it had zero percent removals. The apparent effluent loads for carbamazepine increased compared to the influent loads which possibly indicates some chemical activity occurred through the unit processes, such as potentially liberating the compound from particulate matter, or changes in the presence of interfering compounds through the treatment processes

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Table 5-7. Summary of EC Loads and Removal Rates at Wastewater Treatment Facilities

Pharmaceuticals	Load in influent (mg/d/1000 inh)	Removal rate in STP (%)	Residual load in effluent(mg/d/1000 inh)	Occurrence in particulate (+/-) *
atenolol	494	21	281	+
ofloxacin	360	57	233	+
Ibuprofen	122	55	28	-
Sulfamethoxazole	65	24	10	-
Carbamazepine	12	0	28	**+**

Castiglioni, et al. (2006)
*presence or absence of pharmaceutical (qualitative)

The wastewater treatment plant in the Rosal (2010) study is located in Alcala de Henares in Madrid, Spain. Table 5-8 summarizes the plant performance. This plant treats a mixture of domestic and industrial wastewater with a capacity of 3,000 m^3/h (33,020 gpd) (Rosal, et al. 2010).The facility serves a population of more than 10,000 inhabitants. It uses secondary biological treatment, although they do not specify which biological treatment process was used. The treatment plant had an influent pH of 7.54 (0.24) and effluent pH of 7.63 (0.17) (Rosal, et al. 2010). Treatment takes place in anaerobic, anoxic and oxic zones. This study showed that gemfibrozil and triclosan possessed the highest removal rates, at 76 percent and 75 percent, respectively. Trimethoprim and carbamazepine showed the lowest removal rates at 5.1% and 9.5%, respectively. For most compounds, the removal rates during biological treatment increased with higher hydrophobicity with many non-polar substances being sorbed to the sludge.

Table 5-8. Dissociation Constants, Influent and Effluent Concentrations of ECs

Compound	Caffeine	***Carbamazepine***	***Gemfibrozil***	Naproxen	***Sulfamethoxazole***	***Triclosan***	***Trimethoprim***
pKa	10.4	13.9	4.7	4.2	5.7	7.8	6.8
Influent (ng/L) Max Min Avg	65 x 10^3	173	17 x 10^3	5228	530	2417	197
	5 x 10^3	106	415	1196	162	<LOQ	78
	23 x 10^3	129	3.5 x 10^3	2363	279	860	104
Effluent (ng/L) Max Min Avg	1589	173	5233	2208	370	512	148
	<LOQ	69	3	359	104	<LOQ	<LOQ
	1176	117	845	923	231	219	99
Removal Efficiency (%)	94.5	9.5	76.0	60.9	17.3	74.5	5.1

(Rosal, et al. 2010)

Lishman (2006) studied twelve wastewater treatment facilities. Treatment processes used included lagoons, activated sludge, and activated sludge with filtration. The treatment facilities treated residential and industrial wastewaters. Average daily flow rates ranged from 1,984 m^3/d to 105,300 m^3/d. All activated sludge systems studied used primary clarification. Table 5-9 is a compilation of the plant systems' influent and effluent concentrations.

Table 5-9. Influent and Effluent Concentrations, Detection Limits and Percent Reductions

Analyte	MDL (µg/L)	Point source	Median (µg/L)	Mean (µg/L)	Maximum (µg/L)	Percent reductions (%)
Ibuprofen	0.061	Influent	8.84	8.45	16.5	
		Effluent	0.353	0.384	0.773	95.4%
Gemfibrozil	0.077	Influent	0.418	0.453	0.965	
		Effluent	0.255	0.246	0.436	45.7%
Naproxen	0.074	Influent	5.22	5.58	17.1	
		Effluent	0.351	0.452	1.189	91.9%
Triclosan	0.031	Influent	1.86	1.93	4.01	
		Effluent	0.106	0.108	0.324	94.4%
Diclofenac	0.062	Influent	0.140	0.204	1.01	
		Effluent	0.140	0.194	0.748	4.9%

(Lishman, et al. 2006)

The Lishman study (Table 5-10) reported ibuprofen and triclosan removal rates of more than 90 percent, while gemfibrozil and diclofenac had very low removals. Gemfibrozil and diclofenac both have been shown in the literature to have moderate removals: 46 percent (Lishman, et al. 2006) and 69 percent (Ternes, et al. 1998). Clara, et al. (2003) showed moderate removals for diclofenac and gemfibrozil of between 53 percent and

74r percent (Lishman, et al. 2006). Eight of the twelve WWTP under investigation were conventional wastewater treatment systems. The others were lagoon wastewater treatment systems.

Ibuprofen and triclosan all had higher removals at conventional wastewater treatment facilities. Ibuprofen has the highest removals with low variability. Naproxen and triclosan both had relatively high removal percentages, but triclosan has a slightly higher variability between the conventional treatment systems. Gemfibrozil varied in concentration removal but overall, it was lower than seventy percent. Some of the removal rates were as low as 38 percent.

Table 5-10. Percent reductions of ECs at conventional activated sludge wastewater treatment facilities

CAS plant	IBP	NPX	GMF	DCF	TCL
4	95	79	43	-88	74
5	98	96	###	**#	98
6	###	95	69	22	97
7	94	86	38	-103	93
8a	98	98	###	###	93
8b	94	81	66	28	85
9	91	90	71	-143	89
10	###	98(#)	###	77	98

(Lishman, et al. 2006)

*--number of times there was non-quantifiable values; #--measurable in the influent and non-quantifiable in the effluent

Miege (2009) prepared a comprehensive literature review, compiling wastewater treatment removal data for ECs from 117 publications. Table 5-11 is a summary of the treatment plant data for conventional activated sludge facilities. This review examined the targeted emerging contaminants and also the metabolites of carbamazepine. For this set of data, ibuprofen and naproxen had high removals ranging from 87 percent to 94 percent. Trimethoprim had a medium removal rate of 74 percent. Triclosan, gemfibrozil and sulfamethoxazole all had lower removal rates of less than 70 percent. Carbamazepine had a 30 percent removal rate and their metabolites ranged from negative 80 percent to 51 percent, consistent with other literature values. Ibuprofen shows relatively high removal rates in the literature. There is significant variability of each analyte, possibly a result of each contaminant’s physical and chemical properties.

Table 5-11. Comparison of Influent and Effluent and Percentage Reductions for ECs

Analyte	Sample location	Median (µg/L)	Mean (µg/L)	Min (µg/L)	Maximum (µg/L)	n	Frequency of quantification (%)	Percent reduction (%)
Ibuprofen	Influent	3.20	14.6	0.170	83.5	3	100	
	Effluent	0.800	1.96	0.0020	24.6	109	93	86.5
Gemfibrozil	Influent	1.49	1.63	0.700	3.00	4	25	
	Effluent	0.600	0.564	0.0600	1.34	21	70	65.4
Naproxen	Influent	6.00	26.4	1.79	611	45	96	
	Effluent	0.880	1.89	0.170	33.9	53	87	92.8
Triclosan	Influent	*****	0.380	*****	*****	1	100	
	Effluent	0.130	0.150	0.0700	0.430	19	100	60.5
Diclofenac	Influent	0.997	1.34	0.105	4.11	91	81	
	Effluent	0.420	0.680	0.0350	1.95	101	85	49.2
CBZ-10OH	Influent	*****	0.0222	*****	*****	3	100	
	Effluent	*****	0.0325	*****	*****	3	100	-46.3
CBZ-2OH	Influent	*****	0.0390	*****	*****	3	100	
	Effluent		0.0704			3	100	-80.5
CBZ-3OH	Influent	*****	0.0554	*****	*****	3	100	
	Effluent	*****	0.0692	*****	*****	3	100	-24.9
CBZ-DiOH	Influent	*****	1.001	*****	*****	3	100	
	Effluent	*****	1.08	*****	*****	3	100	-7.9
CBZ-EP	Influent	*****	0.0392	*****	*****	3	100	
	Effluent	*****	0.0191	*****	*****	3	100	51.3
Carbamazepine	Influent	0.732	0.968	0.100	1.90	64	100	
	Effluent	0.520	0.674	0.150	2.30	63	100	30.4
Sulfamethoxazole	Influent	0.157	0.342	0.0200	1.25	10	71	
	Effluent	0.0700	0.115	0.0180	0.320	11	73	66.4
Trimethoprim	Influent	0.281	0.449	0.0800	1.30	10	100	
	Effluent	0.0600	0.118	0.0200	0.550	27	93	73.7

(Miege, et al. 2009)
*****no value reported

Radjenovic (2007) did a comparison of the treatability between a membrane bioreactor system (MBR) wastewater system and a conventional activated sludge (CAS) treatment system, as shown on Table 5-12. The MBR is a suspended growth activated sludge system that uses microporous membranes for solid/ liquid separations instead of secondary clarifiers (Stephen Chapman and Law). A MBR of approximately 21 L active volume equipped with two flat sheet membranes was installed in a municipal WWTP. Although the nominal porosity of the membrane was 0.4µm, a fouling layer of proteins and microorganisms formed on the surface, reduced the effective porosity to 0.01µm (Radjenovic, et al. 2007). The MBR was operated in parallel with the aeration tank and secondary settling tank. The Rubi CAS wastewater treatment plant was designed for a population of 125,550. The WWTP was operating with an average daily flow rate of 22,000 m^3/d. The treatment plant was designed to treat municipal, hospital and industrial wastewater. Treatment was a biological activated sludge system with standard pretreatment and primary treatment. The hydraulic retention time was approximately 12 hours and the sludge retention time was approximately three days.

There is a greater variability in removal for all of the compounds for CAS facilities. Gemfibrozil had the largest differences in treatability with the MBR removal at 90 percent and the CAS removal at 39 percent. Diclofenac showed an 80 percent t removal for MBR facilities, while removal at the CAS facilities was only 50 percent. Carbamazepine showed no removal for either treatment system. Ibuprofen, naproxen and sulfamethoxazole displayed small differences in removals between the treatment plant types.

Table 5-12. Comparison of Membrane Bio Reactor and Conventional Activated Sludge

Compound	Elimination percentage	
	MBR	CAS
Analgesic/Anti-inflammatory drugs		
Naproxen	99.3(1.52)	85.1(11.4)
Ibuprofen	99.8(0.386)	82.5(15.8)
Diclofenac	87.4(14.1)	50.1(20.1)
Anti-epileptic drugs		
Carbamazepine	No elimination	No elimination
Antibiotic		
Sulfamethoxazole	60.5(33.9)	55.6(35.4)
Lipid Regulator/Cholesterol lowering statin drug		
Gemfibrozil	89.6(23.3)	38.8(16.9)

Source: Radjenovic, et al. 2007

This current research did not investigate hormones, but their reported treatability offers some insight on the treatment potential of other ECs. Some personal care products act as EDCs, thus understanding their behavior in wastewater treatment systems is important. Hormones have a range of log K_{ow} values but tend to range above three. Andersen et al (2003) observed removals of estrogen at one conventional activated sludge facility, as shown on Table 5-13. The project examined the municipal wastewater treatment plant in Wiesbaden, Germany. The primary effluent is directed to an activated sludge system for biological and chemical treatment, including phosphate removal, denitrification, and nitrification (Anderson, et al. 2003). Fe(II)Cl_2 is added in the first denitrification tank for efficient mixing in the water before oxidation to Fe(III) and subsequent precipitation with phosphate in the aerated nitrification tanks. After settling in the secondary clarifier, the activated sludge is returned to the inlet of the first denitrification tank. The secondary effluent is discharged into the river Rhine. The activated sludge system is operated with a solids retention time of 11-13 d, which is typical for a nitrifying plant with predenitrification. The range of concentrations for E1, E2, and EE2 were in the nanograms per liter range throughout the treatment system. When being treated in the primary clarifier, there was an increase in E1 concentrations and in the combination of E1 and E21. This is possibly due to the hormones reacting with each other and metabolites in the primary clarifier. All hormones showed almost total removal after nitrification and denitrification. Hormones were significantly reduced only after biological treatment.

Table 5-13. Estrogen Influent and Effluent Concentrations

Concentration of dissolved estrogen in WTP Wiesbaden (ng/L)						
	Inlet	Primary effluent	Denitrification 1	Denitrification 2	Nitrification	Secondary effluent
E1 (estrone)	65.7 (54.9-76.6)	74.9 (66.2-83.6)	37.3 (29.7-44.9)	2.8 (2.2-3.5)	1.8 (1.8-1.9)	<1
E2(17β-estradiol)	15.8 (12.2-19.5)	10.9 (9.2-12.6)	10.3 (9.2-11.4)	<1	<1	<1
E1 + E2	81.5 (67.1-96.0)	85.8 (75.4-96.1)	47.6 (38.9-56.3)	2.8	1.8	<2
EE2 (17α-Ethinylestradiol)	8.2 (6.2-10.1)	5.2 (3.5-7.0)	1.5 (0.9-2.1)	1.2 (1.1-1.3)	<1	<1

(Anderson, et al. 2003)

Ternes (1998) studied fourteen pharmaceuticals at German wastewater treatment plants. Composite samples were taken from a municipal STP in Frankfurt/Main, Germany, daily over a period of six days. The treatment plant serves a population of 312,000. Treatment consists of primary treatment, using an aerator tank with the addition of Fe (II) chloride for phosphate removal (Ternes 1998). The average daily flow rates ranged from 58,100 to 89,900 m^3/d. Propanolol and ibuprofen were the two ECs with the highest removals at 96 percent and 90 percent, respectively. The lowest removals were for gemfibrozil (69 percent) and carbamazepine (7 percent). The removals of several antiphlogistics and lipid regulating agents were investigated during another sampling event, which included rainfall on the fourth day leading to an elevated flow rate of about fifty percent, from an average of 59,300 m^3/day to 89,900 m^3/day. The removals of bezafibrate, diclofenac, naproxen and clofibric acid were significantly reduced on the rainfall day and only bezafibric (<5% reduction) recovered by the sixth day.

These results indicate that rainfall affected the treatment, possibly by reduced residence times in the unit processes, reduced microbial activity, or altered sorption and/or flocculation conditions in this rainfall period (Ternes 1998). Joss (2005) noted that biological removal varied strongly from compound to compound, with no evident correlation to the compound structure. Ibuprofen was removed to below the quantification limit at the outfall (>90% removal). There was no removal for carbamazepine or sulfamethoxazole (although there was significant removal of the metabolite N4-acetyl- sulfamethoxazole). The data did not show whether biological transformations occurred because the estimated elimination is significantly smaller than the data accuracy (95 percent confidence interval) (Joss 2005).

Removal rates for each compound observed for pharmaceuticals had high variabilities for the different compounds. Ibuprofen consistently had high removals for each study, while sulfamethoxazole and triclosan showed varying removals (triclosan ranged from 61 to 94%, while sulfamethoxazole ranged from -140 to 66 percent removals. Sulfamethoxazole has more than one form and possibly undergoes chemical alteration in the treatment process. Gemfibrozil and carbamazepine has lower variability removals, but at consistently lower values. Estrogen activity in wastewater has been examined during some studies (Teske and Arnold 2008; Anderson, et al.2003). Estrogen was included in this literature review because they are identified as endocrine disruptor chemicals. They are also biological active showing similarity to pharmaceuticals and personal care products. Their removals in wastewater treatment facilities, based on their physical and chemical characteristics, are similar to pharmaceutical removals.

Properties of Endocrine Disruptors Affecting their Treatment

As noted above, some personal care products (PPCPs), pharmaceuticals, synthetic estrogens, and pesticides imitate natural estrogens that affect the endocrine system. These chemicals are called endocrine disruptor chemicals (EDCs). The United States' EPA defines an EDC as "an exogenous agent that interferes with the synthesis, secretion, transport, binding, action, or elimination of natural hormones of natural hormones in the body that are responsible for the maintenance of homeostatis, reproduction, development, and/or behavior" (Campbell, et al. 2006). Table 5-14 summarizes some of the properties of endocrine disruptive chemicals.

Table 5-14. Properties of Endocrine Disruption Chemicals

EDC	Molecular weight (g/mol)	Water solubility at 20^oC (mg/L)	Log K_{ow}
Estrone (E1)	270.4	13	3.43
17β-Estradiol (E2)	272.4	13	3.94
Estriol (E3)	288.4	13	2.81
Ethinyl Estradiol (EE2)	296.4	4.8	4.15
Bisphenol A	228.0	300	3.40
Octylphenol (OP)	206.3	12.6	4.12
Nonylphenol (NP)	220.0	5.43	4.48
Nonylphenol polyethoxylates (n≥3-5)	352.0-440.0	5.88-9.48	4.2-4.3
Nonylphenoxy ethoxy acetic acid	322	soluble	1.34

(Teske and Arnold 2008)

Hormones are classified as endocrine disrupting compounds because they cause hormonal abnormalities in aquatic wildlife such as fish. Many EDCs have moderate to high log K_{oc} values, so they tend to sorb to sediments or suspended solids (Campbell, et al. 2006). In their sediment associations, there is the potential for biological uptake, degradation and transformations to less or more mobile forms (Campbell, et al. 2006). The solubility values suggest they would not stay in solution; however, most EDCs are identified in water samples. Campbell (2006) also found a poor correlation between colloidal partitioning coefficient and the water octanol partitioning coefficients (log K_{ow}), indicating the dominant mechanism for the binding of EDCs to colloidal particles may not be controlled by its log K_{ow}.

Estrogens are one of the main endocrine disruptors present in influent and effluent at wastewater treatment facilities. The most common synthetic hormone used for contraceptives is 17 α-ethynylestradiol, with concentrations being 30 to 50 µg per pill (Beausse 2004). Synthetic compounds with estrogenic activity include 17α-ethinylestradiol (EE2), and alkylphenol polyethoxylates (NPnEO) (Teske and Arnold 2008). In the Teske literature review, chemical and biological characteristics such as chemical structure, molecular weight, water solubility at 20°C and the log K_{ow} are listed. Estrogens have low solubility and high log K_{ow} values that suggest sorption is a key component in the removal of estrogen during wastewater treatment.

Campbell's (2006) review showed estradiol exhibits log K_{oc} of 2.55-4.01 L/kg; water solubility of 13.0-32 mg/L and pKa of 10.5-10.71. The same literature shows 17β-Estradiol (E2) has similar properties of log K_{oc} 3.10-4.01 and water solubility of 13.0 mg/L. The estrogens have low solubility and moderately high octanol-water partitioning coefficient. The log k_{ow} that are generally above 3 suggest they would not remain in solution. Some studies show estrogens present in the effluent and not sorbed to particulates. Campbell (2006) argue: (1) there are more soluble precursors of metabolites being transport (i.e. nonylphenol carboxylics); (2) there is more colloid facilitated transport; (3) there is an enhanced solubility through elevated pH (many e-EDCS have a pka around 10); and (4) there is the formation of micelles which can greatly enhance the stability of the compound.

In some of the literature, commonly measured physicochemical properties are not always the best predictors affecting the treatment behavior of EDCs. Literature records other factors that could be pivotal in predicting EDC removal in wastewater treatment facilities. Researchers found certain EDCs were reduced in wastewater systems due to the increase of sludge retention time. Some compounds are transformed throughout the treatment process. Seasonal conditions could affect the treatability of wastewater systems.

Combined Sewer Systems

In order to better understand how wet weather flows affect municipal wastewater treatment facilities, one should examine performance at treatment facilities for combined sewers. Wastewater that enters combined sewers consists of both raw sewage and stormwater. Stormwater increased inflow is similar to municipal sewers during wet weather from I&I (inflow and infiltration).

Combined sewers are single drainage systems than simultaneously collect stormwater and wastewater in the same collection system. During dry weather, the sanitary wastewater is drained to the treatment plant, but during wet weather, the combined flows commonly exceed the treatment plant's capacity, and the excess overflow is discharged mostly untreated to the receiving water.

In combined sewers, the stormwater affects the concentrations of the pollutants in the influent to the treatment plant (likely decreasing the concentrations of most PPCPs, while increasing concentrations of PAHs and pesticides), and increase the flows being treated, with associated decreased residence times in the treatment unit processes. In addition, combined sewer overflows (CSOs) occur with the discharge of untreated influent when the flows exceed the capacity of the treatment plant. Weyrauch, et al. (2010) reported CSOs occurring when rain events exceeded 4.7 mm (0.19 in). Numerous studies emphasize the importance of pollutant loads conveyed by combined wet weather discharges and their adverse impacts on receiving waters (Kafi, et al. 2008). Also, in Kafi's study, there was an increase in suspended solids, organic matter and hydrocarbon concentrations. A decrease was found in heavy metal concentrations at the outfall during wet weather periods.

Boyd, et al. (2004) found concentrations of ibuprofen and triclosan in urban receiving water canals in New Orleans after 7 cm or more rainfalls (Phillips and Chalmers 2009). Phillips, et al. (2009) reported that the concentrations and numbers of organic wastewater compounds were higher in storm flow samples collected than in baseflow samples: 1.5 to 9.4 µg/L in stormwater and 0.05 to 0.17 µg/L in baseflow samples.

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons are compounds derived from petroleum products such as tar, oil and coal, and are byproducts of burning these materials. They are comprised of several benzene rings. As petroleum products are combusted, many PAHs are emitted in the atmosphere. PAHs are ubiquitous environmental pollutants with carcinogenic and mutagenic properties that can have adverse effects if exposed to humans (Busetti, et al. 2006). Stormwater transports PAHs from sources such as asphalt, oil and gas usage, and from wet and dry atmospheric deposition. PAHs can enter sanitary wastewater through I&I. In this study, the monitoring of typical stormwater PAHs at the wastewater treatment facility was done to investigate their wet weather contributions and to determine their treatability under both dry and wet weather conditions. PAHs are differentiated by the number of rings and the placement of hydrocarbons connected to the rings reveal physical and chemical properties. At wastewater treatment facilities, PAHs can undergo changes in physical and chemical compositions. PAHs are typically insoluble in water and are very lipophilic. Due to their strong hydrophobic characteristics, PAHs are mostly removed from wastewaters during the activated sludge treatment process through sorption onto particulates that are then removed from the wastewater by sedimentation (Busetti, et al. 2006).

PAHs are divided into two groups: those with low molecular weights and those with high molecular weights. PAHs containing four or fewer rings are easier to biodegrade than PAHs with five rings or greater (Hazardous Substance Database 2012). PAHs such as naphthalene and acenaphthene both have low molecular weights. Acenaphthene is also a non-carcinogenic EPA priority pollutant with a two-ring chemical structure. Acenaphthene and naphthalene are easily biodegradable because they are lower in molecular weight and have smaller ring structures. With solubility in water of 31.7 mg/L and a Henry's law constant of 4.6×10^{-4}; it is likely that volatilization will be an important route of naphthalene loss from water (ATSDR 2011). PAH compounds such as benzo(a)pyrene and chrysene have more cyclic rings and have higher molecular weights. There is a correlation between increasing molecular weight of these compounds and decreasing solubility. Anthracene and pyrene have three to four cyclic carbon rings, causing an increase in sorption capacity and reduction in aqueous solubility. Fluoranthene has a slightly higher molecular weight and is highly lipophilic, with a log K_{ow} of 5.14 and solubility of 0.20 to 0.26 mg/L (Crunkilton and DeVita 1997). Chrysene has a high molecular weight of 228.3 g mol^{-1}, log K_{ow} of 5.16, and solubility of 2.8µg/L (ATSDR 2011). PAHs such as benzo[b]fluoranthene (log K_{ow}=6.04) and benzo[a]pyrene (log K_{ow}=6.06) all have very high log octanol-water coefficients and correspondingly very low solubilities. The toxicities of PAHs have a wide range. Many are above the concentration ranges found at wastewater treatment plants as indicated in the literature and from the experimental data during this research. Table 5-15 summarizes various characteristics of PAHs.

Table 5-15. Characteristics of PAHs

Compound	Molecular weight (g/mol)	Solubility (water)(mg/L)	Log K_{ow}	Volatility atm^{-3}/mol	Toxicity **
naphthalene	128.2	31.7*	3.37*	$4.6x10^{-4}$ *	LC50 Pimephales promelas 7.76 mg/L
acenaphthylene	152.2	3.93*	3.89**	1.45×10^{-3} *	
acenaphthene	154.2	1.93*	4.02**	7.91×10^{-5} *	LC50 Salmo gairdneri 1570 µg/L
fluorene	166.2	1.68-1.98 *	4.12**	1.0×10^{-4} *	EC 50 V. fischeri 4.10 µg/mL
anthracene	178.2	0.076 *	4.53**	1.77×10^{-5} *	D.magna EC 50=211 µg/L
phenanthrene	178.2	1.20 *	4.48**	2.56×10^{-5} *	EC50; Daphnia magna 678.41 µg/L
pyrene	202.2	0.077 *	5.12**	1.14×10^{-5} *	D.magna EC 50=67000 µg/L
fluoranthene	202.2	0.20-0.26 *	5.14**	6.5×10^{-6} *	S. capricornutum EC 50=54,400 µg/L
benzo[a]anthracene	228.3	0.010*	5.61*	n/a	
chrysene	228.3	2.8×10^{-3} *	5.16*	n/a	LC50 Daphnia magna 1.9 mg/L
benzo[b]fluoranthene	252.3	0.0012	6.04*	n/a	
benzo[a]pyrene	252.3	1.6×10^{-3}	6.06*	n/a	EC50: Daphnia magna; 40 µg/L

*ATSDR; **Crunkilton 1997

PAHs are also known as semivolatile organic compounds. Under certain conditions they can sorb onto particulates, have some solubility in water, or enter into a gaseous phase depending on their individual properties. PAHs with higher Henry's constants are more volatile. Some of the LMW PAHs are more soluble than HMW PAHs. PAHs with lower molecular weights are less likely to adsorb onto particulate matter and be volatized or remain in solution. The phase distribution of any PAH depends on the vapor pressure of the PAHs, the atmospheric temperature, the PAH concentration, the affinity of the PAH for the suspended particles (k_{ow}), and the nature and concentration of the particles (ATSDR 2011). Table 5-16 lists some PAHs by molecular weight category.

Table 5-16. PAH Categories

Low Molecular Weight PAHs	High Molecular Weight PAHs
Naphthalene	Benzo(a)anthracene
Acenaphthene	Pyrene
Acenaphthylene	Benzo(a)pyrene
Fluorene	Chrysene
Phenanthrene	Benzo(b)flouranthene
Anthracene	Fluoranthene

Sorption onto particulates is directly related to sorption coefficients, solubility and the amount of organic material, but biodegradation of PAHs vary considerably. Ogawa (1982) observed that microorganisms in stored groundwater samples completely degraded acenaphthene and acenaphthylene within three days, while other studies determined that, based on estimated reaction rates or half-lives, acenaphthene, acenaphthylene, and fluorene may not readily biodegrade in water (ATSDR 2011). Vapor pressure, temperature and the Henry's constant are other properties that may affect how PAHs are treated throughout the unit processes of the treatment plant, but log K_{ow} is most likely to be the most important parameter indicating their treatability.

PAHs in Combined Sewer Overflows (CSOs)

Blanchard (2001) tested samples from five combined sewer wastewater treatment plants near Paris, France. The effluents were collected from the five sewers entering the Ache`res. The average flow rates were: (1) 220,000 $m^3$/d (58.1 MGD) for the Se`vres 1-Ache`res Rueil;(2) 360,000 $m^3$/d (95.1 MGD) for the Saint Denis-Ache`res (3); 900,000 m^3/d (237 MGD) for the Clichy-Ache`res junction of Argenteuil; (4) 600,000 $m^3$/d (159 MGD) for the Clichy-Ache`res junction of Bezons and (5) 600,000 m^3/d (159 MGD) for the Se`vres 2-Ache`res junction of Saint-Cloud Nanterre (Blanchard, et al. 2001, 3679-3687). Samples from the Ache'res were taken during both dry weather and for wet weather, as shown on Figure 5-1. Atmospheric fallout was also monitored for this study.

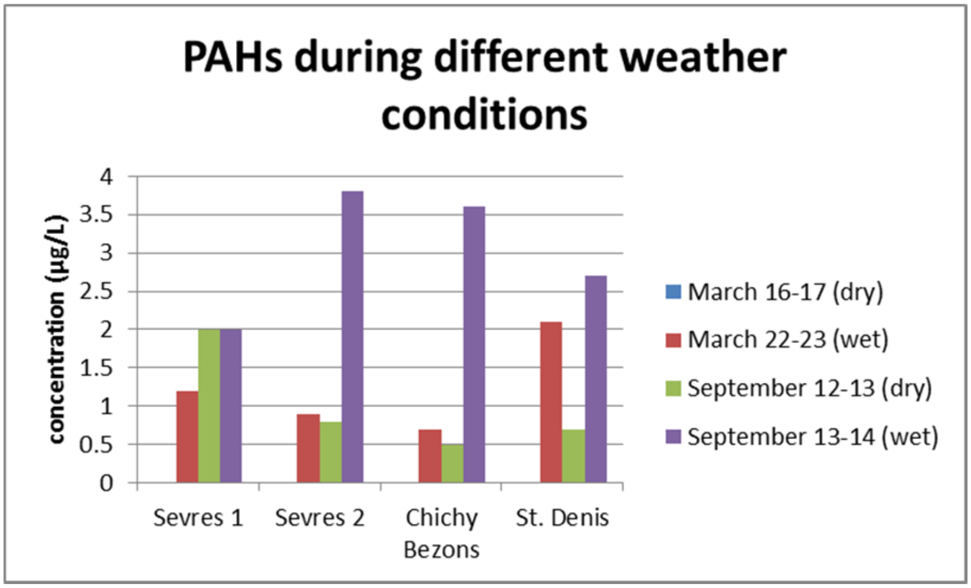


Figure 5-1. Comparison of dry and wet weather concentrations for total PAHs (Blanchard, et al. 2001)

Blanchard (2001) observed a relationship between influent PAH concentrations during two dry weather events and during two wet weather events at four wastewater treatment plants in the same area. They found PAHs increase in the influent to the treatment plant during large rains due to stormwater influences.

There does appear to be a correlation between the reductions of PAHs and their molecular weights (Manoli and Samara 1999, 176-186). Pham (1997) collected samples from the Montreal, Canada Urban Community (MUC) wastewater treatment system. The MUC wastewater treatment plant receives combined domestic, industrial and stormwater wastewaters since its opening in 1988 (Pham and Prouix 1997). The MUC wastewater treatment plant serves approximately 1.4 million people (out of a total population of 1.8 million), and approximately 15 percent of its total flow is contributed by industry (Pham and Prouix 1997). There are two intercepting areas connected to the plant: (1) the north and southwest sector of Montreal Island and the (2) southeast sector. The MUC treatment plant treats 1.3 million m^3/day, (343 MGD), however the southeast sector was only partially collected. Under heavy rainfall conditions, this flow rate can triple. The capacity for this facility, including the southeast sector is 2.8 million m^3/d (740 MGD).

Pham (1997) investigated several PAHs and their removals, as shown in Table 5-17. Each PAH showed a variety of reductions. Naphthalene had the lowest reductions which indicate minimal sorption to particulate matter and also low biodegradation. Naphthalene has a low molecular weight and is one of the more soluble PAHs, so there may be aqueous forms of it throughout the treatment plant. Many of the low molecular weight compounds, such as fluorene, anthracene and phenanthrene, had moderate removals, ranging from 57 to 65 percent. Acenaphthylene is a LMW PAH, but during these observations, it had high removals. Chrysene had the highest removals, at 93 percent. It is a high molecular weight PAH so it was consistent with the theory that most of HMW PAHs are removed in the primary sedimentation stage.

Table 5-17. Mean, Standard Deviations and Removal Percentages of Influent and Effluent

	N=10		N=6		
	Avg Influent μg/L	std Influent μg/L	Avg Effluent μg/L	std Effluent μg/L	Overall Average Removal rates %
Naphthalene	0.147	0.084	0.088	0.049	40
Acenaphthylene	0.021	0.051	0.002	0.005	90
Acenaphthene	0.016	0.011	0.005	0.003	67
Fluorene	0.037	0.025	0.015	0.008	59
Phenanthrene	0.333	0.228	0.109	0.055	67
Anthracene	0.028	0.034	0.012	0.007	58
Fluoranthene	0.150	0.193	0.020	0.007	86
Pyrene	0.138	0.157	0.023	0.007	83
Chrysene	0.080	0.122	0.005	0.002	93

(Pham and Prouix 1997)

Manoli (1999) collected samples from the Thessaloniki, Greece, combined sewage wastewater treatment plant. It is a conventional activated sludge treatment facility which includes the addition of a flocculant and chlorine dioxide for disinfection. The plant receives a dry weather flow of approximately 40,000 m^3/d, consisting mainly of the residential discharges from the city of Thessaloniki (Manoli and Samara 1999). The treatment unit processes include: (1) pre-treatment with aerated sands and grease removal units; (2) a primary sedimentation tank with a detention time of three hours, (3) an aeration tank with surface aerators with a detention time of three hours, and a secondary sedimentation tank with a detention time of 6 hours. Table 5-18 summarizes the observed concentrations of PAHs within this treatment plant.

Table 5-18. PAH Concentrations through each unit process (μg/L)

Pollutant	Influent	Primary effluent	Secondary effluent	Final effluent	Percent reduction
naphthalene	7.3	7.6	5.7	5.0	32
acenaphthene	0.7	0.3	0.17	0.11	84
fluorene	0.7	0.5	0.5	0.23	67
phenanthrene	1.7	0.57	0.18	0.2	88
pyrene	0.47	0.12	0.07	0.06	87
benzo(a)anthracene	0.05	0.015	0.0052	0.0047	91
chrysene	0.16	0.033	0.014	0.015	91

(Manoli and Samara 1999)

Each of the PAHs varied in removal. In Table 17, naphthalene showed the lowest removal rate. Naphthalene also showed an increase in the primary effluent, before its reduction in the secondary and final treatment process. Benzo(a)anthracene and chrysene had the highest reduction rates. Most of these two compounds were removed during primary treatment. These compounds were higher in molecular weight, which imply sorption was likely the primary removal mechanism for those compounds. The lower molecular weight PAHs are more likely to be removed in the secondary treatment unit processes of the facility.

Pesticides

Pesticides and herbicides are used to reduce damaging or nuisance insects, weeds or other pests that have a negative impact on agriculture or public health. Chemical pesticides contributed to increased yields of agriculture by controlling pests and diseases (AHMAD, et al. 2010); however, excessive amounts of pesticides can have detrimental effects on wildlife and human populations. Highly chlorinated pesticides are known as persistent organic pollutants (POPs). POPs tend to have low water and high fat solubility, stability during degradation processes, low vapor pressure and are persistent in the environment (Katsoyiammis and Samara 2004). Pesticide contaminants enter wastewater treatment plants by surface runoff from treated sites, in contaminated rinses from cleaning of pesticide applicators and containers, and/or from disposal of unused pesticides (Monteith, et al. 2995).

The major types of pesticides are organochlorine pesticides and organophosphorus pesticides. These categories are further divided into four types: insecticides, fungicides, herbicides and bactericides (Badawy, et al. 2006). Chlorinated phenoxy acid herbicides, which account for the majority of pesticides worldwide, are characterized by high polarity and thermal lability (Petrovic, et al. 2003).

Organochlorine pesticides are known for their persistence in the environment and their bioaccumulation in the food chain (Jiries, et al. 2002). Organophosphorus pesticides degrade faster in the environment than organochlorine pesticides (Jiries, et al. 2002). Researchers in Switzerland analyzed the fate and transport of azole fungicides and found the fungicides were unaffected by wastewater treatment. Azole fungicides in wastewater are moderately lipophilic and fairly persistent with half-lives of weeks to months (Kahle, et al. 2008). Chlorinated hydrocarbon pesticides and chlorophenoxy herbicides are used worldwide and have been detected in the nanogram per liter and microgram per liter levels in almost every major U.S. river and lake (Saleh, et al. 1980). 2, 4-D, butoxyethyl ester and 2, 4-D, isooctyl ester have a water solubility of 10-12 mg/L. 2, 4-D, isopropyl ester has a higher solubility at 46 mg/L and also may not be effectively removed at wastewater treatment plants, depending on biodegradation. The pesticides prochloraz, flusilazole and epoxiconazole have relatively high log K_{ow} values of 4.38, 3.7 and 3.4 respectively. Although these values generally indicate these compounds are highly lipophilic and less soluble, studies at several wastewater treatment plants show they were not significantly removed.

Most likely, pesticide sources entering the wastewater treatment plant are from stormwater I&I entering the wastewater treatment plant. A number of pesticides are implicated as endocrine disruptors in aquatic and wildlife species (US EPA 2001). Table 5-19 summarizes the properties of pesticides that affect their treatability.

Table 5-19. Properties of Pesticides Affecting their Treatability

Pesticide	Log k_{ow} *	Solubility (mg/L)*	Toxicity (LC_{50}) ***	Biodegradation (half-life) ***
Methoxychlor(	4.68-5.08	0.1	D. magna (EC 50) 16µg/L	7-29 days; >100 days
Aldrin	6.5	0.027	Salmo gairdneri (rainbow trout) 2.6 µg/L	20-100 days
Dieldrin	6.2	0.1	Salmo gairdneri (rainbow trout) 1.2 µg/L	Did not find
Chlordane	~5.54	Insoluble	Chironomus plummosus (10 µg/L	10 to 20 yrs**
Arochlor Σ	5.6-6.8	Insoluble	P. subcapitata 182nmol/L	volatilization half-life from a model pond is 82 days-58 years
Lindane	3.8	17	D. magna (EC 50) 1.64 mg/L	69.41 hours/ 15 months
Heptachlor	6.10	0.056	S. capricornutum 26.7 µg/L	6 months-3.5 years
Heptachlor-epoxide	5.40	Not found	Not found	Not found

*ATSDR; **Bondy 2000; ***HSDB;

Lindane is an insecticide used for the protection of fruits and vegetables. It can cause acute symptoms such as irritation of the nose and throat and chronic symptoms such as adverse effects on the liver, blood, nervous, cardiovascular and immune systems if inhaled or ingested (US EPA 2001). The EPA classified lindane as a possible human carcinogen. Lindane is also known as the gamma isomer of 1, 2, 3,4,5,6 hexachlorocyclohexane (HCH). It is a white crystalline powder volatile in the atmosphere but insoluble in water. It has a molecular weight of 290.83 g/mol and its octanol-water coefficient (log K_{ow}) is 3.8. Lindane is persistent in the environment and can travel long distances from its application location (Walker, et al. 1999). It is an isomer and can be conformed to other more toxic compounds. Sorption onto particulate matter is used to remove lindane from water. Volatilization may also be a removal mechanism.

Chlordane is an organochlorine insecticide that contains a complex mixture of more than forty-five individual isomers and congeners (Kawano, et al. 1988). Chlordane was first produced in 1947 and used as an insecticide. The EPA banned chlordane in 1988 because it was found to be a carcinogen, causing ecological damage. Chlordane has an environmental half-life of ten to twenty years (Bondy, et al. 2000). Because it is fat soluble, it can accumulate in animal tissue causing harmful effects to humans. Chlordane acts as an endocrine disrupting compound, having estrogenic effects on human breast cells. Thus, chlordane mimics biological activities of hormones, such as the hormone 17β-estradiol (Bonefeld-Jorgensen, et al. 2001). The hormone 17β-estradiol is important for stimulating breast cell proliferation in mature breast tissue. Pure chlordane has a molecular weight of 409.76 g/mol. It has a low water solubility and high log K_{ow} value (~5.54). At wastewater treatment facilities, it is expected that most of the chlordane would be removed because it tends to sorb to particulates.

Methoxychlor is an insecticide that replaced the carcinogen DDT. It is a pale yellow solid with a light odor. When created commercially, between 88-90% of the pesticide is pure methoxychlor (ATSDR 2011). It is virtually insoluble in water and it binds to soil when applied to plants(ATSDR 2011). The log K_{ow} of methoxychlor is approximately 4.68 to 5.08, which is relatively high. The EPA does not classify methoxychlor as a carcinogen, but it does simulate estrogens in the body which affects the reproduction of certain species. Methoxychlor causes a negative impact to the nervous system if exposed directly.

Heptachlor is an insecticide used extensively in the past for killing insects in homes, buildings, and on food crops (ATSDR 2011). Application of the insecticide ceased in 1988 and is now permitted only for fire ant control in underground power transformers (ATSDR 2011). Heptachlor epoxide is formed from the breakdown of heptachlor by bacteria and animals (ATSDR 2011). It is more soluble in water than heptachlor and it very persistent in the environment. EPA classified both heptachlor and heptachlor epoxide as possible human carcinogens. Both chemicals are a white solid with camphor like odor. The molecular weights are 373.32 g/mol for heptachlor and 389.40 g/mol for heptachlor epoxide. The log K_{ow} for heptachlor is 6.10 and the log K_{ow} for heptachlor epoxide is 5.40. They bind to soil and are expected to be treated by wastewater treatment facilities primarily by sedimentation.

Aldrin and dieldrin are organochlorine pesticides commercially manufactured since 1950. They were used throughout the world until the early 1970s (International Labor Organisation, UN 2988). Aldrin breaks down into dieldrin which kills disease carrying insects, such as the tsetse fly. Since the early 1970s, the two compounds have been severely restricted or banned in several countries, especially for agriculture use (International Labor Organisation, UN 2988). Nevertheless, they are still used in some other countries for termite control (International Labor Organisation, UN 2988). Both aldrin and dieldrin are insoluble in water (although dieldrin has higher solubility) having a relatively high molecular weight being 364.91 g/mol and 380.91 g/mol respectively. Both compounds have high log K_{ow} values, 6.5 and 6.2 respectively. Both aldrin and dieldrin often bind to particulates and are expected to be removed through sedimentation processes.

Arochlor (Table 5-20) is a mixture of several polychlorinated biphenyl (PCB) congeners sold in the U.S. from 1930 to 1977 (ATSDR 2011). The Aroclors are identified by a four-digit numbering code in which the first two digits indicate the type of mixture and the last two digits signify the approximate chlorine content by weight percent (ATSDR 2011). Thus, Aroclor 1242 is a chlorinated biphenyl mixture of varying amounts of mono- through heptachlorinated homologs with an average chlorine content of forty-two percent (ATSDR 2011). The exception to this code is Aroclor 1016, which contains mono- through hexachlorinated homologs with an average chlorine content of forty-one percent (ATSDR 2011).

Table 5-20. Physical and Chemical Properties of Aroclors Affecting their Treatment (ATSDR 2011)

Arochlor congener	Molecular weight (g/mol)	Solubility (water) (mg/L) at 25°C	Vapor pressure (mm Hg) at 25°C	Henry's Constant (atm-m^3/mol) at 25°C	Log K_{ow}
1016	257.9	0.42	4×10^{-4}	2.9×10^{-4}	5.6
1221	200.7	0.59 (24°C)	6.7×10^{-3}	3.5×10^{-3}	4.7
1232	232.2	0.45	4.06×10^{-3}	No data	5.1
1242	266.5	0.34	4.06×10^{-3}	5.2×10^{-4}	5.6
1248	No data	No data	No data	No data	No data
1254	328	0.012	7.71×10^{-5}	2.0×10^{-3}	6.5
1260	357.7	0.0027	4.06×10^{-5}	4.6×10^{-3}	6.8
1262	389	0.052 (24°C)	No data	No data	No data
1268	453	0.300 (24°C)	No data	No data	No data

All of the Arochlor congeners are insoluble in water and have a high affinity for oil and fat. They have very high molecular weights and the octanol-water coefficients are high for all of them. PCBs tend to sorb onto particulate matter rather than dissolve in aqueous solutions and are therefore likely to be removed at wastewater treatment plants by sedimentation. The most effective treatment of most pesticides usually involves carbon adsorption using activated carbon. This is mostly available with stormwater filters for the treatment of wet weather flows.

Increases in the infiltration rate of surface water and removals of some pesticides were observed using vegetative filter strips. The pesticide removals were associated with sorption to soil and vegetation (Arora, et al. 1996). The addition of vegetation in the stormwater flow path increased the microbial activity, leading to some pesticide degradation (Staddon, et al. 2001). These researchers found that soil type, slope, length, vegetation density, and vegetation type influence the efficiency of microbial degradation of pesticides.

Pesticides in CSOs

Pesticides have a high affinity for particulate matter, degrade at a slow rate and are insoluble in water. The combined sewage wastewater treatment facility of the city of Thessaloniki, Greece, serves about 1 million residents (Katsoyiammis and Samara 2004). About five to ten percent of the total flow comes from industrial dischargers. The treatment process includes screening, grid removal, primary sedimentation without use of chemical coagulants, conventional activated sludge treatment, and effluent disinfection using Cl_2. During the Katsoyiannis (2004) study, much of the pesticide concentrations were reduced during both the primary and secondary treatment processes, as shown on Figure 5-2. This is consistent with their physicochemical properties, although other factors affect treatment, such as retention time. Although there were significant removals for all pesticides observed, most of the concentrations in the secondary effluent ranged from 10-25 ng/L.

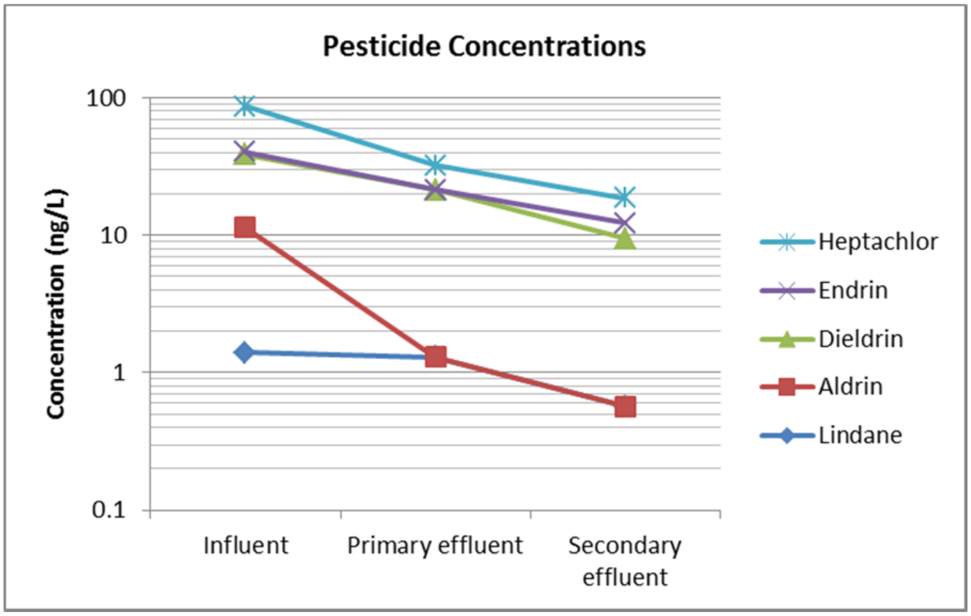


Figure 5-2. Concentrations of pesticides at Thessaloniki wastewater treatment plant (Katsoyiammis and Samara 2004).

Polychlorobiphenyls (PCBs) are discharged by various industries as congener mixtures. Blanchard (2004) conducted a study of PAH and PCB concentrations from five combined sewers near Paris entering the Ache`res region: (1) the  Se`vres 1-Ache`res Rueil (220,000 $m^3$/d or 58.1 MGD), (2) the Saint Denis-Ache`res (360,000 m^3/d or 95.1 MGD); (3) the Clichy-Ache`res junction of Argenteuil (900,000 $m^3$/d or 237 MGD), for the Clichy-Ache`res junction of Bezons (600,000 m^3/d or 158 MGD), and the Se`vres 2-Ache`res junction of Saint-Cloud Nanterre (600,000 m^3/d or 158 MGD). Arochlor, which is a polychlorinated biphenyl, were observed by Blanchard (2004) to be significantly reduced during the primary treatment process. Figure 5-3 shows how the different treatment unit processes reduced PCBs.

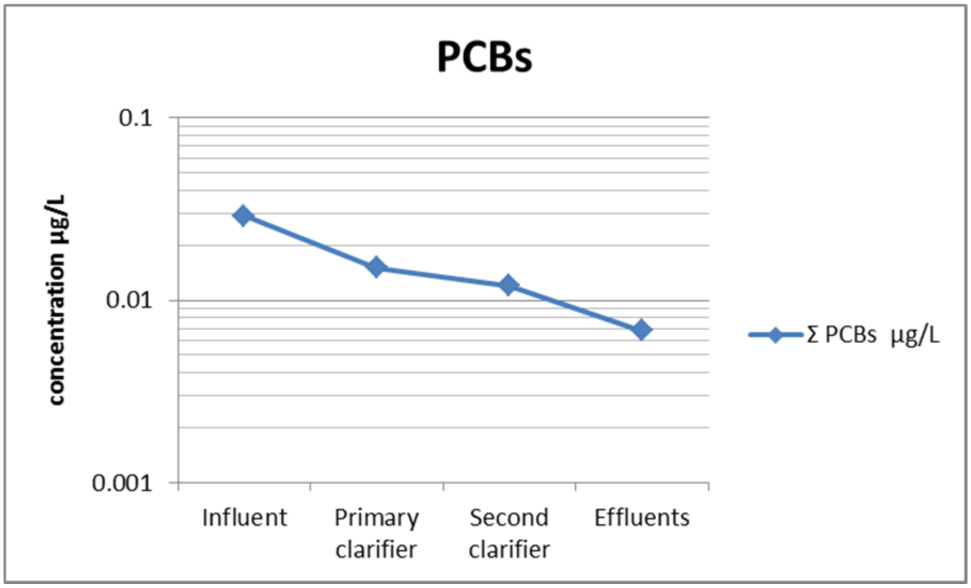


Figure 5-3. Concentration of ΣPCBs (Blanchard, et al. 2004).

Monitored Treatment of PPCP at the Tuscaloosa Wastewater Treatment Plant

Line graphs showing the concentrations throughout each of the unit processes at the treatment plant are a visual representation of the treatability of each compound for each unit process. Dry weather and wet weather sample concentration patterns are compared to represent the differences in treatment during varied weather conditions. The wet weather samples were taken during days with anticipated rain, with the total daily rain amounts ranging from 0.05 to 2.7 inches. Rains larger than 0.1 inches were considered wet weather, while the very small rains (not expected to result in runoff) were included in the dry weather category.

Table 5-21 summarizes the average concentrations obtained at each of the four sampling locations at the Tuscaloosa Earl N. Hilliard (ENH) wastewater treatment plant and indications of the likely most important unit treatment process. The pharmaceuticals have low to moderate removals (about 50%) while the PAHs show larger removals (about 90%). A combination of unit treatment processes affected the pharmaceuticals and PAH concentrations, as expected.

Table 5-21. Performance Data for Earl Hilliard WWTP, Tuscaloosa, AL

Constituent	Avg Influent conc. (µg/L)	Avg Primary effluent conc. (µg/L)	Avg Secondary effluent conc. (µg/L)	Avg concentration after UV (final effluent) (µg/L)	Avg Overall Percentage Removal at ENH wastewater treatment facility	Apparent most Important treatment unit process
Pharmaceuticals						
Gemfibrozil (w)	32.4	31.7	18.1	17.1	45	Secondary
Gemfibrozil (d)	80.3	23.4	22.3	18.6	71	Primary
Ibuprofen (w)	21.6	21.0	17.6	9.6	58	UV
Ibuprofen (d)	44.7	35.3	20.8	15.3	67	Secondary
Triclosan (w)	33.9	16.9	15.0	12.3	63	Primary
Triclosan (d)	16.7	3.3	12.9	0.4	98	UV
Carbamazepine (w)	2.4	5.0	5.0	2.6	-8	UV
Carbamazepine (d)	15.9	10.5	2.5	1.4	94	Primary
Fluoxetine (w)	14.1	41.7	3.3	1.9	86	Secondary
Fluoxetine (d)	61.7	36.8	11.6	9.6	84	Secondary
Sulfamethoxazole (w)	10.4	18.4	14.1	13.1	-33	None
Sulfamethoxazole (d)	68.7	42.6	31.1	24.4	65	Secondary
Trimethoprim (w)	3.1	3.1	3.9	2.0	33	UV
Trimethoprim (d)	16.3	28.3	21.1	21.0	-31	None
Polycyclic Aromatic Hydrocarbons						
Naphthalene (w)	15.3	4.7	25	22.7	-47	None
Naphthalene (d)	7.1	11.1	3.8	1.3	82	Secondary
Acenaphthene (w)	16.9	5.1	0.4	0.6	96	Primary
Acenaphthene (d)	7.7	0.8	0.1	0.02	99	Primary
Fluorene (w)	10.3	1.0	0.6	0.6	91	Primary
Fluorene (d)	0.7	1.2	0.04	0.05	93	Secondary
Fluoranthene (w)	10.3	4.2	0.5	0.5	95	Primary
Fluoranthene (d)	0.3	0.5	0.02	0.04	87	Secondary
Acenaphthylene (w)	10.5	0.6	0.6	0. 7	92	Primary
Acenaphthylene (d)	0.1	0.6	0.01	0.02	75	Secondary
Phenanthrene (w)	6.1	4.4	0.05	0.2	98	Secondary
Phenanthrene (d)	1.6	0.8	0.2	0.1	90	Primary and secondary
Anthracene (w)	198	2.3	9.7	0.8	100	Primary
Anthracene (d)	60.1	0.2	0.2	0.2	100	Primary
Pyrene (w)	10.2	4.0	0.7	0.5	95	Primary and secondary
Pyrene (d)	0.7	1.0	0.1	0.1	80	Secondary

Figure 5-4 through 5-7 are line-treatability plots for the pharmaceutical fluoxetine, and the PAHs acenaphthene, phenanthrene, and pyrene at different sampling locations at the Tuscaloosa wastewater treatment facility. The locations are the influent to the treatment facility and the effluent after the primary sedimentation and secondary biological unit processes, and the final effluent after ozone disinfection. These four examples are the most consistent in indicating pollutant removals through the treatment facility. The largest reductions, for all but acenaphthene, occur during secondary biological treatment, where most of the removal of particulates occurs along with biological digestion of the solids. The primary treatment had little effect. Phenanthrene actually indicated an increase in concentrations with primary treatment, likely due to removal of particulates that interfered with the extraction of the compound. Acenaphthene is an example where all of the treatment processes were effective for partial removal of the compound, including the primary, secondary, and disinfection unit processes. For many of the samples, acenaphthene was not detected after the secondary treatment phase.

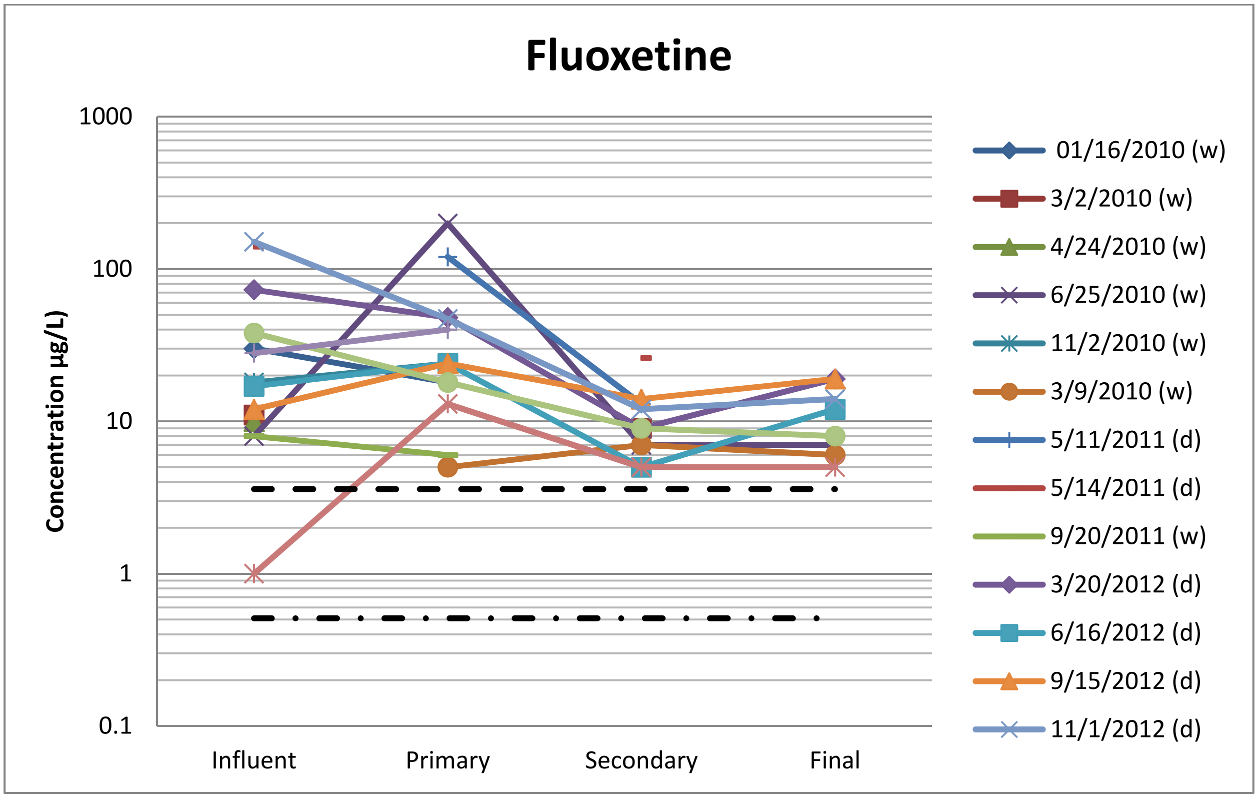


Figure 5-4. Line graph for the pharmaceutical Fluoxetine at different sampling locations

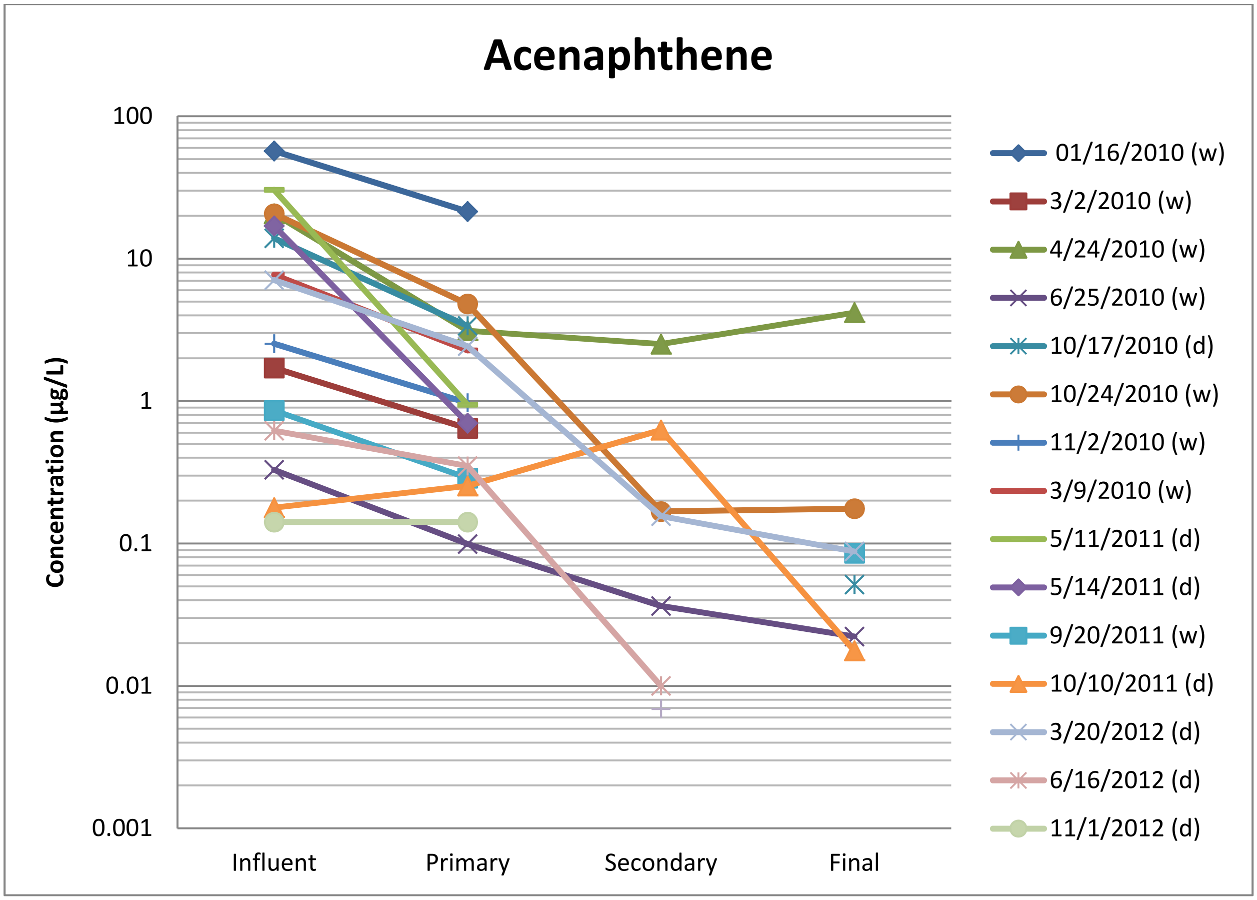


Figure 5-5. Line graph for the PAH Acenaphthene at four different sampling locations

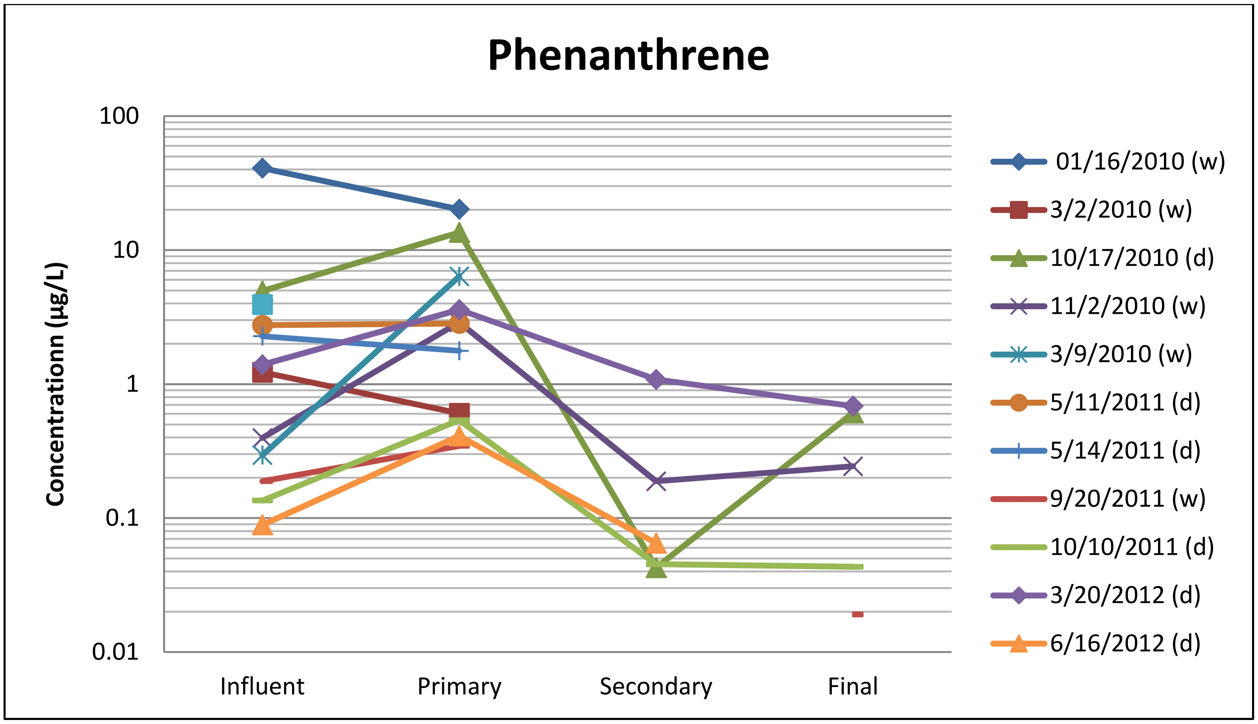


Figure 5-6. Line graph for the PAH Phenanthrene at four different sampling locations

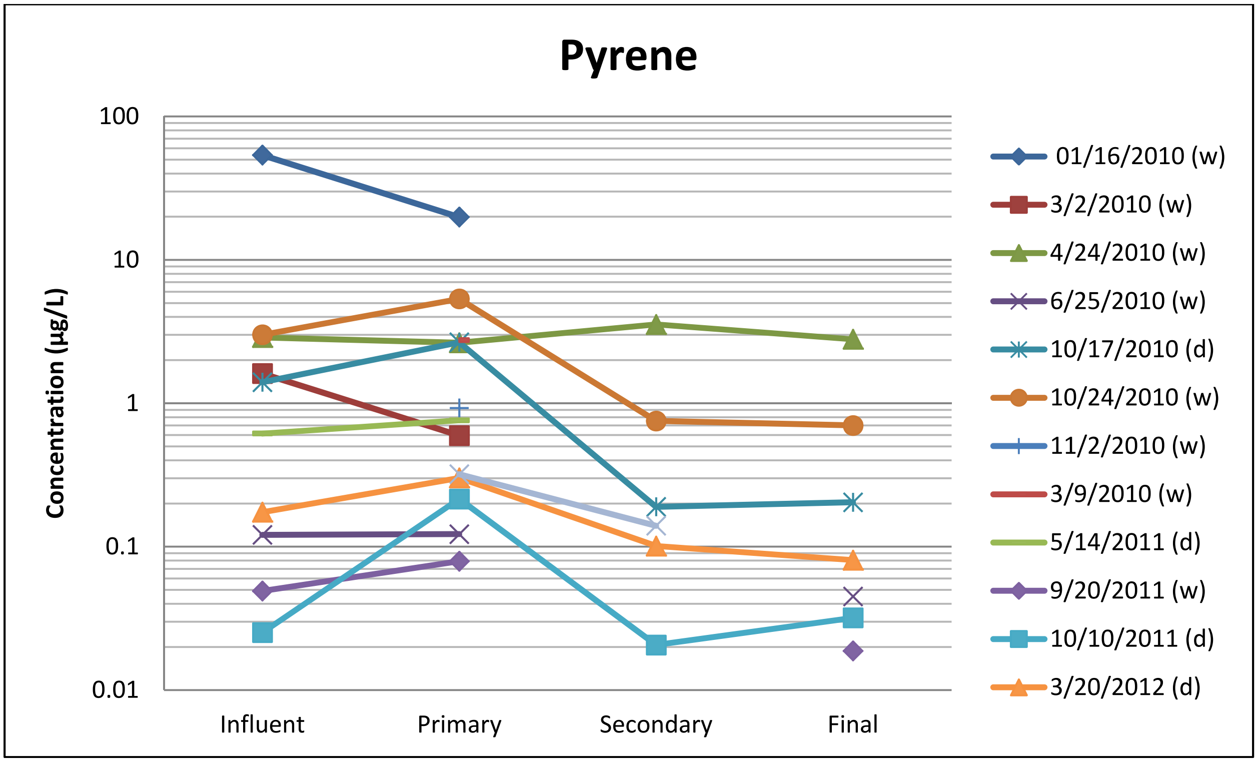


Figure 5-7. Line graphs for the PAH Pyrene at four different sampling locations

Figures 5-8 to 5-22 are box and whisker plots for all of the pharmeuciticals and PAHs examined. These plots show the ranges and medians of concentrations at the different locations at the Tuscaloosa wastewater treatment plant.

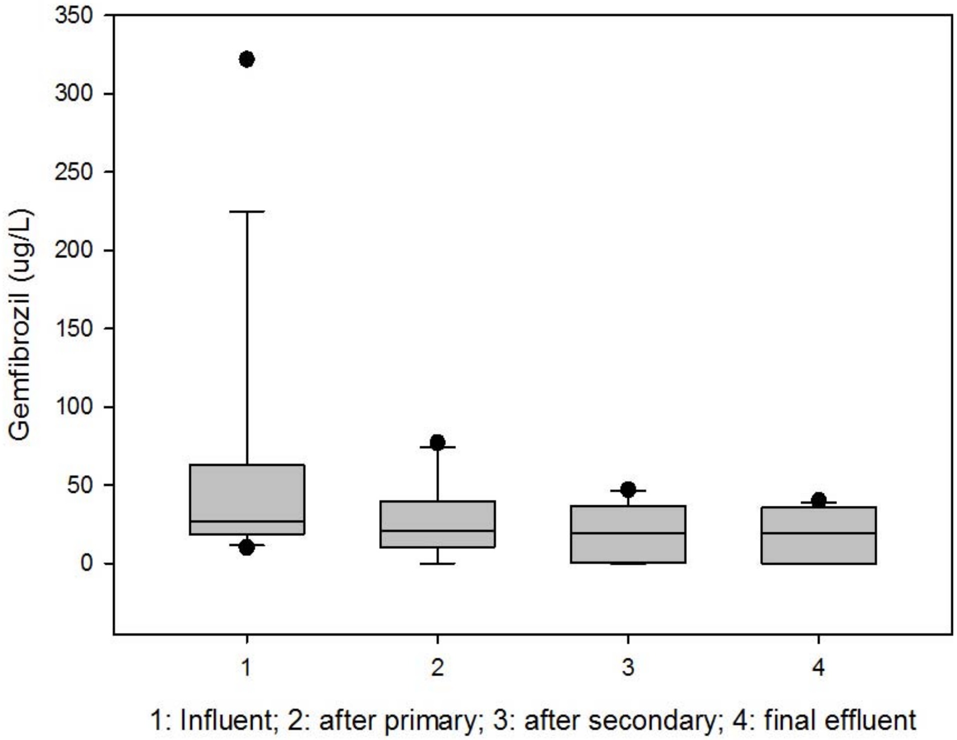


Figure 5-8. Box and Whisker plots for Gemfibrozil

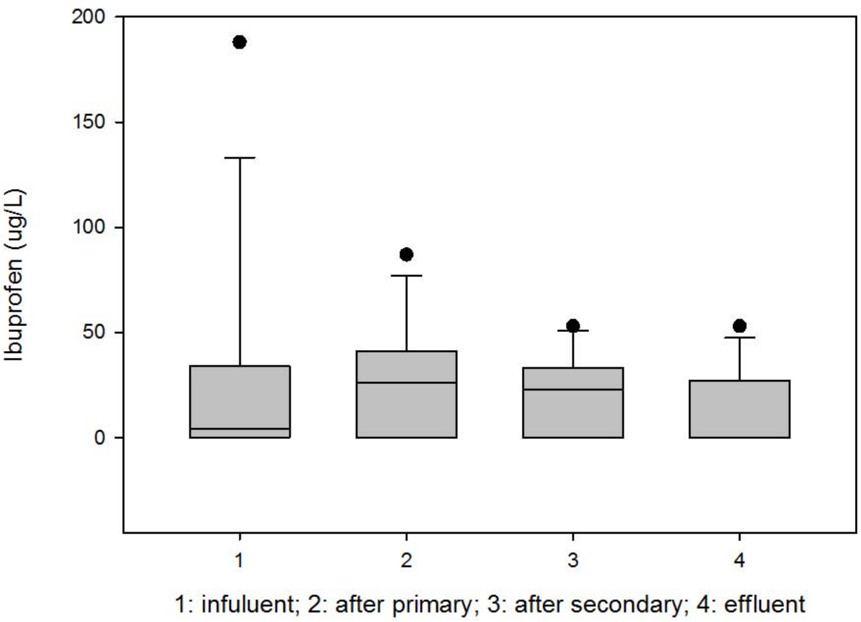


Figure 5-9. Box and Whisker plots for Ibuprofen

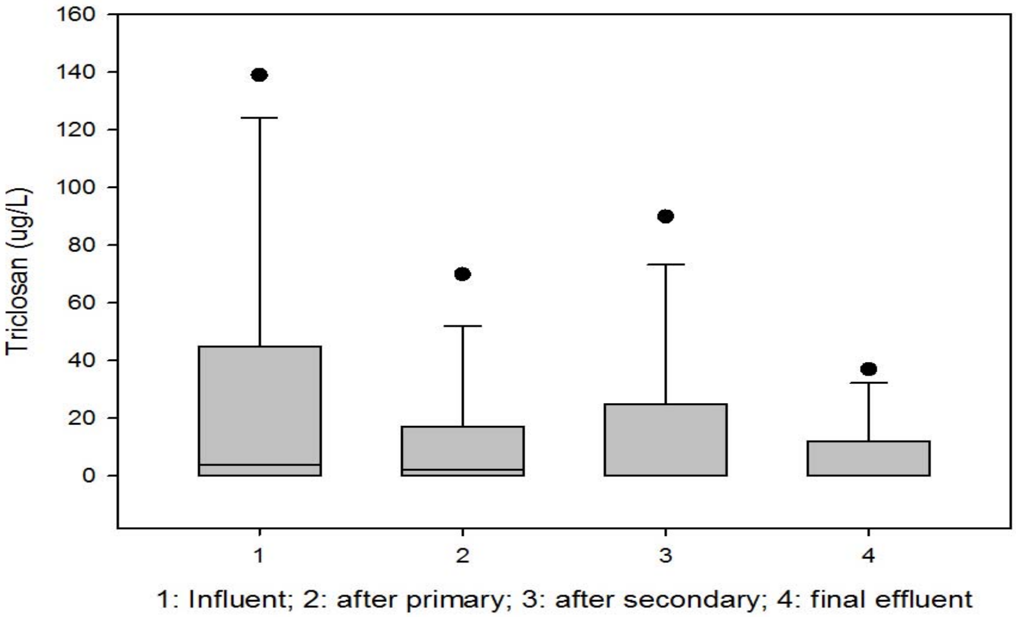


Figure 5-10. Box and Whisker plot of Triclosan

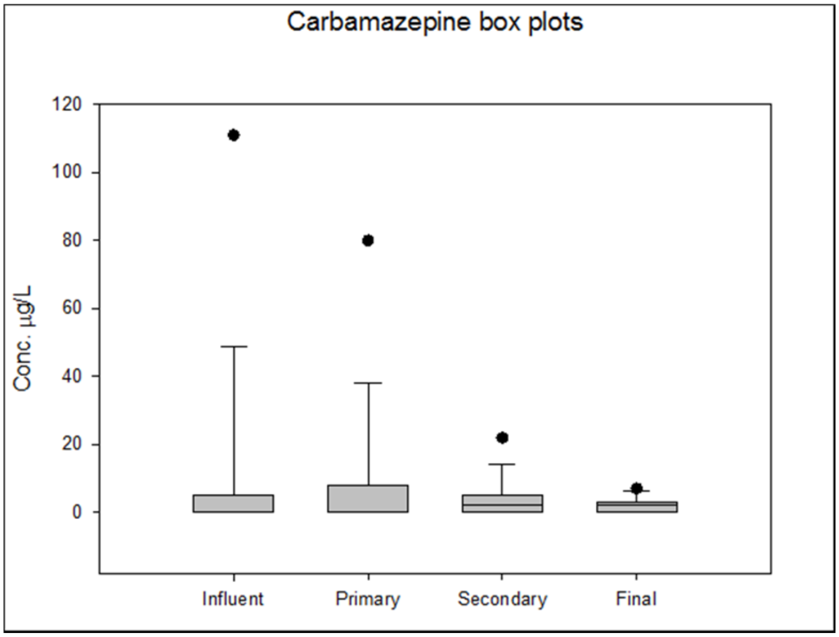


Figure 5-11. Box and Whisker Plots for Carbamazepine

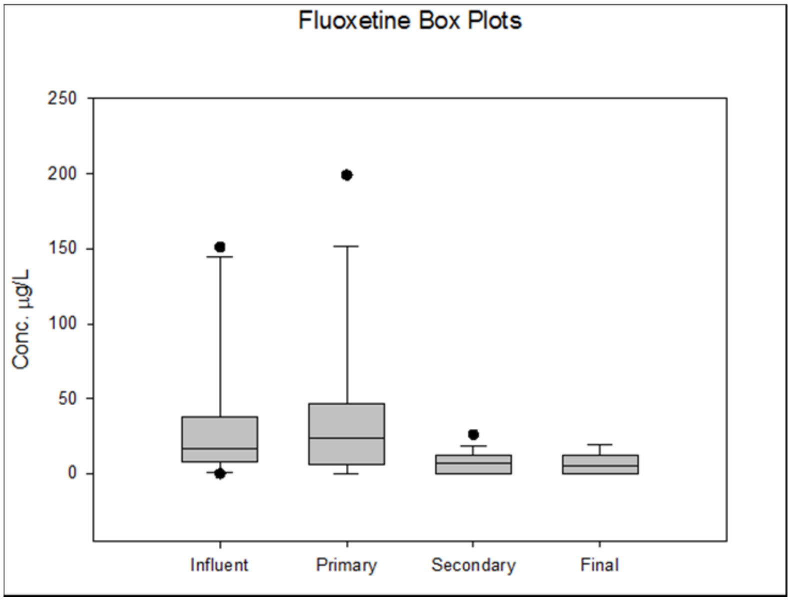


Figure 5-12. Box and Whisker Plots for Fluoxetine

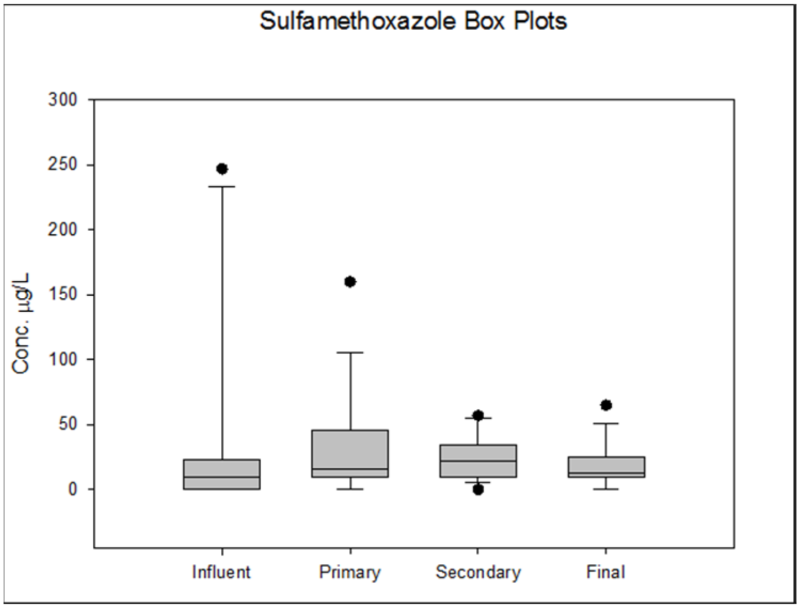


Figure 5-13. Box and Whisker Plots for Sulfamethoxazole

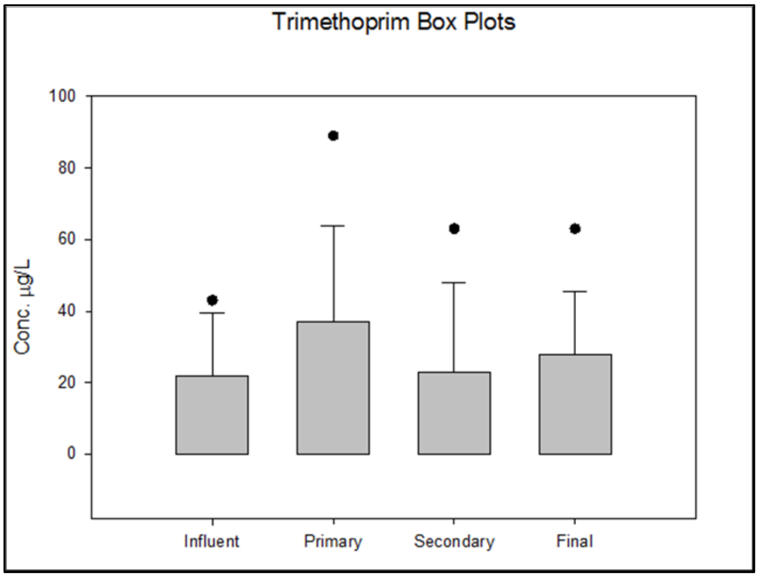


Figure 5-14. Box and Whisker Plots for Trimethoprim

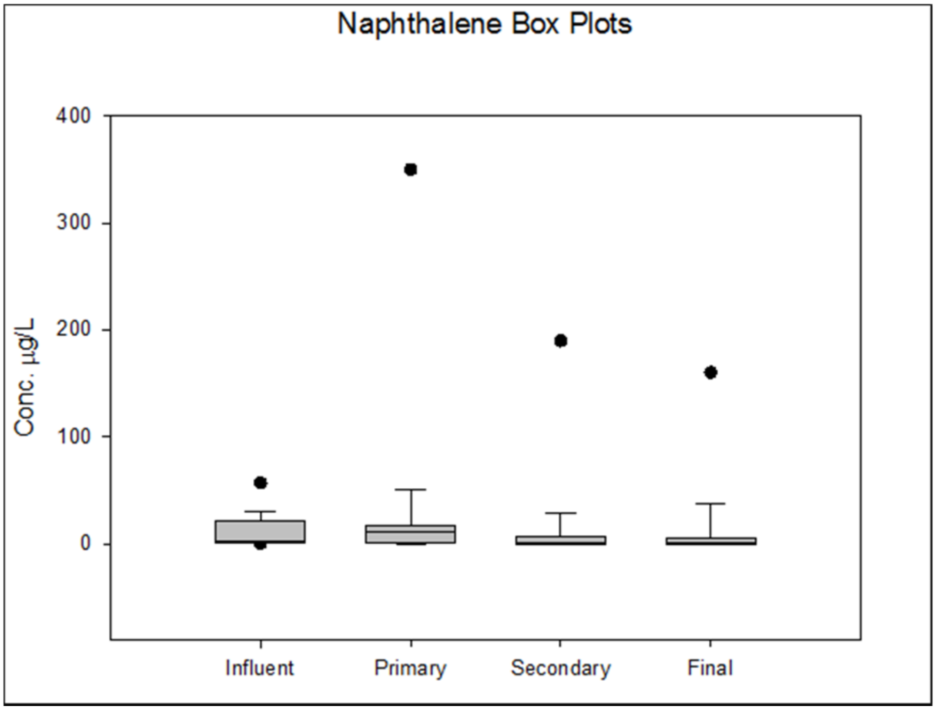


Figure 5-15. Box and Whisker plot for Naphthalene

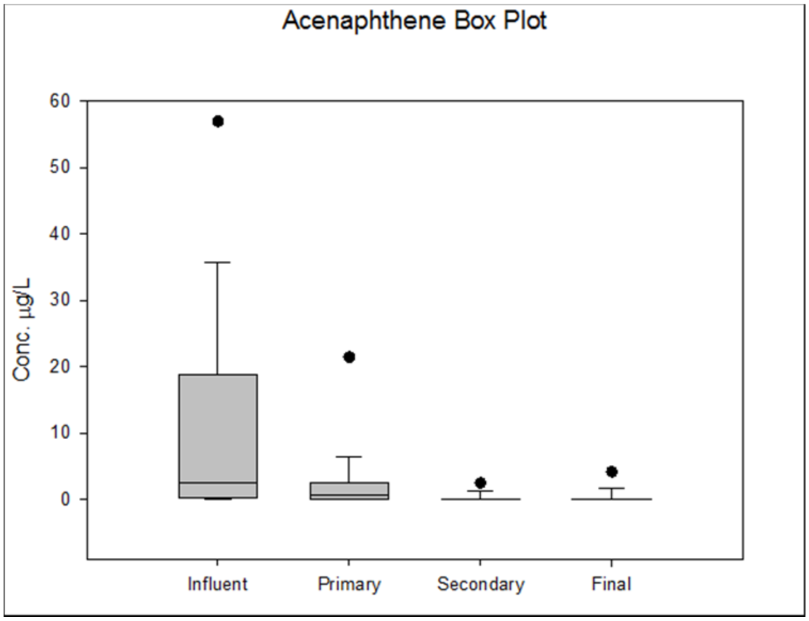


Figure 5-16. Box and Whisker Plot for Acenaphthene

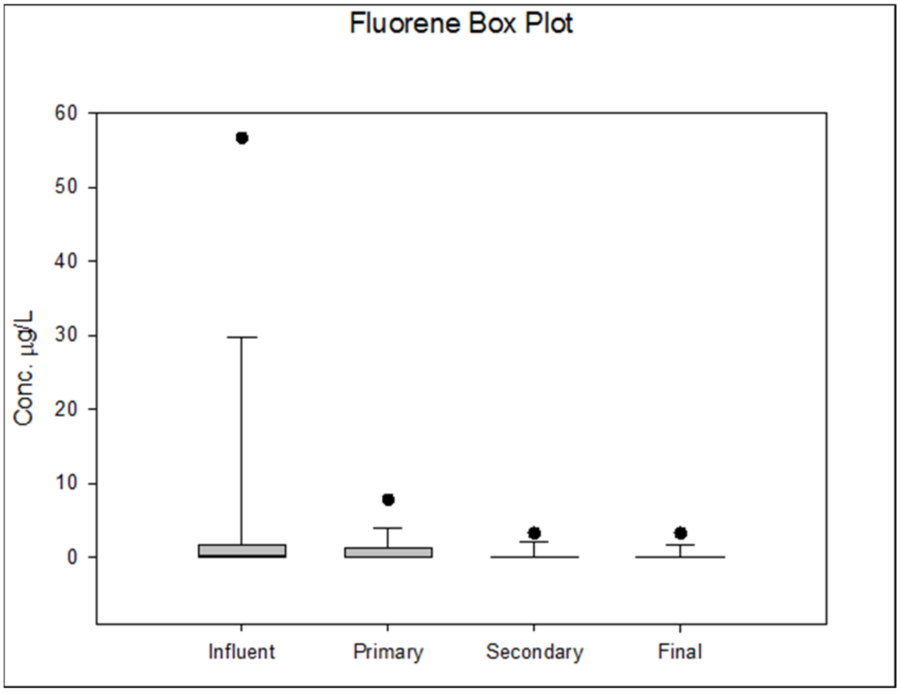


Figure 5-17. Box and Whisker Plots for Fluorene

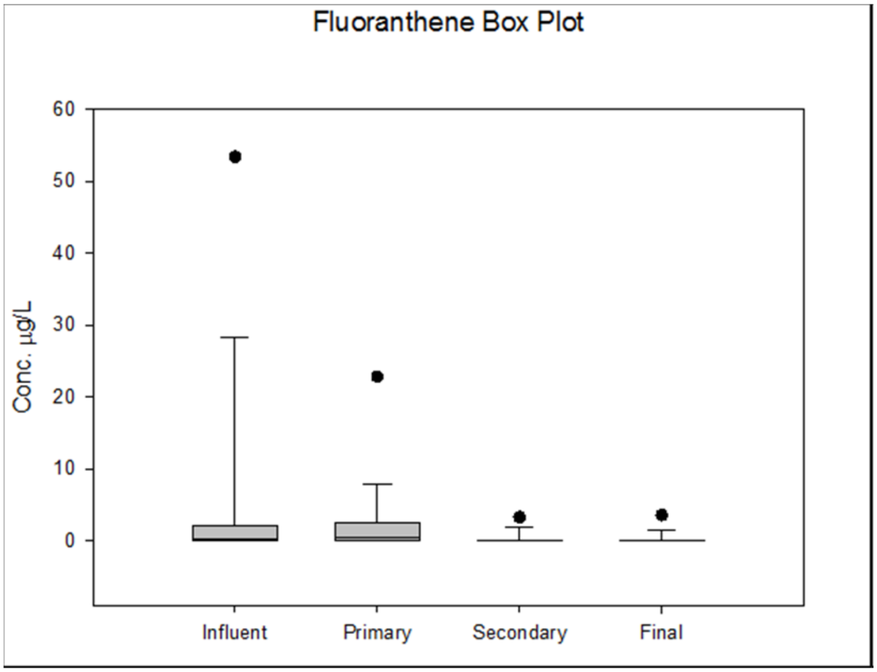


Figure 5-18. Box and Whisker Plots for Fluoranthene

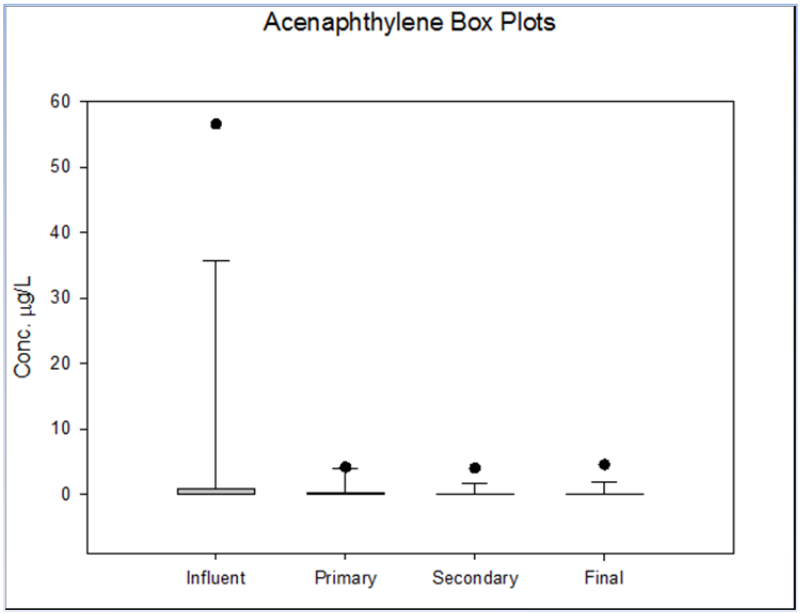


Figure 5-19. Box and Whisker Plots for Acenaphthylene

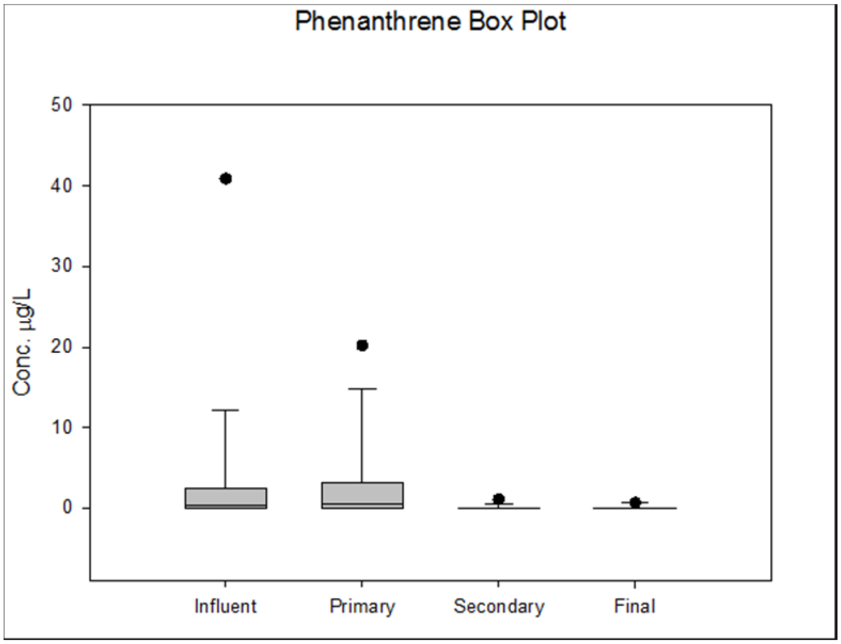


Figure 5-20. Box and Whisker Plots for Phenanthrene

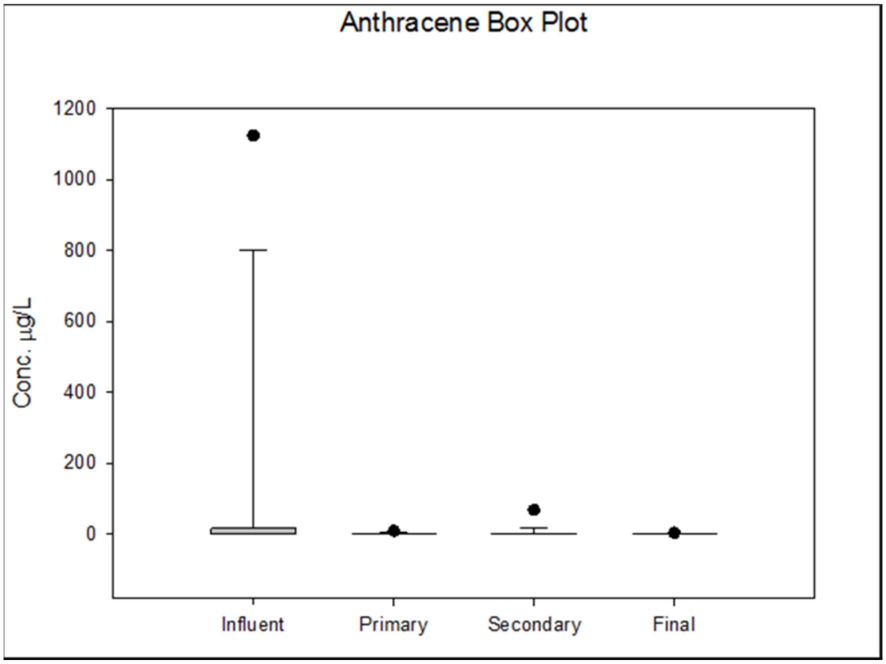


Figure 5-21. Box and Whisker Plots for Anthracene

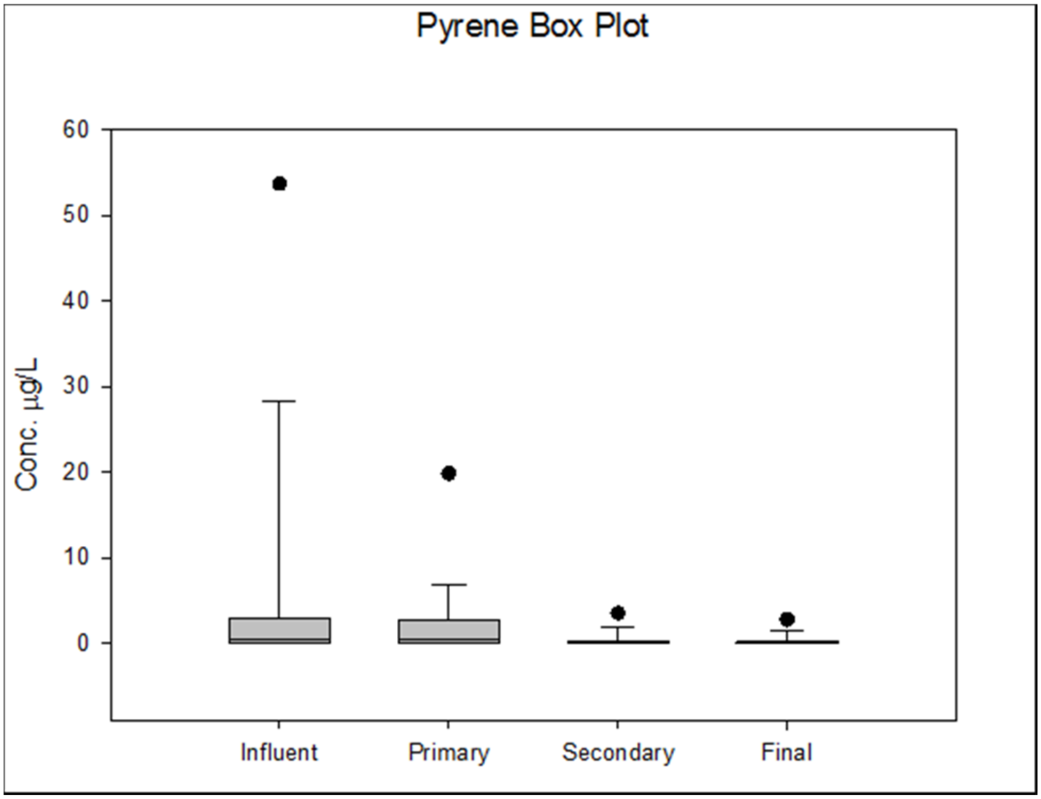


Figure 5-22. Box and Whisker Plots for Pyrene

Table 5-22 is a summary of the detected semivolatile compounds, analyzed using EPA method 525 (phthalates, pesticides, and some PAHs) conducted by Penn State Harrisburg and their local laboratory (ALS Environmental, Middletown, PA). Surrogate recoveries, blanks, and external standards were also analyzed along with these samples. Table 5-23 shows some of the removals for the most consistently detected consitituents using this analytical method.

Table 5-23a. Summary of Phthalates, Pesticides, and Other Constutent Removals at Tuscaloosa Wastewater Treatment Plan

	Butylbenzylphthalate	**Di-n-Butylphthalate**	**bis(2-Ethylhexyl)phthalate**
Detection frequency in influent	50%	67%	92%
Median concentration in influent	1.3 – 2.6 µg/L	3.4 µg/L	8.9 µg/L
Detection frequency in primary effluent	33%	58%	75%
Median conc. in primary effluent	0 – 2.5 µg/L	2.7 µg/L	7.1 µg/L
% reduc. after primary treatment	23 - 60%	20 – 41%	41 – 50%
Detection frequency in secondary effluent	8.3%	42%	0%
Median conc. in secondary effluent	0 – 2.5 µg/L	0 – 2.5 µg/L	0 – 5 µg/L
% reduc. after secondary treatment	40 - 91%	29 – 59%	66 – 100%
Detection frequency in final effluent	17%	25%	0%
Median conc. In final effluent	0 – 2.5 µg/L	0 – 2.5 µg/L	0 – 5 µg/L
% reduc. after all treatment	43 - 89%	32 – 70%	66 – 100%

Table 5-23b. Summary of Phthalates, Pesticides, and Other Constutent Removals at Tuscaloosa Wastewater Treatment Plan (continued)

	Di(2-Ethyhexl)adipate	**Naphthalene**	**Phenanthrene**
Detection frequency in influent	33%	50%	50%
Median concentration in influent	0 – 2.5 µg/L	0.6 – 1.1 µg/L	0.3 µg/L
Detection frequency in primary effluent	42%	58%	33%
Median conc. in primary effluent	0 – 2.5 µg/L	0.6 – 1.1 µg/L	0.3 – 0.6 µg/L
% reduc. after primary treatment	6.7 – 47%	-25 – 20%	-2 – 57%
Detection frequency in secondary effluent	25%	0%	8%
Median conc. in secondary effluent	0 – 2.5 µg/L	0 – 1 µg/L	0 – 0.5 µg/L
% reduc. after secondary treatment	18 – 70%	8 – 100%	10 – 91%
Detection frequency in final effluent	25%	0%	0%
Median conc. In final effluent	0 – 2.5 µg/L	0 – 1 µg/L	0 – 0.5 µg/L
% reduc. after all treatment	21 – 73%	8 – 100%	12 – 100%

The treatment removals were large for many consistuents, with many of the secondary and final effluent concentrations below the concentration detection limits, indicating that all of the remaining analytes were removed during secondary treatment. No pesticides were detected at the 0.5 to 1 µg/L detection limits. Phthalates are commonly thought of as frequent contaminants in laboratory analyses of semi-volatiles. They are plasticizers and are found in much labware. However, the pattern of many of the phthalates clearly show that they were detected at much higher frequencies and concentrations in the influent samples, with many not detected in the treated samples; however, some are more evenly found in all samples, possibly implying possible contamination.

Table 5-22. Semivolatile analyses results (phthalate esters, PAHs, and pesticides)

Sample date, treatment plant daily flow, and daily rain total	Influent	Primary Effluent	Secondary	Final
1/16/2010	Butylbenzylphthalate 11.1	Butylbenzylphthalate 3.5	all ND	all ND
18.2 MGD	Di-n-Butylphthalate 3.9	Di-n-Butylphthalate 2.7		
0.55 inches	Diethylphthalate 12.3	Diethylphthalate 6.3		
	bis(2-Ethylhexyl)phthalate 53.9	bis(2-Ethylhexyl)phthalate 17.8		
	Naphthalene 2.0	Naphthalene 1.0		
3/2/2010	bis(2-Ethylhexyl)phthalate 6.9	bis(2-Ethylhexyl)phthalate 8.6	all ND	all ND
23.3 MGD		Fluorene 0.52		
0.68 inches	2-Methylnaphthalene 2.2	2-Methylnaphthalene 2.0		
	Naphthalene 1.1	Naphthalene 1.1		
		Metribuzin 1.9		
4/24/2010	bis(2-Ethylhexyl)phthalate 8.8	bis(2-Ethylhexyl)phthalate 7.1	all ND	all ND
16.5 MGD				
1.01 inches				
6/25/2010	Benzo(a)anthracene 0.63			
20.7 MGD	Butylbenzylphthalate 13.3	Butylbenzylphthalate 9.0	all ND	all ND
0.59 inches	bis(2-Ethylhexyl)phthalate 26.2	bis(2-Ethylhexyl)phthalate 15.8	all ND (duplicate)	
	Chrysene 0.77			
		Di-n-Butylphthalate 2.6		
	Phenanthrene 0.77			
	Pyrene 0.52			
11/2/2010	Butylbenzylphthalate 4.6	Butylbenzylphthalate 3.3	all ND	all ND
20.5 MGD	Di-n-Butylphthalate 4.5	Di-n-Butylphthalate 3.2		
0.88 inches	Diethylphthalate 7.8	Diethylphthalate 6.7		
	bis(2-Ethylhexyl)phthalate 9.6	bis(2-Ethylhexyl)phthalate 10.4		
	2-Methylnaphthalene 4.6	2-Methylnaphthalene 6.0		
	Naphthalene 2.5	Naphthalene 3.7		

Table 5-22. Semivolatile analyses results (phthalate esters and pesticides) (continued)

Sample date, treatment plant daily flow, and daily rain total	Influent	Primary Effluent	Secondary	Final
3/9/2011	Anthracene 0.54		all ND	all ND
42.2 MGD	Fluoranthene 0.57			
2.67 inches	2-Methylnaphthalene 3.9	2-Methylnaphthalene 3.8		
	Naphthalene 2.0	Naphthalene 1.9		
	Phenanthrene 0.87	Phenanthrene 0.86		
	Pyrene 0.55			
9/20/2011	Butylbenzylphthalate 2.6			all ND
26.5 MGD	Di-n-Butylphthalate 5.3	Di-n-Butylphthalate 2.6	Di-n-Butylphthalate 4.3	
0.64 inches	Di(2-Ethyhexl)adipate 5.0	Di(2-Ethyhexl)adipate 2.5	Di(2-Ethyhexl)adipate 2.9	
	bis(2-Ethylhexyl)phthalate 6.3	bis(2-Ethylhexyl)phthalate 7.0		
		2-Methylnaphthalene 3.2		
		Naphthalene 1.4		
	Phenanthrene 0.62			
10/10/2011	Butylbenzylphthalate 6.3		Butylbenzylphthalate 4.8	Butylbenzylphthalate 2.6
16.9 MGD				Chrysene 1.3
0.07 inches	Di-n-Butylphthalate 13.0	Di-n-Butylphthalate 4.3	Di-n-Butylphthalate 10.2	Di-n-Butylphthalate 5.7
	Di(2-Ethyhexl)adipate 10.7	Di(2-Ethyhexl)adipate 2.5	Di(2-Ethyhexl)adipate 7.0	Di(2-Ethyhexl)adipate 4.2
	bis(2-Ethylhexyl)phthalate 15.0	bis(2-Ethylhexyl)phthalate 6.0	Phenanthrene 0.6	
	Fluoranthene 0.66			
	Phenanthrene 1.0			

Table 5-22. Semivolatile analyses results (phthalate esters and pesticides) (continued)

Sample date, treatment plant daily flow, and daily rain total	Influent	Primary Effluent	Secondary	Final
11/9/2011		Butylbenzylphthalate 2.6	all ND	
	Di-n-Butylphthalate 3.9	Di-n-Butylphthalate 4.9		Di-n-Butylphthalate 3.4
0.03 inches	Di(2-Ethyhexl)adipate 2.8	Di(2-Ethyhexl)adipate 3.4		
	bis(2-Ethylhexyl)phthalate 9.0	bis(2-Ethylhexyl)phthalate 6.8		
		Phenanthrene 0.51		
3/20/2012	Di-n-Butylphthalate 2.6		Di-n-Butylphthalate 3.3	
17.1 MGD		Butylbenzylphthalate 3.8		Butylbenzylphthalate 2.9
0 inches		Di-n-Butylphthalate 8.1		Di-n-Butylphthalate 6.0
	bis(2-Ethylhexyl)phthalate 5.3			
		Di(2-Ethyhexl)adipate 4.5	Di(2-Ethyhexl)adipate 3.2	Di(2-Ethyhexl)adipate 6.6
	Naphthalene 1.2	Naphthalene 1.1		
		Phenanthrene 0.55		
6/16/2012	Butylbenzylphthalate 8.7	Butylbenzylphthalate 5.8		Butylbenzylphthalate 3.1
13.5 MGD	Di-n-Butylphthalate 18.3	Di-n-Butylphthalate 13.0	Di-n-Butylphthalate 3.9	Di-n-Butylphthalate 7.4
0 inches	Di(2-Ethyhexl)adipate 14.9	Di(2-Ethyhexl)adipate 10.9	Di(2-Ethyhexl)adipate 3.3	Di(2-Ethyhexl)adipate 4.1
	bis(2-Ethylhexyl)phthalate 23.9	bis(2-Ethylhexyl)phthalate 9.1		
	Fluoranthene 0.70			
	Fluorene 0.67			
	Naphthalene 1.3	Naphthalene 1.3		
	Phenanthrene 1.4	Phenanthrene 0.85		
9/15/2012	Di-n-Butylphthalate 2.8	Di-n-Butylphthalate 4.5	Di-n-Butylphthalate 2.7	Di-n-Butylphthalate 4.6
14.5 MGD	bis(2-Ethylhexyl)phthalate 8.2			
		Di(2-Ethyhexl)adipate 3.8		Di(2-Ethyhexl)adipate 3.6
0 inches	Phenanthrene 0.62	Phenanthrene 0.63		

Trace Heavy Metal Treatability

The form of the pollutant species plays an important role in selecting an appropriate treatment technology (Clark and Pitt 2012). Many heavy metals are associated predominantly with particulates, and therefore their treatability is influenced by the removal of the associated particulates. The association of heavy metals with particulates depends on pH, oxidation-reduction potential, particulate organic matter. The treatability of stormwater solids and associated heavy metals is dependent on their size (Morquecho, et al. 2005; House, et al. 1993; Li, et al. 2005; Kim and Sansalone, 2008). Sedimentation and physical filtration can be used to remove the particulates with the attached pollutants from stormwater (Pitt, et al. 1996). For sedimentation, the median suspended solids removal efficiency is between 70 and 80% (Clark and Pitt 2012; Hossain, et al. 2005; International Stormwater BMP Database 2011). The sedimentation effectiveness is dependent upon the size of suspended solids. The removal of large suspended solids is efficient; however the suspended solids removal diminishes with the increase of content of smaller particulates (Clark and Pitt 2012; Greb and Bannerman, 1997). The heavy metal removal by sedimentation is very efficient at locations where the particulates are large (highways, for example) and the heavy metals are predominantly associated with the larger particulates (Clark and Pitt 2012; Kim and Sansalone, 2008).

Effectively designed wet detention ponds have restricted short-circuiting and low surface overflow rates (SOR). The sedimentation basins are not very effective for the removal of very small particles (< 2 µm) due to the repulsive forces caused by the negative charges on colloids and clay-sized particles that keep solids in suspension and prevent the particles from settling (Clark and Pitt 2012). The sedimentation can be improved by coagulation/flocculation that neutralized the electrical charges on the particles and causes the solids to settle out. Testing will be necessary since it is impossible to predict the settling of the floc theoretically (Clark and Pitt 2012; Metcalf and Eddy, 2003). For metals that are predominantly associated with particles in the range of colloidal and clay particles (< 1 µm), filtration with a chemically-active media may be necessary if low numeric discharge limits must be met (Clark and Pitt 2012; Pitt and Clark, 2010). Sand with oxide coatings can be used to remove colloidal pollutants (Clark and Pitt, 2012, Sansalone and Kim, 2006).

The removal of dissolved contaminants may be needed due to their high mobility and to meet permit requirements and reduce surface and groundwater contamination potential (Pitt, et al. 1996; Clark and Pitt 2012). Heavy metals in ionic forms are the most bioavailable. The toxicity of a heavy metal is affected by metal bioavailability which is controlled by speciation and partitioning of a metal. Metals in ionic forms are generally more bioreactive than metal complexes. Treatment techniques for metals associated with dissolved fractions include chemical treatment. To remove dissolved metals from stormwater, organic filter media (such as compost or peat), a mix of peat moss and sand, zeolite, and compost can be used. Zn^{2+} is highly reactive and is more amenable to ion exchange.

In physisorption reactions, the electrical bonds between the contaminants and the media are reversible and weak. On the other hand, during chemisorption and precipitation reactions stronger bonds are formed and the pollutant retention is permanent if the solution pH and dissolved oxygen level do not change significantly (Evangelou, 1998; Watts, 1998; Clark and Pitt 2012). Sorption and ion exchange remove pollutants through electrostatic interactions between the media and contaminants (Clark and Pitt 2012). The high sodium content during the snowmelt can regenerate the ion exchanging media and release the already retained heavy metals back into the effluent (Clark and Pitt 2012), in addition to increasing the sodium adsorption ratio (SAR) that can greatly hinder infiltration rates in soils or media having even small amounts of clay. Granular activated carbon (GAC) technology is costly and therefore is not regularly used for stormwater applications, but is used when very low permit limits must be met (Pitt and Clark 2012).

The valence charge of a metal and its complexation, among other contaminant properties, influence the choice of stormwater treatment technology (Clark and Pitt 2012). Strongly charged, small molecules can be removed effectively by zeolites (Clark and Pitt 2011 and 2012). Zeolites are not effective in the removal of compounds of zero valence and compounds with large size (Clark and Pitt 2012). Peat, compost and soils remove pollutants by chemisorption that is generally irreversible (Watts 1998; Evangelou 1998). Peat can be used as a filtration media for treatment of heavy metals and likely their complexes (Clark and Pitt 2012 and 1999). Peat's effectiveness is due to the wide range of binding sites (carboxylic acid, etc.) present in the humic materials and ligands in the peat (Cohen, et. Al. 1991; Sharma and Foster 1993; Clark and Pitt 2012). An advantage of peat media is that it can treat many heavy metals during relatively short (10 minutes) contact times (Pitt and Clark 2010; Clark and Pitt 2012). The peat's drawbacks (especially for Sphagnum peat) includes the leaching of colored humic and fulvic acids and the release of hydronium ions (H_3O^+) in exchange for metals which can lower the pH of the treated water by as much as 1 to 2 pH units and increase the solubility of the metals that were associated with stormwater runoff solids or media (Clark and Pitt 2012, 1999). Another disadvantage of using peat is the release of nutrients from the filter during the first flush under microanaerobic conditions in the media which may occur between storms (Clark and Pitt 2009b), although this is not as problematic as for compost media. Compost (including municipal leaf waste compost) can also be used to treat metals (Sharma and Foster 1993; Guisquiani, et al. 1995). The advantage of compost is that it is not likely to reduce the pH of the treated water (Clark and Pitt 1999). However, the disadvantage is that it can release nutrients, depending on the compost's source material, during the first few years of its life (Hathaway, et al. 2008, Pitt, et al. 1999; Pitt and Clark 2010). Treatment trains, like the multi-chambered treatment train (MCTT) can be effectively used for metal treatment and include catch basins for retaining the largest sediment, settling chambers for retaining fine sediment and particle-bound pollutants, and an sorption/ion exchange chamber with mixed media (peat moss, sand) for capturing filterable contaminants through sorption/ion-exchange (Pitt, et al. 1999). The upflow filter was also found to be an effective method for controlling stormwater and uses sedimentation, screens for floatable solids, sorption, and ion exchange (Togawa and Pitt, available online). Grass swales may be effective for removing metals. They capture heavy metals by sedimentation, infiltration/sorption, and biological uptake, can treat high volumes of water and are relatively inexpensive (Johnson, et al. 2003).

The data for total and filtered metal concentrations of lead, copper, zinc, and aluminum analyzed after three months of exposure during the buffered tests was compared to estimate metal association with the particulate matter (Appendix D). Analytical methods having smaller detection limits are necessary to account for non-detected values. Tables 5-24 and 5-25 summarize particulate and filterable lead and zinc fractions in different samples during the buffered pH tests. Generally, most of the lead was associated with the particulate fraction under pH 5 conditions and with the dissolved fraction (> 76%) under pH 8 conditions during the buffered tests after three months of exposure. For pH 5 waters, no detectable concentrations of lead were associated with the dissolved fraction. Under pH 8 conditions, most of the lead was associated with the dissolved fraction, while24% of the lead was associated with particulates for galvanized steel pipe, and only 4% for galvanized steel gutter.

Practically all copper was associated with the dissolved fraction (>67 %) for all the pipes under pH 5 and pH 8 conditions after three months of exposure. The exception was for copper gutter samples under pH 8 conditions for which the filtered copper concentration was 83%.

For plastic PVC and HDPE pipes immersed in the pH 5 water, almost all of the zinc concentrations were in dissolved forms. For metal pipes under pH 5 conditions, from 49% to more than 92% of the zinc was associated with particulates, with the exception of the aluminum gutter sample where all zinc was associated with the filterable fraction. For HDPE, vinyl, and copper materials under pH 8 conditions, all zinc was associated with the dissolved fraction. For the rest of the materials (concrete, PVC, aluminum, and galvanized steel pipe and gutter) immersed into pH 8 water, from 67% to practically 100% of zinc was associated with particulates.

Under both pH 5 and 8 conditions, aluminum was predominantly associated with the dissolved fraction (from 50 to 100%).

Table 5-24. Filterable and particulate fractions of lead and zinc in buffered waters after three months of exposure

Water	Material	% Filterable Pb	% Particulate Pb	% Filterable Zn	% Particulate Zn
pH 5	Concrete Pipe	n/a	n/a	n/a	n/a
	PVC Pipe	n/a	n/a	89	11
	HDPE Pipe	n/a	n/a	83	17
	Steel Pipe	< 2.0	> 98	24	76
	Vinyl Gutter	n/a	n/a	n/a	n/a
	Aluminum Gutter	n/a	n/a	100	0
	Steel Gutter	< 13.5	> 86	51	49
	Copper Gutter	n/a	n/a	< 15	> 85
pH 8	Concrete Pipe	n/a	n/a	< 67	> 33
	PVC Pipe	n/a	n/a	18	82
	HDPE Pipe	n/a	n/a	100	0
	Steel Pipe	76	24	0.34	100
	Vinyl Gutter	n/a	n/a	100	0
	Aluminum Gutter	n/a	n/a	24	76
	Steel Gutter	96	4	1.7	98
	Copper Gutter	n/a	n/a	100	0

Table 5-25. Filterable and particulate fractions of copper and aluminum in buffered waters after three months of exposure

Water	Material	% Filterable Cu	% Particulate Cu	% Filterable Al	% Particulate Al
pH 5	Concrete Pipe	n/a	n/a	n/a	n/a
	PVC Pipe	96	4	100	0
	HDPE Pipe	100	0	n/a	n/a
	Steel Pipe	n/a	n/a	n/a	n/a
	Vinyl Gutter	100	0	n/a	n/a
	Aluminum Gutter	133	0	100	0
	Steel Gutter	n/a	n/a	n/a	n/a
	Copper Gutter	100	0	n/a	n/a
pH 8	Concrete Pipe	n/a	n/a	n/a	n/a
	PVC Pipe	71	29	< 100	> 0
	HDPE Pipe	100	0	100	0
	Steel Pipe	67	33	n/a	n/a
	Vinyl Gutter	100	0	50	50
	Aluminum Gutter	100	0	100	0
	Steel Gutter	100	0	50	50
	Copper Gutter	17	83	n/a	n/a

Table 5-26 summarizes particulate and filterable iron fractions during natural pH tests. After three months of exposure during natural pH tests, iron in containers with PVC and HDPE pipes and with vinyl and aluminum gutters were associated predominantly with dissolved fraction (70% and greater), while iron in containers with the rest of the materials were mainly associated with particulates.

Table 5-26. Filterable and particulate fractions of iron in natural pH waters after three months of exposure

Water	Material	% Filterable Fe	% Particulate Fe
Bay	Concrete Pipe	29	71
	PVC Pipe	90	10
	HDPE Pipe	84	16
	Steel Pipe	49	51
	Vinyl Gutter	92	8
	Aluminum Gutter	88	12
	Steel Gutter	41	59
	Copper Gutter	43	57
River	Concrete Pipe	18	82
	PVC Pipe	73	27
	HDPE Pipe	77	23
	Steel Pipe	6	94
	Vinyl Gutter	69	31
	Aluminum Gutter	70	30
	Steel Gutter	19	81
	Copper Gutter	16	84

Morquecho, et al.2005 studied the percent of pollutant reductions that were associated with removal of particulates of different sizes. It was found the tin sheetflow samples collected in Tuscaloosa, AL, a large percentage of copper (> 60%) was associated with particles smaller than 0.45 µm and are not removed by sedimentation and physical filtration techniques (Morquecho, et al. 2005; Clark and Pitt 2012). For these samples, lead was reduced on the average by 62% and zinc by 70% by removing the particles greater than 5µm and lead was reduced by 76% and zinc by 70% by removing the particles greater than 1 µm, indicating that sedimentation and physical filtration would be an appropriate pretreatment technologies since it is considered that the reliable sedimentation is occurring for particles in the range of 2 to 5 µm (Camp 1952; Clark and Pitt 2012). Frequently, lead that is in ionic form (approximately < 0.45 µm) is in very low quantities, but if necessary, it can be treated with ion exchange technology using zeolites (Clark and Pitt 2012). Chemically-active media filtration using compost, peat, and soil can be used to treat lead complexes formed with hydroxides and chlorides (Clark and Pitt 2012).

Zero-valent iron (ZVI) was found to be an efficient medium for treating stormwater heavy metal ions as Cu^{2+} and Zn^{2+} (Rangsivek and Jekel 2005, Shokes and Moller 1999; Wilkinan and McNeil 2003). Rangsivek and Jekel (2005) found that a significant fraction of Cu^{2+} is transformed to insoluble CuO and Cu_2O species. Zn^{2+} is removed by adsorption and co-precipitation with iron oxides. Zero-valent iron removes inorganic pollutants via cementation (reduction of redox sensitive compounds to insoluble forms, for example, $Cu^{2+}+Fe^0 \rightarrow Cu^0+Fe^{2+}$), adsorption and metal hydroxide precipitation

(Rangsivek and Jekel 2005, Cantrell, et al. 1995; Shokes and Moller 1999; Blowes, et al. 2000; Naftz, et al. 2002; Wilkin and McNeil 2003). Higher values of water pH, dissolved oxygen (DO), temperature, and ionic strength increased the removal rates of Zn^{2+}. At higher pH values and in the presence of dissolved oxygen (DO), adsorption and co-precipitation with iron oxide are predominantly occur (Rangsivek and Jekel 2005). On the other hand, at low pH values in the absence of DO, the cementation is very effective (Rangsivek and Jekel 2005; Strickland and Lawson 1971; Ku and Chen 1992).

ZVI was found to have capacity comparable to a commercial adsorbent granular ferric hydroxide (GFH). The advantages of zero-valent iron (ZVI) are that it is inexpensive and can provide environmental benefits when used in the reclamation of solid waste (Rangsivek and Jekel 2005). Also, ZVI can be installed in an on-site remediation system as a fixed-bed barrier (Morrison, et al. 2002). Drawbacks of ZVI include the release of dissolved iron and complexes of iron oxides with other heavy metals. Therefore, a post-treatment process that includes aeration and sand filtration may be necessary. The removal of such substances as oil from iron's surfaces may be required if iron was acquired as solid waste.

A virgin coconut hull granular activated carbon (GAC), which has a limited chemical capacity, can be used for nitrate (NO_3^-) treatment (Pitt and Clark 2010). To remove nitrate and nitrite, vegetated systems can be utilized (Baker and Clark 2012; Lucas and Greenway 2008, 2011; Hunt, et al. 2006; Hunt, et al. 2008). For nitrogen removal, zeolites, commercial resins, and some native soils may be used. Current work on the removal of nitrogen compounds is focusing on denitrification in anaerobic systems and on bacterial processes in subsurface gravel wetlands and biofilters.

Sedimentation can be utilized to treat particulate bound phosphorus. To remove phosphorus associated with colloids or are in dissolved forms, vegetative systems may be used (Clark and Pitt 2012).

Ionic fractions for zinc, copper, and cadmium can range from 25 to 75% (Clark and Pitt 2012). Sedimentation and physical filtration can be used to treat metals that are bound to particles. These metals can be associated with very small particles, therefore the efficiency of physical filtration to remove metals will depend on size of associated particulates. Treatment technologies for metals associated with dissolved fraction include chemical methods. To remove dissolved metals from stormwater, peat moss, mixtures of peat moss and sand, zeolite, and compost can be used, especially with long contact times. These metals can form soluble complexes with different inorganic and organic ligands. The complex valence can range from -2 to +2. Organic and inorganic complexes may be treated by chemically active filtration through compost, peat, and soil. Also, granular activated carbon (GAC) can be used to remove complexes with organic matter.

The choice of treatment methods depends on form of heavy metals and desired level of metal removal. If high degree of metal reduction is required, it is necessary to use multiple techniques (Clark and Pitt 2012). Generally, low numeric discharge limits can be met through combinations of pre-treatment by sedimentation and filtration with a chemically and biologically active media.

Concrete Stability and Calcium Carbonate Saturation using the Langelier Index

The Langelier Index was calculated to determine whether the leaching water for the concrete materials was in equilibrium, oversaturated, or undersaturated with respect to $CaCO_{3(s)}$. Langelier Index indicates whether concrete will deteriorate as a result of $CaCO_{3(s)}$ dissolution from the concrete. Also, the Langelier Index can indicate whether $CaCO_{3(s)}$ that is present in the water will precipitate and form scale that may protect pipe materials from corrosion. The Langelier Index was calculated for the test samples at three months of exposure. $H_2PO_4^-$ and HPO_4^{2-} concentrations were calculated from weighed chemicals. During the calculations of ionic strength μ, $H_2PO_4^-$ and HPO_4^{2-} concentrations were assumed to be in ionic form.

The Langelier Index was calculated twice: once utilizing the activity coefficients in aqueous solution determined using the DeBye-Huckel equation, and second time using the Maclinnes assumption to estimate the activity coefficients. Both methods produced the same results (Tables 5-27 and 5-28). The Langelier Index showed that all samples with buffered pH 5 and pH 8 waters were undersaturated with respect to $CaCO_{3(s).}$ Therefore, the water in the containers with concrete pipes had a tendency to dissolve $CaCO_{3(s)}$ from the concrete. The water in the containers with the remaining pipe and gutter materials didn't have a tendency to precipitate $CaCO_{3(s)}$ from the solution. During the second testing stage, the samples with galvanized steel pipe and gutter materials immersed into bay and river waters were undersaturated with respect to $CaCO_{3(s).}$ However the samples with the rest of the materials (including concrete) were oversaturated with $CaCO_{3(s)}$ indicating the water in these samples had a tendency to precipitate $CaCO_{3(s)}$ from the solution and there was no degradation of the concrete pipe after 3 months of exposure.

Table 5-27. Langelier Index. Buffered pH 5 and pH 8 Waters.

				γ:DeBye-Huckel Equation			γ: The Maclinnes Assumption		
		μ	pHa	pHs	L.I.	Water with respect to CaCO3	pHs	L.I.	Water with respect to CaCO3
pH 5	**P. Concrete**	0.069	6.37	12.59	-6.22	undersaturated	12.61	-6.24	undersaturated
	P. PVC	0.070	5.23	11.81	-6.58	undersaturated	11.82	-6.59	undersaturated
	P. HDPE	0.068	4.84	13.66	-8.82	undersaturated	13.67	-8.83	undersaturated
	P. Steel	0.069	5.80	13.04	-7.24	undersaturated	13.05	-7.25	undersaturated
	G. Vinyl	0.068	4.83	13.89	-9.06	undersaturated	13.90	-9.07	undersaturated
	G. Aluminum	0.068	4.84	14.10	-9.26	undersaturated	14.11	-9.27	undersaturated
	G. Steel	0.068	5.43	13.36	-7.93	undersaturated	13.37	-7.94	undersaturated
	G. Copper	0.068	5.13	15.79	-10.66	undersaturated	15.81	-10.68	undersaturated
pH 8	**P. Concrete**	0.196	8.96	12.90	-3.94	undersaturated	12.93	-3.97	undersaturated
	P. PVC	0.196	8.50	12.01	-3.51	undersaturated	12.04	-3.54	undersaturated
	P. HDPE	0.196	8.47	12.79	-4.32	undersaturated	12.83	-4.36	undersaturated
	P. Steel	0.196	8.90	13.13	-4.23	undersaturated	13.16	-4.26	undersaturated
	G. Vinyl	0.196	8.48	12.98	-4.50	undersaturated	13.01	-4.53	undersaturated
	G. Aluminum	0.196	8.50	14.68	-6.18	undersaturated	14.72	-6.22	undersaturated
	G. Steel	0.196	9.07	13.04	-3.97	undersaturated	13.07	-4.00	undersaturated
	G. Copper	0.196	8.76	13.52	-4.76	undersaturated	13.55	-4.79	undersaturated

Footnote: pH$_a$ = actual pH of water; pH$_s$ = pH of water if it were in equilibrium with $CaCO_{3(s)}$ at the existing solution concentrations of HCO_3^- and Ca^{2+}. L.I. = Langelier Index.

Table 5-28. Langelier Index. Natural Bay and River Waters.

				γ: DeBye-Huckel Equation			γ: The Maclinnes Assumption		
		μ	pHa	pHs	L.I.	Water with respect to CaCO3	pHs	L.I.	Water with respect to CaCO3
Bay	**P. Concrete**		8.39	7.49	0.90	oversaturated	7.50	0.89	oversaturated
	P. PVC		7.90	7.82	0.08	oversaturated	7.83	0.07	oversaturated
	P. HDPE		7.84	7.80	0.04	oversaturated	7.82	0.02	oversaturated
	P. Steel		7.00	8.72	-1.72	undersaturated	8.73	-1.73	undersaturated
	G. Vinyl		7.97	7.72	0.25	oversaturated	7.73	0.24	oversaturated
	G. Aluminum		8.00	7.60	0.40	oversaturated	7.62	0.38	oversaturated
	G. Steel		7.84	8.44	-0.60	undersaturated	8.45	-0.61	undersaturated
	G. Copper		8.01	7.75	0.26	oversaturated	7.76	0.25	oversaturated
River	**P. Concrete**		8.74	8.12	0.62	oversaturated	8.12	0.62	oversaturated
	P. PVC		8.43	7.84	0.59	oversaturated	7.84	0.59	oversaturated
	P. HDPE		8.35	7.94	0.41	oversaturated	7.94	0.41	oversaturated
	P. Steel		8.87	9.06	-0.19	undersaturated	9.07	-0.20	undersaturated
	G. Vinyl		8.31	7.97	0.34	oversaturated	7.97	0.34	oversaturated
	G. Aluminum		8.34	7.93	0.41	oversaturated	7.93	0.41	oversaturated
	G. Steel		6.93	9.02	-2.09	undersaturated	9.02	-2.09	undersaturated
	G. Copper		8.31	7.93	0.38	oversaturated	7.93	0.38	oversaturated

Indicator Microorganism Survival on Urban Surfaces

These experiments are described elsewhere in this report and focus on the initial die-off and subsequent re-growth. These results also affect the fate of these organisms after their discharge. Disinfection of a wastewater containing the indicators *E. coli* and enterococci may result in significantly reduced populations initially, but are likely to undergo significant re-growth during subsequent periods. The re-growth may occur on surfaces (as shown during these tests) or in the receiving water (although the specific rates may vary for different conditions). The following briefly describes how these results may be applicable to treatment of wet weather flows.

E. coli

Results from breakpoint analyses of the *E. coli* dataset are complex. One treatment (warm/wet/dark, similar to gut conditions of warm blooded hosts) showed no significant decrease in populations. Two treatments (warm/dry/UV and warm/wet/UV) showed an initial decline, a rebound of growth, and a subsequent second decline. Cool treatments were nearly indistinguishable from each other, and resulted in more rapid declines than warm/shade treatments. All treatments exhibiting multiple declines showed slower declines later in the study period than in the initial die-off period. The initial declines occurred over a few day period, but were rarely sustained for longer periods. By the end of the study period (about two weeks) all of the *E. coli* populations were about 2 to 4 orders of magnitude lower than their original populations after a second die-off period.

Enterococci

Survival characteristics were less complex for enterococci than for *E. coli*. The warm/wet/dark test conditions had much lower declines in populations with time than for the other test conditions. The clear trend of greater net survival in warm treatments seen for *E. coli* is not evident for enterococci. All treatments exhibited an initial decline, with all three environmental factors (temperature, humidity, and UV exposure) contributing (either as main effects or within interactions). The rates of decline, however, are only about half of those shown by *E. coli*. By the end of the study period (about two weeks) all enterococci had rebounded to within about 10% of their original populations.

Treatment of Emerging Contaminants using Media in Stormwater Filtration and Biofiltration Systems

The following is summarized from a recent publication by Clark and Pitt (2012) that reviewed recent research on the selection of treatment media that can be used in many situations for the control of a wide variety of targeted pollutants.

Treatability of Dissolved Organic and Inorganic Pollutants of Concern

A number of literature references describe laboratory tests of media for the control of stormwater. However, conventional laboratory batch tests need to be interpreted carefully when selecting media and when completing the design of biofilters or bioretention facilities. Johnson et al. (2003) ran stormwater batch tests at two concentrations: one typical of stormwater and one typical of low-to-medium strength industrial wastewater. The results showed the importance of testing at the anticipated runoff concentrations because, at higher concentrations, the isotherms had different shapes and were more favorable than those at typical runoff concentrations (Johnson et al. 2003). Fixed-bed adsorber equations address the impact of contact time in the media. Applying batch testing results to a fixed-bed column requires assuming an instantaneous equilibrium, with all adsorption sites available to a pollutant during movement through the bed (Watts 1998; McKay 1996). However, for many media, not all active sites are available, especially the interstitial sites, when the contact time is minutes instead of many hours. Typical contact time for treating stormwater is much less than normally assumed for batch tests due to the small area and high flow rates. Contact times are usually from about 10 minutes to an hour. Recent research has focused on diffusion limitations, assuming that adsorption is instantaneous once the pollutant reaches the active site. Clark (2000) showed the difficulty of applying fixed-bed models for the treatment of wet weather flows. These models assume a substantial concentration gradient between the pollutant and the media surface, with adsorption overwhelming desorption. Large concentration gradients often do not exist in stormwater runoff treatment (the influent concentrations of many pollutants of concern are usually much lower than the industrial applications for which these models were developed. In addition, pollutant removal, especially in natural systems, is due to many phenomena, most of which cannot currently be mathematically quantified. Therefore, long-term, intermittent flowing pilot-scale column testing of media performance using actual stormwater is needed to measure and compare the ability of alternative treatment media.

Sand without surface amendments, such as oxide coatings, is considered relatively inert compared to other media and minimal removal likely would occur for colloidally-sized pollutants. Sand, though, often is incorporated into stormwater media to provide structure and to minimize fluctuations in flow rate through the media (Clark 2000). Sand removal efficiencies typically increase as the media/filter ages because the trapping of particles typically decreases the pore openings, especially on the surface, allowing smaller particles to be captured, plus the coating of chemically active materials and biofilms on the inert sand particles occurs with time (Metcalf and Eddy 2003; Geesey, et al. 1998).

Clark and Pitt (2011) found that zeolites can be effective for metals in the +2 valence state. The effectiveness of ion exchange decreases as the valence charge approaches zero and as the size of the complex increases. Therefore, the overall effectiveness of zeolites, and potentially other ion-exchange media such as oxide-coated sands, is likely reduced because a substantial fraction of the metals likely exist in valence forms other than +2 due to complexation with inorganic ions and organic matter. Organic compounds and larger, less charged complexes of metals, can be chemically bonded with a media having strong sorption capacities. K_{OW} is an indication of the preference for the molecule to attach to an organic media (peat, compost, GAC) versus remaining in the stormwater runoff. K_S indicates the likelihood that the organic compound will remain dissolved in solution. The removal of some inorganic anions is difficult because most stormwater treatment media specifications stress high cation exchange capacities

(CEC). High CEC media typically have low anion exchange capacities (AEC). CEC and AEC provide an estimate of the potential for exchanging a less-desirable compound with a pollutant whose chemical characteristics are more favorable. Table 5-29 lists some of the pollutants of concern in stormwater runoff and potential treatment options, based on their chemical properties and the results of laboratory, pilot-scale, and full-scale treatment tests.

Table 5-29. Selecting Treatment Technologies for Stormwater Pollutants (summarized from Clark and Pitt 2012)

Pollutant	**Treatment Process**	**Design Notes**
Metals		
Lead	Sedimentation or filtration, possibly followed with ion-exchange and chemically-active media.	Lead attaches strongly to solids. Substantial removal by sedimentation and/or physical filtration of solids to which lead is attached. Lead < 0.45 µm may be ionic and could be removed using ion-exchange with zeolites, but filtered, ionic lead is usually at very low concentrations and it would be unusual to require treatment. Lead complexes with hydroxides and chlorides to a certain extent. Removed in media with a variety of binding sites (peat, compost, soil) would be needed.
Copper, Zinc, Cadmium	Sedimentation or filtration, likely followed with chemically-active media.	These metals can attach to very small particles, with attachments being a function of the particulate organic content, pH, and oxidation-reduction conditions (filterable fractions vary from 25 to 75+%). Physical filtration may be limited depending on size association of the pollutants. These metals complex with a variety of organic and inorganic ligands to create soluble complexes of varying valence charges (-2 to +2). Typical major ions in the stormwater reduce ion-exchange effectiveness of targeted pollutants. Complexes require a variety of types of sorption/exchange sites. Organic complexes may be removed by GAC, Peat, compost and soil will remove most inorganic and organic complexes.
Organics and Pesticides		
PAHs/Oil and Grease (O&G)/Dioxin	Sedimentation or filtration, possibly followed with chemically-active media.	These compounds have high K_{OW} and low K_S and are strongly associated with particulates. Sedimentation's effectiveness is function of particle size association. Preferential sorption to organic media, such as peat, compost, soil. Some O&G components can be microbially degraded in filter media. Reductions to very low levels with filtration may be difficult if parent material is contaminated. If low permit limits, may have to use clean material such as GAC.
Organic Acids and Bases	Chemically-active filtration	Tend to be more soluble in water than PAHs and more likely to be transported easily in treatment media. Need media with multiple types of sorption sites, such as peat, compost and soil. GAC possible if nonpolar part of molecule interacts well with GAC or if GAC has stronger surface active reactions than just van der Waals strength forces.
Pesticides	Chemically-active filtration	Tend to be soluble in water and need multiple reaction sites to be removed. Breakdown time in biologically-active filtration media is compound-dependent. Breakdown has the potential to restore surface-active sites, and may result in more soluble daughter products, which may or may not be more toxic. Organic media such as peat, compost, soil, GAC likely to be most effective since size of pesticide compounds will exclude substantial removal in ion-exchange resins such as zeolites.
Microorganisms		
Bacteria	Physical filtration and organic media (chemically-active) filtration	Most bacteria are in the lower limits of the size range for effective physical filtration using a sand medium. Removal not 100% effective, but can be important as the bacteria can be highly associated with larger particulates. However, as the filter ages, removals will tend to increase, partly due to reduction in the effective pore sizes and due to the exopolymers that many bacteria excrete. These

Pollutant	Treatment Process	Design Notes
		exopolymers will provide surface reactive sites, even on a relatively-inert sand media. Exopolymers and surface active sites on cell membranes also enhance the attachment of bacteria to surface sites on filtration media. Because of negative surface charge, bacteria can be removed by media with high AEC, with potential for predation, but also regrowth. Organic media provide a location for captured bacteria to reside and grow. Challenge is encouraging capture and potential growth to create reactive sites, but without excessive growth that sloughs off the media and is washed out with successive storms.

Summary of Fate and Treatment of Emerging Contaminants in Wet Weather Flows

The main physical and chemical properties that affect EC treatment are the octanol/water coefficient, water solubility, pH, sorption coefficient, structure and the molecular weight of the compound. The octanol-water coefficient is a surrogate measure of how the compound may be absorbed by organic matter. Solubility and log K_{ow} are inversely proportional. If pollutants have a higher log K_{ow} and lower solubility, they tend to sorb on organic particulate matter and can be removed in primary treatment (sedimentation).

Treatment of Pharmaceuticals and PAHs

Tables 5-30 and 5-31 summarize the chemical characteristics and their treatability as reported in the literature review for the emerging contaminants examined during this research. These tables shows the most likely means of removal, the reported ranges of influent and effluent concentrations, and the ranges of the percentage removals for each constituent.

The pharmaceuticals gemfibrozil, ibuprofen, triclosan and fluoxetine were reported to be best reduced by biodegradation. The overall range of influent concentrations ranged from 0.3 to 14.6 µg/L. The removals for these compounds varied. Ibuprofen showed the highest level of treatability ranging from 82 to 95 percent. Triclosan had reduction rates of 75 percent and gemfibrozil had a reduction range from 38 to 76 percent.

Carbamazepine had the lowest reported reduction rates of zero to 30 percent. . Carbamazepine is difficult to treat, as it is resistant to biodegradation. Because carbamazepine is soluble in water, it is also not treatable by sedimentation in the primary unit processes. Carbamazepine concentration increases in the effluent compared to the influent were observed. Possible treatment mechanisms of carbamazepine are not clearly understood.

Sulfamethoxazole is highly soluble in water and therefore difficult to remove. Photodegradation removes sulfamethoxazole at some treatment facilities. The reported influent concentrations ranged from 0.25 to 0.35 µg/L, and the effluent concentrations ranged from 0.11 to 0.23 µg/L. The reduction rates of sulfamethoxazole ranged from 17 to 66 percent.

Low molecular weight (LMW) PAHs (naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, and anthracene) had reported reduction rates between 31 and 91 percent. Naphathlene had the lowest reduction rates ranging from 31 to 40 percent. Naphthalene has a Henry's Law constant of 0.019 atm-m^3/mol, making it more volatile than the other PAHs and more likely to volatize during wastewater treatment. Acenaphthene, acenaphthylene, fluorene, phenanthrene and anthracene have Henry's

Law constants of about 10^{-3}, and their solubilities range from 0.045 to 16.1 mg/L. Volatization and oxidation were the primary means of reported treatment for PAHs having lower molecular weights. High molecular weight (HMW) PAH compounds (such as pyrene, fluoranthene, chrysene, and benzo(a)pyrene) had higher reduction percentages ranging from 83 to 91 percent. Adsorption is a primary removal factor for the HMW compounds. Influent concentrations for LMW PAHs ranged from 0.016 to 7.3 µg/L. Effluent concentrations for LMW PAHs had a range from 0.002 to 0.7 µg/L. Influent concentrations for the HMW PAHs ranged from 0.044 to 0.47 µg/L. Effluent concentrations for HMW PAHs ranged from 0.013 to 0.06 µg/L.

Table 5-30. Summary of Characteristics and Treatability of Targeted Pollutants

Constituent	**Log Kow**	**Solubility (mg/L)**	**pka**	**Biodegradation half-life * **rate**	**Toxicity**
Pharmaceuticals					
Gemfibrozil	4.78	5.0	4.7	1.5 hours	EC 50 D. Magna 22.85 mg/L
Ibuprofen	3.5-4.0	41.5	4.9	2 hours	EC 50 Daphnia. 108 mg/L
Triclosan	4.8-5.4	2-4.6	7.8	125 hours	IC 50 P. subcapitata. 1.4 µg/L
Carbamazepine	2.25	17.7	13.9	10-20 hours	LC 50 D. magna >100 mg/L
Fluoxetine	4.05	38.4	9.5	24-72 hours	LC 50 P. subcapitata 24 µg/L
Sulfamethoxazole	0.9	600	5.7	10 hours	IC 50 P. subcapitata. 1.5 mg/L
Trimethoprim	0.79	400	6.8	8-10 hours	IC 50 P. subcapitata. 80.3 to 130 mg/L

Table 5-30. Summary of Characteristics and Treatability of Targeted Pollutants (continued)

Polycyclic Aromatic Hydrocarbons	**Log kow**	**Solubility**	**Volatility**	**Biodegradation rate**	**Toxicity**
Napthalene	3.37	31.7	4.6 x 10^{-4}	0.8-43 days	LC 50 Pimephales promelas 7.76 mg/L
Acenaphthene	4.02	1.93	7.91 x 10^{-5}	1-25 days	LC 50 Salmo gairdneri 1570 µg/L
Fluorene	4.12	1.68-1.98	1.0 x 10^{-4}	2-64 days	EC 50 V. fischeri 4.10 µg/mL
Fluoranthene	5.14	0.20-0.26	6.5 x 10-^{6}	880 days	EC 50 S. capricornutum 54,400 µg/L
Acenaphthylene	3.89	3.93	1.5 x 10^{-3}	21-121 days	Did not find
Phenanthrene	4.48	1.20	2.56 x 10^{-5}	19 days ; 35-37 days;	Did not find
Anthracene	4.53	0.0076	1.77 x10^{-5}	108-139 days	EC 50 D.magna 211 µg/L;
Pyrene	5.12	0.0.077 (Dabestani and Ivanov 1999, 10-34)	4.3 x 10^{-4}	34 to 90 weeks	EC 50 D.magna 67000 µg/L
Benzo(a) anthracene and chrysene	5.61-5.71	0.0016-0.011	n/a	n/a	n/a
Benzo(b) fluoranthene, Benzo(k) fluoranthene, Benzo(a) pyrene, and indeno(1,2,3,cd) pryene			n/a	n/a	n/a
Benzo(a,h) anthracene and Benzo(g,h,i) perlene			n/a	n/a	n/a

Table 5-30. Summary of Characteristics and Treatability of Targeted Pollutants (continued)

Pesticides	Log kow	solubility	Reported most important treatment method	Biodegradation rate	Toxicity
Methoxychlor	4.68-5.08	0.1	Adsorption/ biodegradation	7 to 29 days	D. magna EC 50=1800 µg/L
Aldrin	6.5	0.027	Adsorption/ biodegradation	20-100 days	Salmo gairdneri LC 50 2.6 µg/L
Dieldrin	6.2	0.1	Adsorption/ biodegradation	None found	Salmo gairdneri LC 50 1.2 µg/L
Chlordane	~5.54	insoluble*	Adsorption/ biodegradation	60 days	Chironomus plummosus LC 50 10 µg/L
Arochlor Σ	5.6-6.8	insoluble*	Adsorption/ biodegradation	Variable. Depends on chlorination of compound	P. subcapitata 182nmol/L
Lindane	3.8	17	Adsorption/ biodegradation	69.41 hours	D. magna EC 50=1.64 mg/L
Heptachlor	6.10	0.056	Adsorption/ biodegradation	6 months-3.5 years	S. capricornutum LC 50 26.7 µg/L
Heptachlor-epoxide	5.40	not found	Adsorption/ biodegradation	None found; metabolite	None found
	4.68-5.08	0.1	Adsorption/ biodegradation		

Table 5-31. Summary of Characteristics and Treatability of Targeted Pollutants

Constituent	**Reported most important treatment method**	**Range of influent concentration (µg/L)**	**Range of effluent concentration (µg/L)**	**Range of removal at conventional wastewater treatment facility**
Gemfibrozil	Biodegradation	1.5-3.5	0.4-0.8	38%-76%
Ibuprofen	Biodegradation	0.45-14.6	0.02-1.96	82%-95%
Triclosan	Biodegradation	0.38-1.93	0.108-0.219	60%-75%
Carbamazepine	Not widely known due to increase in effluent	0.13-1.85	0.117-1.61	0%-30%
Fluoxetine	Biodegradation			
Sulfamethoxazole	Adsorption (minor), photodegradation	0.250-0.350	0.110-0.230	17%-66%
Trimethoprim	Chlorination (UV was not effective) Batt et al	0.104-0.450	0.099-0.110	70%-75%
	Reported most important treatment method	**Range of influent concentration (µg/L)**	**Range effluent concentration (µg/L)**	**Range of removal at conventional wastewater treatment facility**
Napthalene	Volatization/oxidation	0.147-7.3	0.088-0.7	31%-40%
Acenaphthene	Oxidation/Sorption	0.016-0.7	0.005-0.11	67%-85%
Fluorene	Oxidation/sorption	0.037-0.7	0.015-0.23	59%-68%
Fluoranthene	Sorption	0.15-0.24	0.02-0.03	86%-88%
Acenaphthylene	Oxidation/sorption	0.021	0.002	91%
Phenanthrene	Oxidation/sorption	0.333-1.7	0.109-0.2	67%-89%
Anthracene	Oxidation/sorption	0.028-0.09	0.007-0.012	75%-87%
Pyrene	Adsorption	0.138-0.47	0.023-0.06	83%-88%
Benzo(a) anthracene and chrysene	Adsorption	0.21	0.019	91%
Benzo(b) fluoranthene, Benzo(k) fluoranthene, Benzo(a) pyrene, and indeno(1,2,3,cd) pryene	Adsorption	0.42	0.076	82%
Benzo(a,h) anthracene and Benzo(g,h,i) perlene	Adsorption	0.044	0.013	71%
Heptachlor	n/a	n/a	n/a	n/a
Heptachlor-epoxide	n/a	n/a	n/a	n/a

Observed Treatment of PPCPs at the Tuscaloosa Wastewater Treatment Plant

Table 5-32 summarizes the average concentrations obtained at each of the four sampling locations at the Tuscaloosa Earl N. Hilliard (ENH) wastewater treatment plant and indications of the likely most important unit treatment process. The pharmaceuticals have low to moderate removals (about 50%) while the PAHs show larger removals (about 90%), although the observed removals varied substantially for different compounds in each constituent group. A combination of unit treatment processes resulted in the best pharmaceuticals and PAH reductions, as expected.

Table 5-32. Performance Data for Earl Hilliard WWTP, Tuscaloosa, AL

Constituent	Avg Influent conc. (µg/L)	Avg Primary effluent conc. (µg/L)	Avg Secondary effluent conc. (µg/L)	Avg concentration after UV (final effluent) (µg/L)	Avg Overall Percentage Removal at ENH wastewater treatment facility	Apparent most Important treatment unit process
Pharmaceuticals						
Gemfibrozil (w)	32.4	31.7	18.1	17.1	45	Secondary
Gemfibrozil (d)	80.3	23.4	22.3	18.6	71	Primary
Ibuprofen (w)	21.6	21.0	17.6	9.6	58	UV
Ibuprofen (d)	44.7	35.3	20.8	15.3	67	Secondary
Triclosan (w)	33.9	16.9	15.0	12.3	63	Primary
Triclosan (d)	16.7	3.3	12.9	0.4	98	UV
Carbamazepine (w)	2.4	5.0	5.0	2.6	-8	UV
Carbamazepine (d)	15.9	10.5	2.5	1.4	94	Primary
Fluoxetine (w)	14.1	41.7	3.3	1.9	86	Secondary
Fluoxetine (d)	61.7	36.8	11.6	9.6	84	Secondary
Sulfamethoxazole (w)	10.4	18.4	14.1	13.1	-33	None
Sulfamethoxazole (d)	68.7	42.6	31.1	24.4	65	Secondary
Trimethoprim (w)	3.1	3.1	3.9	2.0	33	UV
Trimethoprim (d)	16.3	28.3	21.1	21.0	-31	None

Table 5-32. Performance Data for Earl Hilliard WWTP, Tuscaloosa, AL (continued)

Polycyclic Aromatic Hydrocarbons						
Naphthalene (w)	15.3	4.7	25	22.7	-47	None
Naphthalene (d)	7.1	11.1	3.8	1.3	82	Secondary
Acenaphthene (w)	16.9	5.1	0.4	0.6	96	Primary
Acenaphthene (d)	7.7	0.8	0.1	0.02	99	Primary
Fluorene (w)	10.3	1.0	0.6	0.6	91	Primary
Fluorene (d)	0.7	1.2	0.04	0.05	93	Secondary
Fluoranthene (w)	10.3	4.2	0.5	0.5	95	Primary
Fluoranthene (d)	0.3	0.5	0.02	0.04	87	Secondary
Acenaphthylene (w)	10.5	0.6	0.6	0. 7	92	Primary
Acenaphthylene (d)	0.1	0.6	0.01	0.02	75	Secondary
Phenanthrene (w)	6.1	4.4	0.05	0.2	98	Secondary
Phenanthrene (d)	1.6	0.8	0.2	0.1	90	Primary and secondary
Anthracene (w)	198	2.3	9.7	0.8	100	Primary
Anthracene (d)	60.1	0.2	0.2	0.2	100	Primary
Pyrene (w)	10.2	4.0	0.7	0.5	95	Primary and secondary
Pyrene (d)	0.7	1.0	0.1	0.1	80	Secondary

The largest reductions, for all but acenaphthene, occur during secondary biological treatment, where most of the removal of particulates occurs along with biological digestion of the solids. The primary treatment had little effect. Phenanthrene actually indicated an increase in concentrations with primary treatment, likely due to removal of particulates that interfered with the extraction of the compound during the laboratory tests. Acenaphthene is an example where all of the treatment processes were effective for partial removal of the compound, including the primary, secondary, and disinfection unit processes. For many of the samples, acenaphthene was not detected after the secondary treatment phase. Figures 5-23 and 5-24 illustrate how the wide range of influent concentrations were reduced with the different treatment processes.

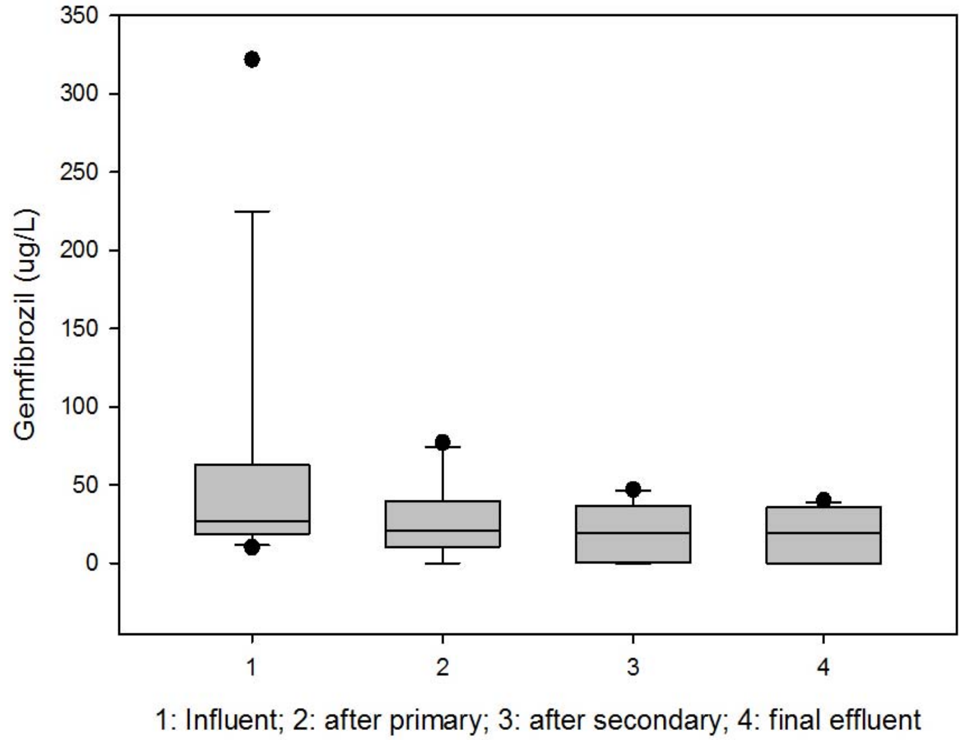


Figure 5-23. Box and Whisker plots for Gemfibrozil

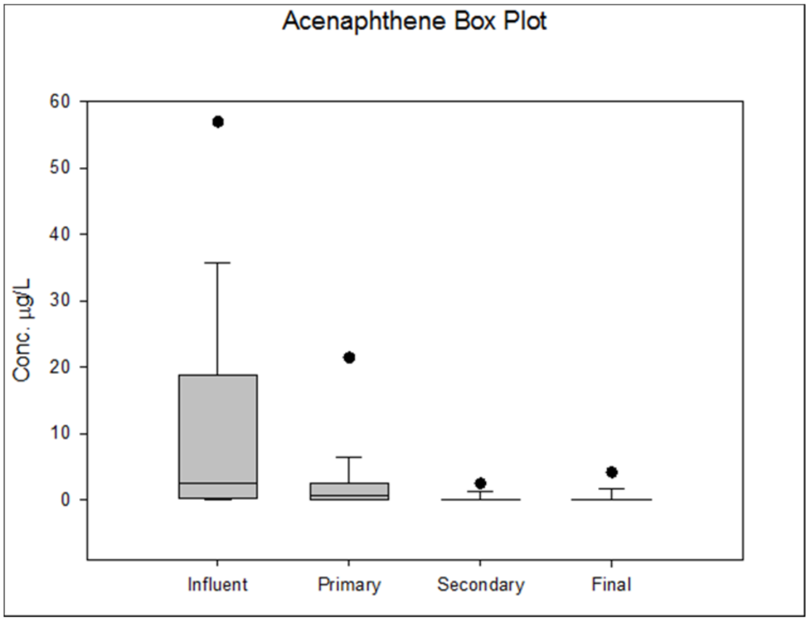


Figure 5-24. Box and Whisker Plot for Acenaphthene

In most cases, the median concentration reductions for the ECs are modest; however, extremely large periodic influent concentrations are usually significantly reduced by the primary treatment unit process. The biological secondary treatment processes and the final ozone disinfection processes provided additional benefit, approaching the “irreducible” concentrations. The secondary treatment did result in a very narrow range of effluent quality for acenaphthene, fluorene, fluoranthene, phenanthrene, and pyrene, although most of the removals for these compounds occurred during with primary sedimentation treatment. No pesticides were detected at the 0.5 to 1 µg/L detection limit at any of the sampling locations at the treatment facility.

Heavy Metal Treatability

Many heavy metals are associated predominantly with particulates, and therefore their treatability is influenced by the removal of the associated particulates. The association of heavy metals with particulates depends on pH, oxidation-reduction potential, and particulate organic matter. The treatability of stormwater solids and associated heavy metals is dependent on their size. The removal of dissolved contaminants may be needed to meet stringent numeric discharge permit requirements and reduce surface and groundwater contamination potentials.

The valence charge of a metal and its complexation, among other contaminant properties, influence the choice of stormwater treatment technology. Strongly charged, small molecules can be removed effectively by zeolites. Zeolites are not effective in the removal of compounds of zero valence and compounds with large size. Peat can be used as a filtration media for treatment of heavy metals and likely their complexes. Peat’s effectiveness is due to the wide range of binding sites (carboxylic acid, etc.) present in the humic materials and ligands in the peat. An advantage of peat media is that it can treat many heavy metals during relatively short (as short as 10 minutes) contact times.

Tests were conducted over a three month exposure period of pipe, gutter, and storage tank materials. Generally, most of the lead was associated with the particulate fraction under pH 5 conditions and with the dissolved fraction (> 76%) under pH 8 conditions after three months of exposure. Practically all copper was associated with the dissolved fraction (>67 %) for all the pipes under pH 5 and pH 8 conditions after three months of exposure. For plastic PVC and HDPE pipes immersed in pH 5 buffered stormwater, almost all of the zinc concentrations were in dissolved forms. For metal pipes under pH 5 conditions, from 49% to more than 92% of the zinc was associated with particulates, with the exception of the aluminum gutter sample where all zinc was associated with the filterable fraction.

Prior research found that ionic fractions for zinc, copper, and cadmium in stormwater can range from 25 to 75%. These metals can be associated with very small particles, therefore the efficiency of physical filtration to remove metals will depend on size of associated particulates. Treatment technologies for metals associated with dissolved fractions include chemical methods. To remove dissolved metals from stormwater, peat moss, mixtures of peat moss and sand, zeolite, and compost can be used, especially with long contact times. These metals can form soluble complexes with different inorganic and organic ligands. The complex valences can range from -2 to +2. Organic and inorganic complexes may be treated by chemically active filtration through compost, peat, and soil. Also, granular activated carbon (GAC) can be used to remove complexes with organic matter.

Indicator Microorganism Survival on Urban Surfaces

Laboratory experiments were also conducted that focused on initial die-off and subsequent re-growth (and later die-off) on concrete test specimens. These results also affect the fate of these organisms after their discharge. Disinfection of a wastewater containing the indicators *E. coli* and enterococci may result in significantly reduced populations initially, but are likely to undergo significant re-growth (and possibly another period of slower die-off) during subsequent periods. The re-growth may occur on surfaces or in the receiving water (although the specific rates may vary for different conditions).

One treatment (warm temperatures/humid moisture/dark conditions, similar to gut conditions of warm blooded hosts) showed no significant decreases in *E. coli* populations. Two treatments (warm/dry/UV and warm/wet/UV) showed an initial decline, a rebound of growth, and a subsequent second decline period. Cool treatments were nearly indistinguishable from each other, and resulted in more rapid declines than warm/shade treatments. All treatments exhibiting multiple declines showed slower declines later in the study period than in the initial die-off period. The initial declines occurred over a few days period, but were rarely sustained for longer periods. By the end of the study period (about two weeks) all of the *E. coli* populations were about 2 to 4 orders of magnitude lower than their original populations after a second die-off period.

Survival characteristics were less complex for enterococci than for *E. coli*. The warm/wet/dark test conditions had much lower declines in populations with time than for the other test conditions. The clear trend of greater net survival in warm treatments seen for *E. coli* is not evident for enterococci. All treatments exhibited an initial decline, with all three environmental factors (temperature, humidity, and UV exposure) contributing (either as main effects or within interactions). The rates of decline, however, are only about half of those shown by *E. coli*. By the end of the study period (about two weeks) all enterococci had rebounded to within about 10% of their original populations.

Section 6. Other Potential Sources of PAHs in Urban Receiving Waters and their Treatability and Fate

Introduction

This report section summarizes several related research tasks that investigated some potential PAH sources in urban areas (asphalt degradation and petroleum spills), urban stormwater PAH characteristics and their treatability, and the fate of discharged PAHs focusing on urban stream sediments. This material is excerpted from the research reports conducted by Sree Usha Verravalli as part of her MSCE program and from research conducted by Jejal Reddy Bathi as part of his PhD program in the Department of Civil, Construction, and Environmental Engineering at the University of Alabama. These research efforts were jointly funded as part of this emerging contaminant project supported by the US EPA and by a related grant funded by the National Science Foundation (grant no. EPS-0447675). The NSF project included tasks conducted at UA supporting the Center for Optical Sensors and Spectroscopies (COSS) at UAB's Department of Physics by applying emerging technologies to solve current environmental problems. These activities are identifying and quantifying environmental contaminant levels associated with current environmental disasters that can then be used by the COSS team to develop performance objectives of newly developed laser instrumentation. The NSF requires the following statement: any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

The following three tasks conducted as part of the NSF project are summarized in this report chapter (other project tasks are not addressed herein):

- Sources of polycyclic aromatic hydrocarbons (PAHs) associated with pavement degradation
- Changes in IR spectra of Deepwater Horizon and other gulf coast crude oil when exposed to natural degradation processes
- Environmental hydrocarbon levels in urban stream sediments and contamination associated with massive hurricanes

Sources of PAHs in the Environment

PAHs are ubiquitous environmental contaminants. Sources of PAHs can be broadly classified as pyrogenic (combustion origin) and petrogenic (petroleum origin). A greater abundance of high molecular weight (HMW) PAHs indicates likely pyrogenic sources, while a greater abundance of low molecular weight (LMW) PAHs implies likely petrogenic origins of the PAHs (Boehm and Farrington 1984). Naphthalene, Fluorene, Anthracene, Phenanthrene are examples of low molecular weight PAHs, while benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(*cd*)pyrene and benzo(*ghi*)perylene are examples of high molecular weight PAHs. Tracking the sources of PAHs based on the molecular weight of PAHs alone may not be accurate. Table 6-1 lists frequently detected PAHs in the environment, and their likely primary sources (Pitt et al.1995). In contrast to what one would expect, high molecular weight PAHs, which are assumed to be pyrogenic in origin, were noted to be from original petroleum sources. Of course, some of these primary petroleum materials have undergone combustion in transportation and industrial operations. Tracking the sources of PAHs based on the presence of LWM or HMW PAHs also becomes questionable as the PAHs are released into the environment and undergo chemical, physical and biological changes (Countway et al. 2003). Physical changes (such as evaporation, or physical transport of by air or water from one location to another), chemical changes (such as photo transformation of PAHs to daughter products), and biological changes (such as biotransformation of the PAHs), changes their profile in the environment. Differentiating the sources of PAHs based on observed PAH molecular weights may be a useful tool if the samples analyzed for PAHs are assumed not to be affected by any of these modifications.

Table 6-1. Organic Compounds Detected at Different Urban Source Areas (Source: Pitt, *et al*.1999)

Toxicant	**Maximum Concentration (µg/L)**	**Detection Frequency at Urban Source Areas (%)**	**Likely Primary Source**
Benzo(a)anthracene	60	12	Gasoline, Wood Preservative
Benzo(b)fluoranthene	226	17	Gasoline, Motor Oils
Benzo(k)fluoranthene	221	17	Gasoline, Bitumen, Oils
Benzo(a)pyrene	300	17	Asphalt, Gasoline, Oils
Fluoranthene	128	23	Oils, Gasoline, Wood Preservative
Naphthalene	296	13	Coal Tar, Gasoline, Insecticides
Phenanthrene	69	10	Oils, Gasoline, Coal Tar
Pyrene	102	19	Oils, Gasoline, Bitumen, Coal Tar, Wood Preservative

Over time, many changes have occurred affecting industrialization with the effect of increased discharges of pollutants. Prior to the 1800s, the bulk of PAH discharges to the environment were of natural origin, or received limited contributions from anthropogenic sources (Van Metre, *et al*. 2000). Van Metre, *et al*. (2000) reported modest to dramatic increases over time in total PAH concentrations in sediment cores of ten lakes and reservoirs in six U.S. metropolitan areas. This study indicated there was a shift in the sources of PAH contamination from uncombusted to combusted fossil fuels. The increase in PAH sediment concentrations was in coincidence with the increase in automobile use and power production, both major consumers of fossil fuels. Similarly, Kuklick, *et al.* (1997) examined sediment samples from three South Carolina estuaries, Winyah Bay, Charleston Harbor and the North Edisto River estuary. The concentrations of total PAHs were extremely variable, ranging from 33 µg kg^{-1} dry weight in the Edisto River estuary to 9,600 µg kg^{-1} dry weight in some areas of urbanized Charleston Harbor. These data show the large effect that urbanization has on sediment PAH contamination.

PAHs are considered to be some of the most important organic toxicant pollutants in stormwater runoff. The magnitude of PAH pollution in runoff can depend on the type of the contributing source area. Pitt, *et al.* (1999) examined stormwater PAHs from more than 100 samples collected from different source area sheetflows, and some receiving waters, in and around Birmingham, AL. The source areas represented by the samples included roofs, parking areas, storage areas, streets, loading docks, and vehicle service areas, plus nearby urban creeks, in residential, commercial, industrial and mixed land use areas. The concentrations of the different PAHs detected varied considerably among the different source areas. Vehicle servicing areas and parking areas were found to have the highest concentrations of PAHs in the runoff, and higher concentrations were associated with longer interevent periods between rains. McCready, *et al.* (2000) also examined PAH contamination of stormwater runoff and resultant contamination of aquatic systems. They examined surface sediment samples from 124 sites in Sydney Harbor, Australia, for 16 of the EPA identified priority PAHs. They also found that the PAH concentrations varied widely, from < 100 to 380,000 µg kg^{-1} total PAHs, depending on the sampling location. The spatial distribution of PAHs indicated increased concentrations of PAHs nearer to areas where stormwater enters the harbor, indicating that urban runoff is a major source of PAHs into Sydney Harbor.

Dry deposition of prior industrial and automobile emissions of PAHs is likely a major source of PAHs to urban waters. However, it is important to factor the yield of these materials to the actual runoff and receiving waters when conducting mass balances. As an example, Pitt (1987) found that only about half of the smallest particulates (<50 µm) on impervious surfaces actually are removed during most rains. If these surfaces are directly connected to the drainage system, these particulates would be effectively transported to the receiving waters. Impervious surfaces that drain to landscaped areas have less of their washed-off particulates actually enter receiving waters, and dry deposition to pervious areas would have very little of their contributions enter receiving waters. Dry deposition falling directly onto water surfaces would obviously have 100% yields to the receiving waters. Therefore, dry deposition of PAHs to receiving waters is more obvious in urban areas than in non-urban areas due to the greater land surface coverage of impervious surfaces in urban areas.

When PAHs are discharged to the atmosphere they will partition between particulate and gaseous phases. The PAH contributions to wet and dry deposition are a function of their vapor exchange across the air-water interface. Wet and dry deposition have been reported as the major transport processes for atmospheric PAHs to the aquatic environment (Terzi, *et al.* 2005). The density and magnitude of PAH emission sources in an area affects the amount of dry deposition. For example, emissions from vehicular exhaust and from industries in urban areas will increase the deposition rate of PAHs. Webber (1983) investigated dry deposition of PAHs in urban and non-urban locations of southeastern Virginia over a 16 month period from November 1980 to February 1982. They found that the mean PAH deposition rate was 27 µg $m^{-2}yr^{-1}$, and was higher in urban locations compared to non-urban locations.

Seasons may also have an effect on the deposition rates of PAHs. Seasonal differences in environmental conditions such as rain characteristics, temperature, and wind speed, plus possible changes in source area contributions, likely affect the deposition characteristics of PAHs in any area. Ollivon, *et al.* (2001) found from their study in Paris, France that the bulk deposition rate (wet plus dry deposition) for six selected PAHs during the summer was 69 $\mu gm^{-2}yr^{-1}$, the winter deposition rate was higher, at 165 $\mu gm^{-2}yr^{-1}$. The observed higher deposition rates in the winter could have been caused by increases in source PAH emissions to the atmosphere in the form of domestic heating. PAHs in urban runoff can occur in both particulate and soluble forms, although studies have identified the particulate forms as being the most predominate (Pitt, *et al.* 1999). According to the Hwang and Foster (2005) study on urban stormwater runoff in Washington DC, particulate-associated PAHs account for 68-97% of total PAHs in the runoff. The particulate-bound PAHs tend to settle and accumulate in receiving water sediments. The following chapter sections address some of these potential sources of PAHs associated with pavement use and petroleum product spillage, and then summarizes a study on PAH associations with urban stream sediment.

Pollutant Releases during the Initial Aging of Asphaltic Pavements

Prior studies have shown that PAH releases associated with coal-tar sealants applied to asphaltic pavements can be significant sources of PAHs to receiving water sediments. Other research has examined the long-term degradation of highway construction materials (including pavements) as pollutant sources. The research summarized in this report section, was conducted by Sree Usha Veeravalli as part of her MSCE program in the Department of Civil, Construction, and Environmental Engineering at the University of Alabama (Veeravalli 2011). She examined the role of freshly constructed asphaltic materials as pollutant sources during the initial exposure period. During aging of asphalt, the pavement undergoes physical and chemical changes which are expected to affect the quality of the runoff; this research investigated the early exposure periods as these changes were thought to be most rapid for freshly placed asphalt.

Exposure tests under natural conditions using three square pavement slabs were examined during this project for a six month period. Two (a hot-mix asphalt pavement and a warm-mix asphalt pavement) were freshly constructed, while the third was a two year old pavement which was freshly coated with an asphalt sealant. The test slabs had a surface area of 0.25 m^2 and were 5 cm thick. They were prepared especially for this project by the National Center for Asphalt Technology (NCAT), at Auburn University, in Auburn, AL. The pavement slabs were set up outdoors in mostly full sun and exposed to rain and other weather factors. During the project period, a 0.5 in simulated rain (using prior collected roof runoff from an adjacent building) was applied to each of the pavement slabs for each controlled sampling period every two weeks. The resulting runoff was analyzed for PAHs, heavy metals (Zn, Cd, Cr, Pb, and Cu), and nutrients (total phosphorous, total nitrogen, nitrate plus nitrite, ammonia, and COD). The samples were also tested for toxicity using the Microtox screening procedure which makes use of bioluminescent bacteria, *Vibrio Fischeri*. The presence of anionic detergents in the samples was also measured using MBAS test kits.

Background

Asphalt is a widely used paving material due to its ability to act as a binder and hold together stone and gravel (aggregate) and due to its water-resisting properties. Its' wide use is also attributed to its ability to withstand heavy traffic loads on busy roads. Asphalt is a viscoelastic material and is a crude oil derivative obtained by controlled distillation of crude oil where the lighter fractions are separated out and the heavy bitumen residue (the asphalt) is left behind (Robinson 2005).

Asphalt is a high molecular weight compound with complex structure and properties. Its' primary composition is hydrocarbons, with many other compounds, including calcium, iron, manganese, nitrogen, oxygen, sulfur and vanadium. The composition of asphalt varies with the source of the Crude oil (Robinson 2005); however, most bitumen contains about:

- Carbon 82-88%
- Hydrogen 8-11%
- Sulfur 0-6%
- Oxygen 0-1.5%
- Nitrogen 0-1%

Other than the source of the crude oil, the manufacturing process and aging in service also leads to different compositions of asphalt (Shell Bitumen Handbook 2003). In general, asphalt's chemical composition is broadly classified in asphaltenes and maltenes, with the maltenes further divided into saturated aromatics and resins. However, the four groups are not well defined and tend to overlap. Asphalt chemistry is approximately determined using a saturated aromatics-resins-asphaltenes (SARA) analysis to compare composition (Robinson 2005).

According to Mack (1932) asphalt consists of five groups of compounds:

- Oily Constituents – These are primarily hydrocarbons, viscous and fluorescent in nature with a high percentage of sulfur and oxygen.

- Asphaltic Resins – These are intermediate products formed during the formation of asphaltenes from oil constituents due to oxidation with air. The molecular weight is always slightly higher than that of the oily constituents.
- Asphaltenes – These are formed when sulfur or oxygen acts on asphaltic resins. They have a black or dark brown powder-like texture and tend to swell on heating. They are soluble in benzene, chloroform, and carbon tetrachloride, while being insoluble in alcohol, ether, and petroleum ether.
- Carbenes and Carboids – These compounds constitute only a small percentage of the asphalt. Carbenes are soluble in only carbon bisulphide, while carboids are insoluble in all solvents.
- Asphaltic acids and their Anhyrides – These are present in small amounts in petroleum derived asphalt, but are present in higher amounts in natural asphalt (12%). Asphaltic acids are brownish black in color with tar-like texture and tend to form their respective anhydrides on heating.

Manufacturing of Asphalt

About 1,500 sources of crude oil occur worldwide, mainly from the USA, Mexico, South America, the Caribbean, the Middle East, and the old Soviet bloc states, although all are not suitable for the production of bitumen. Based on the different crude oil sources, different physical and chemical properties are attributed to asphalt. Refining of crude oil involves heating the crude oil to a temperature of 350° to 380° in a furnace before sending the liquid and vapor components of the crude oil into a distillation tower. Once in the distillation tower, the lighter fractions of the crude oil are in the vapor phase and rise in the tower through holes in trays placed in the tower. As the lighter fractions rise, they lose their heat energy and condense when the temperature is just below its boiling point and are drawn away by pipes. The lighter fractions separating out include propane, butane, naptha, and kerosene. The heavier factions at the bottom of the column are subjected to further distillation under higher pressure to obtain short residue, which can then be used in the manufacture of different grades of bitumen. The short residue is then subjected to a blowing process where oxidation, dehydrogenation and polymerization of asphaltenes and formation of additional asphaltenes from maltenes takes place, and bitumen suitable for road construction is formed (*Shell Bitumen Handbook*, 2003).

Asphalt-Aggregate Interactions

Asphalt-aggregate interactions are important to ensure that the asphalt binds the aggregate to maintain the integrity of the mixture for road bed construction. The ratio of asphalt to aggregate in a mix is typically 5-6 wt% of asphalt to 94-95 wt% of aggregate. The aggregate present varies in size ranging from ¾ inch fractions to fines that are in the 200 mesh range.

Asphalt coats each of the aggregate particles and also provides cohesion between the aggregate particles to maintain the integrity of the mixture. Asphalt can also enter the pores and crevices of the aggregates. Aggregates have active sites for binding asphalt molecules at different levels. Their surface is frequently either fully charged or partially charged. Asphalt, being a mixture of hydrocarbons that is organomettalic (contains nickel, vanadium and iron) is polar in nature and gets attracted to the active sites on the aggregate surface. The bonds formed may include hydrostatic, electrostatic, or Vander Waal's forces. According to the SHRP (1993), autoradiographic experiments with labeled molecules, having a similar structure as asphalt, confirmed the presence of active sites on the aggregates.

The asphalt adhering to, and between, the aggregate must remain in contact with the aggregate under all environmental condition, serving a cohesive role to maintain the integrity of the system. However, this integrity of the cohesion and adhesion of the asphalt-aggregate is damaged in the presence of moisture. In the presence of moisture, the pH of the local environment may substantially change and this pH value depends on whether the aggregates are siliceous or calcareous. The acidity and basicity of the asphaltic components can influence the effect of pH under such environmental conditions. It is recommended that asphalt with amphoteric characteristics be used, since amphoteric species can either assume an acidic or basic character and the amphoterics may bond in either acidic or basic environments (SHRP, 1993)

Moisture damage does not occur as one mechanism, a list of theories that explain the mechanisms of moisture damage are given in the Table 6-2.

Table 6-2. Mechanisms explaining moisture damage of asphalt-aggregate interaction

Theory	Principle
Contact Angle	When the contact angle of water is less than that of the asphalt molecules, asphalt is displaced.
Interfacial Energy or Molecular Orientation	When the surface energy of water molecule is than asphalt molecules, asphalt is displaced.
Chemical Reaction Theory	pH changes around the aggregates results in the buildup of negative charge and electrical double layer on the aggregate and asphalt layer.
Pore Pressure	Asphalt may rupture when the pore pressure of entrapped water molecules increases with the densification of the mixture with traffic.
Spontaneous Emulsification	Inverted emulsion can result in the loss of adhesion between the asphalt and aggregate.

Source: Adopted from Dong-Woo Cho and Kyoungchul Kim 2010.

Asphalt Aging

There are three major factors causing hardening of asphalt in asphalt mixtures associated with aging:

1) loss of oily components by volatility or absorption,
2) changes in composition by reaction with atmospheric oxygen, and
3) molecular structuring that produces thixotropic effects (steric hardening).

Asphalt ages (oxidizes) in the presence of air and oxidation leads to bitumen hardening and embrittlement of the pavement. This leads to asphalt failure due to adhesion failure with aggregate and cracking. However, asphalt hardening in the base layers is thought to be helpful due to improved stiffness which contributes to improved performance. The factors that contribute to the aging of the asphalt are the composition of the asphalt mixture, the binder film thickness, the air void content of the asphalt, and the composition of the asphalt itself. Air voids are particularly important because in dense asphalt mixtures, air is unable to penetrate easily, and the rate of oxidation will be much slower compared to an open graded (a lower density, porous material – basically less dense due to the aggregate grading) material (Robinson 2005).

Oxidative aging of asphalt leads to the formation of ketones, carboxylic acids and sulfoxides. According to SHRP (1993), the oxidative aging products produced were found to be uniform and dependent on the amount of sulfur present in the asphalt. The chemical composition of the asphalt and the composition of the aggregate were found to have little or no influence on the oxidative products being formed (SHRP 1993). Infrared spectrometric studies on aged asphalt pavements also found that the principle components formed as a result of aging were carbonyl groups, sulfoxides and sulfones. The embrittlement and increased viscosity of the pavement is a result of formation of highly polar groups and functional groups that contain oxygen that strongly interact (Usmani 1997).

Laboratory Testing of the Aging of Asphalt
Under natural conditions, short term asphalt aging occurs during the construction phase, primarily dominated by volatilization of an asphalt pavement. It begins at the mixing plant and ends when the compacted pavement has cooled. Long-term aging occurs during the service life of the pavement due to oxidation. Both factors cause an increase in viscosity of the asphalt and a consequent stiffening of the mixture. These conditions are studied in an asphalt test laboratory using the following means:

Short- term aging:

- The SHRP recommended procedure for short-term asphalt aging tests is to age a loose mixture (to simulate pre- compaction phase) in a forced-draft oven for 4 h at 135°C (275°F). The aging achieved with the extended mixing method is similar to the aging achieved using this method, however, the advantage of this approach over extended mixing is that several trays of material can be aged at the same time.

- The extended mixing test method may also be used where a modified rolling thin film oven (RTFO) is used. An attachment to the RTFO drum enables loose mixtures to be rolled, thus extending the mixing time. This method was found to produce more uniform aging in the mix than oven aging.

Long-term aging:

- The SHRP recommended procedure for long-term asphalt aging tests is to precondition compacted samples for two days at 60°C (140°F). The compacted mixture specimens are then aged in a forced-draft oven for 5 days at 85°C (185°F). This procedure is best suited for dense-graded mixtures. A temperature of 100°C (212°F) for two days may also be used, however; such a high temperature may cause damage to the test specimens.

- The other long-term aging test method includes triaxial cell aging and requires conditioning of the sample, followed by passing oxygen or air through the sample. A flow rate of 0.11 cubic m per h (4 cubic ft per h) is used, at a pressure of about 345 kPa (50 psi) and 85°C (185°F) temperature. The low-pressure oxidation (triaxial cell) technique is recommended for long-term aging of open-graded mixtures or dense-graded mixtures using soft grades of asphalt. A temperature of 85°C (185°F) is recommended for a period of five days.

A study conducted by the NCHRP (Nelson, *et al.* 2001) to observe the toxicity of runoff from construction materials involved the use of a loose mixture of open graded asphalt concrete with MSWIBA (Municipal solid waste incinerated bottom ash) and was aged in a forced draft oven for 4 hrs at 135°C for short term aging tests, and for 5 days at 85°C for long term aging, as recommended by the SHRP protocol. Long term oven aging of 5 days is representative of a sample of 10 years old.

Summary of Asphalt Characteristics and Aging Mechanisms

Asphalt has a complex structure and rheological properties that gradually change with time. The effect of aging is more rapid in the presence of light and air. Oxidation on the exposed surface of the pavement causes aging and the extent of aging is proportional to the surface area exposed (the surface and voids) to the atmosphere and the rate of diffusion of air into the pavement. Therefore, during the service of the pavement, asphalt undergoes aging forming insoluble, condensation products as a result of the oxidation and the loss of volatile compounds from the pavement. As a result of these changes, the composition and the concentration of contaminants that leaches into the runoff is likely to vary with aging (Zakar 1971).

When pavements are aged under laboratory conditions, the runoff profile may vary depending on the aging method used. For instance, in the NCHRP study when leachate samples were collected at regular intervals from specimens' under-going long term aging tests, no change was observed in either the toxicity or the chemistry of the leachate during the aging process. However, when the long term aging process was modified and oxidation was provided (10 atms in a pressure aging vessel (PAV) system at 85°C for 30 days), a significant drop in the algal toxicity with time was observed (Nelson, *et al.* 2001).

Contamination of Runoff from Asphalt Surfaces

According to the NCHRP research (Nelson, *et al.* 2001), asphalt (AC) and concrete (PCC) roads, and the constituents used in their production, account for the largest volume of construction materials used in the US. Almost 90% of surfaced roads in the US are asphaltic, while 6% (2000 km^2 area) of the surfaced roads are of concrete. Stormwater runoff from paved roads includes organic toxicants, metals, nutrients and PAHs (Azizian, *et al.*, 2003). The extensive use of additives in pavement mixtures also present potential water quality problems. The additives enhance the properties of AC and PCC by increasing strength, temperature stability, durability, aging etc. The additives include organic salts, detergents, calcium chloride, carbonates, coloring agents, and ammoniacal-copper-zinc-arsenate (ACZA) (Azizian, *et al*. 2003).

In the study conducted by National Cooperative Highway Research Program in 2001 (Nelson, *et al.*) on the impact of construction materials on surface and groundwater, individual components and the aggregates of the pavements were subjected to exposure and aging tests. Testing of individual components may not result in complete insight into the impact they may have on the environment since the assemblage of all components is exposed to the environment. The NCHRP study of individual components did offer relative findings of the toxicity of the chemicals used in pavements. They reported that although the individual components of AC and PCC showed high toxicity levels, this was reduced when incorporated into the complete assemblage. They reported that the overall toxicity is much lower when field conditions are considered due to the lower leaching rates and greater dilution under rain conditions in the field.

In 2005, parking lot sealants were identified as a major source of PAHs in Austin, TX runoff. Parking lots with coal tar based sealants were found to contribute 65 times more PAH mass in the runoff compared to unsealed parking lots. The sealing layer on these parking lots tend to wear off by vehicle use, with the crumbled seal coat losses producing up to 2,200 mg PAH/kg sediment of 12 PAHs, compared with 27 mg/kg from unsealed parking lots . Sealcoats are applied to asphaltic pavements because they act as a protective coating on the pavement by decreasing ultraviolet ray exposures, weathering, petrochemical losses, and degradation from deicing salts (Mahler, *et al.* 2005).

The sealant forms a coating on the parking lot surface until it begins to wear off. A photographic sealant wear study was conducted in Austin by Scoggins, *et al.* (2009). The rate of wear of the sealants was estimated to be about 7% per year in the drive areas. The rate of wear is dependent on the traffic, the rainfall energy, and wind. Another study was conducted by Mahler, *et al.* (2005) who used an artificial washoff rig with low rainfall energy on small parking lots (50m^2). They found that the sealant wears of at a rate of about 0.2% per year, with no traffic activity.

Two types of sealants are commonly used, coal tar based and the asphalt based, as described below:

(a) **Coal tar based sealant:** This sealant is a shiny, black emulsion applied on asphalt pavements. Its most active compounds are PAHs, comprising 3.4 to 20% PAHs by dry weight. It was originally assumed that the pavement sealant would not be able to desorb the PAHs. Light rains, however, have been shown to transport significant amounts of PAHs from coal tar sealers into nearby water bodies. In a study conducted by Bryer, *et al.* (2006), coal tar pavement sealers appeared to affect the growth and development of amphibians, at low parts per million concentrations.

(b) **Asphalt based sealant:** Following the Mahler, *et al.* (2005) study, the City of Austin in 2005 also studied the direct amounts of PAHs in the sealant products by sampling scrapings and particulates from the parking lots. They found that the profile of the PAHs in the sealant products although similar, showed that the coal tar had a significantly higher percentage of PAHs when compared to asphalt sealants (a maximum of 1,800 ppm total PAHs for asphalt-based vs. 50,000 ppm for coal-tar based sealants on a dry weight basis). These asphalt-based sealants are advertised as an environmentally friendly alternative to coal tar based sealants as they contains lower amounts of PAHs (usually 0.03% to 0.66% of PAHs by dry weight, according to Bryer, *et al.* 2006). Other alternatives suggested by the USGS (2006) included concrete or unsealed pavements.

The results of a recent study (DeMott, *et al.* 2010) on the PAH levels in Austin streams, conducted two years after the ban of sealants, showed that there was no change in the level of the PAHs in the sediments. They concluded that sealants may not have been the principal source of PAHs in the sediments as concluded by the earlier studies. However, PAHs have very long half-lives during natural exposures (several years to decades, as reported by MacKay, *et al.* 1997) and unless physically removed or scoured, they would remain in the receiving water sediments at high levels for extended periods, even after their sources were removed.

Toxicity of runoff samples

The NCHRP study (Nelson, *et al*. 2001) tested the toxicity of leachate samples from highway construction materials using Selenastrum capricornutum (algae) and Daphnia magna. The alga represents plant species while the Daphnia represents animal species. These organisms were chosen based on their wide geographical availability, sensitivity, feasibility to culture in the laboratory, and availability of standardized protocols for the tests. The NCHRP research showed that construction materials, especially the additives used to incorporate special characteristics to the pavements, were found to be significantly toxic, however the toxicity was reduced when they were incorporated in the pavements.

A toxicity study conducted in Sweden on leachates from road construction materials used Vibrio fischeri and Phaseolus aureus. They found that in comparison to roads built with conventional materials, roads built with municipal solid waste incineration ash released higher concentrations of Al, Cl, Cr, Cu, K, Na, NO_2–N, NH_4–N, total N, TOC and SO_4. However, the release of Ca, Co, Fe, Mn, Ni, NO_3–N and Pb did not differ significantly between the two pavement types. From their study, they concluded that more than one kind of toxicity test may be needed since different species may respond differently to the same environmental sample (Ore, *et al.* 2007).

Experimental Setup and Analyses

Three square pavement slabs were examined during this project. Two (a hot-mix asphalt pavement and a warm-mix asphalt pavement) were freshly constructed to represent unsealed pavement types, while the third was a two year old pavement which was freshly coated with asphalt sealant (it was planned to also test a coal-tar sealant, but it was not possible to purchase that sealant type in the area). The test slabs had a surface area of 0.25 m^2 and were 5 cm thick. They were prepared for this project by the National Center for Asphalt Technology (NCAT), at Auburn University, in Auburn, AL. The preparation method used to prepare the pavement slabs is given in Appendix I. The pavement slabs were set up outdoors in mostly full sun and exposed to rains and other natural conditions for a six month period. During the project period, a 0.5 in rain was simulated on each of the pavement slabs and the resulting runoff was being analyzed for pollutants.

The pavements were supported by un-treated wooden boxes and placed on bricks such that they were slightly inclined to allow the sheetflow runoff to flow into the sample containers. All three pavements were placed adjacent to each other at about the same inclination to the ground. The water used for simulating the rainfall for sampling was from prior collected roof runoff from an adjacent building. The roof runoff was repeatedly poured onto the pavement slabs to allow a contact time of about five minutes. The resulting final runoff was collected in Nalgene HDPE and glass sample bottles and transported to the lab for analyses.

The hot mix pavement and the warm mix pavement were five days old when the first runoff samples were collected (Table 6-3). The two year old pavement was coated with driveway asphalt-based sealant and allowed to dry for 2 days before the first sample was collected.

The following equipment was brought to the sampling site for sample collection.

- 1 L amber glass bottles (for PAHs analysis)
- 100 mL Nalgene NDPE bottles (for heavy metals, nutrients and detergent analyses)
- 20 mL glass vials (for Microtox analysis)

- Labels for bottles
- Marker pens
- Glass jars (for pouring the roof runoff onto the pavement)
- Trough-like plastic containers (placed near the lower edge of the slabs for collecting the runoff)
- Stop watch

Table 6-3. Pavement Degradation Sampling Schedule

Date of Sample collection	Average mean temperature (°F) on day of sampling	Observations
05/30/2010 (asphalt tests started on this date)	75	The runoff was collected from only HMA and WMA pavement slabs. The third pavement was freshly sealed with asphalt driveway sealant. The runoff from the pavements looked clean, free of any sediment.
06/02/2010 (sealant tests started on this date)	87	The runoff from the pavements looked clean, free of any sediment.
06/11/2010	89	The runoff from all the three pavements was pale yellow, with dust and deposited soil particles on the pavement.
06/25/2010	91	The runoff from all the three pavements was pale yellow but relatively less pale than from the previously collected samples.
07/08/2010	82	The runoff from all the three pavements was cleaner than from the previously collected samples. It was free of soil deposits on the pavements.
07/21/2010	93	The runoff from all the three pavements was pale yellow, with dust and deposited soil particles on the pavement.
08/04/2010	93	The runoff from all the three pavements was cleaner than from the previously collected samples. It was free of soil deposits on the pavements.
09/14/2010	88	The runoff from all the three pavements was pale yellow, with dust and deposited soil particles on the pavement.
10/19/2010	77	The runoff from all the three pavements was pale yellow, with dust and deposited soil particles on the pavement.
11/18/2010	66	The runoff from all the three pavements was pale yellow, with dust and deposited soil particles on the pavement.

Samples that were collected after a recent wet period appeared cleaner compared to samples after a dry period.

Chemical Analyses

For each set of samples, blanks and standards were also analyzed. A DR 2010 spectrophotometer and incubator were used to perform the nutrient analyses using HACH methods. All the methods were USEPA approved for the measurement of the respective nutrients. All the nutrient and detergent tests were performed within 48 hrs after the collection of the samples.

pH: All the samples were measured for pH soon after they were delivered to the laboratory from the sampling site. An IQ 160 pH meter was used for measuring the pH. Before each set of measurements, the pH meter was calibrated with pH 7 and pH 4 standard solutions provided by the manufacturer. The calibration required approximately three minutes after which the pH meter was used to measure the pH of the samples. Between each sample reading, the probe was rinsed with deionized water.

COD (0-150mg/L COD): The sample CODs were measured within 48hrs after the sample collection. This test was performed using HACH Method 8000 which uses a strong oxidant (dichromate) to digest the COD. The test method contains premeasured reagents to which the water samples are added and digested at high temperature for 2 hrs, followed by cooling of vials and reading the values directly in a spectrophotometer.

Nitrate: This test was performed using the HACH AccVac Ampuls method. The principle behind the method is cadmium present in the ampul reagent mix reduces the nitrates in the sample to nitrites and the nitrites then reacts with sulfanilic acid to form an intermediate dizonium salt, which in turn binds to gentisic acid to form an amber colored product. It takes approximately 10 minutes to measure each sample using this method.

Ammonia-Nitrogen (0-2.5 mg/L NH_3-N): The HACH Salicylate Method was used to determine the ammonia-nitrogen levels in the samples. The principle is that the ammonia in the water samples combines with chlorine to form monochloramine, which then reacts with salicylate to form 5-aminosalicylate, which is then oxidized in the presence of a catalyst and a colored compound is formed in the reaction related to the ammonia concentration. This test takes approximately 45 min for a set of three samples.

Total Nitrogen (0-25 mg/L N): The total nitrogen in the samples was measured using the HACH Test N Tube method. The principle behind the test is that all forms of nitrogen are converted to nitrate, which then reacts with chromotropic acid in a strong acidic environment to form a yellow complex which has an absorbance at 410 nm. Sodium metabislfite is added to the samples after digestion to remove any halide interferences. This test takes approximately 1.5 hrs for a set of three or more samples.

Total Phosphate (0-3.5 mg/L PO_4^{3-}): For this test, PhosVer 3 with Acid Persulfate Digestion from HACH was used. The principle behind the method is that the Orthophosphate reacts with molybdate under acidic conditions to produce a phosphomolybdate complex, which is then reduced by ascorbic acid to give the molybdenum blue color. This test takes approximately 1.5 hrs for a set of three or more samples.

Detergents (0-3ppm): The anionic detergent method from CHEMetrics was used for these tests. This test uses the methylene blue extraction method. Anionic detergents react with methylene blue to form a blue complex which is extracted into an immiscible organic solvent. The intensity of the blue color gives an indication of the concentration of methylene blue active substances in the sample. It takes approximately 10 minutes per sample to perform the test.

Microtox: The Microtox toxicity test use luminescent bacteria and measures the light intensity before and after its exposure to the sample which gives a measure of the toxicity of the contaminant with the reducing light intensity. Any component present in the sample that interferes with the respiration of the bacteria results in reduced light output. The lower the EC_{50} value, the higher the toxicity. This reduction in light output is compared to that of a control sample to calculate relative toxicity. The procedure used is given in the Appendix I (adapted from Stormwater Effect Handbook, Pitt et al., 2001).

Heavy Metals Analysis: The water samples in Nalgene HDPE bottles were preserved in 2% nitric acid and sent to Stillbrook Laboratories, in Fairfield, AL for acid digestion and ICP/MS analyses.

PAH Analysis: The water samples were collected in amber glass bottles and sent to Miles College, AL, for analysis. EPA Method 625 was used after liquid-liquid extraction of the samples. A GC/MS was used for analyses.

The Kruskal-Wallis test was performed on the groups of data of each of the pollutants analyzed to identify any significant differences that were present. This was followed by pair-wise ANOVA and Mann-Whitney tests to detect any significant differences between the initial and final exposure periods of each of the pollutants from each of the pavement types. A one-way linear regression analysis was also performed on the nutrients to identify trends in the loss of these components from the pavements.

Results and Discussion

The rainfall accumulation during the project duration is as shown Figure 6-1. This chart also includes the 0.5 in simulated rainfall on the slabs on the ten sampling days, for an additional approximately 5 inches of “rain” added to the 18 inches of natural rain during this six month period. Most of the sample results were compared for two exposure periods: an initial phase (0-2 months aging) and the final phase (2-6 months aging). The regression equations corresponding to the trend lines on the graphs are significant based on ANOVA analyses. If the ANOVA analysis indicated that the intercept was not significant, the regression analysis (and ANOVA) was repeated with the intercept equal to zero. If the slope (trend) coefficient was not significant, then the result was a constant, and the average and COV (coefficient of variation) values are shown on the figures.

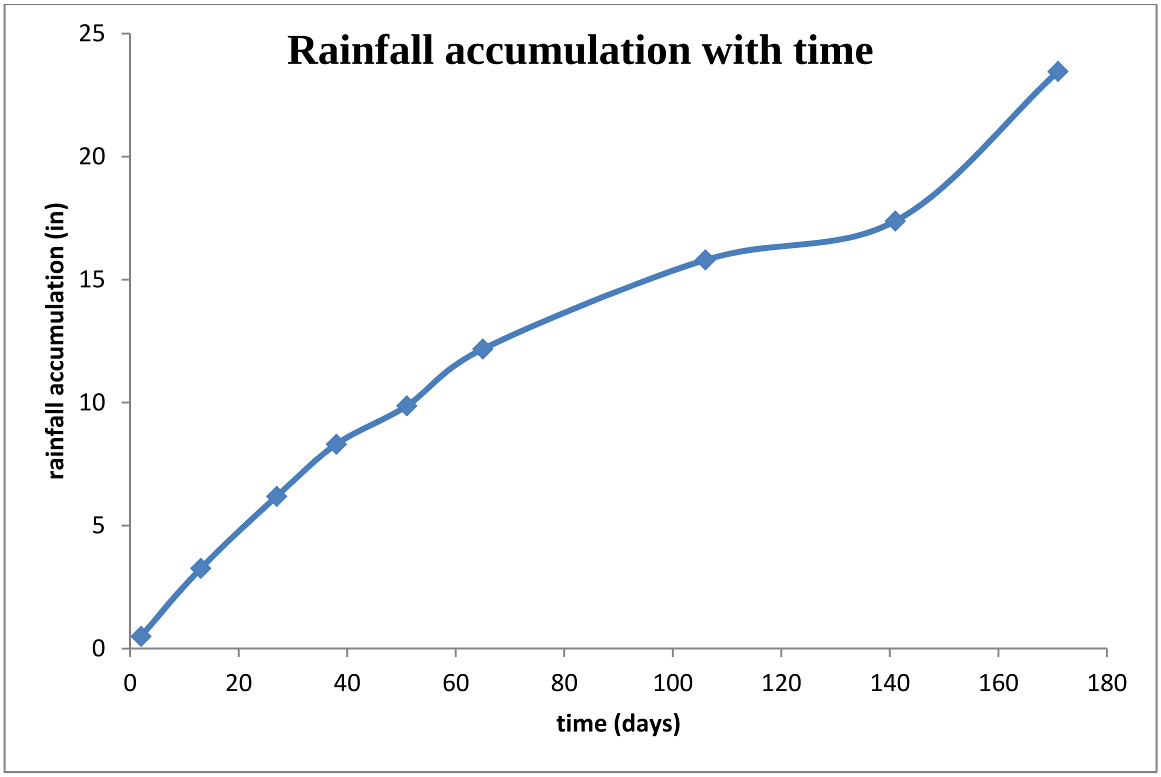


Figure 6-1. Rainfall accumulation during the project period.

Nutrient Releases from Pavement Test Slabs

Nitrate concentrations (mg/L as N) from all three pavements showed a weak increasing trend in concentrations with the aging of the pavements over the six months exposure period. The highest nitrate releases from the pavements were observed towards the final experimental stages, with concentrations of 4 to 6 mg/L during the 5 month sampling.

A significant difference (p = 0.012) was found from the Kruskal-Wallis test for the six groups of data, indicating that there is a significant difference in the medians in at least one of the leaching patterns from the pavements. The box and whisker plot of the nitrate loss, from the initial and the final phases is given in Figure 6-2. A Mann-Whitney test was performed to find if any significant difference existed between the initial and final phases for each of the pavement types and the p-values from the test are presented in Table 6-4.

Table 6-4. Mann-Whitney test results for loss of Nitrate

Mann-Whitney test results for loss of Nitrate	
Asphaltic Sealant (AS)	0.02
Hot Mix Asphalt (HMA)	0.04
Warm Mix Asphalt (WMA)	0.06

Significant differences between the loss of nitrate from the AS and HMA pavement samples comparing the initial and final phases were observed (with a somewhat weaker difference indicated form the WMA sample). One-way ANOVA test results examined differences between the initial values from all three samples and the final values from all three samples. These tests indicated they were similar, with little likely difference in behavior between the three pavement types.

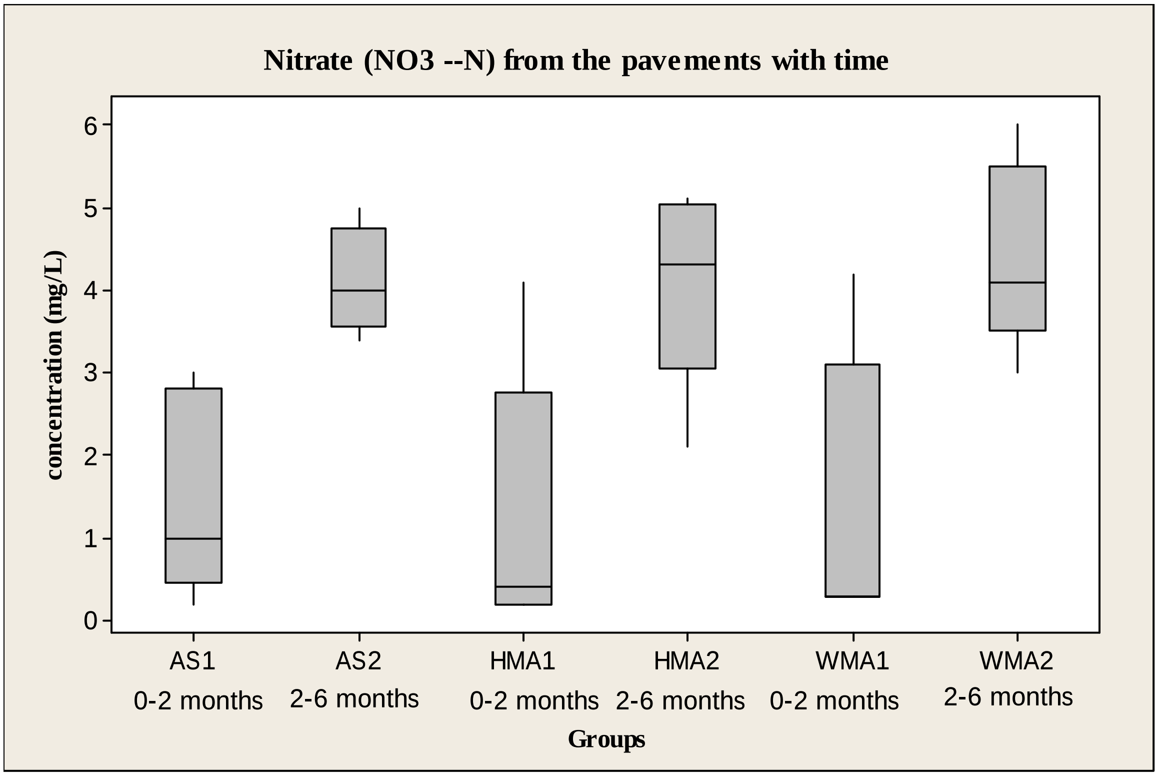


Figure 6-2. Nitrate loss from the pavements during the initial and final experimental stages.

The hot mix asphalt pavement and the pavement with the asphalt sealer showed significant increasing concentrations with time for total phosphorus, while the warm mix asphalt showed a weak decreasing trend with time. ANOVA on the linear regression however showed that the trend from the warm mix pavement was not significant.

The Kruskal-Wallis test for the six groups of data for total phosphorous leaching resulted in a p-value of 0.41, indicating no significant differences in the medians in the leaching data from the pavements for the number of samples available. A box and whisker plot of the total phosphorous losses for the initial and the final exposure phases is given in Figure 6-3. A Mann-Whitney test was performed to find if any significant difference exist between the initial and final phases for each of the pavement types and the p-values from the test are presented in Table 6-5. None of the three pavements indicated any significant differences in the total phosphorous concentrations between the two exposure periods; however, ANOVA test results comparing the differences do show an apparent change for the asphalt sealant observations (a decrease) for the WMA sample.

Table 6-5. Mann-Whitney test results for loss of total phosphorous

Mann-Whitney test results for loss of total phosphorous	
AS	0.18
HMA	0.47
WMA	0.68

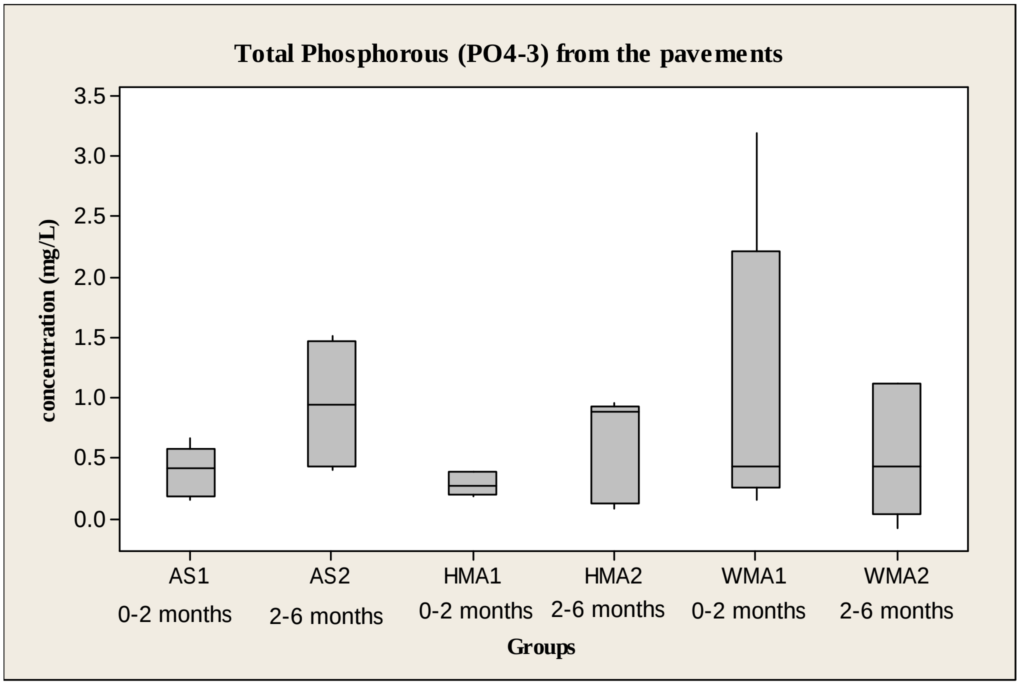


Figure 6-3. Loss of Total Phosphorous from the pavements during the initial and the final experimental stages.

A significant difference was observed in the leaching of total nitrogen from the pavements amongst the three pavement samples (p = 0.037, from the Kruskal-Wallis test. The ANOVA pairwise tests showed significant differences for the hot mix asphalt and the sealer samples, with a somewhat weaker change for the warm mix sample. For the loss of ammonia and COD from the pavements, the six groups of data did not show any significant differences, with higher Kurskal-Wallis p-values of 0.128 and 0.312 for ammonia and COD respectively. The box and whisker plots of the loss of total nitrogen, ammonia and COD from the pavements in initial and the final phases is given in Figure 6-4 through 6-6. The Mann-Whitney test was performed to find if any significant difference existed between the initial and final phases for each of the pavement types and the p-values from the test are presented in Table 6-6; the total nitrogen loss from the hot mix pavement shows a significant difference, similarly for COD from the pavement with the sealer. The short-term concentrations from all three samples are all very similar, as are the long-term concentrations for these constituents, with little apparent differences in concentration behavior for the different samples.

Table 6-6. Mann-Whitney test results for loss of nutrients

Mann-Whitney test results for loss of nutrients		
Total N	AS	0.09
	HMA	0.04
	WMA	0.14
Ammonia	AS	0.71
	HMA	0.06
	WMA	0.12
COD	AS	0.04
	HMA	0.84
	WMA	0.60

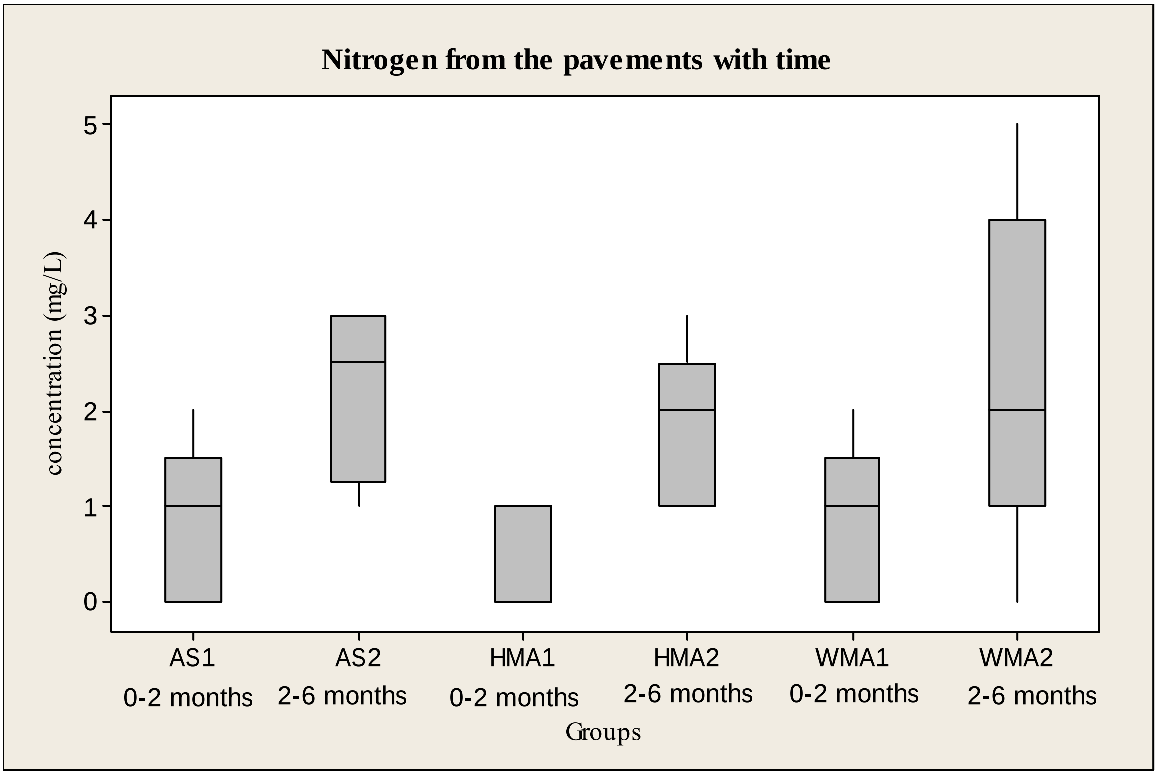


Figure 6-4. Nitrogen loss from the pavements between the initial and final experimental stages.

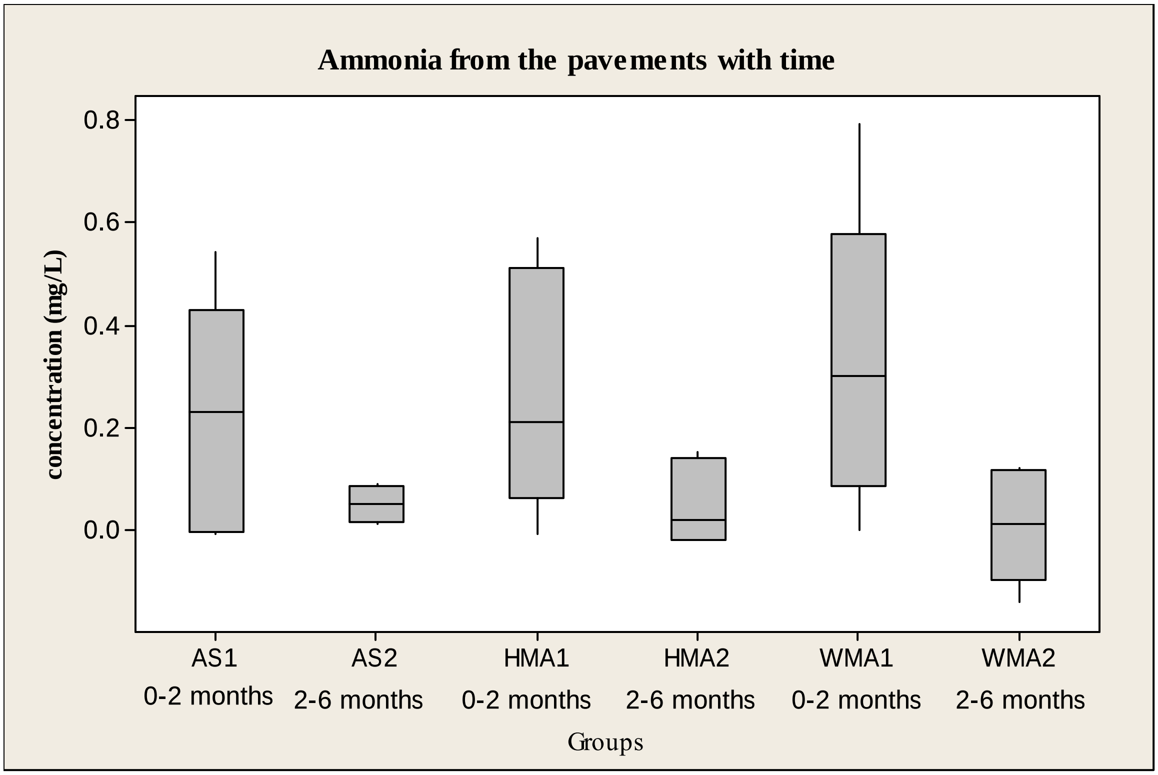


Figure 6-5. Ammonia loss from the pavements between the initial and final experimental stages.

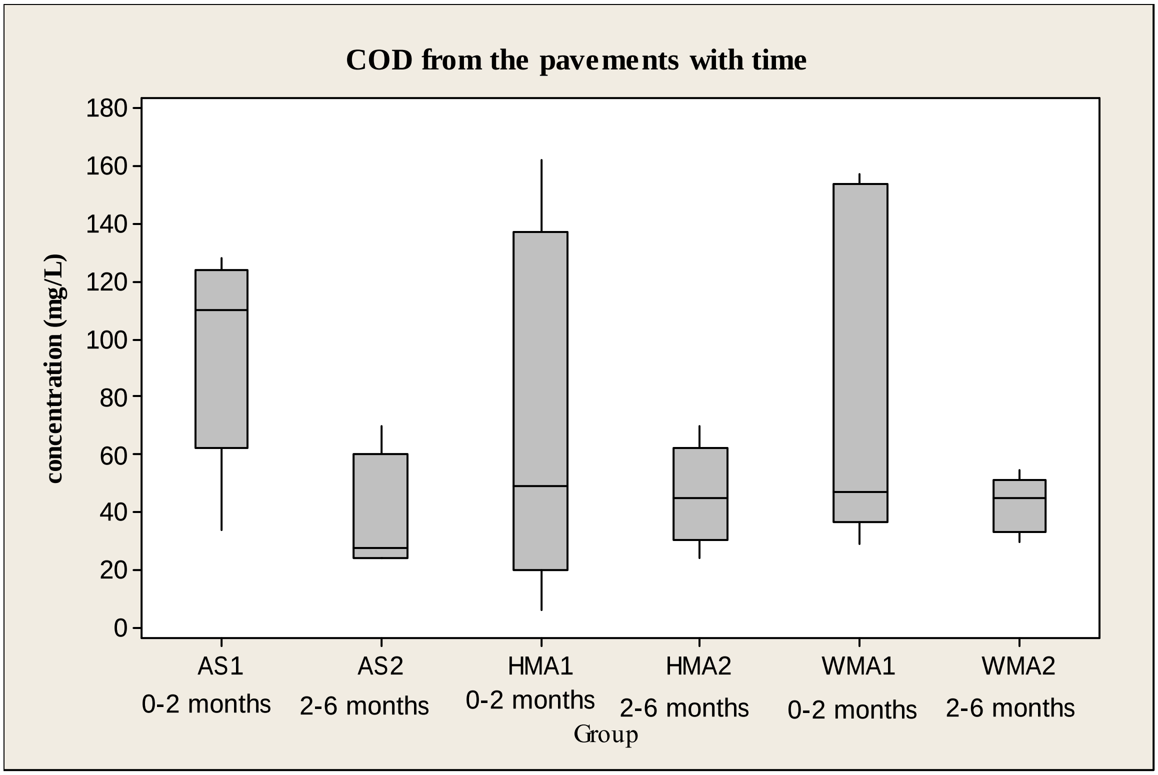


Figure 6-6. COD loss from the pavements between the initial and final experimental stages.

Detergent Releases from Pavement Test Slabs

The pavements runoff during the tests had anionic detergent concentrations between 0.25 mg/L to 1.75 mg/L during the six months of aging of the pavements; however no patterns were observed or statistically detected between the different time frames or the different samples. The p-values from the Mann-Whitney test are shown in Table 6-7. The pairwise ANOVA test results also indicated no significant differences for the number of samples available.

Table 6-7. Mann-Whitney test results for loss of detergents.

Mann-Whitney test results for loss of nutrients		
Total N	AS	0.33
	HMA	1.00
	WMA	0.84

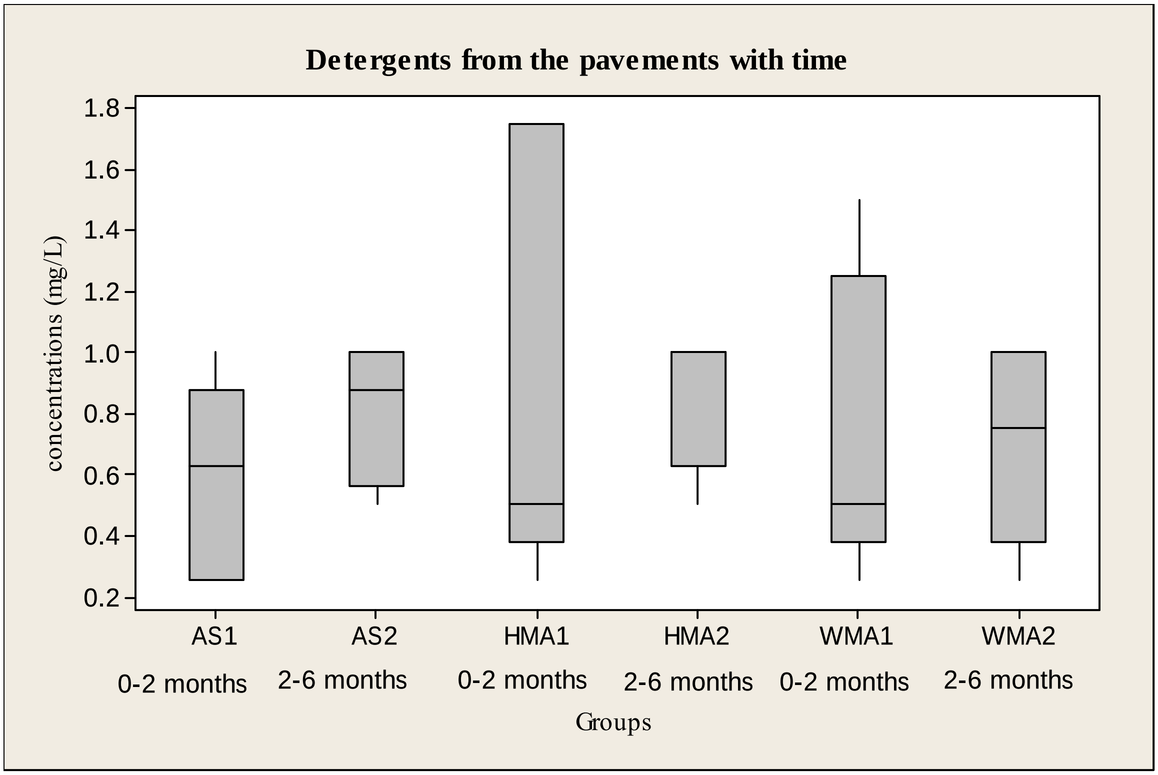


Figure 6-7. Detergents from the pavements during the initial and final experimental stages.

Heavy Metals Releases from Pavement Test Slabs
Amongst the heavy metals analyzed, cadmium and chromium were always below the detection limits for all the samples. Lead was only detected in the 2 week exposure samples from the pavements at 0.008 to 0.017 mg/L concentrations, and in the 7th week for the sealer sample (at 0.006 mg/L). Zinc was also below detection limits for the first sampling event, however with aging (2-6 months period) both zinc and copper showed an increasing trend from all three pavement samples as seen in Figures 6-8 and 6-9. The leaching from all three pavements showed a similar pattern for the heavy metals examined.

The Kruskal-Wallis test results for copper and zinc showed high p-values, 0.32 and 0.76 respectively, also supported by the Mann-Whitney and pairwise ANOVA results and the box plots, indicating no significant differences for the number of samples available (Table 6-8). However, the time series plots show apparent large increases in copper and zinc concentrations during the last few samples for the longest exposures.

Table 6-8. Mann-Whitney test results for loss of heavy metals.

Heavy metal	Pavement type	p-value
Cu	AS	0.27
	WMA	0.53
	HMA	0.84
Zn	AS	0.39
	WMA	0.18
	HMA	0.53

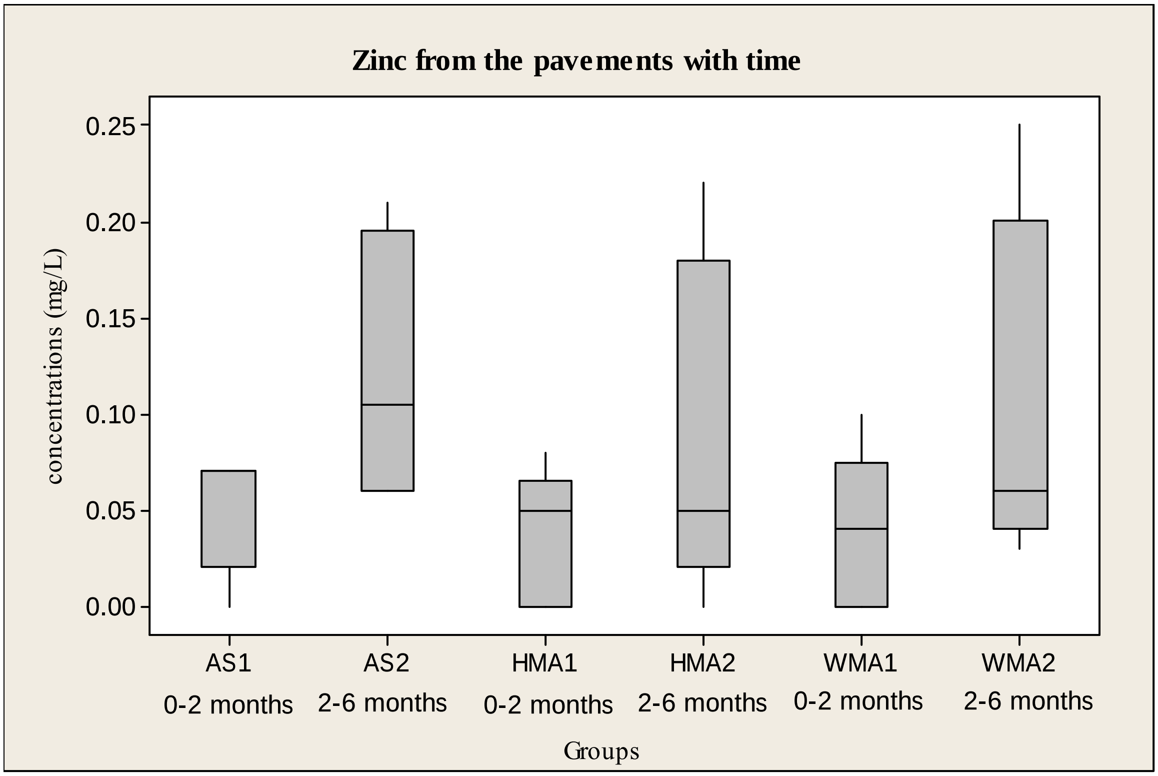


Figure 6-8. Zinc loss from the pavements during the initial and final experimental stages.

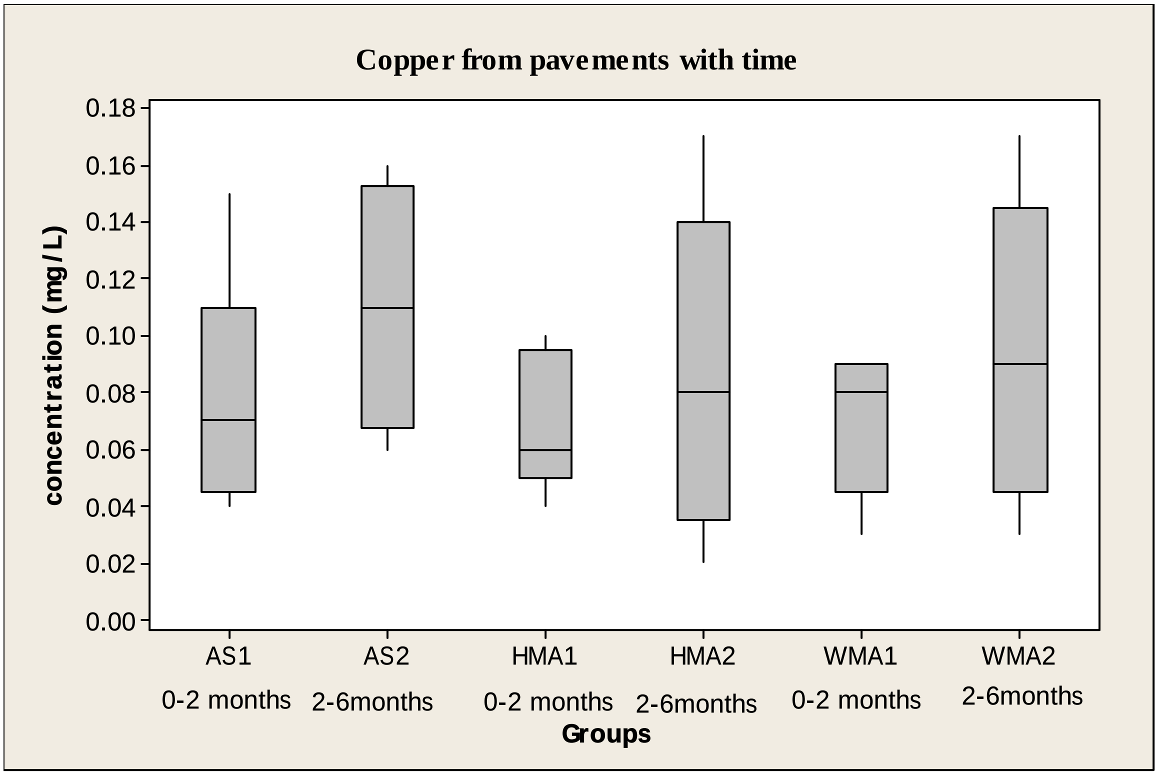


Figure 6-9. Copper loss from the pavements during the initial and final experimental stages.

Toxicity Associated with Runoff from Pavement Test Slabs

The pavements showed high levels of toxicity, but with no significant changes with time of exposure, or differences between the pavement types, for the number of samples available. The results for the Microtox toxicity screening test are presented in Figure 6-10.

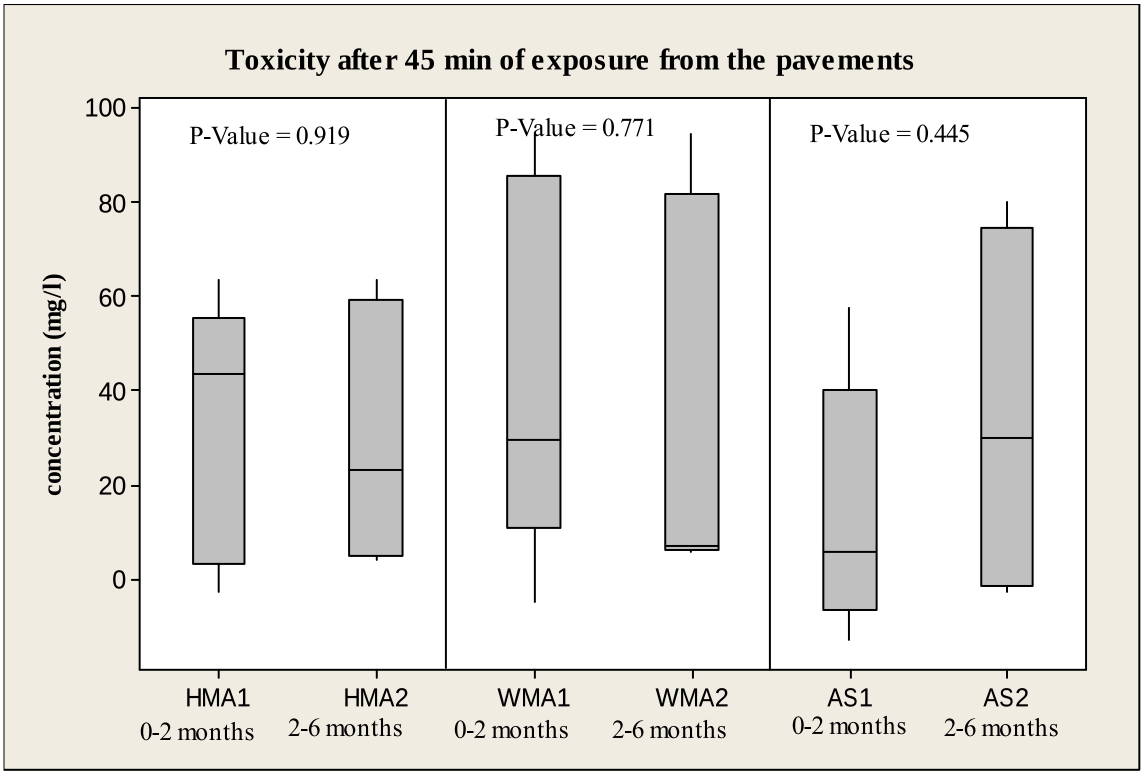


Figure 6-10. Toxicity after 45 min exposure of the samples from the pavements.

PAHs in Runoff from Pavement Test Slabs

A p-value of 0.10 was noted as being marginally significant for the PAH concentration differences for the different exposure periods. Acenapthene, fluoranthene, pyrene, and benzo(ghi)perylene had p values <0.1 based on the Kruskal-Wallis test, as shown on the box and whicker plots in Figures 6-11 to 6-14. The Mann Whitney test was used to examine differences in each pavement type with aging (Table 6-9). Acenapthene in the hot mix pavement and warm mix samples indicated significant differences with aging. Similarly, warm-mix pavement samples had significant differences in benzo(k)fluoranthene concentrations with time period.

Table 6-9. Mann-Whitney test results for PAHs with significant p-values from Kruskal-Wallis test.

Mann-Whitney test results for PAHs with significant p-values from Kruskal-Wallis test		
Acenapthene	AS	0.38
	HMA	0.06
	WMA	0.09
Fluoranthene	AS	0.31
	HMA	0.67
	WMA	0.47
Pyrene	AS	0.31
	HMA	1.00
	WMA	0.19
Benzo(k)fluoranthene	AS	1.00
	HMA	0.67
	WMA	0.03
Benzo(ghi)perylene	AS	0.31
	HMA	0.11
	WMA	0.89

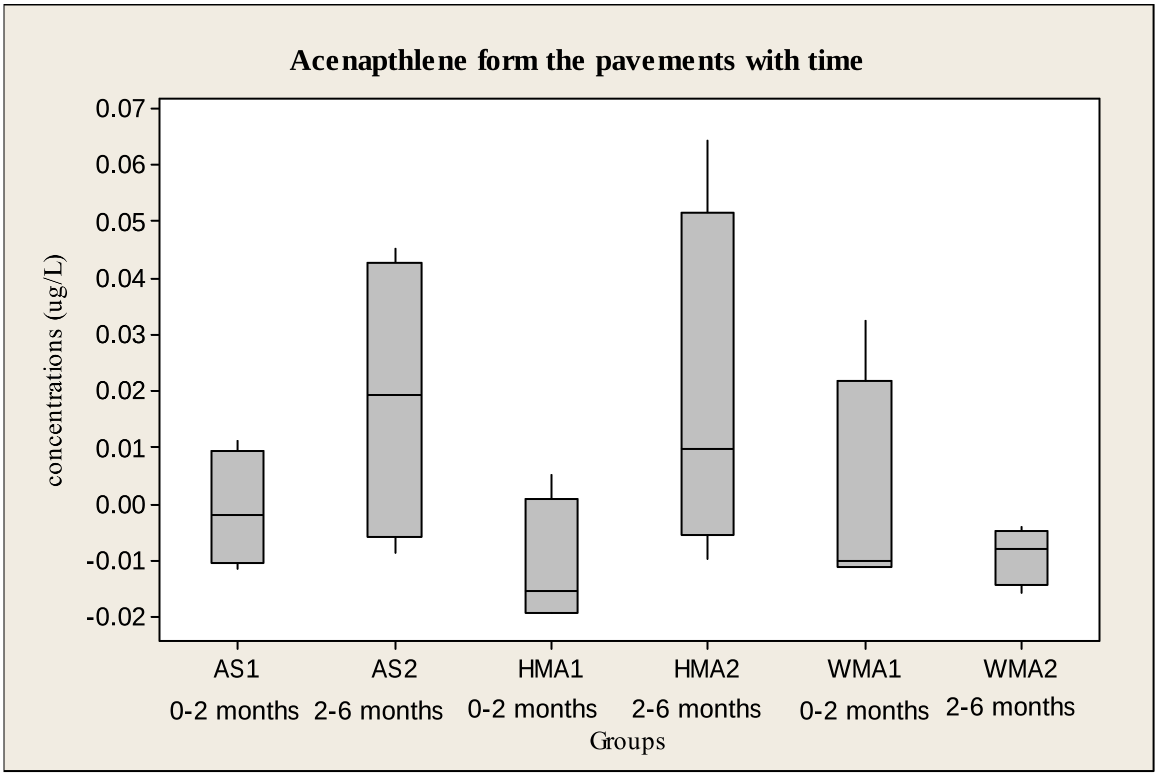


Figure 6-11. Acenapthlene from the pavements with aging.

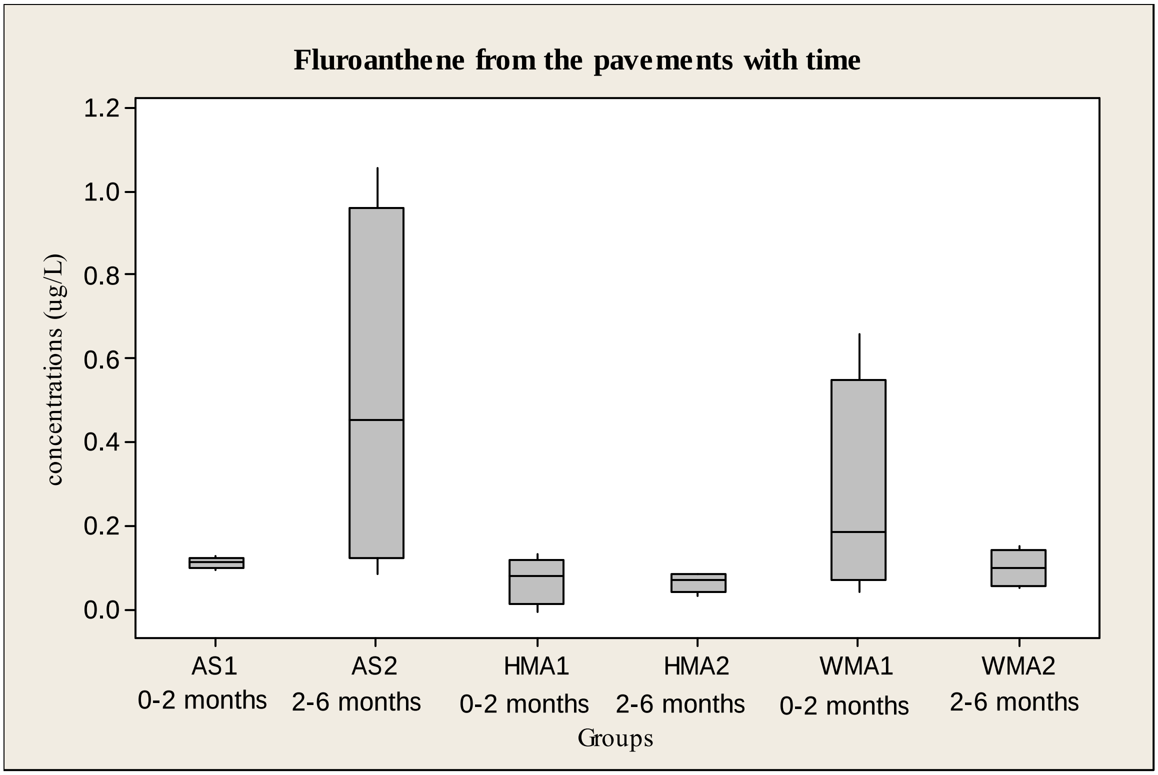


Figure 6-12. Fluroanthene from the pavements with aging.

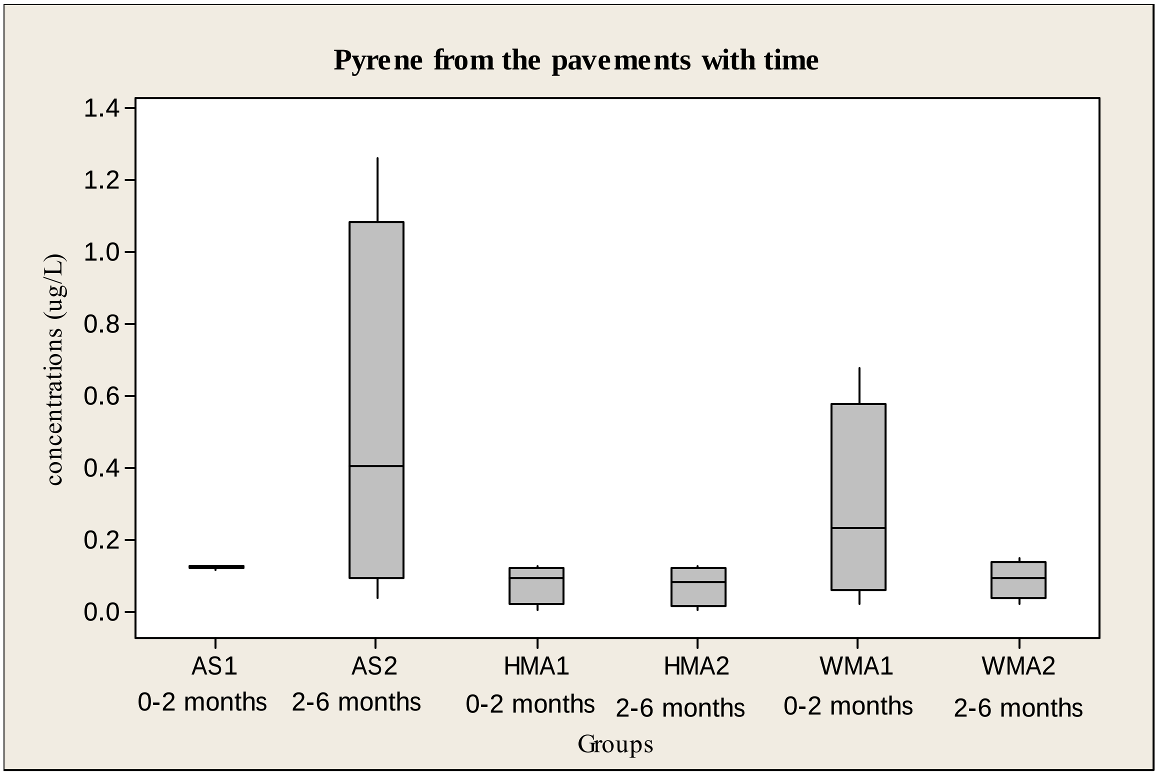


Figure 6-13. Pyrene from the pavements with aging

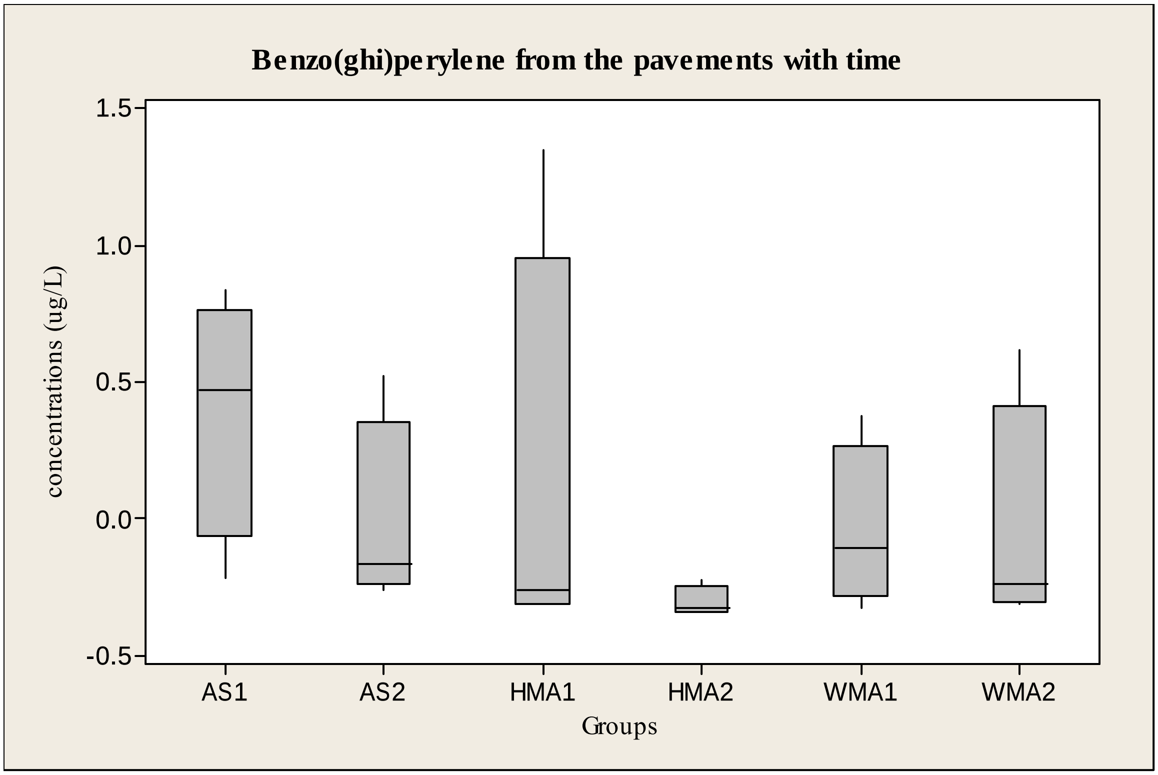


Figure 6-14. Benzo(ghi)perylene from the pavements with aging.

No significant differences were observed for the remainder of the PAHs analyzed based on the Kruskal-Wallis one-way ANOVA tests for the number of samples available. The box-plots for these are presented in Figures 6-15 through 6-22. The Mann Whitney tests examined difference for each pavement type with aging, and these results are presented in Table 6-10. Anthracene from both the asphalt sealer and the warm mix pavement samples indicated significant concentration differences with time (at p = 0.03), although this is not clear for the WMA plot.

Table 6-10. Mann-Whitney test results for the rest of the PAHs.

Mann-Whitney test results for PAHs with insignificant p-values from Kruskal-Wallis test		
Naphthalene	AS	0.31
	HMA	0.89
	WMA	0.11
Acenaphthylene	AS	0.25
	HMA	0.31
	WMA	1.00
Fluorene	AS	0.19
	HMA	0.89
	WMA	0.89
Anthracene	AS	0.03
	HMA	1.00
	WMA	0.03
Benzo(a)anthracene	AS	0.47
	HMA	0.67
	WMA	0.31
Chrysene	AS	0.31
	HMA	1.00
	WMA	0.47
Benzo(b)fluoranthene	AS	0.47
	HMA	0.31
	WMA	0.47
Benzo(a)pyrene	AS	0.31
	HMA	0.67
	WMA	0.89
Indeno(1,2,3-cd)pyrene	AS	0.19
	HMA	0.89
	WMA	0.895
Benzo(a,h)anthracene	AS	0.895
	HMA	1.00
	WMA	0.47

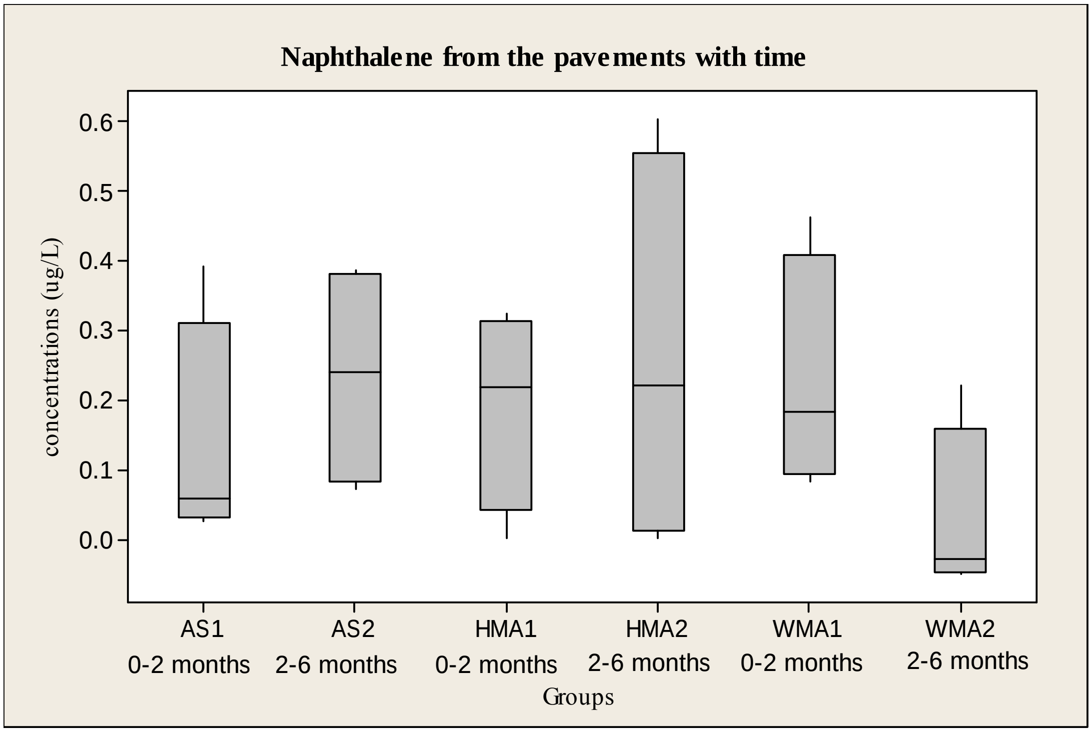


Figure 6-15. Naphthalene from the pavements with aging.

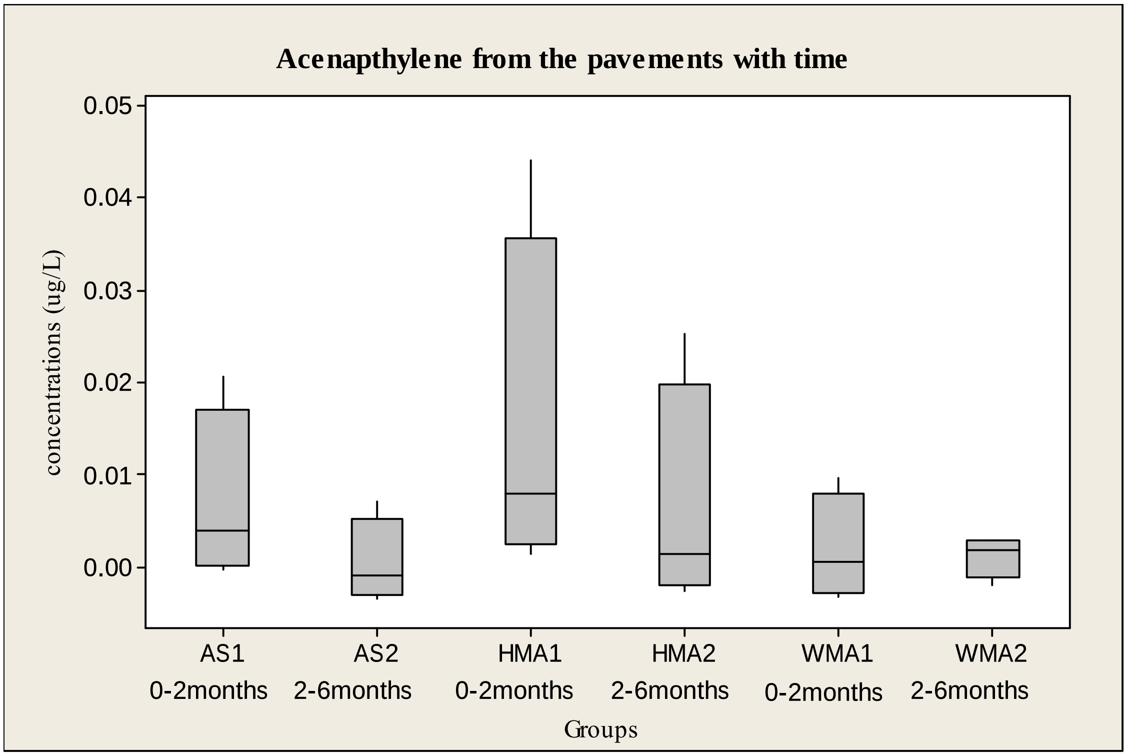


Figure 6-16. Acenapthylene from the pavements with aging.

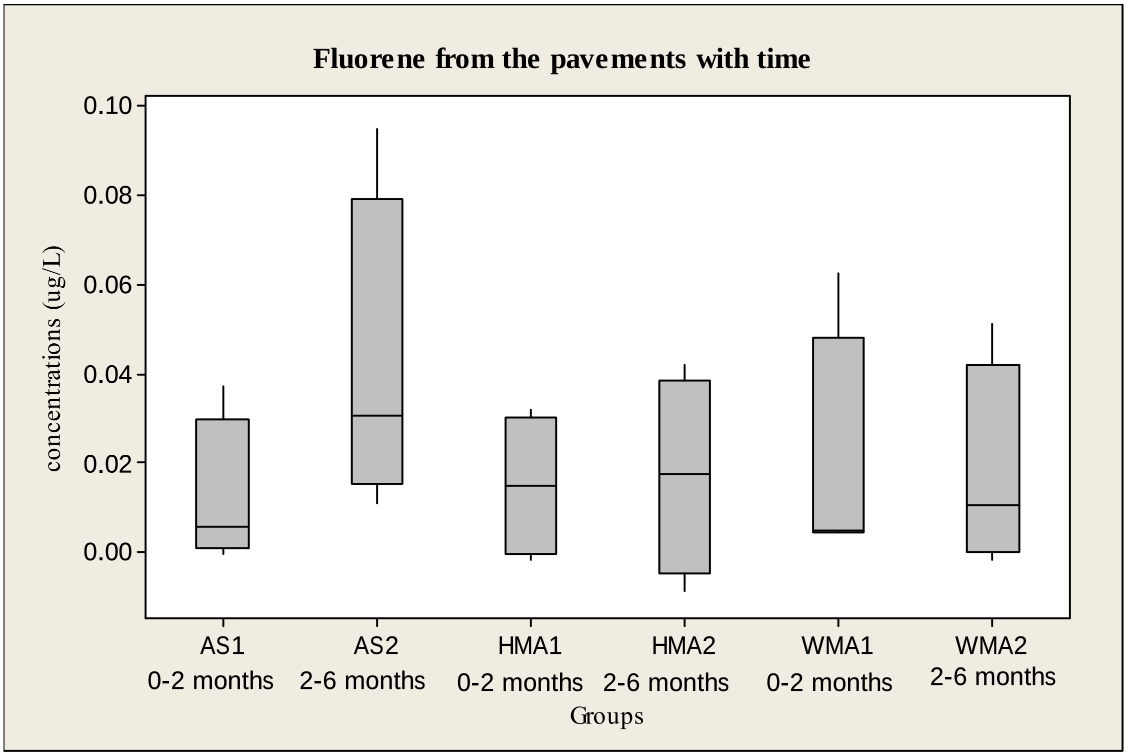


Figure 6-17. Fluorene from the pavements with aging.

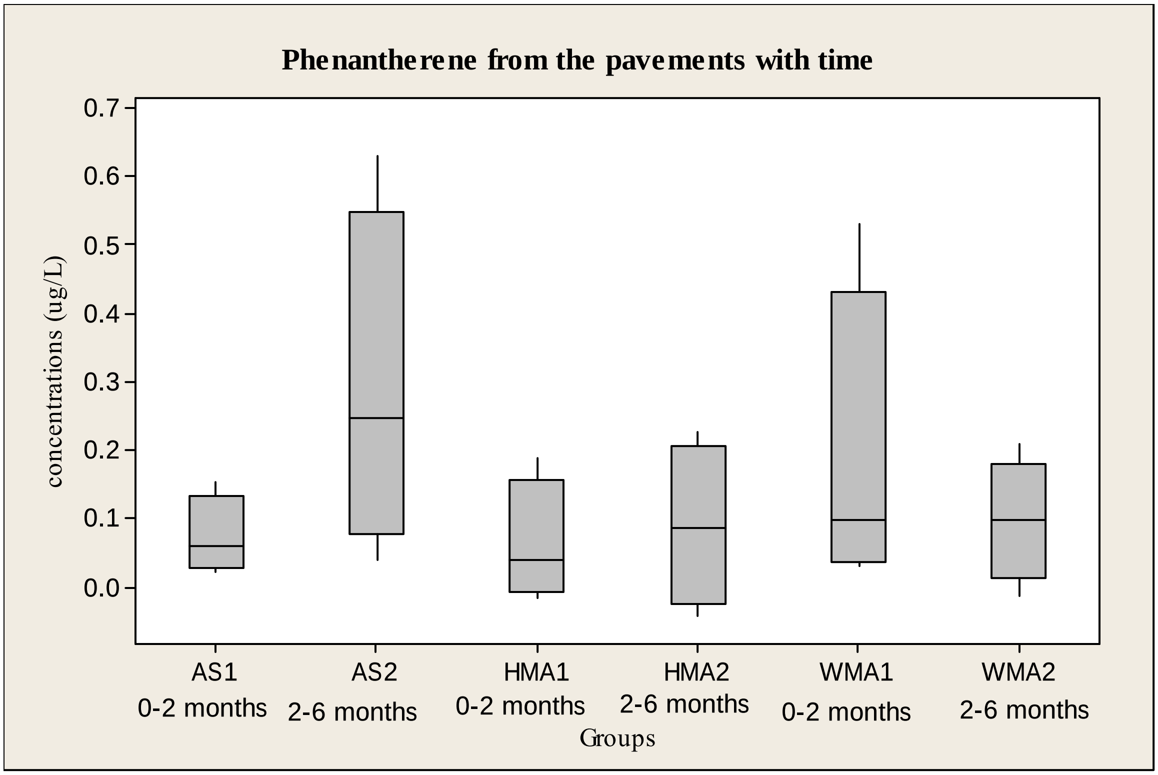


Figure 6-18. Phenanthrene from the pavements with aging

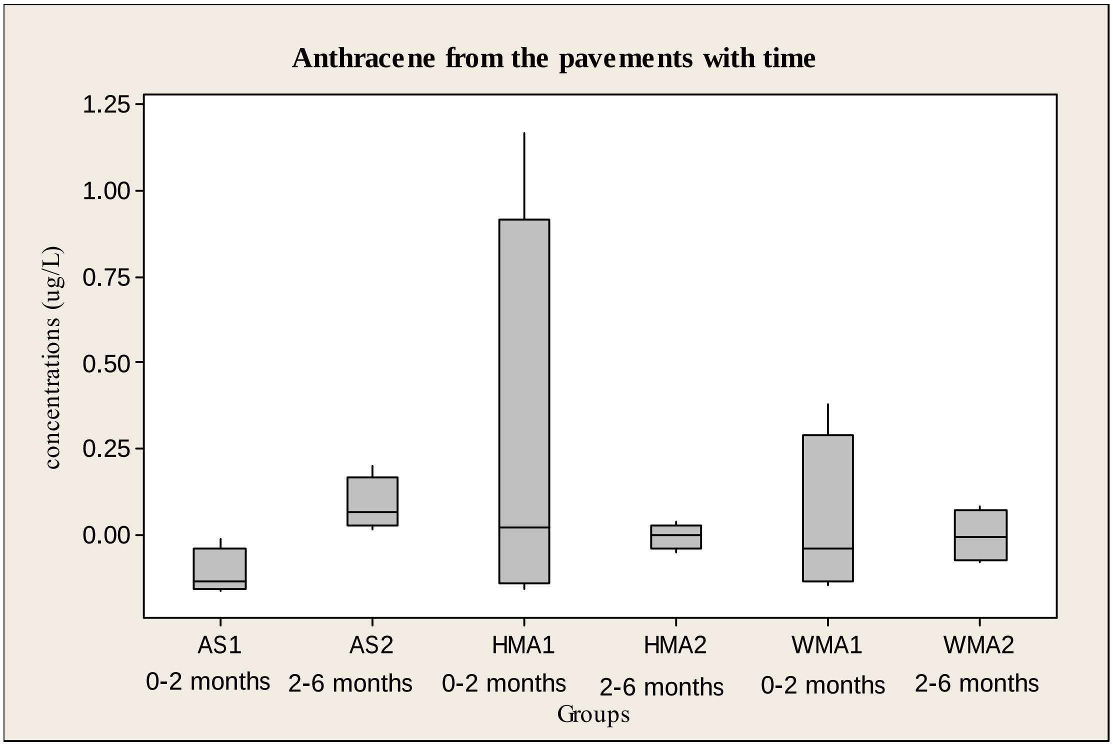


Figure 6-19. Anthracene from the pavements with aging.

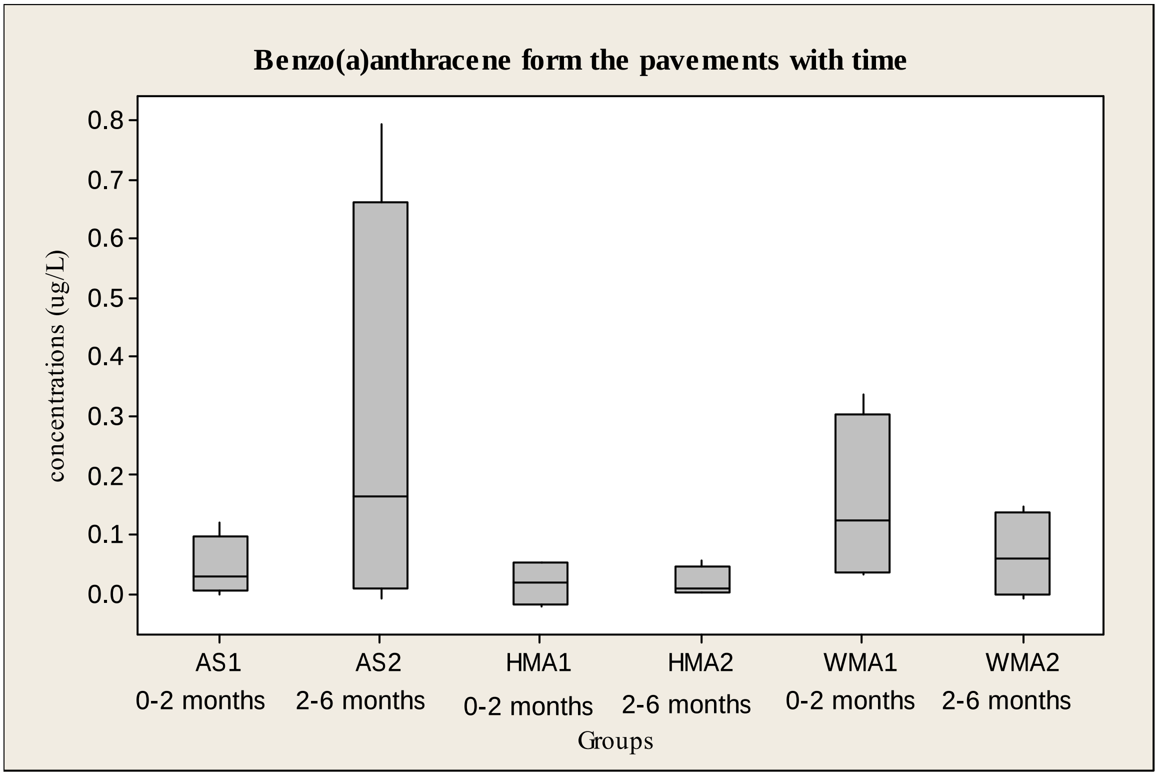


Figure 6-20. Benzo(a)anthracene from the pavements with aging.

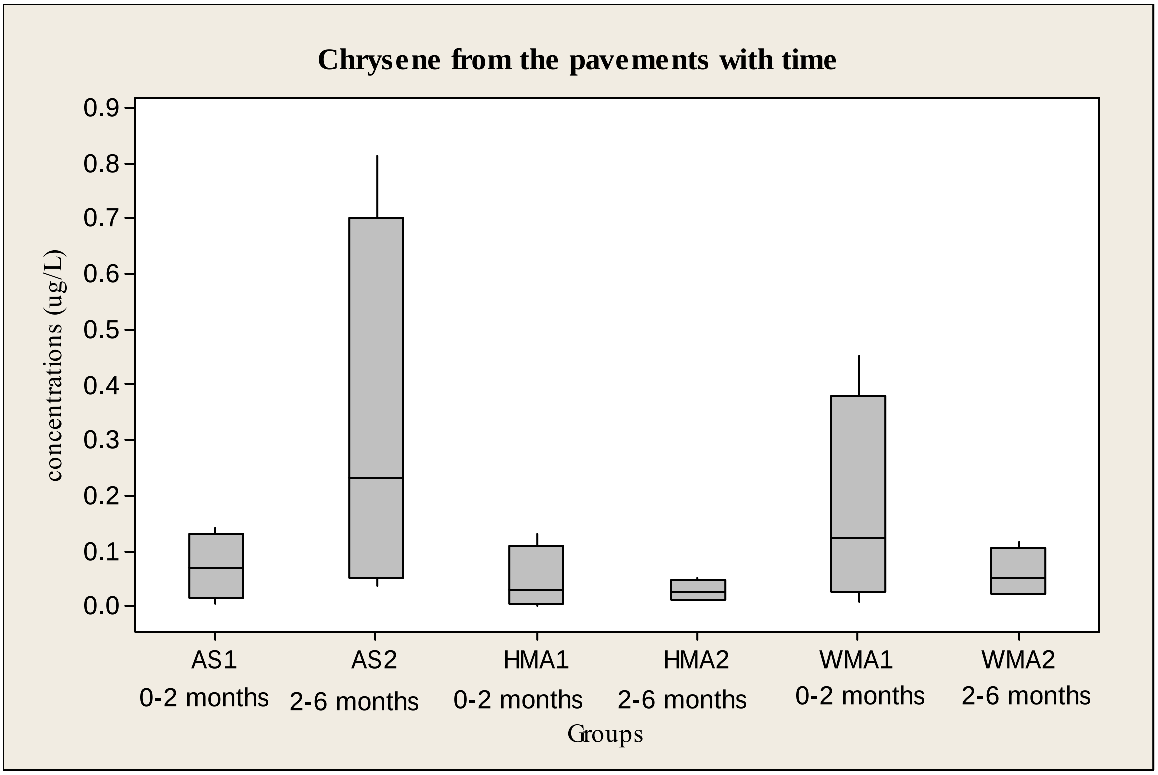


Figure 6-21. Chrysene from the pavements with aging.

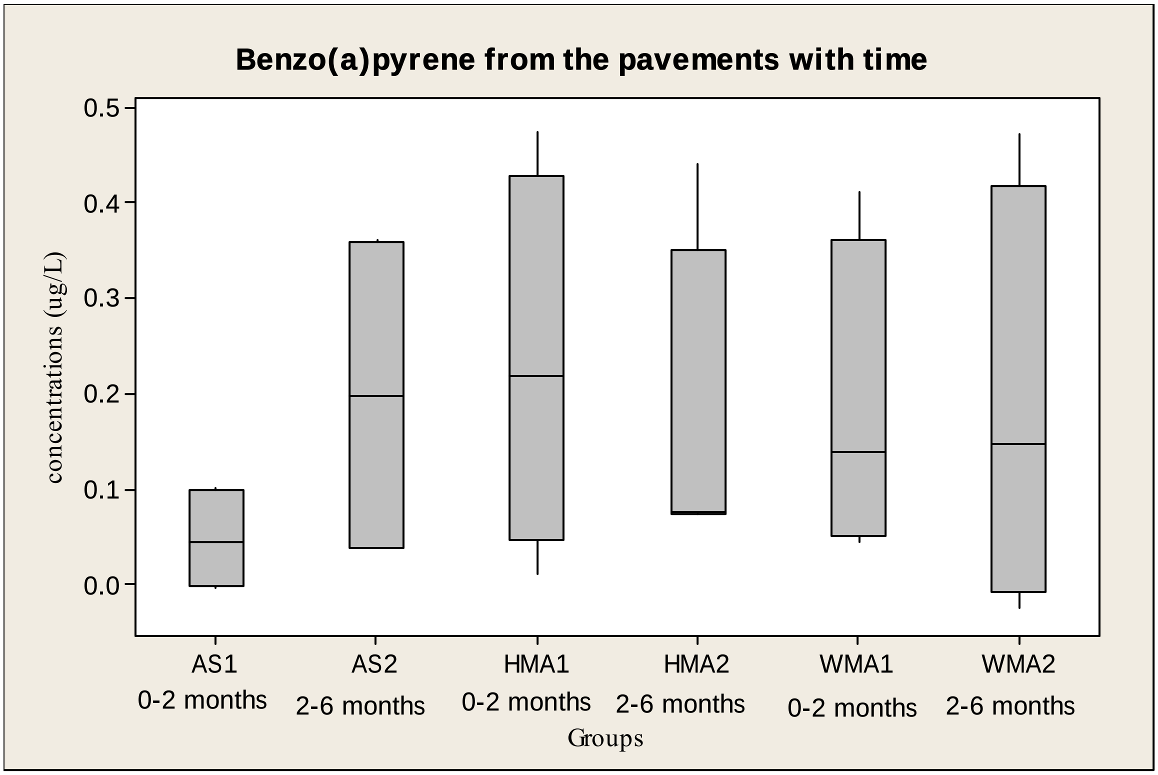


Figure 6-22. Benzo(a)pyrene from the pavements with aging.

Summary of Findings for Pavement Degradation

Tables 6-11 through 6-15 shows the average concentrations of the different constituents in each exposure group for the major constituents studied, along with the corresponding pairwise ANOVA p results comparing the short-term and long-term exposure values. As indicated above, many constituents did not indicate significant differences in concentration between the different pavement types or exposure periods for the limited numbers of samples (ten samples) obtained during the 6 month exposure period. However, nitrates, ammonia, total nitrogen, and COD did have significant differences for exposure periods for some of the sample sets ($p<0.05$), while total phosphorus, zinc, and naphthalene also had large (but less significant) differences.

Table 6-11. Pairwise ANOVA test results for short-term vs. long-term runoff concentrations

		average concentrations in group for all exposure periods						p values		
		HMA1	HMA2	WMA1	WMA2	AS1	AS2	HMA1 vs. HMA2	WMA1 vs. WMA2	AS1 vs. AS2
Nitrate	mg/L as N	1.3	4.1	1.4	4.4	1.5	4.1	***0.02***	***0.01***	***<0.01***
Ammonia	mg/L as N	0.27	0.05	0.32	0.01	0.22	0.05	0.09	0.06	0.2
Total Nitrogen	mg/L as N	0.4	1.8	0.8	2.4	0.8	2.3	***0.01***	0.11	***0.05***
Total Phosphorus	mg/L as P	0.28	0.59	1.01	0.54	0.38	0.94	0.16	0.41	0.07
COD	mg/L	73	46	86	43	97	38	0.39	0.17	***0.03***
Detergents (MBAS)	mg/L	0.95	0.85	0.75	0.7	0.58	0.81	0.78	0.86	0.26
Copper	µg/L	0.07	0.086	0.07	0.094	0.076	0.11	0.58	0.4	0.28
Zinc	µg/L	0.036	0.09	0.038	0.11	0.05	0.12	0.24	0.16	0.09
Napthalene	µg/L	0.19	0.26	0.23	0.03	0.13	0.23	0.67	0.11	0.43
Phenanthrene	µg/L	0.062	0.089	0.19	0.1	0.07	0.29	0.74	0.48	0.14
Flouranthene	µg/L	0.07	0.06	0.27	0.1	0.11	0.51	0.83	0.27	0.12
Pyrene	µg/L	0.078	0.072	0.29	0.003	0.12	0.53	0.86	0.21	0.18
Benzo(a)anthracene	µg/L	0.019	0.018	0.16	0.065	0.044	0.28	1	0.31	0.25
Chrysene	µg/L	0.049	0.029	0.18	0.06	0.07	0.33	0.52	0.28	0.2

Table 6-12. ANOVA on the linear regression for the nutrients (significant slope terms shown)

	average values (mg/L)			COV values			p - values (slope term/intercept term)		
	HMA	WMA	AS	HMA	WMA	AS	HMA	WMA	AS
Nitrate	2.68	2.92	2.65	0.76	0.72	0.63	0.0001/NA	0.00002/NA	0.00004/NA
Total Phosphorous	0.44	0.80	0.63	0.78	1.19	0.76	0.00003/NA	NA/NA	0.00005/NA
Ammonia	0.16	0.17	0.14	1.26	1.61	1.31	NA/0.03	NA/0.05	NA/0.04
Total Nitrogen	1.1	1.60	1.44	0.90	0.99	0.78	0.0003/NA	0.002/NA	0.006/NA
COD	59.4	64.2	70.3	0.77	0.74	0.61	NA/0.03	NA/0.01	0.02/0.0003
Detergent	0.9	0.73	0.68	0.57	0.55	0.44	NA/0.01	NA/0.02	NA/0.01

Table 6-13. Average and COV values for PAHs with no differences between samples or exposure periods

	Average (µg/L)			COV		
	HMA	WMA	AS	HMA	WMA	AS
Napthalene	2.7	1.5	2.2	0.9	1.3	0.8
Acenapthlylene	0.12	0.02	0.04	1.4	2.7	2.0
Fluorene	0.19	0.21	0.3	1.1	1.2	1.1
Phenanthrene	0.91	1.7	2.2	1.1	1.1	1.1
Benzo(a)anthracene	0.22	1.3	1.9	1.5	1.0	1.6
Chrysene	0.47	1.4	2.4	0.99	1.1	1.3
Benzo(a)pyrene	2.4	2.2	1.5	0.84	0.9	1.1

Table 6-14. Average and COV values for metals with no differences between samples or exposure periods

	Average (mg/L)			COV		
	HMA	WMA	AS	HMA	WMA	AS
Zinc	0.06	0.07	0.08	1.1	1.05	0.77
Copper	0.08	0.08	0.09	0.55	0.51	0.49

Table 6-15. Average and COV values for the toxicity results with no differences between samples or exposure periods

	Average values (% toxicity)			COV values		
Microtox exposure period	HMA	WMA	AS	HMA	WMA	AS
5 min	35	41	25	0.62	0.7	1
15 min	25	31	14	1.21	1.2	1.7
25 min	34	42	23	0.69	0.8	1.2
45 min	31	41	21	0.79	0.9	1.4

Conclusions of Pavement Deterioration Tests

Significant trends in concentrations with exposure periods were observed for some constituents, but not all. Ten sampling times were obtained at irregular periods (more frequent at the beginning and fewer near the end), for this study. Additional data observations would increase the power of the analyses allowing smaller trends to be identified as being significant. The observed trends were contradictory to what was expected from the literature review, in that the observed runoff concentration trends increased with time during the six month exposure period.

- Nitrate concentrations from the pavement with asphalt sealant, total nitrogen from the hot mix pavement, and COD from the pavement with sealant indicated significant concentration increases with time.

- Detergents were observed in runoff from all of the pavement samples, but with no apparent trends.

- Consistently observed heavy metals in the runoff samples were zinc and copper, with apparent increasing concentration trends, especially noticeable towards the end of the experiment. Cadmium and chromium were not detected in any runoff samples, while lead was only detected in a few of the samples.

- PAHs were observed in the pavement runoff samples at very low concentrations (generally <1 μg/L). Some of the PAHs in the asphalt sealant samples indicated apparent increasing trends with aging, compared to the unsealed pavements.

- Toxicity in the runoff from all three pavement types was moderate to high during the six months test duration. However, no significant trends were observed in the patterns of the toxicity from the runoff for the number of samples available. Runoff samples from the warm mix pavement had the highest toxicity values.

These tests focused on pavement runoff characteristics during a relatively short six month exposure period for three asphalt samples: two unsealed samples (hot mix and warm mix) and one sealed sample (using an asphaltic sealer). The original plan was also to examine a coal tar sealant but that was no longer available. The majority of the observed significant concentration trends increased with time with increasing concentrations with longer exposures. The opposite trend was expected based on minimal literature information. It is likely that the observed concentrations would decrease eventually with longer exposure periods.

Degradation of Crude Oil Spilled in the Environment

During Sree Usha Verravalli’s graduate research at the University of Alabama (Veeravalli 2011) concerning pollutant losses from asphalt, the tragic Deepwater Horizon oil well blowout occurred in the Gulf of Mexico. Samples were therefore obtained and studied as part of a parallel study funded by NSF. This chapter section summarizes her findings on the degradation of the spilled crude oil by using FTIR spectrophotometry, along with additional degradation surveys using standard crude oil samples obtained from other oil fields throughout the world. This information will be useful to stormwater researchers working in coastal areas and studying the effects of the hydrocarbons from multiple sources, especially when trying to differentiate natural (or spilled) crude oil hydrocarbons from similar materials discharged as part of the stormwater.

The oil-sand mixtures obtained from the contaminated beaches completely degraded over several days under continuous UV exposure in the lab. Unfortunately, the oil on the beaches did not degrade as rapidly under natural conditions, and submerged oil that sank (or remained on the sea floor) is degrading very slowly, and periodically comes ashore during storm conditions, resulting in a continuous source of hydrocarbons. As noted above, this can cause confusion when attempting to determine the contributions of stormwater associated hydrocarbons in near-shore coastal waters under storm conditions.

The standard crude samples, however, were chemically stabilized by the supplier and did not degrade upon laboratory UV exposure. One of the primary purposes of these tests were to identify the main IR wavelengths associated with the crude oils to help in developing advanced laser instrumentation for environmental analyses, as part of a parallel NSF project. Some of those primary wavelengths are included here to supplement the UV wavelengths that are more commonly used for hydrocarbon spectrophotometric analyses.

Site Description

Six soil samples were collected from Gulf of Mexico and infrared scans were performed on the samples to test for presence of oil. The samples were collected in glass jars from six different locations from Grand Isle, LA. Since the beach was off limits, the pictures of the sample location sites were taken from a pier overlooking the beach as seen in Figures 6-23 through 6-30.

Figure 6-23. Cleanup crews, view towards southwest from the pier.

Figure 6-24. Same view as previous panned slightly right (less south, more west): showing accumulated

Figure 6-25. First available access past (southwest of) State Park boundary, looking southwest. Left-to-right, shows clean-up personnel, oily-sand pile, sand collector (that looked a lot like a street-sweeper collecting about 3 to 4 inches per sweep), sand pile, massive dump truck (and an apparent front-end loader beside a sand pile is out of view), multiple sand piles, and security-fence to the horizon. All above are from Gulf of Mexico (marine) side of the island.

Figure 6-26. First available access to Barataria Bay (estuarine) side of the island (was dominated by gated residential communities and fenced/guarded industrial sites, latter of which included the local FEMA HQ).

Figure 6-27. Site of sample 1, Apparent “tar balls” (gray in color, texture that would be best described as slick/sticky* but no sandy grit in interior) on shore of a seafood-company boat-slip (situation picture at Image 5, looking generally north, from the un-fenced side of the slip). [*slick/sticky – If you rub it back and forth between your fingers, it’s fairly frictionless. If you then try to pull your fingers apart, they really try to stick together]

Figure 6-28. First available access to the marine (Gulf) waterfront (terminus of security fence easily visible to the northeast from this location). Site of Sample-3, very dark gray, sprinkles appeared to be actively washing ashore in (calm) surf. Sprinkles were slick/sticky but not gritty when ground between fingers. Sample-3 included a few “brown gobs” (slick/greasy*, but with incorporated sandy texture, visually more like what was described as weathered tar balls on TV) that were intimately co-located. Sample-2 was also taken near here (directly up-gradient) above the apparent high-tide line (well dried rind, smelled distinctly of hydrocarbon when broken, but nothing but sticky inside). [*slick/greasy - little friction when rubbed (except for obvious sand), little resistance to pulling fingers apart]

Figure 6-29. Marine side. Denser (further from active clean-up activities and further from Macondo) wash-up of sprinkles. Material obviously washing up with every wave, and actively being disgorged from clam holes between waves. Site of Sample-5. Note that Sample-5, by necessity of location in active wave region, included a good deal of sand and seawater. Sampling location, however, allowed for exclusion of any apparent brown gobs. Sample-4 (all brown gobs) was collected about 1 meter (near the apparent high-tide line) up-gradient from this picture.

Figure 6-30. Not on Grand Isle, Estuarine side, but very near pass between island and mainland. Location is at boat-slip for a bait-shop/marina. Similar to Sample-1.

Sample Descriptions


SAMPLE 1


SAMPLE 2


SAMPLE 3


SAMPLE 4


SAMPLE 5


SAMPLE 6

Sample 1: This was loose soil, with small clayey lumps. When in contact with solvent it gave a pale yellow color to the colorless solvent.

Sample 2: This sample had asphalt-like structure and when it was cut open, it had a shiny black surface. It disintegrated rapidly when it was in contact with denatured alcohol, turpentine and toluene and turned the solvent to black but remained unchanged in presence of acetone.

Sample 3: This was loose soil and looked similar to sample 1 but it was free of any clayey lumps. In presence of solvent, it gave the solvent a brown color.

Sample 4: This sample looked similar to sample 1 but it contained less of the loose particles and more clayey structures. It turned the solvent brown.

Sample 5: This sample contained water and had an oily layer on the water surface. When analyzing, the oily layer from the jar was also used. It did not affect the solvent color greatly.

Sample 6: This sample had large clay-like lumps.

Materials and Methods

Acetone, denatured alcohol, turpentine and toluene were used as candidate solvents for the analysis. The objective was to find a solvent that had a minor IR response in the same region as the sample extracts. For each solvent, six 60 mL Nalgene bottles had 10 grams of sample. Using a graduated cylinder, 30 mL of solvent was added to each bottle, the caps were closed and shaken vigorously, after which it was allowed to sit undisturbed for 30 min. Using a Pasteur pipette, samples (solvent with the extracted oils) from these bottles were transferred to the sampling cell of a Spectrum RX 1 FTIR and analyzed with the corresponding solvent as the background (background IR spectra was automatically subtracted). Pure solvent samples were also analyzed to determine the extent of the background spectra in the IR. The sample cell had “salt” (calcium fluoride) plates (windows) to contain the sample while scanning. A 0.2 mm thick Teflon^{TM} spacer was used to separate the calcium fluoride windows to provide a small analytical volume.

Results

Acetone

When using acetone as the solvent, samples 1 and 2 showed straight horizontal lines, indicating no contaminants were extracted into the solvent. Whereas samples 3, 4, 5, and 6 showed peaks in the regions of 3500, 3000, and 1600 cm^{-1}, indicating the presence of contaminants that were extracted from the respective sand/oil samples. The area of the peaks varied between the samples.

Table 6-16. Principle IR Peaks for Analyzed Deepwater Horizon Oil and Sand Samples Extracted using Acetone

Sample ID	Peaks at wavelength	Height of the peak	Width of the peak at 50% height
Sample 1	-	-	-
Sample 2	-	-	-
Sample 3	3500 cm-1	14.4 cm	1.9 cm
	3000 cm-1	8.5 cm	0.05 cm
	2000 cm-1	3.3 cm	1.5 cm
	1650 cm-1	13.8 cm	0.6 cm
	1250 cm-1	6.5 cm	1.3 cm
	1200 cm-1	8 cm	0.05 cm
	1125 cm-1	4.3 cm	0.6 cm
	1000 cm-1	4.4 cm	1.2 cm
Sample 4	3625 cm-1	13.5 cm	1.15 cm
	3000 cm-1	7.1 cm	0.05 cm
	1937.5 cm-1	1.8 cm	2.1 cm
	1625 cm-1	11 cm	0.5 cm
	1250 cm-1	4.1 cm	0.7 cm
	1187.5 cm-1	2.8 cm	0.7 cm
Sample 5	3500 cm-1	14.5 cm	2.3 cm
	2062.5 cm-1	6.3 cm	1.8 cm
	1625 cm-1	13.6 cm	0.7 cm
	1250 cm-1	6.1 cm	0.5 cm
	1125 cm-1	7.3 cm	0.65 cm
	937.5 cm-1	11.15 cm	1.3 cm
Sample 6	3500 cm-1	13.5 cm	2 cm
	2000 cm-1	4 cm	1.4 cm
	1625 cm-1	11 cm	0.5 cm
	1281.5 cm-1	1.4 cm	0.2 cm
	1125 cm-1	3.7 cm	1.45 cm
	1000 cm-1	5.2 cm	1.2 cm

Denatured Alcohol

With denatured alcohol, all the samples showed peaks in the regions 900, 1600, 2100, and 3600 cm^{-1} indicating the presence of a similar compound being extracted into the solvent. However, the height and width of the peaks varied greatly among the samples.

Table 6-17. Principle IR Peaks for Analyzed Deepwater Horizon Oil and Sand Samples Extracted using Denatured Alcohol

Sample ID	Peaks at wavelength	Height of the peak	Width of the peak at 50% height
Sample 1	3625 cm-1	14.1 cm	0.4 cm
	2187.5 cm-1	7.8 cm	2 cm
	1625 cm-1	14.5 cm	1.6 cm
	1281.25 cm-1	3.8 cm	<0.05 cm
	1125 cm-1	10.5 cm	0.8 cm
	984.375 cm-1	12.5 cm	0.5 cm
Sample 2	3625 cm-1	13 cm	0.4 cm
	2187.5 cm-1	6.8 cm	1.9 cm
	1625 cm-1	13.8 cm	1.9 cm
	1406.25 cm-1	7.5 cm	<0.05 cm
	1281.25 cm-1	1.5 cm	<0.05 cm
	1125 cm-1	6.3 cm	0.9 cm
	984.375 cm-1	12 cm	0.6 cm
Sample 3	3625 cm-1	13.6 cm	0.5 cm
	2187.5 cm-1	7.5 cm	1.8 cm
	1625 cm-1	14.4 cm	1.5 cm
	1406.25 cm-1	5.4 cm	<0.05 cm
	1125 cm-1	9.2 cm	0.8 cm
	984.375 cm-1	11.8 cm	0.7 cm
Sample 4	3625 cm-1	12.6 cm	0.4 cm
	3250 cm-1	1.5 cm	<0.05 cm
	2187.5 cm-1	6.4 cm	1.9 cm
	1625 cm-1	13.5 cm	1.2 cm
	1125 cm-1	6.5 cm	1 cm
	984.375 cm-1	10.2 cm	0.5 cm
Sample 5	3625 cm-1	14.5 cm	0.7 cm
	2187.5 cm-1	11.9 cm	2.1 cm
	1625 cm-1	14.5 cm	3.3 cm
	1281.25 cm-1	13.3 cm	<0.05 cm
	1125 cm-1	11.1 cm	1 cm
	984.375 cm-1	13 cm	0.5 cm
Sample 6	3625 cm-1	14.5 cm	0.5 cm
	2187.5 cm-1	11 cm	2.1 cm
	1625 cm-1	14.5 cm	2.6 cm
	1125 cm-1	12.7 cm	1 cm
	984.375 cm-1	13 cm	0.5 cm

Turpentine
With turpentine, all the samples showed very narrow, sharp peaks in the 3000 cm^{-1} region, while samples 2, 3 and 6 showed a short and wide peak in the region between 3000 and 3500 cm^{-1}, indicating the presence of a similar compound being extracted into the solvent.

Table 6-18. Principle IR Peaks for Analyzed Deepwater Horizon Oil and Sand Samples Extracted using Turpentine

Sample ID	Peaks at wavelength	Height of the peak	Width of the peak at 50% height
Sample 1	2812.5 cm-1	4.4 cm	<0.05 cm
	1437.5 cm-1	8.5 cm	<0.05 cm
	1000 cm-1	3 cm	0.004 cm
Sample 2	3250 cm-1	1 cm	1.2 cm
	2812.5 cm-1	8.7 cm	0.05 cm
	1062.5 cm-1	2 cm	0.6 cm
Sample 4	Not analyzed	Not analyzed	Not analyzed
Sample 3	3250 cm-1	1 cm	1.1 cm
	3000 cm-1	11.5 cm	<0.05 cm
	2812.5 cm-1	2 cm	<0.05 cm
	1437.5 cm-1	5.5 cm	<0.05 cm
	1062.5 cm-1	2.3 cm	0.5 cm
	750 cm-1	5.5 cm	<0.05 cm
Sample 5	3000 cm-1	0.6 cm	<0.05 cm
	1468.75 cm-1	5 cm	<0.05 cm
	1437.5 cm-1	7.4 cm	<0.05 cm
	1000 cm-1	4.8 cm	<0.05 cm
	890.625 cm-1	6.7 cm	0.2 cm
Sample 6	3250 cm-1	2.4 cm	1.1 cm
	3000 cm-1	2.3 cm	<0.05 cm
	2875 cm-1	7 cm	<0.05 cm
	1000 cm-1	3.7 cm	0.4 cm

Toluene
With toluene as the solvent, all the samples showed narrow peaks in the 3000 cm^{-1} region. The peaks were short for sample 5, but relatively higher for the samples 1, 2 and 3. Samples 4 and 6 could not be analyzed with this solvent because of insufficient sample.

Table 6-19. Principle IR Peaks for Analyzed Deepwater Horizon Oil and Sand Samples Extracted using Toluene

Sample ID	Peaks at wavelength	Height of the peak	Width of the peak at 50% height
Sample 1	3000 cm-1	13.1 cm	<0.05 cm
	2875 cm-1	12 cm	0.3 cm
	1062.5 cm-1	5 cm	<0.05 cm
Sample 2	3000 cm-1	11.8 cm	0.1 cm
	2875 cm-1	10.8 cm	0.1 cm
	1593.75 cm-1	5.7 cm	0.1 cm
	1062.5 cm-1	7.6 cm	<0.05 cm
Sample 3	3000 cm-1	5.1 cm	0.1 cm
	2875 cm-1	10 cm	0.05 cm
Sample 4	Not analyzed	Not analyzed	Not analyzed
Sample 5	2875 cm-1	4.7 cm	0.05 cm
	1062.5 cm-1	14.5 cm	<0.05 cm
Sample 6	-	-	-

IR Scans of Crude Oil Samples

After oil-sand samples from the Deepwater Horizon spill were analyzed using the IR spectroscope, a crude oil sample from Fayetteville, AL mixed with sand were aged in a UV exposure chamber and periodically sampled and analyzed to determine the degradation of the oil. Acetone was used as the solvent. The aging tests of this local crude oil sample were followed by analyzing crude oil samples from ONTA, Ontario, Canada. Six sets of crude oil samples were obtained from the company, four of the sets contained four crude oil samples and two sets contained six crude oil samples and the oils were numbered 1 to 4 and 1 to 6 in the sets and the oils increased in viscosity, with crude oil # 1 being the least viscous to crude oil # 6 being the most viscous.

For example, Crude oil set # 5 numbered 1005, 2005, 3005, 4005, 5005 and 6005 are paraffinic (light, sweet), paraffinic-naphthenic (light-medium, sweet-sour*), naphthenic (medium, sour*), aromatic- intermediate (medium-heavy, sour*), aromatic-naphthenic (heavy, sour*), and aromatic-asphaltic (extra-heavy, sour*) oils, respectively.
These crude oil sets were collected from different parts of the world, from the USA, Nigeria, Iraq, and South America. The crude oil set # 1 and set # 2 are replicates, set # 3 and set # 4 are replicates and set # 5 and set # 6 are replicates. Set # 5 and set # 6 were found to be more viscous than the remaining sets. Set # 6 could not be analyzed because of its high viscosity; it could not be spread easily on the salt plates and it stained the plates.

Some of these samples (sample # 1001,1002,1003,1004, and 1005) were also aged under UV, similar to the above method but without the sand.

Materials and Methods

30 mL of Fayetteville crude oil was mixed with 100 grams of sand in a glass container and mixed such that all the sand particles were coated with the crude oil. The glass container had a wide mouth and was placed in a RPR 100 UV exposure chamber. An oil-sand subsample was periodically taken from this container and analyzed using the Spectrum RX 1 FTIR, with acetone as the solvent. Five grams of the oil-sand mixture was mixed with 30 mL of acetone in 60 mL Nalgene bottles. The Nalgene bottles were then shaken well and allowed to stand for 30 min before pipetting out the oil-acetone mixture into the sampling cell of the Spectrum RX1 FTIR with the calcium fluoride salt plates having 0.2 mm thick Teflon^{TM} spacers.

Results

The initial IR scan showed wide peaks at 3600 to 3400 cm^{-1}, 3000 to 2800 cm^{-1}, 1700 to 1600 cm^{-1}, 1500 to 1350 cm^{-1}, and 1230 to 1250 cm^{-1}. These peak heights and areas were reduced with time with the continued exposure to UV light. After 5 days of aging under the UV light, the scan showed a straight line with no peaks, indicating complete degradation of the Fayetteville crude oil. In contrast, the crude oil standard samples that were aged under UV light without the sand (due to minimal sample volumes) did not show any degradation, even after three weeks of UV light exposure. These standard samples had been stabilized to resist degradation and likely do not reflect typical environmental conditions, but did result in usable IR peak wave lengths.

Appendix I includes tables of the major peaks for these scans along with the IR scans of selected crude oil samples.

The Treatability and Fate of PAHs Discharged to Surface Waters in the Urban Environment

This chapter section is derived from Jejal Bathi's PhD dissertation (Bathi 2008) investigating sediment associations of PAHs by particle size and location in three urban creeks in the Tuscaloosa, AL, area. His fugacity modeling, method development activities, and data results indicate that stream sediments are the most likely fate of PAHs discharged in stormwater to local receiving waters. The strong PAH associations with particulates also support the high levels of PAH removal when using advanced stormwater controls that are capable of removal of very small stormwater particulates. His research was partially funded by the NSF under grant no. EPS-0447675. The NSF project included tasks conducted at UA supporting the Center for Optical Sensors and Spectroscopies (COSS) at UAB's Department of Physics by applying emerging technologies to solve current environmental problems. These activities are identifying and quantifying environmental contaminant levels that can then be used by the COSS team to develop performance objectives of newly developed laser instrumentation.

Fates of PAHs in Aquatic Receiving Waters

PAHs present in surface waters can volatilize photolyze, oxidize, biotransform, bind to suspended particles or sediment, or accumulate in aquatic organisms. In sediments, PAHs can biodegrade or accumulate in aquatic organisms (Agency for Toxic Substances and Disease Registry).

Photodegradation of PAHs involves their transformation to different intermediate products which are finally transformed to end products of carbon dioxide and water. Environmental conditions, such as presence of humic acids, concentrations of oxygen, etc., play an important role in the rate of photo transformations of PAHs in the environment. Analyses of the direct photolysis of pyrene by Parmer, *et al.* (1993) (using GS/MS) showed that pyrene yields six compounds or groups of isomers. He also found that direct photolysis products of benzo(a)pyrene included five groups of compounds or isomers. The study identified these photolysis products tentatively as oxygen-addition products, hydroxyl-addition products, phthalate esters, and three or four carbon degradation products. The study also identified that among the four parameters considered (potential sensitizers, humic material, pH, and suspended sediment), the amount of humic material was the most important parameter affecting the rate of photodegradation of pyrene. Similarly, Clark, *et al.* (2007) found that photodegradation of pyrene in aqueous solutions increases as the ionic strength of the solution increases, and decreases with increases in concentrations of humic acid, or decreases in oxygen concentrations.

Similar to photo transformation, biotransformation of PAHs also involves the formation of intermediate products which will then further undergo biotransformation to form final carbon dioxide and water products. According to Atlas, *et al.* (2005), bacterial metabolism of naphthalene represents the typical biotransformation mechanism of this PAH in the environment. The aerobic bacterial metabolism of naphthalene involves the oxidative action of the naphthalene dioxygenase enzyme, which forms intermediate naphthalene dihydrodiols. The dihydrodiols are then dehydrogenated with the help of dehydrogenase enzymes to form salicylic acid, which is finally metabolized via catechols resulting in carbon dioxide and water.

The overall biotransformation rate of hydrocarbons in solids is strictly limited by a variety of parameters (Rockne, *et al*. 2002). The biotransformation, and hence the persistence of environmental contaminants, is mostly influenced by the physical/chemical properties of the contaminant, the presence of a viable microbial population to transform the contaminants, the environmental conditions such as temperature, and pH suitable for microbial biotransformation activities (Alexander 1999). The aqueous solubility of PAHs decreases as the number of rings in the molecules increase, which influences the biodegradability of the compound. Sherrill and Sayler (1980) found that PAH degradation was directly related to temperature. PAH degrading bacteria have been documented to be temperature sensitive; a Mycobacterium sp. that was shown to mineralize a series of PAHs, including pyrene, grew well at temperatures between 24 and 30˚C (Heitkamp, *et al.* 1988). The rate of mineralization and hence the biotransformation of anthracene and naphthalene will be controlled by oxygen content. Similarly, pH and redox potential may affect the biotransformation of PAHs, with the highest degradation rates of benzo(a)pyrene found to occur at pH 8.0, and at all pH values, benzo(a)pyrene and naphthalene biotransformation increased with increasing redox potential (Hambrick, *et al.* 1980).

PAH Partitioning after Releases to the Environment

When PAHs are released into the environment, they will partition into different phases (air, water, solids) which affect their treatability and how they should be analyzed. Sorption plays an important role in the fate of these organic contaminates. Due to their extremely low solubility and their hydrophobic nature, most PAHs are predominantly associated with particulate matter. Partitioning of PAHs between different phases in the environment also depends on the physical and chemical properties of the phases. The solid-water sorption coefficient (K_d) of a contaminant describes its distribution between the aqueous and solid phases of the system at equilibrium. According to Boethling, *et al*. (2000), the organic carbon normalized sorption coefficient (K_{oc}) approach is the most appropriate procedure for estimating the sorption coefficients, where:

$$K_{oc} = \frac{K_d}{oc} \qquad \text{(eq. 6.1)}$$

The K_d is the solid-water sorption coefficient and OC is the organic fraction of the solid. There are many regression models available to estimate the Log K_{oc} of PAHs from Log K_{ow}, where K_{ow} is the octonal water partition coefficient, for example:

Log K_{oc} = 0.904 log K_{ow} – 0.006 (Chiou, *et al.* 1983) (eq. 6.2)

Log K_{oc} = 1.000 log K_{ow} – 0.210 (Karichhoff, *et al.* 1979) (eq. 6.3)

Regression equations relating the Log K_{oc} and Log S are also available in the literature, where S is the solubility of PAH in water, for example:

Log K_{oc} = log S + 0.44 (Karichhoff, *et al.* 1979) (eq. 6.4)

In general, the relationship between the dissolved and sorbed chemical concentrations of PAHs is non-linear in nature which can be represented by the Freundlich isotherm:

$$C_{sorb} = K_f \,.\, (C_w)^n \,; \qquad \text{(eq. 6.5)}$$

The C_{sorb} is the concentration of the sorbed chemical, K_f is the Freundlich constant, C_w is the concentration of the dissolved chemical, and n reflects the nonlinearity, with n equal to one representing a linear partition relationship.

Under equilibrium conditions, the partition coefficients discussed above may be effective in predicting the PAH partition concentrations in the liquid and solid phases, but these predictions may not be accurate for real time systems which are not usually at equilibrium. Differences between predicted sorption coefficients and actual measured observations were seen by Hwang, *et al*. (2006) in their study of PAHs in stormwater samples along the lower Anacostia River in Washington, D.C. Though the report did not provide the details about how different the predicted and observed values were, they reported that the concentrations of particulate-bond PAHs were higher than the predicted concentrations, as one could expect based on analyses of the solid-water partition coefficient (K_d).

High K_{oc} (or high K_{ow}) values of a pollutant indicate its higher affinity to adsorb to solids in the environment. PAHs are hydrophobic in nature, with their relatively high K_{oc} and K_{ow} constants. Due to their hydrophobic nature, in the aquatic environment, PAHs tend to accumulate more on particulate matter than in the liquid partition, and this is most obvious for high molecular weight PAHs. Many researchers have examined the partitioning behavior of PAHs in the aquatic environment. As shown on Table 6-20, Pitt, *et al*. (1998 and 1999) examined stormwater samples in different locations in the United States and found that PAHs are more predominant in the particulate form than in the dissolved form.

Table 6-20. Concentrations and partitioning of selected PAHs in urban stormwater samples (Pitt, *et al*. 1999)

Contaminant	**Amount of Contaminant (µg/L)**			**% Association**	
	Non-filtered water	**Filtered water (In water Phase)***	**Associated with particulate solids (by difference)**	**Water**	**Particulate Solids**
Fluoranthene	28	7	21	25	75
Pyrene	31	2	29	8	92
Benzo(a)anthracene	32	<0.5	>31.5	<1.5	>98.5
Benzo(b)fluoranthene	61	<0.5	>60.5	<0.8	>99.2
Benzo(k)fluoranthene	47	<0.5	>46.5	<1.1	>98.9
Benzo(a)pyrene	70	<0.5	>69.5	<0.7	>99.3
Benzo(g,h,i) perylene	20	<0.5	>19.5	<2.5	>97.5

* The detection limits for the PAHs was about 0.5 µg/L

Factors that affect the PAH associations with the particulate matter in the aquatic environment include the physical and chemical properties of the specific PAH contaminant, the physical and chemical properties of the aquatic medium, and the physical and chemical properties of the particulate matter. For the purpose of understanding such effects, Zhou, *et al*. (1998) studied the relationships between the concentrations of fluoranthene and pyrene on suspended solids with salinity, suspended solids concentrations, and particulate organic carbon content, in the Humber estuary, UK. The concentrations of selected PAHs on suspended solids showed no correlation with the salinity of the samples, while concentrations of suspended solids and particulate organic carbon showed a clear relationship with concentrations of PAHs on the suspended solids. Concentrations of suspended solids in the samples showed negative correlations with the concentrations of selected PAHs on suspended solids, whereas particulate organic content showed positive correlations with the concentrations of particulate-associated PAHs. This study also showed that higher concentrations of PAHs are likely associated with the finer particles (generally classified as clay material which have large surface areas per unit weight), compared to the coarser particles (generally classified as sand particles which have comparatively less organic matter which are needed for greater sorption of PAHs).

A similar pattern was observed by Aryal, *et al.* (2005) who monitored suspended solids and PAHs associated with fractionated suspended solids in highway runoff for four rain events (samples were only collected during the initial 3 mm of runoff) at an inlet point of treatment facilities for a highway drainage system in Winterthur, Switzerland. The measured concentrations of PAHs in fine fractions (<45µm) were higher than their concentrations in coarse fractions (>45µm).

Mahler, *et al*. (2005), of the U.S. Geological Survey, examined PAHs in simulated rainfall water runoff and particulates collected from four parking lot test plots. Results indicated that the coal-tar-sealed parking lots had higher concentrations of PAHs than those from any other examined type of surface. The reported average total PAH concentrations in particulates in the runoff from the parking lots were 3,500,000 µg/kg from coal-tar-sealed, 620,000 µg/kg from asphalt-sealed, and 54,000 µg/kg from unsealed parking lots.

Rushton, *et al.* (2006) studied the association of selected PAHs on gross solids while analyzing the performance of a Continuous Deflection Separation (CDS) retrofit unit installed to control stormwater discharging to the Hillsborough River, south Florida. The gross solids, consisting of litter, leaves, trash and sediment, collected by the CDS unit was found to have a wide range of concentrations for the selected PAHs. They found high concentrations of PAHs on the gross solids that had high organic content.

Fugacity-based Partition Calculations for an Environmental System under Equilibrium Conditions

Mackay fugacity level 1 (Mackay, *et al.* 1992) calculations to predict the partitioning of PAHs among the environmental phases is only applicable for equilibrium conditions. Prediction fate model calculations for selected PAHs were performed based on typical environmental conditions and with the assumption of system equilibrium. Based on this model, the partition percentages of selected PAHs into different phases were calculated. The equations involved in the model calculations are:

$$C = Z * f \quad \text{(or)} \quad f = \frac{M}{\sum(V_i * Z_i)} \qquad \text{(eq. 6.6)}$$

Where, C = Concentration of contaminant, mol/m^3; Z = fugacity capacity constant, mol/m^3; f = fugacity, Pa; V_i = Volume of the corresponding phases; and Z_i = fugacity capacities of phases for air, water, sediment, suspended sediment, and fish for i =1, 2,3, 4, 5 respectively and are defined as follows.

$$Z_1 = \frac{1}{RT} \qquad \text{(eq. 6.7)}$$

$$Z_2 = \frac{1}{H} \qquad \text{(eq. 6.8)}$$

$$Z_3 = Z_2 * \mathrm{P}_3 * \phi_3 * \frac{K_{OC}}{1000} \qquad \text{(eq. 6.9)}$$

$$Z_4 = Z_2 * \mathrm{P}_4 * \phi_4 * \frac{K_{OC}}{1000} \qquad \text{(eq. 6.10)}$$

$$Z_5 = Z_2 * \mathrm{P}_5 * L * \frac{K_{OW}}{1000} \qquad \text{(eq. 6.11)}$$

Where R = gas constant (8.314 J/mol K), T = absolute temperature (K), H= Henry's law constant (Pa.m^3/mol), K_{OC} = Organic-water partition coefficient, K_{OW} = Octonal-water partition coefficient, P_3 = density of sediment (kg/m^3), P_4 = density of suspended sediment (kg/m^3), $Ø_3$= organic fraction of sediment, $Ø_4$= organic fraction of suspended sediment, P_5 = density of fish in the aquatic system (kg/m^3), L= Lipid content of fish. Predicted partition values calculated using this model were employed in studying the effect of selected environmental parameters on the associations of PAHs with different media compartments. Factorial analyses techniques are used for studying the effect of the parameters, namely, organic content of sediment particles, temperature of the system, concentration of selected PAH, and concentration of sediment particles in the system.

The percentage of the total quantity of each PAH that was partitioned into individual phases were calculated using the system volumes, densities, and organic fractions as shown on Table 6-21.

Table 6-21. Assumed System Parameters

Parameter	**Air**	**Water**	**Soil**	**Sediment**	**SS**	**Fish**
Volume (m^3)	1.0E+14	2.0E+11	9.0E+09	1.0E+08	1.0E+06	2.0E+05
Density (kg/m^3)	1.2E+00	1.0E+03	2.4E+03	2.4E+03	1.5E+03	1.0E+03
Organic Fraction	-	-	0.02	0.04	0.2	0.05 (Lipid Content Weight/Weight)

The model predicted fugacity capacities and the percentage partition by weight for selected PAHs into air, water, suspended sediment, sediment and fish (biota) are shown on Table 6-22. The values indicate, as expected, that for many of the PAHs, the compounds are mostly partitioned with the sediment phase than with the other phases. The low molecular weight PAHs naphthalene, fluorene, phenanthrene, and anthracene (which have fewer carbon rings) are mostly partitioned into the air or water phases compared to those having higher molecular weights. Figure 6-31 shows the relationship between percentage partitioning of PAHs onto sediment phase and their Log (K_{OW}), Log (K_{OC}). PAHs with Log (K_{OW}) or Log (K_{OC}) values greater than about 4.5 are mostly partitioned with the sediment phase compared to other phases. Of the PAHs examined, only naphthalene, fluorene, and phenanthrene are expected to be predominantly associated with the air phase.

Table 6-22. MacKay Level 1 Calculated Fugacity Capacities and Percentage Partitioning of Selected PAHs with Different Environmental Phases

PAH	**Z_1**	**Z_2**	**Z_3**	**Z_4**	**Z_5**	**F**	**% Partition by Weight**				
							Air	**Water**	**Sediment**	**SS**	**Fish**
Naphthalene	4.0E-04	2.1E-02	3.3E+00	1.0E+01	9.3E-01	1.7E-05	89.7	9.5	0.7	0.0	0.0
Fluorene	4.0E-04	4.7E-02	3.3E+01	1.0E+02	2.0E+00	1.1E-05	76.0	17.7	6.2	0.2	0.0
Phenanthrene	4.0E-04	3.9E-02	5.2E+01	1.6E+02	1.7E+00	7.0E-06	73.5	14.4	13.0	0.3	0.0
Anthracene	4.0E-04	5.6E-01	7.6E+02	2.4E+03	4.1E+03	2.8E-06	17.5	49.3	29.8	1.0	0.4
Fluoranthene	4.0E-04	1.5E+00	5.5E+03	1.7E+04	6.6E+01	5.4E-07	4.4	33.2	60.5	1.9	0.0
Pyrene	4.0E-04	5.3E-01	1.9E+03	6.0E+03	2.3E+01	1.1E-06	11.7	30.6	55.9	1.8	0.0
Benzo(a) anthracene	4.0E-04	1.5E+01	2.9E+05	9.0E+05	1.1E+05	2.0E-08	0.1	9.2	87.9	2.8	0.1
Chrysene	4.0E-04	1.2E+14	2.4E+18	7.5E+18	5.4E+15	2.4E-21	0.0	9.2	88.1	2.8	0.0
Benzo(b) flouranthrene	4.0E-04	8.2E-01	4.3E+04	1.4E+05	6.1E+03	1.4E-07	0.9	3.5	92.7	2.9	0.0
Benzo(a) Pyrene	4.0E-04	2.0E+01	1.1E+07	3.3E+07	1.5E+05	5.9E-10	0.0	0.4	96.6	3.0	0.0
Indeno(1,2, 3-cd)pyrene	4.0E-04	3.3E+14	5.1E+19	1.6E+20	1.5E+16	6.9E-23	0.0	1.3	95.8	3.0	0.0
Dibenz(a,h) anthracene	4.0E-04	1.3E+03	4.3E+08	1.3E+09	5.9E+04	1.5E-11	0.0	0.6	96.4	3.0	0.0
Benzo(ghi) perylene	4.0E-04	7.0E+01	1.1E+07	3.4E+07	5.2E+05	5.8E-10	0.0	1.3	95.7	3.0	0.0

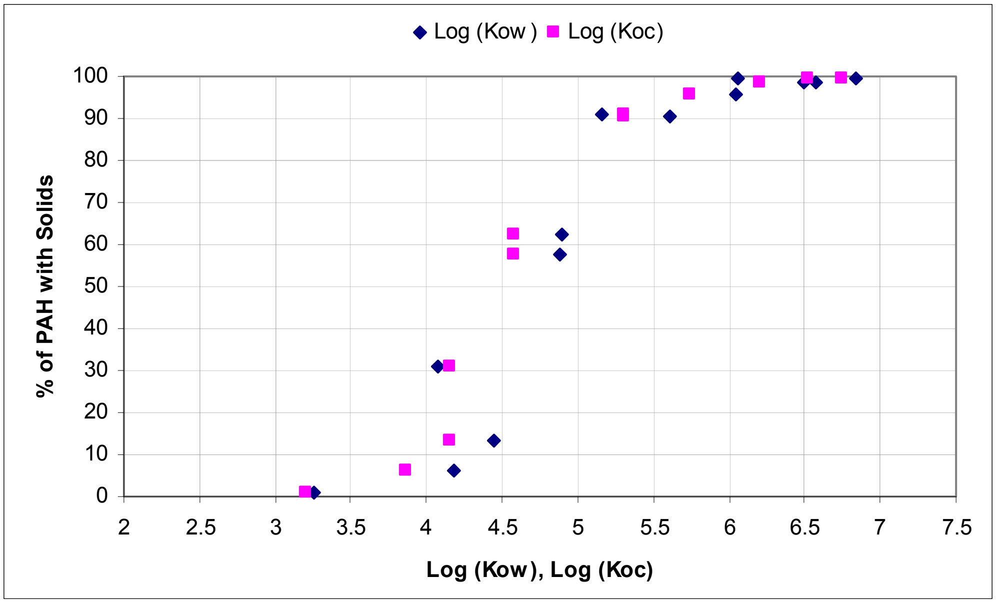


Figure 6-31. Percentage of PAH partitioning with solids versus PAH Log (K_{OW}), Log (K_{OC})

Multi Chamber Treatment Train (MCTT) Study: Particulate Bound PAHs and their Control

The Multi-Chambered Treatment Train (MCTT) was developed to control toxicants in stormwater from critical source areas (Pitt, *et al.* 1995 and 1999). The MCTT is most suitable for use at relatively small areas, about 0.1 to 1 ha in size, such as vehicle service facilities, convenience store parking areas, equipment storage and maintenance areas, and salvage yards. The MCTT is an underground device and is typically sized between 0.5 to 1.5 percent of the paved drainage area. It is comprised of three main sections, an inlet having a conventional catchbasin with litter traps, a main settling chamber having lamella plate separators and oil sorbent pillows, and a final chamber having a mixed sorbent media (usually peat moss and sand).

As a part of the MCTT study, Pitt, *et al.* (1995 and 1999) collected stormwater sheetflow samples from source areas in three different land uses (residential, commercial, and industrial) that were analyzed for PAHs, and other constituents to identify critical source areas of toxicants. Sheetflow samples were obtained from roofs, parking areas, storage areas, streets, vehicle service areas, landscaped areas, urban creeks, and detention ponds. All the samples collected were divided and analyzed twice: one split was analyzed un-filtered and the second split was filtered first through a 0.45 µm membrane filter to remove the particulate solids and analyzed to represent only the water-associated fraction of the PAHs. The particulate-associated fraction was determined by difference. PAH concentrations associated with the particulate solids were calculated using the particulate solids concentrations for each sample. Twenty-two of the 58 samples analyzed contained detectable PAH concentrations, but very few had detectable concentrations in the filtered sample fraction.

Table 6.23 shows the percentage of detection of individual PAHs in un-filtered (all phases combined) and filtered samples (aqueous phase alone). The decreased percentage of detection for the filtered samples compared to the un-filtered samples indicates the analytes are mostly associated with the particulate solids in the samples. The decrease in percentage of detection in the filtered samples is more common for the high molecular weight PAHs then for the low molecular weight PAHs, indicating that the high molecular weight PAHs have a greater portion associated with the particulates.

Table 6-23. Percentage of samples detected

	% of Samples Having Detected PAH Concentrations	
PAH	**In Un-filtered Samples**	**In both Un-filtered and Filtered Samples**
Naphthalene	16	12
Anthracene	9	2
Fluoranthene	26	12
Phenanthrene	12	0
Benzo(a)anthracene	12	0
Benzo(b)fluroanthene	22	0
Benzo(k)fluroanthene	22	0
Chrysene	9	0
Pyrene	19	7
Benzo(a)pyrene	22	0

Table 6-24 shows the treatment levels that have been observed during seven tests in Minocqua, WI (during one year of operation) and 15 tests in Milwaukee, WI (also during one year of operation), compared to the pilot-scale Birmingham, AL, test results (13 events). These data indicate high reductions for SS (83 to 98%), COD (60 to 86%), turbidity (40 to 94%), phosphorus (80 to 88%), lead (93 to 96%), zinc (90 to 91%), and for many organic toxicants (generally 65 to 100%). The reductions of dissolved heavy metals (filtered through 0.45 μm filters) were also all greater than 65% during the full-scale tests. None of the organic toxicants were ever observed in effluent water from either full-scale MCTT, even considering the excellent detection limits available at the Wisconsin State Dept. of Hygiene Laboratories that conducted the analyses.

Table 6-24. Performance of Full-Scale and Pilot-Scale MCTTs (median reductions and median effluent quality)

	Milwaukee MCTT (full-scale) (15 events)	Minocqua MCTT (full-scale) (7 events)	Birmingham MCTT (pilot-scale) (13 events)
suspended solids	98 (<5 mg/L)	85 (10 mg/L)	83 (5.5 mg/L)
volatile suspended solids	94 (<5 mg/L)	na[a]	66 (6 mg/L)
COD	86 (13 mg/L)	na	60 (17 mg/L)
turbidity	94 (3 NTU)	na	40 (4.4 NTU)
pH	-7 (7.9 pH)	na	8 (6.4 pH)
ammonia	47 (0.06 mg/L)	na	-210 (0.31 mg/L)
nitrates	33 (0.3 mg/L)	na	24 (1.5 mg/L)
Phosphorus (total)	88 (0.02 mg/L)	80 (<0.1 mg/L)	nd[b]
Phosphorus (filtered)	78 (0.002 mg/L)	na	nd
Microtox® toxicity (total)	na	na	100 (0%)
Microtox® toxicity (filtered)	na	na	87 (3%)
Cadmium (total)	91 (0.1 μg/L)	na	18 (0.6 μg/L)
Cadmium (filtered)	66 (0.05 μg/L)	na	16 (0.5 μg/L)
Copper (total)	90 (3 μg/L)	65 (15 μg/L)	15 (15 μg/L)
Copper (filtered)	73 (1.4 μg/L)	na	17 (21 μg/L)
Lead (total)	96 (1.8 μg/L)	nd (<3 μg/L)	93 (<2 μg/L)
Lead (filtered)	78 (<0.4 μg/L)	na	42 (<2 μg/L)
Zinc (total)	91 (<20 μg/L)	90 (15 μg/L)	91 (18 μg/L)
Zinc (filtered)	68 (<8 μg/L)	na	54 (6 μg/L)
benzo(a)anthracene	>45 (<0.05 μg/L)	>65 (<0.2 μg/L)	nd
benzo(b)fluoranthene	>95 (<0.1 μg/L)	>75 (<0.1 μg/L)	nd
dibenzo(a,h)anthracene	89 (<0.02 μg/L)	>90 (<0.1 μg/L)	nd
fluoranthene	98 (<0.1 μg/L)	>90 (<0.1 μg/L)	100 (<0.6 μg/L)
indeno(1,2,3-cd)pyrene	>90 (<0.1 μg/L)	>95 (<0.1 μg/L)	nd
phenanthrene	99 (<0.05 μg/L)	>65 (<0.2 μg/L)	nd
pentachlorophenol	na	na	100 (<1 μg/L)
phenol	na	na	99 (<0.4 μg/L)
pyrene	98 (<0.05 μg/L)	>75 (<0.2 μg/L)	100 (<0.5 μg/L)

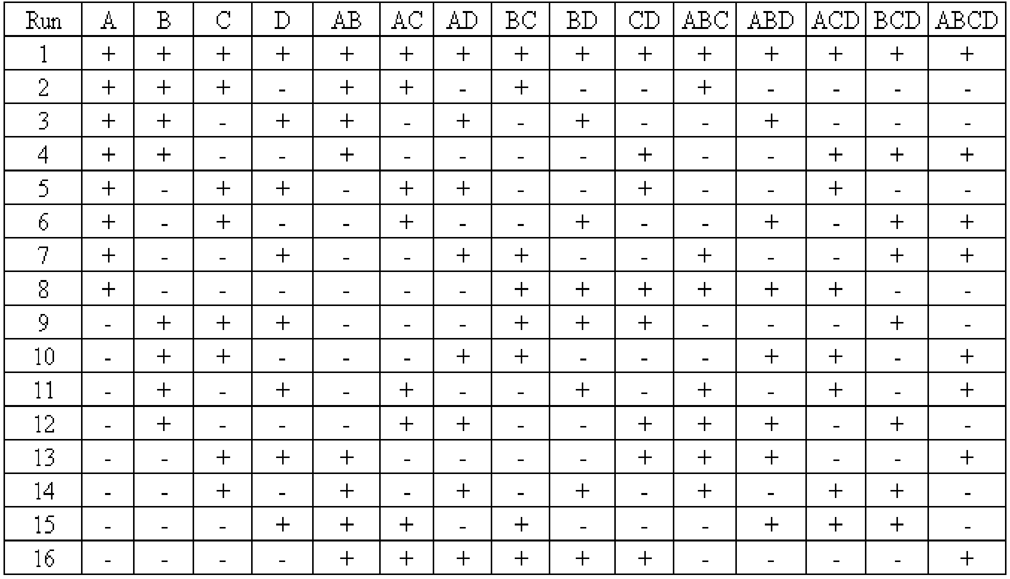
na[a] : not analyzed
nd[b]: not detected in most of the samples

The particulate bound pollutants were most effectively removed by the MCTT. Also, because of its chemically active media filter and relatively long residence time, significant reductions in filterable pollutants were also observed.

Studying the Effects of Environmental Factors on PAHs Associations with Particulate Material using Fugacity Calculations

The effects of assumed important environmental factors on the partitioning of the PAHs with different media were studied using a full 2^4 factorial experimental design (Box, *et al.* 1978). The factorial experimental design identifies the effects of individual variables, and also the effects of interactions of the variables, on the PAH concentrations. These effects were calculated using a table of contrasts. This table shows the averages of the differences between the sums of the analyte concentrations when the factor is at its maximum value and at its minimum value. Probability plots of the calculated effects for the factors identify those factors and interactions that are not likely associated with random processes. The design matrix used in this factorial study is shown in Table 6-25. The '+' and '-' sign in the matrix indicates the factor at its high and low respectively. The low and high values of the factors were chosen based on typical observations for stormwater and urban receiving waters, and are shown in the Table 6-26. Combination of factors, example ‘AB’ shows the interaction of ‘A’ factor and factor ‘B,’ similarly, for example ‘ABCD’ indicates the 4-way interaction of ‘A’, ‘B’, ‘C’, and ‘D.’

Table 6-25. 2^4 Factorial Design Showing Experimental Conditions for 16 Runs (Box et al. 1978)



Run	A	B	C	D	AB	AC	AD	BC	BD	CD	ABC	ABD	ACD	BCD	ABCD
1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
2	+	+	+	-	+	+	-	+	-	-	+	-	-	-	-
3	+	+	-	+	+	-	+	-	+	-	-	+	-	-	-
4	+	+	-	-	+	-	-	-	-	+	-	-	+	+	+
5	+	-	+	+	-	+	+	-	-	+	-	-	+	-	-
6	+	-	+	-	-	+	-	-	+	-	-	+	-	+	+
7	+	-	-	+	-	-	+	+	-	-	+	-	-	+	+
8	+	-	-	-	-	-	-	+	+	+	+	+	+	-	-
9	-	+	+	+	-	-	-	+	+	+	-	-	-	+	-
10	-	+	+	-	-	-	+	+	-	-	-	+	+	-	+
11	-	+	-	+	-	+	-	-	+	-	+	-	+	-	+
12	-	+	-	-	-	+	+	-	-	+	+	+	-	+	-
13	-	-	+	+	+	-	-	-	-	+	+	+	-	-	+
14	-	-	+	-	+	-	+	-	+	-	+	-	+	+	-
15	-	-	-	+	+	+	-	+	-	-	-	+	+	+	-
16	-	-	-	-	+	+	+	+	+	+	-	-	-	-	+

(+indicates factor at its high value, - indicates factor at its low value)

Table 6-26 Values Used in Factorial Analysis of Modeled PAH Associations

Variable	**Low value**	**High value**
Temperature (A), ^{o}C	5	25
Concentration of PAH compound (B), µg/L	10	300
Concentration of Suspended Solids(C), mg/L	10	500
Organic Fraction of Suspended Solids (D)	0.05	0.2

A hypothetical system with air, water, and suspended particulate matter phases was assumed to study the effects of selected factors on the partitioning with different phases. As an example anthracene analyses calculations are shown here. Table 6-27 shows the predicted portioned moles of anthracene into air, water and suspended particulate matter under different combinations of the factors of the 2^4 factorial design. Table 6-28 shows the calculated effects of different combinations of the factors in portioning of anthracene with air, water and suspended particulate matter.

Table 6-27. Model Predicted Partitioning of Anthracene with 2^4 Factorial Design Variables

Factor Value				Moles of Anthracene Partitioned with		
A	**B**	**C**	**D**	**Air**	**Water**	**Particulate Matter**
+	+	+	+	2.3E-13	2.8E-08	3.9E-08
+	+	+	-	4.2E-13	5.0E-08	1.8E-08
+	+	-	+	5.5E-13	6.5E-08	1.8E-09
+	+	-	-	5.6E-13	6.7E-08	4.7E-10
+	-	+	+	7.8E-15	9.3E-10	1.3E-09
+	-	+	-	1.4E-14	1.7E-09	5.9E-10
+	-	-	+	1.8E-14	2.2E-09	6.2E-11
+	-	-	-	1.9E-14	2.2E-09	1.6E-11
-	+	+	+	8.0E-14	1.6E-08	5.1E-08
-	+	+	-	7.8E-14	1.6E-08	5.2E-08
-	+	-	+	3.1E-13	6.3E-08	4.0E-09
-	+	-	-	3.3E-13	6.6E-08	1.0E-09
-	-	+	+	2.7E-15	5.4E-10	1.7E-09
-	-	+	-	6.2E-15	1.3E-09	9.9E-10
-	-	-	+	1.0E-14	2.1E-09	1.3E-10
-	-	-	-	1.1E-14	2.2E-09	3.5E-11

Table 6-28. Calculated Effects of Factors and their Interactions on the Associations of Anthracene with Different Media

Factors/ Interactions	Calculated Effect		
	Air	**Water**	**Suspended Solids**
A	1.0E-13	6.2E-09	-6.2E-09
B	3.9E-13	4.5E-08	2.0E-08
C	-2.5E-13	-2.0E-08	2.0E-08
D	-2.7E-14	-3.4E-09	1.2E-08
AB	8.0E-14	6.0E-09	-6.0E-09
AC	3.0E-15	5.5E-09	-5.5E-09
AD	-2.3E-14	-2.6E-09	2.6E-09
BC	-1.9E-13	-1.9E-08	1.9E-08
BD	-2.5E-14	-3.0E-09	3.0E-09
CD	-2.0E-14	-2.3E-09	2.3E-09
ABC	3.7E-15	5.3E-09	-2.3E-09
ABD	-2.2E-14	-2.6E-09	2.6E-09
ACD	-2.4E-14	-3.0E-09	3.0E-09
BCD	-1.8E-14	-2.0E-09	1.1E-09
ABCD	-2.3E-14	-3.0E-09	3.0E-09

Figures 6-32 through 6-34 are probability plots of the effects of the factors and their interactions on partitioning anthracene into the three main phases. The probability plot for the air phase (Figure 6-32) indicates that the concentration of anthracene (or total amount of anthracene) (B) in the system has positive effects in partitioning of anthracene into the air phase. However, the concentration of suspended particulate matter (C), and combinations of suspended particulate matter concentration and anthracene concentration (BC) have negative effects on anthracene portioning into the air. In the case of partitioning into the water phase (Figure 6-33), the concentration of anthracene (B) was found to have the greatest positive effect, and the concentration of the suspended particulate matter (C) had a significant negative effect (the higher the particulate matter concentration, more of the anthracene is associated with the sediment). Figure 6-34 shows the probability plot of effects of anthracene partitioning with suspended particulate matter. The significant factors were the concentration of the anthracene (B) and the concentration of the particulate matter (C). The organic content (D) of the particulate matter also affects the partitioning of the anthracene with suspended particulate matter, but to a lesser extent. Similar results were also found during the factorial analyses of benzo(a)anthracene.

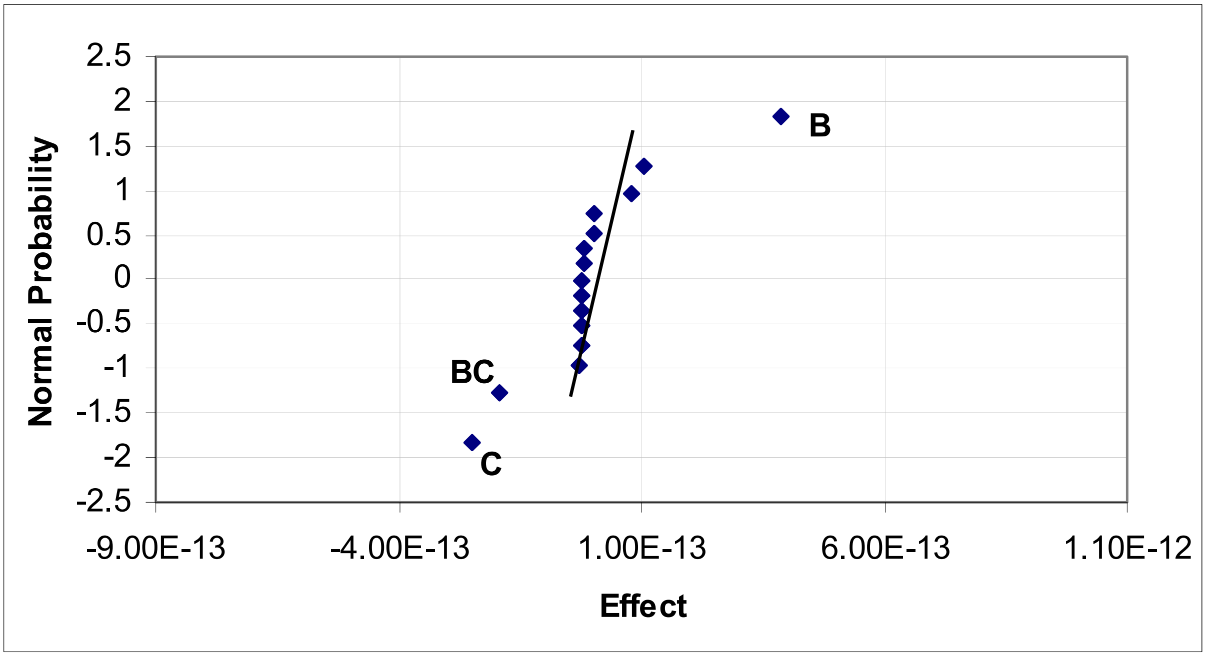


Figure 6-32. Probability plot of effects of partitioning of Anthracene with air.

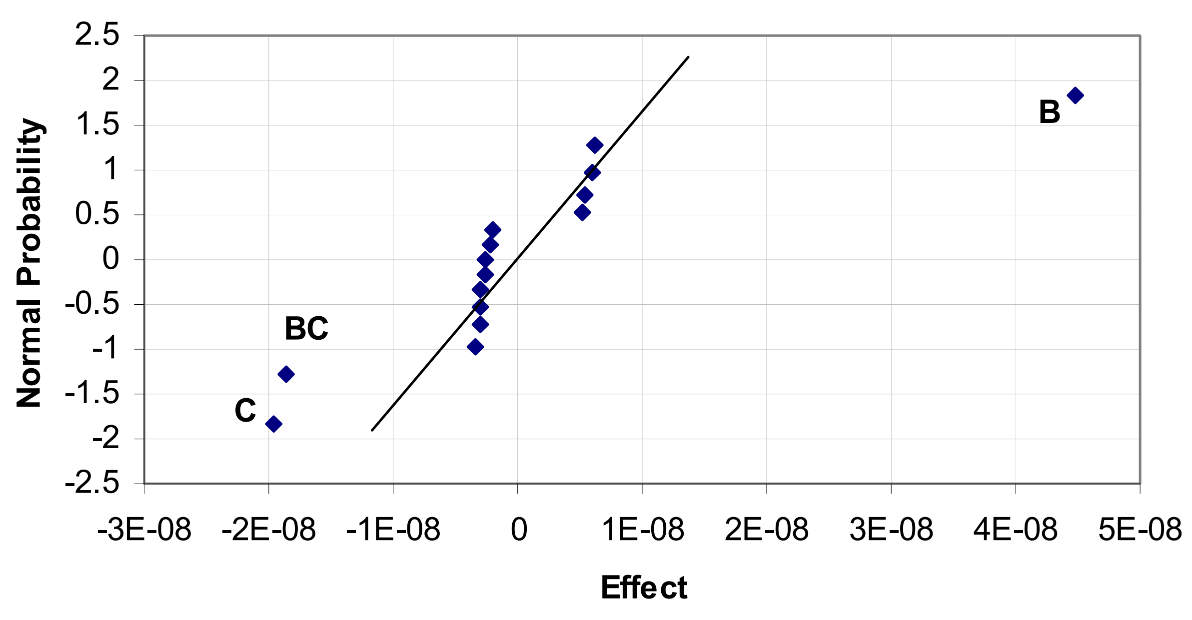


Figure 6-33. Probability plot of effects of partitioning of Anthracene with water.

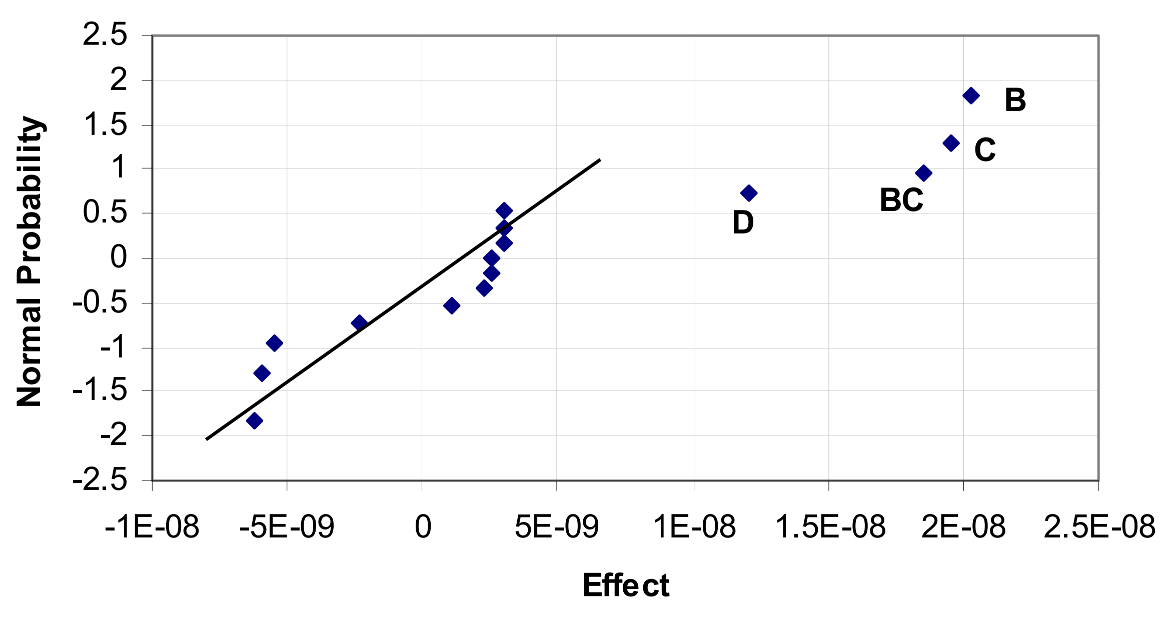


Figure 6-34. Probability plot of effects of partitioning of Anthracene with suspended particulate matter.

Conclusions for Fugacity Modeling of PAHs and Associations with Particulates

MacKay's level I fugacity model was used to predict portioning fractions of selected PAHs associated with different phases (water, sediment, air, biota). This modeling approach indicated that except for the low molecular weight PAHs (naphthalene, fluorene, phenanthrene, and anthracene) all the other studied PAHs are predominantly portioned with the sediment phase. The level I fugacity model, which assumes system equilibrium, was found to under predict the PAH portioning with the particulate matter when compared with observed particulate and filtered PAH observations from prior research that examined stormwater treatment of PAHs. A 2^3 full factorial design study was conducted for an air, water and suspended solids hypothetical system for anthracene and benzo(a)anthracene and chrysene. In this example, PAHs were found to partition into all three phases, and its behavior was mainly affected by their initial concentration in the system components.

Site Descriptions for Urban Stream Sediment Sampling

Sediment samples were collected from three different creeks in and around Tuscaloosa and Northport, AL, for PAH analyses by particle size.

Cribbs Mill Creek

Cribbs Mill Creek is an urban creek in Tuscaloosa, Alabama which originates at a small stormwater runoff ditch at the Veterans Affairs Hospital on Veterans Memorial Parkway. Cribbs Mill Creek then joins Cypress Creek at Friday Lake before emptying into the Black Warrior River. A sampling point along the creek was chosen in a concrete lined channel in a residential neighborhood. Medium density single-family dwellings are located on both sides of this concrete lined creek channel. The chosen sampling point is towards the downstream end of the concrete channel reach which is a few hundred feet long. The sediment (bed load) on the concrete channel is therefore mainly affected by the runoff from the surrounding residential areas, with minimal bank erosion material. This creek was extensively studied by Pitt, *et al.* (2004) as part of an EPA study on inappropriate discharges. No sanitary sewage discharges were ever identified along this creek during this prior three year study.

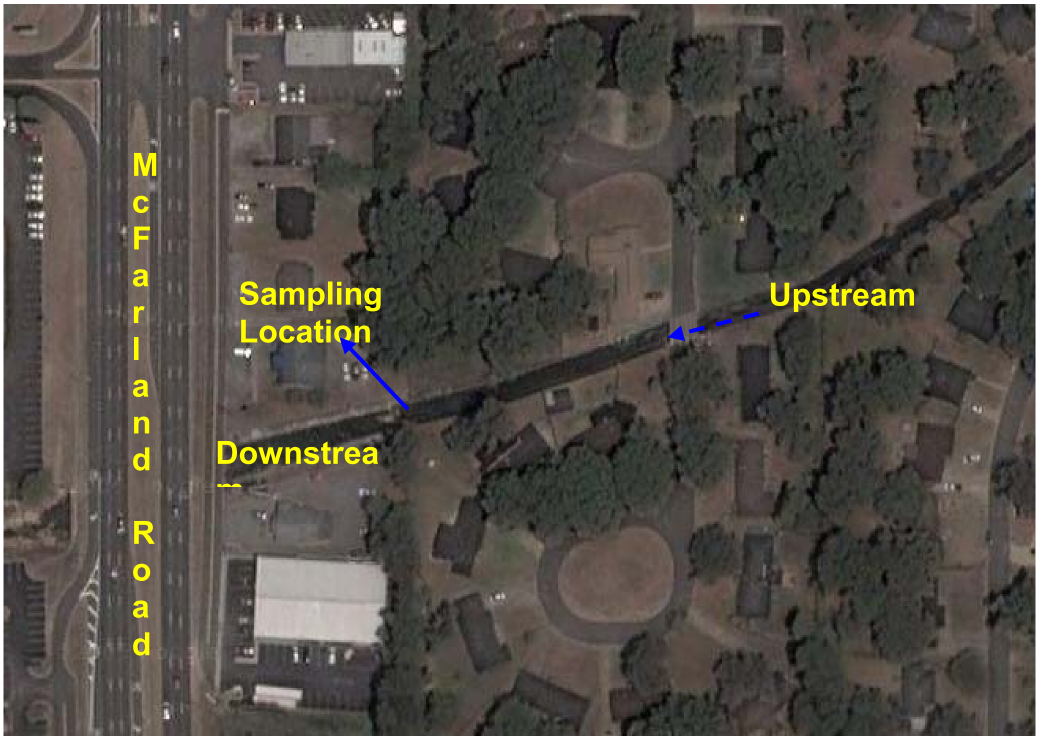


Figure 6-35. Aerial photograph of Cribbs Mill Creek, sampling point (Source: Googlemap, www.google.com)

Figure 6-36. Concrete channel along Cribbs Mill Creek

Hunter Creek
Hunter Creek is an urban creek whose watershed area is within the cities of Tuscaloosa and Northport, AL. Hunter Creek originates in Tuscaloosa County and passes through the Northport city limits before joining the Black Warrior River. The sediment at the

sampling location is mostly affected by runoff from McFarland Blvd, which has heavy traffic, and adjacent commercial areas, and trailer park residential areas. Observations at the site indicate that an outfall from an automobile maintenance shop is directly affecting the sediment at the sampling location. The PAH analyses results from this sampling location represent PAH contamination in creek sediments affected by commercial sources.

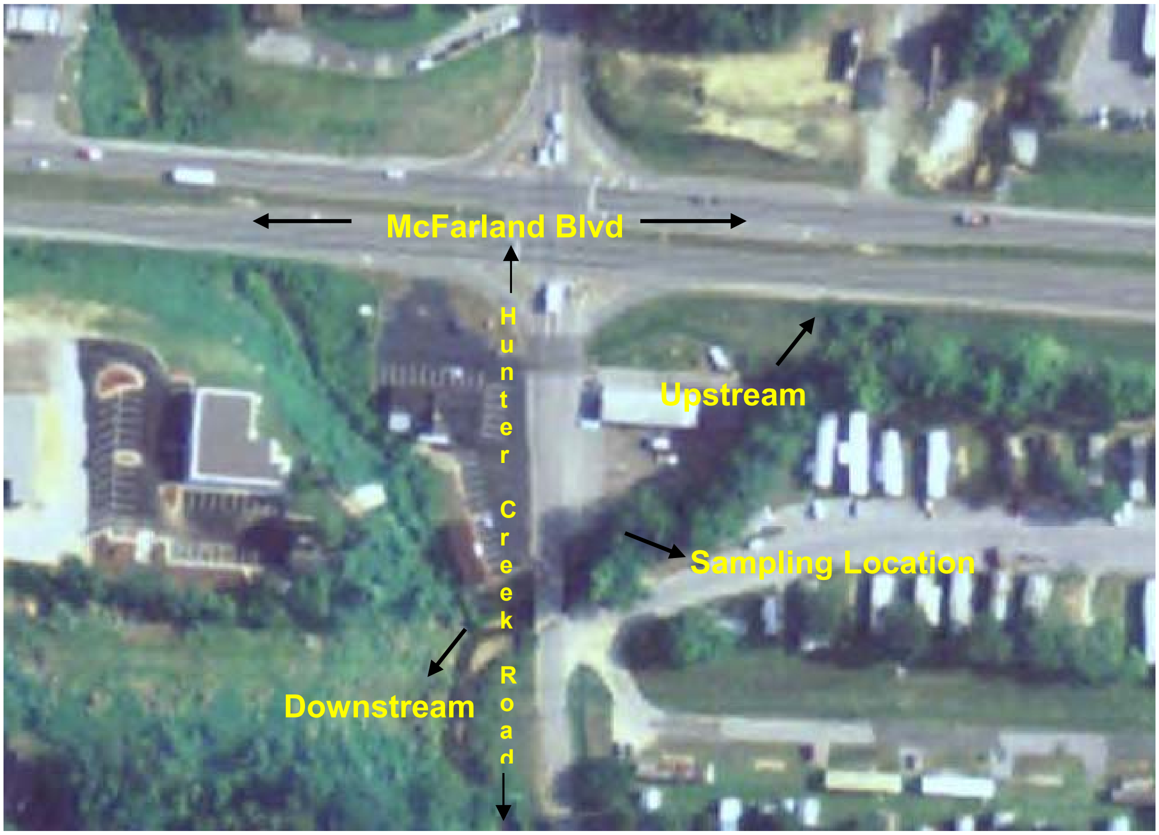


Figure 3-37. Aerial photograph of Hunter Creek sampling location (Google Earth photo)

Figure 3-38. Sampling location at Hunter Creek

Figure 3-39. Layer of grease material at the outfall of automobile maintenance shop which is entering Hunter Creek adjacent to the sampling location

Caroll Creek

Carroll Creek is located in Northport and Tuscaloosa, although most of the watershed is in Northport. The sediment at the sampling location chosen along the creek is directly affected by runoff from a high density residential area on one side of creek and forested lands on the other side of the creek. The residential area near the sampling location has a recent history of sanitary sewer overflows (SSOs). As indicated in Consent Order NO. 07-139-CWP from the Alabama Department of Environmental Management (ADEM) to the City of Northport issued in July 2007, there were three SSO incidents during 2006 at the residential area near the sampling location. In February 2006 sewage overflowed into the creek during an intense lightning storm having high intensity rains. A reported 42,000 gallons of sewage overflowed at this location and entered the creek. The second incident was in March 2006, when a wastewater line ruptured and leaked 2,000 gallons of sewage into the creek. The third reported incident was in July 2006 when 30,000 gallons of SSO discharged into the creek due to a sewer pump failure in the neighborhood.

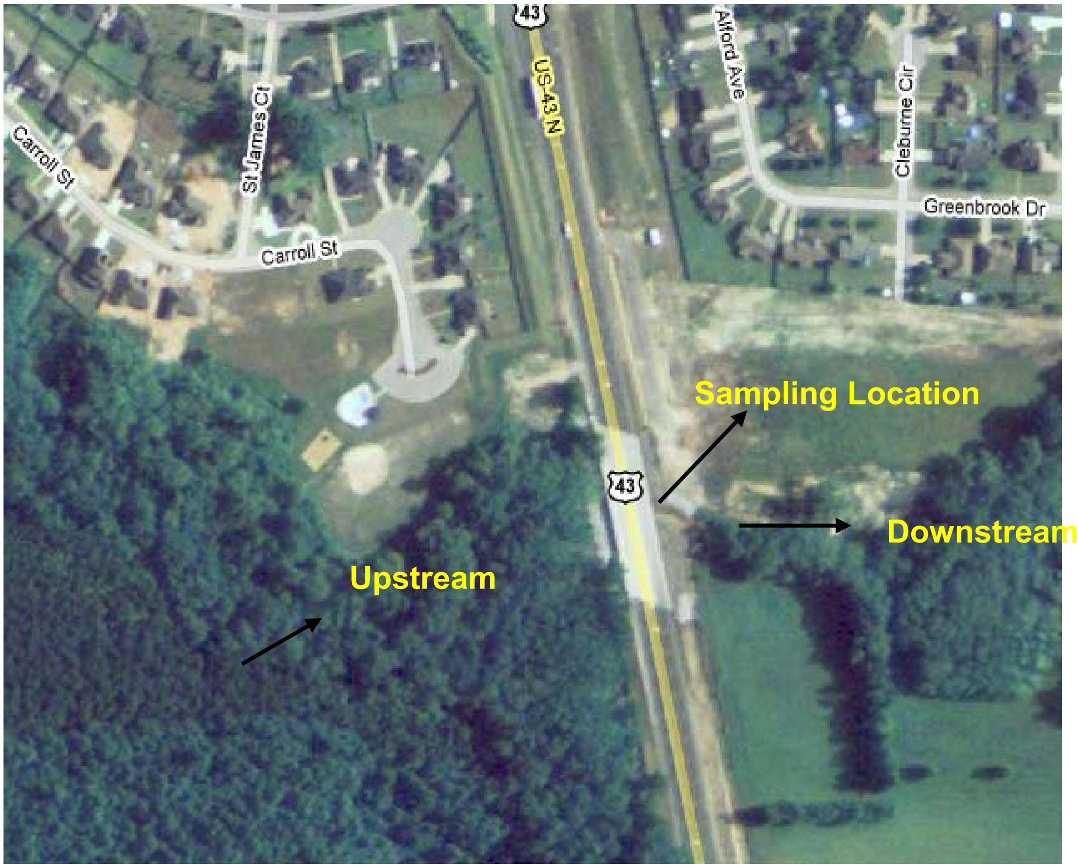


Figure 6-40. Carroll Creek sampling location aerial view (Google Earth photo).

Figure 6-41. Closer view of sampling location along Carroll Creek.

Figure 6-42. Residential area along Carroll Creek.

Thermal Chromatography

A thermal chromatography method was developed by Ray (1997) to identify the components of urban dirt samples. This method was used to identify the major components of the sediment samples. A known amount of sediment sample was placed in a crucible that was heated progressively to higher temperatures, at set intervals, from 105 to 550°C. The heating process started with a temperature of 105°C to dry the samples. After 105°C, 240°C was the next temperature, then 365°C, then 470°C, and finally 550°C to complete the process. A heating time of 1 hour at each temperature was maintained to ensure stable weights. After each heating interval, the crucible (with sample) was cooled and weighed in order to determine the percent mass burned off since the last temperature. Table 6-29 shows the corresponding temperatures where different materials were combusted, based on Ray's (1997) earlier work. Material lost between 240 and 365°C indicates the amount of leaves and grass associated with each particle size that may preferentially sorb PAHs, while material lost between 365 and 550°C indicates rubber and asphalt that likely has substantial PAH as part of the component material.

Table 6-29. Ray (1997) Thermal Chromatography Method Parameters

Temperature (°C)	**Material Lost at These Temperatures**
up to 104	Moisture
104 – 240	Paper debris
240 – 365	Leaves and grass
365 – 470	Rubber
470 – 550	Asphalt
Above 550	Remaining material is inert

A composite sediment sample from the five sediment samples collected at each sampling location was prepared and subjected to the thermal chromatography analysis. Figure 6-43 compares the percentage of the total weight loss for up to 550°C for the different particle sizes and three sampling locations. Almost all of the material was inert, except for the large leaf fraction. The sediment samples from Cribbs Mill Creek are found to have highest weight loss indicating that those sediment samples had higher proportions of combustible components compared to the sediment samples from other two creeks. Figure 6-44 compares the weight losses associated with the temperature range 240 – 365°C associated with organic material such as leaves and grass.

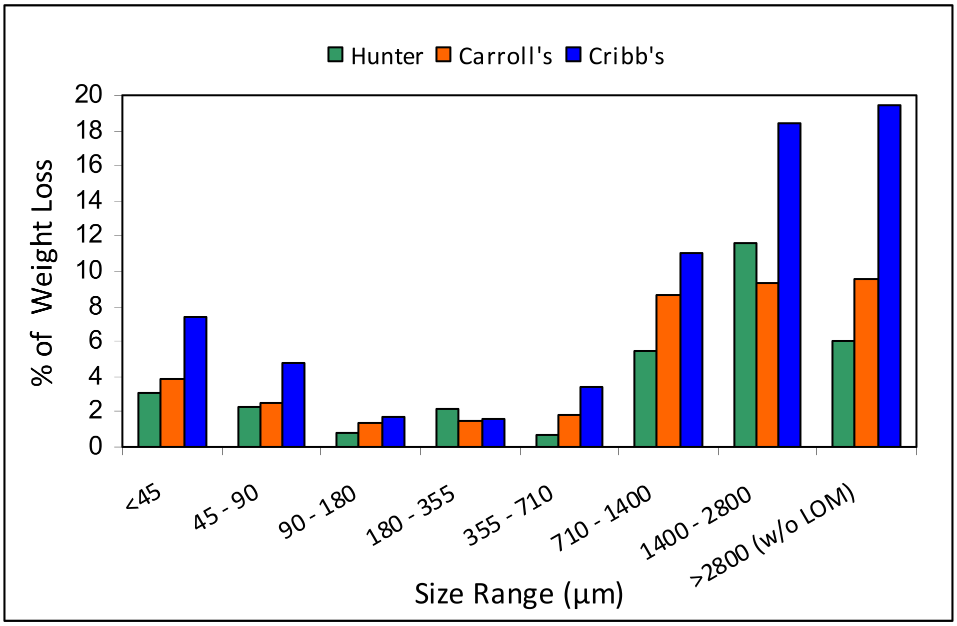


Figure 6-43. Comparison of weight loss over temperature range of 104 – 550°C (total volatile content)

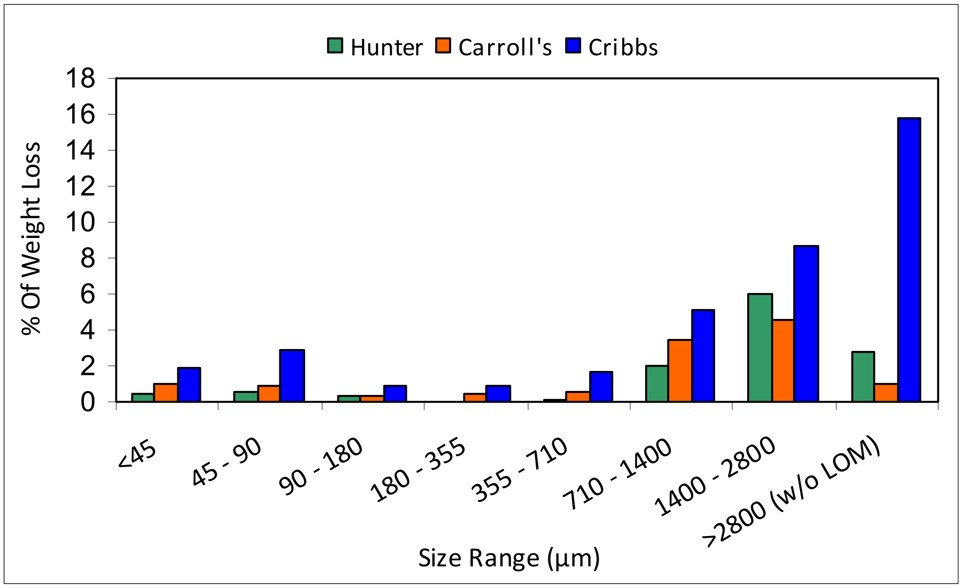


Figure 6-44. Comparison of weight loss over temperature range of 240 – 365°C (leaves and grass)

The thermal chromatography results show that the sediment samples from Cribbs Mill Creek, which did not have any indications of sewage contamination, were associated with the highest weight loss over the temperature range of 240 – 365°C and hence are associated with higher proportions of organic material compared to the other two creeks. Cribbs Mill Creek sediment samples did not have much mass contributions from bank erosion soil material, as the sampling reach was concrete-lined. There was an obvious greater amount of algae present on the channel lining in Cribbs Mill Creek than in the other creeks. Lower proportions of organic material from Carroll's Creek may be due to the sediments at the sampling point were diluted with inert eroded material from eroding stream banks, and the organic material from the sewer overflows were long scoured and transported from the area of historical contamination.

Comparing PAH Concentrations for Different Particle Sizes of Urban Creek Sediments

All the collected samples (15 in total) were separated into nine size fractions ranging from < 45 µm to > 2800 µm. The sediment size fraction 180 – 355 µm was predominant in the samples from all three locations. For samples from Cribbs Mill Creek and Hunter Creek, most of the sediment was distributed in the size range of 180 to 710 µm, whereas most of the particles in the samples from Carroll Creek were between 90 to 355 µm. In addition to runoff water sources of sediments, creek bank erosion might have introduced sediment particles at the sampling locations (likely coarser than particles in typical runoff samples). Creek bank erosion would only be applicable to sampling locations along Hunter and Carroll creeks, as the Cribbs Mill Creek location was a concrete lined channel section. Due to the high density urban development sources of Cribbs Mill and Hunter creeks, these sampling locations were likely affected by high velocity flash floods that could cause increased bank erosion.

All individual sediment fractions were analyzed by TD/GC/MS for PAHs. Thirteen PAHs were selected for quantification as being more harmful than others in the group and also found to be most abundant in urban stormwater during earlier stormwater research (Pitt, *et al.* 1995). These analyses yielded a data set containing 1,755 PAH determinations (15 samples x 9 size fractions x 13 PAHs). Mean concentrations of the PAHs by sediment size fractions and by sampling location are presented in the Tables 6-30 through 6-32 (individual PAH results by sediment size fraction and by creek can be found in Bathi 2008). As for most laboratory analyses, the analytical results presented in the tables are not corrected for the method recovery.

Table 6-30. Mean PAH Concentrations with Standard Deviations (n[a] = 5) , PAH Total Weight, Mean Weight (as percent) of Sediment Size Fractions, of Different Particle Sizes (µm) of Cribb Mill Creek Sediment Samples

Sediment Size Fraction (µm)	<45		45 - 90		90 - 180		180 - 355		355 - 710		710 - 1400		1400 - 2800		>2800 (W/O LOM)		>2800 LOM	
	Mean	SD[b]	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
% of Sediment Dry Weight	0.5	0.3	1.9	1.2	10.9	6.6	38	15	23.7	9.8	12.4	8.9	6.9	3.9	5.7	5.8	1.4	0.5
Naphthalene	436	384	266	200	361	305	135	81	133	130	1917	3483	2143	3338	149	69	2241	1361
Fluorene	223	273	96	71	262	217	169	209	193	209	190	165	303	198	174	85	2117	751
Phenanthrene	135	89	96	64	124	55	58	41	60	28	145	147	332	355	219	234	2817	1838
Anthracene	283	184	246	126	162	169	84	83	287	250	502	276	955	921	231	146	2292	1254
Fluoranthene	238	116	307	145	183	83	117	44	143	10	280	89	355	110	140	88	1944	847
Pyrene	327	177	271	117	225	190	123	57	126	98	219	84	227	105	257	179	2181	769
Benzo(a) anthracene	315	231	280	172	318	276	240	233	207	188	185	146	344	355	443	630	2932	1138
Chrysene	310	205	429	349	331	231	186	113	199	126	253	157	353	305	151	105	2420	792
Benzo(b) fluoranthrene	597	289	257	187	309	194	915	1002	236	98	569	129	635	483	543	588	2491	1405
Benzo(a)pyrene	621	258	596	205	689	199	801	711	388	197	872	734	2559	3321	645	253	2589	1336
Indeno(1,2,3-cd) pyrene	647	165	543	273	1271	908	332	199	435	213	578	436	1205	1393	320	235	2142	1022
Dibenz(a,h) anthracene	607	350	570	451	765	550	390	256	446	287	1085	572	1650	1952	371	265	1954	891
Benzo(g,h,i) perylene	509	303	324	223	444	506	136	36	132	50	677	782	499	360	433	181	1841	1190
$\sum$PAHs$_{13}$ (µg/Kg)	5248		4281		5444		3686		2985		7472		11560		4076		29961	
Mass of $\sum$PAHs$_{13}$ (µg)	26		81		593		1401		707		927		798		232		419	

[a] = Number of Samples; [b] = with the large organic matter removed; [c] = Standard Deviation

Table 6-31. Mean PAH Concentrations with Standard Deviations ($n^a = 5$), PAH Total Weight, Mean Weight (as percent) of Sediment Size Fractions, of Different Particle Sizes (µm) of Hunter Creek Sediment Samples

Sediment Size Fraction (µm)	<45		45 - 90		90 - 180		180 - 355		355 - 710		710 - 1400		1400 - 2800		>2800 (W/O LOM[b])		>2800 LOM	
	Mean	SD[c]	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
% of Sediment Dry Weight	0.2	0.1	0.5	0.3	3.5	2.4	43.7	8.6	47.2	11.1	2.8	1	0.5	0.2	1.6	1.7	0.4	0.3
Naphthalene	130	83	96	60	70	66	78	115	97	92	193	204	238	207	95	65	4053	2967
Fluorene	406	424	310	153	259	221	80	68	109	99	166	178	380	196	145	67	1339	965
Phenanthrene	566	283	435	210	218	239	155	110	150	107	190	176	174	134	155	104	1285	881
Anthracene	562	632	542	323	474	257	248	229	172	146	424	414	265	188	281	200	2515	783
Fluoranthene	1656	864	1489	724	762	379	431	318	543	476	433	317	287	259	308	251	1069	605
Pyrene	1548	575	1188	408	915	798	302	252	488	665	274	222	220	151	135	89	1700	832
Benzo(a) anthracene	1092	706	862	750	418	380	201	163	362	321	174	148	292	256	132	89	1693	804
Chrysene	1215	709	1214	871	585	495	348	276	475	384	189	108	312	236	131	123	1217	480
Benzo(b) fluoranthrene	1049	586	1111	708	617	582	249	227	294	210	327	231	289	311	249	229	1744	1647
Benzo(a)pyrene	3549	2979	3689	4923	525	262	380	326	326	213	390	277	550	448	300	188	2329	2939
Indeno(1,2,3-cd) pyrene	945	773	917	820	339	359	244	105	370	156	782	1262	661	628	569	682	1248	764
Dibenz(a,h) anthracene	2810	2739	1646	1399	469	472	296	283	375	239	500	270	599	569	314	163	1091	445
Benzo(g,h,i) perylene	1329	870	810	598	490	498	375	381	228	126	502	524	396	362	369	349	3178	2513
$\sum PAHs_{13}$ (µg/Kg)	16857		14309		6141		3387		3989		4544		4663		3183		24461	
Mass of $\sum PAHs_{13}$ (µg)	34		72		215		1480		1883		127		23		51		98	

[a] = Number of Samples; [b] = with the large organic matter removed; [c] = Standard Deviation

Table 6-32 . Mean PAH Concentrations with Standard Deviations ($n^a = 5$) , PAH Total Weight, Mean Weight (as percent) of Sediment Size Fractions, of Different Particle Sizes (µm) of Carroll Creek Sediment Samples

Sediment Size Fraction (µm)	<45		45 - 90		90 - 180		180 - 355		355 - 710		710 - 1400		1400 - 2800		>2800 (W/O LOM[b])		>2800 LOM	
	Mean	SD[c]	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
% of Sediment Dry Weight	2.6	1.1	6.1	1	29.1	4.4	48.5	3.6	6.5	1.1	3.1	0.7	2.5	0.7	1.6	0.5	0.1	0.1
Naphthalene	199	214	171	152	59	71	70	57	143	181	261	326	294	271	129	92	1617	936
Fluorene	144	76	163	66	137	94	126	103	108	84	244	82	197	70	329	234	1860	1113
Phenanthrene	92	105	86	91	58	21	69	98	111	83	57	24	87	51	192	161	1920	1200
Anthracene	218	185	77	30	69	33	130	94	87	88	138	128	256	180	144	88	1959	1332
Fluoranthene	85	46	79	65	91	71	60	55	58	30	66	56	69	26	128	91	1549	1133
Pyrene	84	75	99	110	98	95	101	92	107	78	130	112	131	104	125	71	2283	1289
Benzo(a) anthracene	97	61	84	81	72	84	67	39	104	53	142	138	178	115	261	132	1868	868
Chrysene	247	246	163	180	172	234	72	47	144	94	113	71	223	212	231	163	1792	881
Benzo(b) fluoranthrene	148	136	184	232	150	111	42	30	152	114	51	47	200	127	196	81	2301	1429
Benzo(a)pyrene	253	142	287	207	771	769	120	110	329	274	178	145	248	233	230	66	2073	1262
Indeno(1,2,3-cd) pyrene	769	596	473	278	1282	719	197	232	190	125	317	244	251	198	181	108	1931	935
Dibenz(a,h) anthracene	382	180	146	41	790	658	141	84	245	111	522	561	257	228	173	65	1432	797
Benzo(g,h,i) perylene	277	180	210	148	818	1004	121	107	147	148	455	408	293	160	242	72	1689	1020
$\sum PAHs_{13}$ (µg/Kg)	2995		2222		4567		1316		1925		2674		2684		2561		24274	
Mass of $\sum PAHs_{13}$ (µg)	78		136		1329		638		125		83		67		41		24	

[a] = Number of Samples; [b] = with the large organic matter removed; [c] = Standard Deviation

The PAH concentrations for the different size fractions were highly variable, which is similar to the variations found in PAH concentrations of runoff water samples and urban stormwater pond sediments (Polta, *et al.* 2006; Lau, *et.al*. 2009; Weinstein, *et al*. 2009). One-way ANOVA analyses to test the differences of the PAH concentrations for different particle sizes indicated significant differences in PAHs concentration for particle sizes ($p<0.05$, except for naphthalene at Cribbs Mill Creek; and benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene at Hunter Creek). Additionally, cluster analyses of the sediment PAH data by particle size fractions indicated that for most of the analytes, the >2800µm LOM fraction was a separate group compared to all the other sizes combined (analyses results presented by Bathi 2008). These results all demonstrated that generally, smaller sized and larger sized particles (especially in large organic material, LOM) were associated with higher concentrations of selected PAHs compared to medium sized particles. Observed higher concentrations in the LOM fraction were similar to the trend noted by Rushton (2006). Also prior fugacity modeling by Bathi, *et al*. (2007) showed strong associations of PAHs with the organic content of the particulates in aquatic systems, further supporting the observed higher concentration of PAHs in the leaf fractions.

Boehm and Farrington (1984) reported a direct positive relationship between PAH content and the silt/clay fraction of sediments. Higher concentrations of PAHs in the smaller size fractions were believed to be related to higher organic content and larger surface areas of these fractions. The observed bimodal distribution of the PAH concentrations by sediment particle size is similar to the distribution observed for volatile content of sediment fractions. Overall, all analytes were enriched mostly in the smaller sized particles compared to the larger size particles, excluding the LOM fraction. This trend is very evident for the high molecular weight analytes. This observation was similar to the trend reported by Krein and Scholer (2000) for high molecular weight PAHs in road runoff samples. Although the smaller (< 90 µm) and larger (> 710 µm) size fractions of creek sediments were found to contain the highest levels of PAHs, these fractions only represented small fractions of the total sediment mass, hence, only a small PAH load is associated with these extreme size fractions.

Hunter Creek has significantly higher concentrations for many PAHs, especially for the small particle sizes, followed by Cribbs Mill Creek. For smaller sized particles, the observed PAH trend by location is similar to the trend noticed by Banger, *et al.* (2010) in Miami, FL, with commercial areas having the highest PAH concentration, and residential and open lands having the lowest PAH concentrations. For larger sized particles, Cribbs Mill Creek sediment samples have higher PAH concentrations than found in Hunter and Carroll creeks. Hunter Creek sediments are impacted by discharges from a creek-side automobile repair shop, the likely source of the higher PAH concentrations in the sediment samples at that location. However, visual observations at the Hunter Creek sampling location also indicate eroded creek bank material composed of mainly of larger particles. This erosion material is believed to be diluting any larger sediment particles from contaminated sources, resulting in lower PAH concentrations of the larger size fractions at this location.

The total concentrations of the thirteen PAHs (as shown on Figure 6-45), calculated based on mean concentrations and mean weight of the sediment fractions, were about 5,200 µg, 4,000 µg and 2,500 µg per kilogram of sediment samples dry weight for Cribbs Mill Creek, Hunter Creek and Carroll Creek, respectively. PAH enriched 710 – 1400 µm and 1400 – 2800 µm size fractions from Cribbs Mill Creek, resulted in higher levels of total PAHs in sediment samples than in the commercial source area Hunter Creek sediments. Observed total PAHs for the creeks were in the lower range of literature published PAHs concentrations for urban sediments. Polta, *et al*. (2006) noted total PAHs concentration (of the same thirteen PAHs together) ranging from 200 µg to 65,800 µg per kilogram of dry sediment for samples collected from ten different sites of stormwater ponds and lakes from the Twin Cities metropolitan area, Minnesota. Similarly, Weinstein, *et al*. (2009) has reported total PAH concentrations of sixteen stormwater pond sediments ranging from 186 µg to 159,000 µg per kilogram of dry sediment.

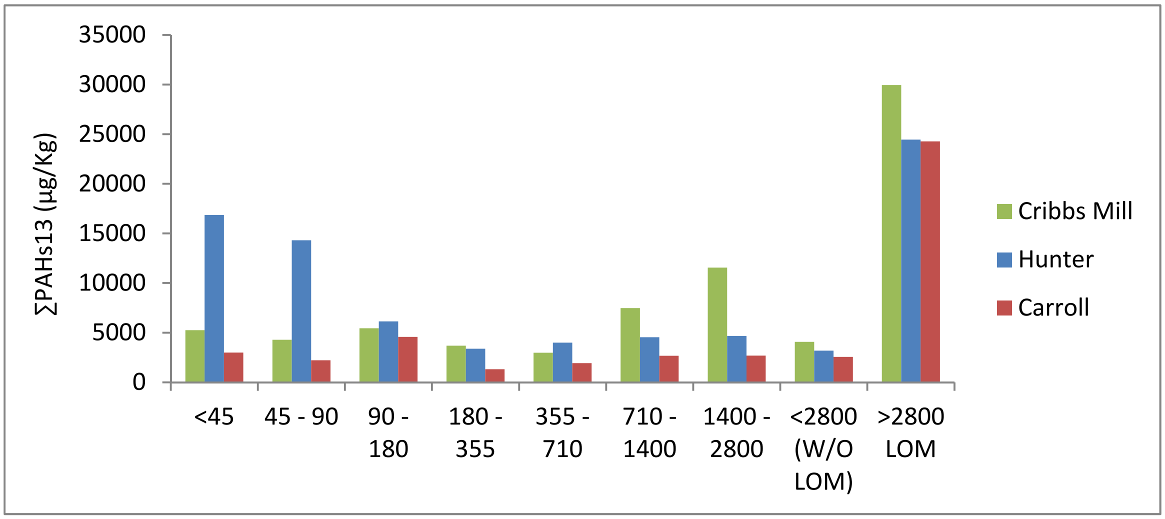


Figure 6-45. Observed Total Concentrations of PAHs by Sediment Size Fractions (µm) for Three Sampling Locations

Conclusions for PAH Treatability and Associations with Urban Stream Sediments

Fugacity level I partitioning calculations were performed for the PAHs in a hypothetical environmental system. This modeling approach indicated that, except for the low molecular weight PAHs (naphthalene, fluorene, phenanthrene, and anthracene), all the other studied PAHs were predominantly portioned with the sediment phase. The model predictions also indicated that the PAHs with Log (K_{OW}) or Log (K_{OC}) values greater than about 4.5 were mostly partitioned with the sediment phase, compared to other phases. The particulate and filterable PAH stormwater concentration data from prior field observations were compared to modeled values. The analytes were mostly associated with the particulate solids in the field samples. The high molecular weight PAHs had a greater portion associated with the particulates than the low molecular weight PAHs.

Sediment characteristics (particle sizes, sediment COD and material composition of the sediment) were measured and studied. Overall, all characteristics studied showed similar trends, the smaller and larger particles were found to have relatively higher values compared to the intermediate sized particles. A strong linear relationship was seen between the calculated CODs and combustible material associated with each particle size. Cluster analyses of the PAH concentrations for the different particle sizes showed that for most cases examined, the LOM fraction was found to be separate (having much higher concentrations) from all other sizes. When examining the other particle sizes (besides the large-sized LOM), Hunter Creek sediments were much greater than the other creeks, especially for the smaller particle sizes. PAH concentrations for the other two creeks were more inconsistent by particle size.

Fugacity modeling, reviews of available data, and the field measurements all strongly demonstrate that most PAHs preferentially associate with particles compared with other phases in aquatic systems. COD and the combustible fraction of the sediments were found to have no consistent effect on the PAH concentrations, except for the large-sized LOM material.

The sediments at Cribbs Mill Creek, Hunter Creek, and Carroll Creek were mainly affected by runoff from residential, commercial and residential areas, respectively. The sediment at Carroll Creek also had a past history of sewage contamination due to SSOs. Other than naphthalene, fluorene, phenanthrene and indeno(1,2,3-cd)pyrene, all the other PAH analytes were affected by the location of the sediment samples. One-way ANOVA of the concentrations on different particles comparing the locations showed that for most of the analytes there were more significant differences between the creek locations for the smaller particle sizes (<45 and 45 – 90 μm) than for the other sizes. Using probability plots and other graphical analyses, Hunter Creek was found to have significantly higher concentrations than the other creeks, especially for the small particle sizes. Hunter Creek sediment had a history of contamination of hydrocarbons from creek-side businesses that caused the increased PAH concentrations. Cribbs Mill Creek generally had higher PAH concentrations than the historically sewage contaminated Carroll Creek sediments. This may be due to the long time since the Carroll’s Creek sediments were affected by the SSOs and that the Cribbs Mill Creek sampling location was in a long concrete channel. The channel had no bank erosion material affecting the sediment concentrations, and the concrete lining had obvious algae levels that could have preferentially sorbed PAHs. In addition, the contaminated sediment at Carroll’s Creek either was flushed from the contamination site, or the contaminated sediment may be buried below the surface sampling depth.

Summary of Other Potential Sources of PAHs and Their Characteristics and Fates in Urban Areas

This report section summarized several related research tasks that investigated some potential PAH sources in urban areas (asphalt degradation and petroleum spills), urban stormwater PAH characteristics and their treatability, and the fate of discharged PAHs focusing on urban stream sediments. PAHs are ubiquitous environmental contaminants;

sources of PAHs can be broadly classified as pyrogenic (combustion origin) and petrogenic (petroleum origin). Generally, a greater abundance of high molecular weight (HMW) PAHs indicates likely pyrogenic sources, while a greater abundance of low molecular weight (LMW) PAHs implies likely petrogenic origins of the PAHs.

Prior studies have shown that PAH releases associated with coal-tar sealants applied to asphaltic pavements can be significant sources of PAHs to receiving water sediments. Other research has examined the long-term degradation of highway construction materials (including pavements) as pollutant sources. The research summarized in this report section was conducted by Sree Usha Veeravalli as part of her MSCE program in the Department of Civil, Construction, and Environmental Engineering at the University of Alabama (Veeravalli 2011). She examined the role of freshly constructed asphaltic materials as pollutant sources during the initial exposure period. During aging of asphalt, the pavement undergoes physical and chemical changes which are expected to affect the quality of the runoff; this research investigated the early exposure periods as these changes were thought to be most rapid for freshly placed asphalt.

Significant trends in concentrations with exposure periods were observed for some constituents, but not all. Ten sampling times were obtained at irregular periods (more frequent at the beginning and fewer near the end), for this study. The observed trends were contradictory to what was expected from the literature review, in that the observed runoff concentration trends increased with time during the six month exposure period, likely due to surface degradation and release of material from the asphalt matrix.

- Nitrate concentrations from the pavement with asphalt sealant, total nitrogen from the hot mix pavement, and COD from the pavement with sealant indicated significant concentration increases with time.

- Detergents were observed in runoff from all of the pavement samples, but with no apparent trends.

- Consistently observed heavy metals in the runoff samples were zinc and copper, with apparent increasing concentration trends, especially noticeable towards the end of the experiments. Cadmium and chromium were not detected in any runoff samples, while lead was only detected in a few of the samples.

- PAHs were observed in the pavement runoff samples at very low concentrations (generally <1 μg/L). Some of the PAHs in the asphalt sealant samples indicated apparent increasing trends with aging, compared to the unsealed pavements.

- Toxicity in the runoff from all three pavement types was moderate to high during the six months test duration. However, no significant trends were observed in the patterns of the toxicity from the runoff for the number of samples available. Runoff samples from the warm mix pavement had the highest toxicity values.

These tests focused on pavement runoff characteristics during a relatively short six month exposure period for three asphalt samples: two unsealed samples (hot mix and warm mix) and one sealed sample (using an asphaltic sealer). The original plan was also to examine a coal tar sealant but that was no longer available. The majority of the observed significant concentration trends increased with time with increasing concentrations with longer exposures. It is likely that the observed concentrations would decrease eventually with longer exposure periods.

During Sree Usha Verravalli's graduate research at the University of Alabama, the tragic Deepwater Horizon oil well blowout occurred in the Gulf of Mexico. Samples were therefore obtained and studied as part of a parallel study funded by NSF. She examined the degradation of the spilled crude oil by using FTIR spectrophotometry, along with additional degradation surveys using standard crude oil samples obtained from other oil fields throughout the world. This information will be useful to stormwater researchers working in coastal areas and studying the effects of the hydrocarbons from multiple sources, especially when trying to differentiate natural (or spilled) crude oil hydrocarbons from similar materials discharged as part of the stormwater.

This section also described Jejal Bathi's research (Bathi 2008) that investigated sediment associations of PAHs by particle size and location in three urban creeks in the Tuscaloosa, AL, area. His fugacity modeling, method development activities, and data results indicate that stream sediments are the most likely fate of PAHs discharged in stormwater to local receiving waters. The strong PAH associations with particulates also support the high levels of PAH removal when using advanced stormwater controls that are capable of removal of very small stormwater particulates.

Fugacity level I partitioning calculations were performed for the PAHs in a hypothetical environmental system. This modeling approach indicated that, except for the low molecular weight PAHs (naphthalene, fluorene, phenanthrene, and anthracene) all the other studied PAHs were predominantly portioned with the sediment phase. The model predictions also indicated that the PAHs with Log (K_{OW}) or Log (K_{OC}) values greater than about 4.5 were mostly partitioned with the sediment phase, compared to other phases. The particulate and filterable PAH stormwater concentration data from prior field observations were compared to modeled values. The analytes were mostly associated with the particulate solids in the field samples. The high molecular weight PAHs had a greater portion associated with the particulates than the low molecular weight PAHs.

The total concentrations of the thirteen PAHs were about 2,000 to 5,000 µg per kilogram of sediment samples dry weighty. PAH enriched 710 – 1400 µm and 1400 – 2800 µm size fractions from Cribbs Mill Creek, resulted in higher levels of total PAHs in sediment samples than in the commercial source area Hunter Creek sediments. Observed total PAHs for the creeks were in the lower range of literature published PAH concentrations for urban sediments.

Section 7. Conclusions

This section presents conclusions from the lab and field tests conducted during this research on the characteristics and treatment of emerging contaminants in wet weather flows, supplemented by findings from the extensive literature reviews conducted by the project participants.

Wet Weather Pharmaceutical and PAH Sources and Treatment

Goals of this research included investigating how stormwater affects the treatment of emerging contaminants at wastewater treatment plants and to determine stormwater contributions of ECs during wet weather. Influent, primary effluent, secondary effluent and final effluent after UV disinfection for wet weather and dry weather were compared to identify any significance differences in treatment for the unit processes during both wet and dry weather conditions. Physical and chemical properties of each EC constituent were summarized from published literature, including descriptions how these properties can affect their treatability by different unit processes. These predictions were compared to the findings during this research to determine the significance of the chemical properties and the unit processes at the treatment plant. Table 7-1 summarizes the observed concentrations and the statistical analyses for these compounds at the Tuscaloosa, AL, wastewater treatment facility.

Table 7-1. Summary Statistical Test Results for Selected ECs Examined during this Research

Constituent	Influent (avg. µg/L)	Effluent (avg. µg/L)	p that influent ≠ primary effluent	p that primary effluent ≠ secondary effluent	p that secondary effluent ≠ final effluent	p that influent ≠final effluent	Overall reduction (based on avg. conc., %	Wet weather increased conc., from sign. regression slope term (avg. µg/L increase per MGD increase; p of slope term)
Pharmaceuticals								
Gemfibrozil	59	18	0.14	0.76	0.68	0.04	53%	2.8 (p = 0.01)
Ibuprofen	28	15	0.51	0.48	0.40	0.64	46%	6.7 (p = 0.02)
Triclosan	28	6.8	0.57	0.92	0.79	0.27	76%	6.9 (p = 0.003)
Carbamazepine	8.6	1.9	0.32	0.98	0.74	0.44	78%	0.38 (p = 0.3)
Fluoxetine	36	6	0.77	0.013	0.42	0.004	83%	2.4 (p < 0.01)
Sulfamethoxazole	38	19	0.17	0.90	0.63	0.15	50%	2.5 (p = 0.02)
Trimethoprim	9.3	12.1	0.58	0.96	0.80	0.70	increase	0.66 (p = 0.05)
Polycyclic Aromatic Hydrocarbons								
Naphthalene	11	11	0.90	0.04	0.74	0.08	none	0.50 (p < 0.01)
Acenaphthene	11	0.30	0.11	0.003	1.00	<0.001	97%	0.31 (p = 0.01)
Fluorene	4.7	0.2	0.65	0.04	0.70	0.04	96%	0.06 (p = 0.02)
Fluoranthene	4.6	0.27	0.83	0.011	0.75	0.04	94%	0.05 (p = 0.01)
Acenaphthylene	4.9	0.32	0.61	0.13	0.72	0.06	99%	0.03 (p = 0.11)
Phenanthrene	3.4	0.1	0.70	0.008	0.90	0.011	97%	0.11 (p = 0.01)
Anthracene	119	0.4	0.17	0.86	0.47	0.069	? (large influent variability)	0.06 (p < 0.01)
Pyrene	4.8	0.3	0.89	0.021	1.00	0.045	94%	0.06 (p = 0.01)

Note: yellow high-lighted values are statistically significant at least at the 0.05 level

The summary table indicates that the only significant removals occurred with the secondary treatment phases. Only two of the pharmaceuticals (gemfibrozil and fluoxetine) had significant removals at the treatment plant for the number of observations available (about 16 sets), while most of the PAHs had significant removals (except for naphthalene and possibly anthracene) had statistically significant removals. All of these constituents, except acenaphthylene, had significant trends of increasing concentrations with increasing daily average flow rates, indicating influences of wet weather flows. However, as noted in the following summaries for each constituent, few had different treatment behaviors during wet compared to dry weather flows.

Ibuprofen has a pKa value of 4.9. Ibuprofen is therefore ionized in wastewaters which usually have pH values above 6. It has a relatively high solubility of 41.5 mg/L, and a concurrent high sorption potential (pKa 3.5 to 4.0). The literature review reported observed removal rates at wastewater treatment plants from 82 to 95 percent, with resulting effluent quality from 0.02 to 2 µg/L. The literature focuses on biodegradation as the most common method of removal of ibuprofen because of its concurrent high solubility and absorption factors. This research found average removal rates of 66 percent for dry weather samples and 55 percent for wet weather samples, which were less than indicated in the literature. The effluent ibuprofen concentrations ranged from 15 µg/L for the dry weather samples and 10 µg/L for the wet weather samples (substantially larger than the values reported in the literature). The most apparent treatment unit process for dry weather samples occurred during secondary treatment, while the final UV disinfection process was highly important for the wet weather samples, although none of the unit process removals were statistically significant based on the number of samples available.

Gemfibrozil has a pKa value of 4.7 which makes this chemical ionize in the nearly neutral wastewater and stormwater aqueous solutions. It has a relatively high solubility of 5.0 mg/L and a log K_{ow} of 4.78. The literature review reported removal rates from 38 to 76 percent with biodegradation as the primary means of removal. The gemfibrozil wastewater treatment plant effluent concentrations ranged from 0.4 to 0.8 µg/L. This research measured removal rates averaging 71 percent during dry weather and 45 percent during wet weather, within the range reported in the literature. The gemfibrozil in the treated effluent ranged from 19 to 89 µg/L during dry weather and from 18 to 33 µg/L during wet weather, which are also substantially larger than reported in the literature. The most significant removal unit process for the dry weather samples was primary treatment, while secondary treatment (which utilizes biodegradation) was the most important unit process during wet weather. None of the unit processes were found to be significant by themselves, but the overall treatment facility process resulted in significant removals of this compound.

Triclosan has a pKa of 7.8 which under typical neutral wastewater and stormwater conditions will not ionize in these aqueous solutions. It also is relatively soluble in water (2 to 4.6 mg/L) and has a high log K_{ow} of 4.8 to 5.4 indicating a high adsorption potential to organic particulates. The literature review reported triclosan removals from 60 to 75%

in wastewater treatment plants; with effluent concentrations from 0.11 to 0.22 µg/L. The most important removal unit process is reported to be biodegradation in the secondary phase of wastewater treatment. During this research, the average removal rates during dry weather were found to be about 97 percent with 64 percent removals during wet weather. Triclosan concentrations in the treated wastewater effluent ranged from 11 to 32 µg/L during dry weather and 2 to 28 µg/L during wet weather, also larger than reported in the literature. The most important removal unit process during dry weather was secondary treatment (incorporating biodegradation through oxidation) and primary treatment (sedimentation) during wet weather conditions, although statistically significant removals were not noted for the number of sample sets available.

Carbamazepine has a log K_{ow} value of 2.45 and a pKa of 13.9. It is a basic compound, so in wastewater with a neutral pH, it is expected to ionize. The solubility of carbamazepine is 17.7 mg/L. With ionization in wastewater and a relatively high solubility, carbamazepine has a low probability of being treated through sedimentation. The LC_{50} of *D. magna* is greater than 100 mg/L in a 24-hour period. The maximum concentrations in the wastewater treatment system were much less than the reported LC_{50} value so toxicity is not expected to have a large effect on the treatment of carbamazepine. The biological half-life of carbamazepine is 10 to 20 hours, which means it is relatively stable and may be transported through the wastewater treatment with small reductions. Literature has shown that carbamazepine is resistant to biodegradation. The literature review shows that carbamazepine removal ranges from 0 to 30%. In our study, wet weather samples and dry weather samples showed carbamazepine was reduced by about 78%. The one way ANOVA and rank sum tests show that there were no statistically significant differences in the treatment of carbamazepine by flow rate or process.

Fluoxetine has a log K_{ow} value of 4.05 and a pKa of 7.9. It also has a relatively high solubility of 38.4 mg/L. Because of its high pKa, there is expected to be some protonation in the wastewater treatment stream. It also has the potential to sorb onto organic particulates. The LC_{50} of *P. subcapitata* exposed to fluoxetine is 24 µg/L. The toxicity value is close to values observed at the treatment plant, indicating potential inhibition. The half-life of fluoxetine ranges from 24 to 72 hours. The one way ANOVA showed some statistical differences in the treatment of fluoxetine by flow rate and unit treatment process. After conducting a Mann-Whitney rank sum test, there was a significant difference noted between the influent and the final effluent concentrations and between the primary effluent and secondary effluent concentrations. The average removal of fluoxetine was 83%, with secondary treatment being the major removal process.

Sulfamethoxazole has a log K_{ow} value of 0.9 and a solubility of 600 mg/L. It also has pKa1 and pKa2 values of 1.7 and 5.6, respectively. It is also classified as a sulfonamide, a member of the amide groups. Amides are known to be soluble in water. *P. subcapitata* exposed to sulfamethoxazole yields an IC_{50} of 1.5 mg/L, so toxicity will not likely affect the microorganisms in the secondary treatment phase. Sulfamethoxazole has a half-life of 10 hours. The literature review gives a range of removals from 17 to 66%. The one way ANOVA and Mann-Whitney rank sum tests indicated that there was not a statistical significant difference in any of the treatment processes in this study for the number of samples available. The research findings indicated that the reduction rates for wet and dry weather for sulfamethoxazole were about 50%.

Trimethoprim has a log K_{ow} value of 0.79 and a solubility of 400 mg/L. Its pKa is 6.6 which is close in value to the neutral pH of wastewater. Trimethoprim is predicted to be soluble in water, making it more difficult to treat. The freshwater green alga *P. subcapitata* has a LC_{50} of 80.3 to 130 mg/L for trimethoprim and therefore is unlikely to affect biological treatability due to toxicity. Trimethoprim has a half-life of 8 to 10 hours. The literature review indicated that trimethoprim has a removal rate of 70 to 75%. The influent concentrations from the literature ranged from 0.1 µg/L to 0.5 µg/L. The effluent concentrations from the literature were about 0.1 µg/L. The reported means of treatment for trimethoprim was through chlorination. The one way ANOVA test shows that there were no statistically significant differences between each of the treatment processes during this research. Trimethoprim had reported slight increases in concentrations at the treatment facility. The average influent concentrations were 16 µg/L for dry weather and 3.1 µg/L for wet weather. The average final effluent concentrations for dry and wet weather samples were 21 and 2.0 µg/L, respectively. The concentrations in the experimental data were much greater than presented in the literature.

Naphthalene has a log K_{ow} of 3.37 and a solubility of 31.5 mg/L. This compound is a lower molecular weight PAH, and therefore is less hydrophobic. It is a semivolatile compound, having a Henry's Law constant of 4.6×10^{-4} atm-m^3/mol, so it could be partially removed in the treatment plant through volatilization. If dissolved in the wastewater stream, it would be removed through biodegradation or oxidation. The removal rates reported in the literature show low to moderate removal rates, ranging from 31 to 40%. Influent concentrations from the literature ranged from 0.15 µg/L to 7.3 µg/L. Effluent concentrations from the literature ranged from 0.09 µg/L to 0.7 µg/L. The one way ANOVA tests showed there were no significant differences when all four sampling locations were compared, but the Mann-Whitney rank sum test showed that there were significant differences in the primary and secondary treatment process effluents. The experimental results indicated no reductions for the wet weather or dry weather separately. The average wet weather concentrations ranged from 15 µg/L for the influent to 23 µg/L for the effluent. There was no apparent method of removal based on the experimental data, which differs from the literature.

Acenaphthene has a log K_{ow} of 4.02 and a solubility of 1.93 mg/L, making it more likely to be associated with the organic particulate materials. It has a Henry's Law constant of 7.91×10^{-5} atm-m^3/mol, so it is not very volatile. From the literature, influent concentrations ranged from 0.02 to 0.7 µg/L and the effluent concentrations ranged from 0.005 to 0.11 µg/L. Reported removal rates ranged from 67 to 85% from the literature. The one way ANOVA tests indicated there were significant differences between the four treatment locations. The experimental results show an average of about 97% removals. These reduction rates are similar to literature findings.

Fluorene has a log K_{ow} value of 4.12 and solubility between 1.68-1.98 mg/L, making fluorene less likely to dissolve in water than to associate with organic particulate matter. Fluorene is predicted to be removed through primary sedimentation, although oxidation is another means of removal for PAHs. It is a semivolatile compound. From the literature, reported removal rates ranged from 59 to 68%. The one way ANOVA indicated that there was a statistically significant difference at the four treatment locations. After doing a Mann-Whitney rank sum test, it was determined that there was a significant difference between the primary and secondary treatment effluent locations. Experimental data indicated average 96% overall removal.

Flouranthene and pyrene have high log K_{ow} values and low solubility rates, so they are predicted to adsorb onto particulate organic matter. The literature review shows flouranthene and pyrene to have reduction rates ranging from 83 to 88%. The statistical tests of the data from this research indicated statistically significant differences in the sampling locations for fluoranthene when comparing the primary and secondary effluent locations, indicating secondary treatment benefits. The samples showed an overall 94% percent removal. The reductions occurred for both the primary (but not statistically significant) and secondary treatment processes.

For pyrene, the statistical analyses indicated statistically significant reductions in the primary and secondary treatment unit processes. The experimental results showed an average 94%, with the secondary process being most important.

From these examples, we see that many of the constituents had concentrations that were not in the same range as reported in the literature. The analytical methods used during this research were generally less sensitive than the methods reported in much of the literature, resulting in only the largest values being detected. The removal rates were also generally lower than the literature reports, especially for the wet weather conditions. The high variability and low concentrations of the constituents resulted in few significant differences between wet and dry weather and between unit processes. The literature indicated large amounts of variability in the treatment of these constituents that indicate that there are other factors other than physical and chemical properties that affect the removals of these compounds.

Characteristics of Emerging Contaminants in Stormwater Sheetflows

Sheetflow samples were analyzed for selected PPCP concentrations, including trimethoprim, sulfamethoxazole, carbamazepine, fluoxetine, ibuprofen, gemfibrozil, and triclosan. Triclosan was not detected in any of the samples, while ibuprofen was only detected in 15% of the samples, and trimethoprim was only detected in 23% of the samples. The nonparametric Kurskal-Wallis one-way analysis of variance on ranks test was applied on these data using SigmaPlot version 11 (SYSTAT Software Inc.) to detect the presence of any significant differences in land use or source area grouping. For the PPCPs, only carbamazepine (detected in 95% of the sheetflow samples) was found to have at least one source area statistically significantly different from the other source area categories. None were found to have any significant differences by land use, for the number of samples available.

Grouped box and whisker plots (using SigmaPlot version 11) were also prepared for all of the PPCPs showing differences by source area and land use. Probability plots (Minitab version 16) were also prepared for the constituents having sufficient data (sulfamethoxazole, bacteriostatic antibiotic, often used with trimethoprim; carbamazepine, an anticonvulsant; fluoxetine, and antidepressant such as Prozac; and gemfibrozil, used to lower lipid levels).

The probability plots were prepared showing each source area separately for carbamazepine to also help distinguish the source areas that were likely different from the others. The probability plots indicate good fits of the data to log-normal statistical distributions, with some very large values and some low values observed, as generally seen for most stormwater constituents. These analyses clearly show that landscaped areas had low average concentrations of carbamazepine (about 1 µg/L), while the other source areas (paved areas and roof runoff) had average concentrations at about 4 µg/L. The reasons for these concentration relationships are not clear.

Polycyclic aromatic hydrocarbons (PAHs) were also analyzed in the sheetflow samples. Naphthalene was detected in 64% of the sheetflow samples, phenanthrene was detected in 29% of the sheetflow samples, and indeno(1,2,3-cd)anthracene was detected in 21% of the sheetflow samples. Anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(a,h)anthracene, and benzo(ghi)perylene were also included in the GC/MSD analyses for the PAHs, but were detected in less than 20% of the samples. The Kurskal-Wallis nonparametric ANOVA test did not identify any significant groupings by source area or land use, for the number of observed data available, for any of the PAHs. Naphthalene had the highest concentrations observed, with about half greater than 2 µg/L (maximum of about 9 µg/L), while phenanthrene and indeno(1,2,3-cd)anthracene were much lower (medians of about 0.3 µg/L and maximums of about 1 µg/L).

No sheetflow samples had detected cadmium (total or filtered), filtered chromium, and filtered lead, while less than 20 percent of the samples had detected total chromium, total lead, and total and filtered nickel. The average filtered percentages of the observed metals were 0% for chromium and lead (but few samples had detected values), and 50 to 100% for copper, zinc, aluminum, and iron. The Kurskal-Wallis non-parametric ANOVA tests indicated the following metal forms that had significant groupings by either source area or land use:

Total aluminum ($p<0.001$) for source areas
Total zinc ($p = 0.012$) for land uses
Filtered zinc ($p = 0.007$) for land uses
Total iron ($p = <0.001$) for source areas
Filtered iron ($p = 0.013$) for source areas

The commercial areas had significantly higher concentrations (140 and 41 µg/L for total and filtered zinc) compared to the institutional (20 and 12 µg/L) and residential (19 and 9 µg/L) areas, apparently reflecting the greater use of galvanized metals in the commercial land use areas. The probability distributions for most of the observed metals fit log-normal statistical distributions.

Enterococci results indicated at least one significantly different source area compared to the others. The roof runoff (median 60 MPN/100 mL) samples appear to have significantly lower counts compared to the highest levels from the landscaped area (median of about 2,000 MPN/100 mL) samples, while the paved area (median of about 600 MPN/100 mL) samples had intermediate levels (but close to the landscaped area samples). The *E. coli* sheetflow values are much lower than typically observed for stormwater, with a median of only 17 MPN/100 mL, but with an observed maximum of about 18,000 MPN/100 mL).

The Kurskal-Wallis nonparametric ANOVA tests indicated that at least one source area subgroup was significantly different from the others for total solids, TSS, and SSC. TDS did not indicate any differences between the source area groups for the number of samples available. From the box and whisker and probability distribution plots, it is apparent that the landscaped areas generate much more sediment than the paved areas or roof runoff. The median TSS concentration in the landscaped runoff was about 300 mg/L, while the paved area median TSS was about 18 mg/L and the roof runoff median TSS was about 3 mg/L. The SSC concentrations were slightly higher than the TSS values and showed the same pattern, as did the total solids values. The TDS were not separated statistically by source area and had a median value of about 23 mg/L.

Heavy Metal Sources from Material Exposures

Another goal of this research was to determine how different drainage and storage system (pipe, gutter, and storage tank) materials and water quality characteristics can affect stormwater heavy metal concentrations (cadmium, chromium, lead, copper, zinc, aluminum, and iron), toxicity, and nutrients (nitrogen compounds and COD). A wide range of materials under various environmental conditions were evaluated. Factors (such as pH, salinity, and major water ions, and their interactions) causing degradation of the materials with time of exposure were examined. During this research, water from each leaching container was periodically analyzed over a three month period for heavy metals, nutrients, toxicity, pH, conductivity, and Eh.

The experiments were performed in two stages. Each section of pipe and gutter material was immersed in containers with stormwater buffered at pH 5 and 8 during the first series of tests. During the second series of experiments, the materials were immersed in containers having un-buffered bay and river waters having different conductivities.

Metal releases were assessed using spearman correlations, cluster analyses, principal component analyses, and factorial analyses. Also, the Medusa water chemistry program was used to predict the chemical forms of the released metals. Eh-pH and log concentration-pH diagrams were constructed (using guidance from Medusa) and metal forms were determined that influence metal fate and toxicity. A simple model was finally prepared that quantified the expected pollutant releases for different materials for different uses (drainage system vs. storage tanks) and water types (low and high pHs, and saline and non-saline waters). The Spearman correlation matrices showed that toxicity is influenced by both pH values and metal releases. During the natural pH tests, the toxicity in the samples with galvanized steel pipes and gutters was strongly associated with zinc releases, and the toxicity in the samples with copper materials was strongly associated with copper losses. Cluster analyses also confirmed that toxicities are influenced by metal releases and pH values, and metal releases are affected by pH, conductivity, and time of exposure.

Principal Component Analyses (PCA) were conducted to identify groupings of parameters with similar characteristics. It was found that the first four principal components account for about 78% of the total variance and can reasonably represent the data set. Toxicity values have high loadings on the first principal component. The second principal component has high loadings of time, Pb, and Zn (also high loading for PC3). Copper and Zn have large loading on the third principal component. Conductivity, pH and material type have high loadings on the fourth principal component.

Full 2^3 Factorial analyses were conducted on Cu, Zn, Pb constituents (expressed in mg per m^2 surface area of exposed material units) and toxicities for 15 and 45 min of bacteria exposure time to determine the effect of the factors. During the natural pH tests, the interaction of conductivity, material, and time had a significant effect on copper and lead releases. For zinc releases, the interaction of material and time was significant. The two-way interactions of conductivity and material, and material and time, had significant effects on toxicity during the second test series.

This research task found that:

- Some stormwater drainage system and tank materials can release large amounts of zinc, copper, and lead under controlled and natural pH and different salinity conditions during both short and long exposure periods.

- Galvanized steel pipes and gutters were the most significant source of lead and zinc, while copper materials were the greatest source of copper.

- During short exposure times, only copper materials were a source of copper under both high and low buffered pH conditions. Under natural pH conditions, copper concentrations were detected only for copper materials during both short and long exposure times and exceeded 35 mg/L in bay samples after 3 months of exposure.
- Concrete pipes were not a source of copper under either controlled or natural pH conditions. Low copper concentrations were found for the HDPE, vinyl,

galvanized steel, and aluminum sample exposure tests during the controlled pH conditions.

- The greatest sources of zinc were galvanized steel materials. Zinc releases from galvanized steel materials were detected during both short (0.5 to 27 h) and long exposure (after 1 to 3 months) for all water conditions. Under controlled pH conditions, zinc releases in the samples with galvanized steel materials were greater and more rapidly released at higher pH values during long exposure times. The least sources of zinc were concrete and plastic materials.

- Galvanized steel materials were found to be the only source of lead releases, with lead concentrations detected during both short and long exposure times, for both controlled and uncontrolled pH tests, and for both high and low salinity conditions.

- For controlled pH conditions, the largest concentrations of iron (>20 mg/L at pH 5) were found to be leaching from galvanized steel materials. During natural pH conditions, concrete and galvanized steel materials were the greatest sources of iron.

- During controlled pH tests, there were low periodic releases of nitrogen compounds from the drainage and pipe materials.

- For controlled pH tests, the toxicities of the roof and pipe materials were much greater under lower pH conditions than under higher pH conditions. The concrete pipes were found to be least toxic under the lower pH conditions. Under higher pH conditions during the controlled pH tests, concrete pipes and vinyl roofing materials were found to be the least toxic, while copper and galvanized materials were the most toxic. For bay and river waters, copper materials had the highest toxicity, followed by galvanized steel materials.

- Concrete, HDPE, and vinyl materials had little or non-detected metal releases during both short and long-term exposure times and therefore can be safely used as drainage system components or storage tanks materials. The use of copper materials for gutter systems is not advised due to high copper releases under a wide range of pH values, especially in the presence of chloride ions in coastal areas. The use of galvanized materials is not advised for drainage systems, and especially for storage tank materials, due to substantial zinc releases under all water conditions.

- Concrete pipes can be used under a wide range of water pH values with minimal heavy metal releases and non detected toxicities. In natural water environments with pH values from 7 to 8 and with low and high salinity values, PVC, HDPE, vinyl, aluminum materials also can be safely used.

- Heavy metals were released from drainage system materials into the water quickly after the water came in contact with the materials. This releases continued during long periods of exposure corresponding to storage facilities. Metallic gutter, pipe, and storage tank materials have the potential to release high concentrations of zinc, copper, and lead under acidic and alkali conditions and at various conductivity values.

Indicator Bacteria Die-off and Regrowth on Urban Surfaces

Bacteria survival models were developed to represent source area processes contributing to the background (i.e. of non-sewage origin) presence of fecal indicators in stormwater. Together with a planned similar study of survival on pervious surfaces (soils), these models should contribute to a mass-balance link between fecal deposition on the landscape and biological stormwater quality. The indicator organisms studied (especially Enterococci) were found to be quite persistent (especially under environmental conditions that most closely approximate enteric conditions) on impervious surfaces subject to the extreme Tuscaloosa, AL environmental conditions. Moreover, under most conditions studied, the rate of disappearance of these organisms from the landscape slowed (or even reversed), rendering short term studies of their survival (or even the simple regression of long term studies) unreliable in predicting their environmental fate.

Treatment of Emerging Contaminants by Conventional and Advanced Wet Weather Wastewater Treatment Facility and Stormwater Controls

Some emerging contaminants may not be adequately treated at wastewater treatment facilities. Studies have demonstrated that wastewater treatment plant removals of pharmaceutical and personal care products (PPCPs) can range between 60% and 90% for a variety of polar compounds (Carballa, *et al*. 2004). The removal rate is mostly contingent on the physical and chemical nature of the pollutant and the effects of the wastewater matrix. It also depends on the treatment plant itself, such as the retention time through each unit process and the specific unit processes used at the treatment facility (Mohapatra, *et al*. 2010).

Wet Weather Flow PPCP Concentrations

There are few obvious sources of PPCPs in stormwater flows (beyond some associated with veterinarian drugs). However, regression analyses of influent concentrations vs. treatment plant flow rates at the Tuscaloosa wastewater treatment plant indicated significant slope terms for all of the pharmaceutical compounds (increasing concentrations with increasing flow rates at the treatment facility), except for carbamazepine. Table 7-2 summarizes the observed concentrations during both low and high flow conditions. In general, the average concentrations for peak flows were about double the dry weather period concentrations, although there was substantial variability.

Table 7-2. Dry and Wet Weather Observed Pharmaceutical Concentrations at Tuscaloosa Wastewater Treatment Plant

	Average dry weather concentrations (at about 18 MGD at treatment plant)	Average wet weather concentrations (at about 40 MGD at treatment plant)
Gemfibrozil, µg/L	55	110
Ibuprofen, µg/L	35	60
Triclosan, µg/L	35	60
Carbamazepine, µg/L	8	15
Fluoxetine, µg/L	45	100
Sulfamethoxazole, µg/L	50	100
Trimethoprim, µg/L	12	25

The PAH concentrations all had statistically significant increasing concentrations with increasing daily average flow rates (except for acenapthtylene), although there were generally wide variations in concentrations during dry weather. In general, the average concentrations for peak flows were also about double the dry weather period concentrations, as shown on Table 7-3.

Table 7-3. Dry and Wet Weather Observed PAH Concentrations at Tuscaloosa Wastewater Treatment Plant

	Average dry weather concentrations (at about 18 MGD at treatment plant)	Average wet weather concentrations (at about 40 MGD at treatment plant)
Naphthalene, µg/L	10	20
Acenaphthene, µg/L	6	12
Fluorene, µg/L	1	2
Fluoranthene, µg/L	0.8	2
Phenanthrene, µg/L	2	4
Anthracene, µg/L	1	2
Pyrene, µg/L	1	2

Table 7-4 shows the significant slope terms for the analyzed pharmaceuticals and PAHs, reflecting the increasing concentrations as the daily average wastewater treatment plant flow increased during different sized rains. These slope terms were used to calculate approximate influent concentrations for these increasing flows, and the loads, expressed as mg/km^2 for each rain category.

Table 7-4. Calculated Influent Mass Loadings for Pharmaceuticals during Different Sized Rain Events

Pharmaceutical compound	Slope term (μg/L/MGD)	Conc. (μg/L) during 0 to 0.5 inch rain (18 MGD; 1.5 hr duration)	Mass per event (mg/km^2)*	Conc. (μg/L) during 0.6 to 1.5 inch rain (23 MGD; 4 hr duration)	Mass per event (mg/km^2)*	Conc. (μg/L) during 1.6 to 2.5 inch rain (34 MGD; 12 hr duration)	Mass per event (mg /km^2)*
Gemfibrozil	2.81	51	1.1	65	4.9	96	32
Ibuprofen	1.85	33	0.74	43	3.2	63	21
Triclosan	1.86	34	0.74	43	3.2	63	21
Fluoxetine	2.44	44	0.97	56	4.2	83	28
Sulfamethoxazole	2.51	45	1.00	58	4.4	85	29
Trimethoprim	0.66	12	0.26	15	1.2	22	7.5

* 74 mi^2 (192 km^2) service area

Table 7-5 contains similar calculations of influent concentrations and mass loadings for PAHs.

Table 7-5. Calculated Influent Mass Loadings for PAHs during Different Sized Rain Events

PAH compound	Slope term (μg/L/MGD)	Conc. (μg/L) during 0 to 0.5 inch rain (18 MGD)	Mass per event (mg/km^2)*	Conc. (μg/L) during 0.6 to 1.5 inch rain (23 MGD)	Mass per event (mg/km^2)*	Conc. (μg/L) during 1.6 to 2.5 inch rain (34 MGD)	Mass per event (mg/mi^2 and mg/km^2)*
Naphthalene	0.5	9.0	0.20	11.5	0.87	17.0	5.7
Acenaphthene	0.31	5.6	0.12	7.1	0.54	10.5	3.5
Fluorene	0.057	1.0	0.02	1.3	0.10	1.9	0.65
Fluoranthene	0.047	0.8	0.02	1.1	0.08	1.6	0.54
Phenanthrene	0.11	2.0	0.04	2.5	0.19	3.7	1.3
Anthracene	0.055	1.0	0.02	1.3	0.10	1.9	0.63
Pyrene	0.059	1.1	0.02	1.4	0.10	2.0	0.67

* 74 mi^2 (192 km^2) service area

Emerging Contaminants Observed in Stormwater Sheetflows in Tuscaloosa, AL

Sheetflow samples were analyzed for selected PPCP concentrations, including trimethoprim, sulfamethoxazole, carbamazepine, fluoxetine, ibuprofen, gemfibrozil, and triclosan. Triclosan was not detected in any of the samples, while ibuprofen was only detected in 15% of the samples, and trimethoprim was only detected in 23% of the samples. The nonparametric Kurskal-Wallis one-way analysis of variance on ranks test was applied on these data using SigmaPlot version 11 (SYSTAT Software Inc.) to detect the presence of any significant differences in land use or source area grouping. For the PPCPs, only carbamazepine (detected in 95% of the sheetflow samples) was found to have at least one source area statistically significantly different from the other source area categories. None were found to have any significant differences by land use, for the number of samples available.

Polycyclic aromatic hydrocarbons (PAHs) were also analyzed in the sheetflow samples. Naphthalene was detected in 64% of the sheetflow samples, phenanthrene was detected in 29% of the sheetflow samples, and indeno(1,2,3-cd)anthracene was detected in 21% of the sheetflow samples. Anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(a,h)anthracene, and benzo(ghi)perylene were also included in the GC/MSD analyses for the PAHs, but were detected in less than 20% of the samples. The Kurskal-Wallis nonparametric ANOVA test did not identify any significant groupings by source area or land use, for the number of observed data available, for any of the PAHs. Naphthalene had the highest concentrations observed, with about half greater than 2 μg/L (maximum of about 9 μg/L), while phenanthrene and indeno(1,2,3-cd)anthracene were much lower (medians of about 0.3 μg/L and maximums of about 1 μg/L).

No sheetflow samples had detected cadmium (total or filtered), filtered chromium, or filtered lead, while less than 20 percent of the samples had detected total chromium, total lead, and total and filtered nickel. The average filtered percentages of the observed metals were 0% for chromium and lead (but few samples had detected values), and 50 to 100% for copper, zinc, aluminum, and iron. The Kurskal-Wallis non-parametric ANOVA tests indicated the following metal forms that had significant groupings by either source area or land use:

- Total aluminum ($p<0.001$) for source areas
- Total zinc ($p = 0.012$) for land uses
- Filtered zinc ($p = 0.007$) for land uses
- Total iron ($p = <0.001$) for source areas
- Filtered iron ($p = 0.013$) for source areas

The commercial areas had significantly higher concentrations (140 and 41 μg/L for total and filtered zinc) compared to the institutional (20 and 12 μg/L) and residential (19 and 9 μg/L) areas, apparently reflecting the greater use of galvanized metals in the commercial land use areas. The probability distributions for most of the observed metals fit log-normal statistical distributions.

Treatment of Pharmaceuticals and PAHs

Table 7-6 summarizes the chemical characteristics and their treatability as reported in the literature review for the emerging contaminants examined during this research. This table shows the most likely means of removal, the reported ranges of influent and effluent concentrations, and the ranges of the percentage removals for each constituent.

The pharmaceuticals gemfibrozil, ibuprofen, triclosan and fluoxetine were reported to be best reduced by biodegradation. The overall range of influent concentrations ranged from 0.3 to 14.6 μg/L. The removals for these compounds varied. Ibuprofen showed the highest level of treatability ranging from 82 to 95 percent. Triclosan had reduction rates of 75 percent and gemfibrozil had a reduction range from 38 to 76 percent.

Table 7-6. Summary of Characteristics and Treatability of Targeted Pollutants as Reported in the Literature

Constituent	**Reported most important treatment method**	**Range of influent concentration (µg/L)**	**Range of effluent concentration (µg/L)**	**Range of removal at conventional wastewater treatment facility**
Gemfibrozil	Biodegradation	1.5-3.5	0.4-0.8	38%-76%
Ibuprofen	Biodegradation	0.45-14.6	0.02-1.96	82%-95%
Triclosan	Biodegradation	0.38-1.93	0.11-0.22	60%-75%
Carbamazepine	Not widely known due to low removal	0.13-1.85	0.12-1.61	0%-30%
Fluoxetine	Biodegradation			
Sulfamethoxazole	Adsorption (minor), photodegradation	0.25-0.35	0.11-0.23	17%-66%
Trimethoprim	Chlorination (UV was not effective)	0.10-0.45	0.10-0.11	70%-75%
	Reported most important treatment method	**Range of influent concentration (µg/L)**	**Range effluent concentration (µg/L)**	**Range of removal at conventional wastewater treatment facility**
Napthalene	Volatization/oxidation	0.150-7.3	0.088-0.7	31%-40%
Acenaphthene	Oxidation/Sorption	0.016-0.7	0.005-0.11	67%-85%
Fluorene	Oxidation/sorption	0.037-0.7	0.015-0.23	59%-68%
Fluoranthene	Sorption	0.15-0.24	0.02-0.03	86%-88%
Acenaphthylene	Oxidation/sorption	0.021	0.002	91%
Phenanthrene	Oxidation/sorption	0.33-1.7	0.11-0.2	67%-89%
Anthracene	Oxidation/sorption	0.028-0.09	0.007-0.012	75%-87%
Pyrene	Adsorption	0.14-0.47	0.023-0.06	83%-88%
Benzo(a) anthracene and chrysene	Adsorption	0.21	0.019	91%
Benzo(b) fluoranthene, Benzo(k) fluoranthene, Benzo(a) pyrene, and indeno(1,2,3,cd) pryene	Adsorption	0.42	0.076	82%
Benzo(a,h) anthracene and Benzo(g,h,i) perlene	Adsorption	0.044	0.013	71%
Heptachlor	n/a	n/a	n/a	n/a
Heptachlor-epoxide	n/a	n/a	n/a	n/a

Carbamazepine had the lowest reported reduction rates of zero to 30 percent. . Carbamazepine is difficult to treat, as it is resistant to biodegradation. Because carbamazepine is soluble in water, it is also not treatable by sedimentation in the primary unit processes. Carbamazepine concentration increases in the effluent compared to the influent were observed. Possible treatment mechanisms of carbamazepine are not clearly understood.

Sulfamethoxazole is highly soluble in water and therefore difficult to remove. Photodegradation removes sulfamethoxazole at some treatment facilities. The reported influent concentrations ranged from 0.25 to 0.35 µg/L, and the effluent concentrations ranged from 0.11 to 0.23 µg/L. The reduction rates of sulfamethoxazole ranged from 17 to 66 percent.

Low molecular weight (LMW) PAHs (naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, and anthracene) had reported reduction rates between 31 and 91 percent. Naphathlene had the lowest reduction rates ranging from 31 to 40 percent. Naphthalene has a Henry's Law constant of 0.019 atm-m^3/mol, making it more volatile than the other PAHs and more likely to volatize during wastewater treatment. Acenaphthene, acenaphthylene, fluorene, phenanthrene and anthracene have Henry's Law constants of about 10^{-3}, and their solubilities range from 0.045 to 16.1 mg/L. Volatization and oxidation were the primary means of reported treatment for PAHs having lower molecular weights. High molecular weight (HMW) PAH compounds (such as pyrene, fluoranthene, chrysene, and benzo(a)pyrene) had higher reduction percentages ranging from 83 to 91 percent. Adsorption is a primary removal factor for the HMW compounds. Influent concentrations for LMW PAHs ranged from 0.016 to 7.3 µg/L, while their effluent concentrations ranged from 0.002 to 0.7 µg/L. Influent concentrations for the HMW PAHs ranged from 0.044 to 0.47 µg/L, while their effluent concentrations ranged from 0.013 to 0.06 µg/L.

Observed Treatment of PPCPs at the Tuscaloosa Wastewater Treatment Plant

Table 7-7 summarizes the average concentrations observed at each of the four sampling locations at the Tuscaloosa Earl N. Hilliard (ENH) wastewater treatment plant and indications of the likely most important unit treatment process. The pharmaceuticals have low to moderate removals (about 50%) while the PAHs show larger removals (about 90%), although the observed removals varied substantially for different compounds in each constituent group. A combination of unit treatment processes resulted in the best pharmaceutical and PAH reductions, as expected.

Table 7-7. Performance Data for Earl Hilliard WWTP, Tuscaloosa, AL

Constituent	Avg Influent conc. (µg/L)	Avg Primary effluent conc. (µg/L)	Avg Secondary effluent conc. (µg/L)	Avg concentration after UV (final effluent) (µg/L)	Avg Overall Percentage Removal at ENH wastewater treatment facility	Apparent most Important treatment unit process
Pharmaceuticals						
Gemfibrozil (w)	32.4	31.7	18.1	17.1	45	Secondary
Gemfibrozil (d)	80.3	23.4	22.3	18.6	71	Primary
Ibuprofen (w)	21.6	21.0	17.6	9.6	58	UV
Ibuprofen (d)	44.7	35.3	20.8	15.3	67	Secondary
Triclosan (w)	33.9	16.9	15.0	12.3	63	Primary
Triclosan (d)	16.7	3.3	12.9	0.4	98	UV
Carbamazepine (w)	2.4	5.0	5.0	2.6	-8	UV
Carbamazepine (d)	15.9	10.5	2.5	1.4	94	Primary
Fluoxetine (w)	14.1	41.7	3.3	1.9	86	Secondary
Fluoxetine (d)	61.7	36.8	11.6	9.6	84	Secondary
Sulfamethoxazole (w)	10.4	18.4	14.1	13.1	-33	None
Sulfamethoxazole (d)	68.7	42.6	31.1	24.4	65	Secondary
Trimethoprim (w)	3.1	3.1	3.9	2.0	33	UV
Trimethoprim (d)	16.3	28.3	21.1	21.0	-31	None
Polycyclic Aromatic Hydrocarbons						
Naphthalene (w)	15.3	4.7	25	22.7	-47	None
Naphthalene (d)	7.1	11.1	3.8	1.3	82	Secondary
Acenaphthene (w)	16.9	5.1	0.4	0.6	96	Primary
Acenaphthene (d)	7.7	0.8	0.1	0.02	99	Primary
Fluorene (w)	10.3	1.0	0.6	0.6	91	Primary
Fluorene (d)	0.7	1.2	0.04	0.05	93	Secondary
Fluoranthene (w)	10.3	4.2	0.5	0.5	95	Primary
Fluoranthene (d)	0.3	0.5	0.02	0.04	87	Secondary
Acenaphthylene (w)	10.5	0.6	0.6	0. 7	92	Primary
Acenaphthylene (d)	0.1	0.6	0.01	0.02	75	Secondary
Phenanthrene (w)	6.1	4.4	0.05	0.2	98	Secondary
Phenanthrene (d)	1.6	0.8	0.2	0.1	90	Primary and secondary
Anthracene (w)	198	2.3	9.7	0.8	100	Primary
Anthracene (d)	60.1	0.2	0.2	0.2	100	Primary
Pyrene (w)	10.2	4.0	0.7	0.5	95	Primary and secondary
Pyrene (d)	0.7	1.0	0.1	0.1	80	Secondary

The largest reductions, for all but acenaphthene, occur during secondary biological treatment, where most of the removal of particulates occurs along with biological digestion of the solids. The primary treatment had little effect. Phenanthrene actually indicated an increase in concentrations with primary treatment, likely due to removal of particulates that interfered with the extraction of the compound during the laboratory tests. Acenaphthene is an example where all of the treatment processes were effective for partial removal of the compound, including the primary, secondary, and disinfection unit processes. For many of the samples, acenaphthene was not detected after the secondary treatment phase.

In most cases, the median concentration reductions for the ECs are modest; however, extremely large periodic influent concentrations are usually significantly reduced by the primary treatment unit process. The biological secondary treatment processes and the final ozone disinfection processes provided additional benefit, approaching the "irreducible" concentrations. The secondary treatment did result in a very narrow range of effluent quality for acenaphthene, fluorene, fluoranthene, phenanthrene, and pyrene, although most of the removals for these compounds occurred during the primary sedimentation treatment stage. No pesticides were detected at the 0.5 to 1 µg/L detection limit at any of the sampling locations at the treatment facility.

Heavy Metal Treatability for Stormwater

Many heavy metals are associated predominantly with particulates, and therefore their treatability is influenced by the removal of the associated particulates. The association of heavy metals with particulates depends on pH, oxidation-reduction potential, and particulate organic matter. The treatability of stormwater solids and associated heavy metals is dependent on their size. The removal of dissolved contaminants may be needed to meet stringent numeric discharge permit requirements and reduce surface and groundwater contamination potentials.

The valence charge of a metal and its complexation, among other contaminant properties, influence the choice of stormwater treatment technology. Strongly charged, small molecules can be removed effectively by zeolites. Zeolites are not effective in the removal of compounds of zero valence and compounds with large size. Peat can be used as a filtration media for treatment of heavy metals and likely their complexes. Peat's effectiveness is due to the wide range of binding sites (carboxylic acid, etc.) present in the humic materials and ligands in the peat. An advantage of peat media is that it can treat many heavy metals during relatively short (as short as 10 minutes) contact times.

Prior research found that ionic fractions for zinc, copper, and cadmium in stormwater can range from 25 to 75%. These metals can be associated with very small particles, therefore the efficiency of physical filtration to remove metals will depend on size of associated particulates. Treatment technologies for metals associated with dissolved fractions include chemical methods. To remove dissolved metals from stormwater, peat moss, mixtures of peat moss and sand, zeolite, and compost can be used, especially with long contact times. These metals can form soluble complexes with different inorganic and organic ligands. The complex valences can range from -2 to +2. Organic and inorganic complexes may be treated by chemically active filtration through compost, peat, and soil. Also, granular activated carbon (GAC) can be used to remove complexes with organic matter.

Advanced Treatment of Trace and Emerging Contaminants using Media in Stormwater Filters or Biofiltration Facilities

Pitt and Clark (2010) review many media available for the removal of heavy metals and organics to very low levels. Critical aspects of these advanced treatment methods include using sufficient pre-treatment for the removal of fine particulates to minimize silting of the treatment media and also to provide sufficient contact time of the water being treated with the media.

Clark and Pitt (2011) found that zeolites can be effective for removal of metals in the +2 valence state. The effectiveness of ion exchange decreases as the valence charge approaches zero and as the size of the complex increases. Therefore, the overall effectiveness of zeolites, and potentially other ion-exchange media such as oxide-coated sands, is likely reduced because a substantial fraction of the metals likely exist in valence forms other than +2 due to complexation with inorganic ions and organic matter.

Organic compounds and larger, less charged complexes of metals, can be chemically bonded with a media having strong sorption capacities. K_{OW} is an indication of the preference for the molecule to attach to an organic media (peat, compost, GAC) versus remaining in the stormwater runoff. K_S indicates the likelihood that the organic compound will remain dissolved in solution. The removal of some inorganic anions is difficult because most stormwater treatment media specifications stress high cation exchange capacities (CEC). High CEC media typically have low anion exchange capacities (AEC). CEC and AEC provide an estimate of the potential for exchanging a less-desirable compound with a pollutant whose chemical characteristics are more favorable. Table 7-8 lists some of the organic pollutants of concern in stormwater runoff and potential treatment options, based on their chemical properties and the results of laboratory, pilot-scale, and full-scale treatment tests.

Table 7-8. Selecting Treatment Technologies for Stormwater Organic Pollutants (summarized from Clark and Pitt 2012)

Organics and Pesticides		
PAHs/Oil and Grease (O&G)/Dioxin	Sedimentation or filtration, possibly followed with chemically-active media.	These compounds have high K_{OW} and low K_S and are strongly associated with particulates. Sedimentation's effectiveness is function of particle size association. Preferential sorption to organic media, such as peat, compost, and soil. Some O&G components can be microbially degraded in filter media. Reductions to very low levels with filtration may be difficult if parent material is contaminated. If low numeric permit limits exist, may have to use clean manufactured material, such as GAC.
Organic Acids and Bases	Chemically-active filtration	Tend to be more soluble in water than PAHs and more likely to be transported easily in treatment media. Need media with multiple types of sorption sites, such as peat, compost and soil. GAC possible if nonpolar part of molecule interacts well with GAC or if GAC has stronger surface active reactions than just van der Waals strength forces.
Pesticides	Chemically-active filtration	Tend to be soluble in water and need multiple reaction sites to be removed. Breakdown time in biologically-active filtration media is compound-dependent. Breakdown has the potential to restore surface-active sites, and may result in more soluble daughter products, which may or may not be more toxic. Organic media such as peat, compost, soil, GAC likely to be most effective since size of pesticide compounds will exclude substantial removal in ion-exchange resins such as zeolites.

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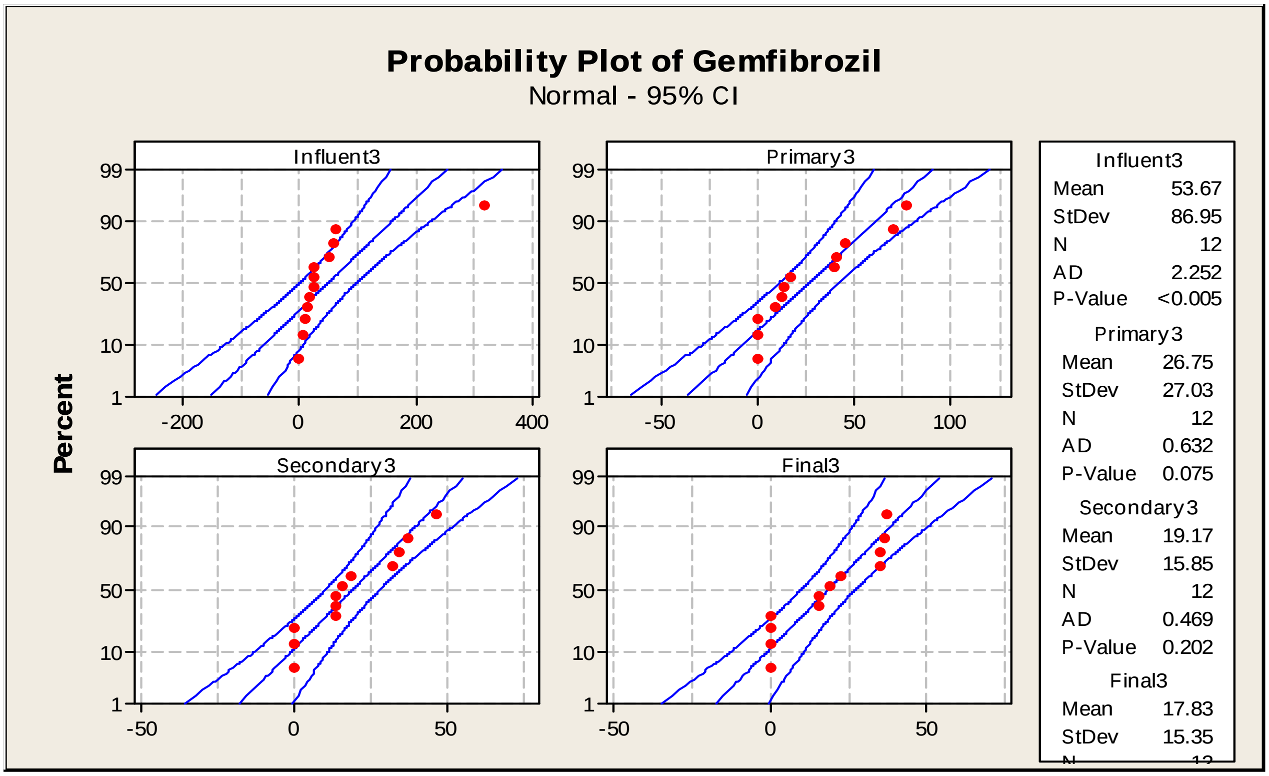
Appendix A. Emerging Contaminant Observations

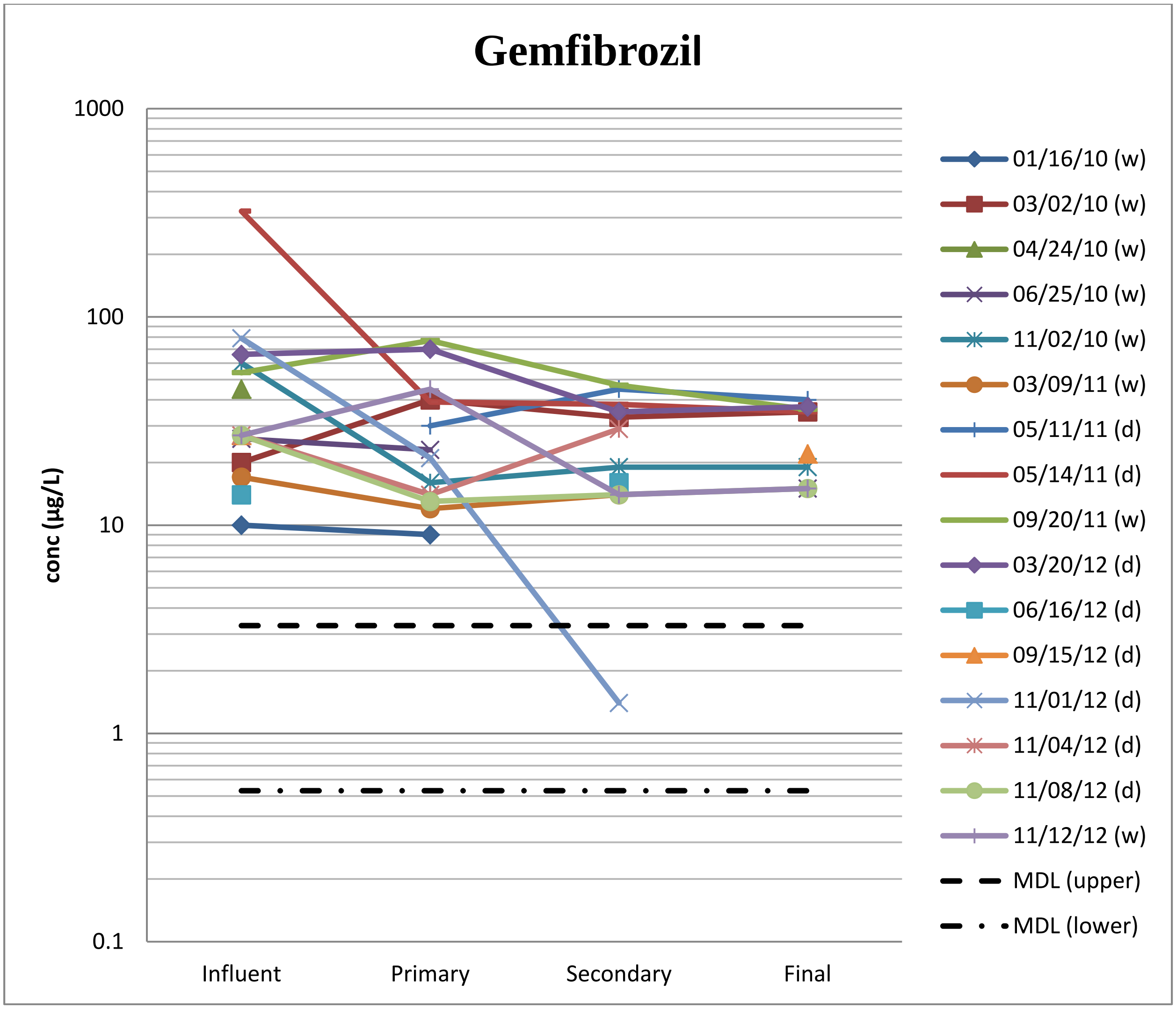
Pharmaceuticals

Gemfibrozil

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	10	9.0	<dl	<dl	18.2	688	0.55	100
3/2/2010	20	40	33	35	23.3	1,761	0.68	-75
4/24/2010	45	n/a	n/a	n/a	16.5	2,807	1.01	n/a
6/25/2010	26	23	<dl	15	20.7	2,034	0.59	42
11/2/2010	60	16	19	19	20.5	4,649	0.88	68
3/9/2011	17	12	14	<dl	42.2	2,712	2.67	100
5/11/2011	n/a	30	45	40	13.5	n/a	0.00	n/a
5/14/2011	322	39	38	35	30.7	37,367	0.00	89
9/20/2011	54	77	47	36	26.5	5,409	0.64	33
3/20/2012	66	70	35	37	17.1	4,266	0.00	44
6/16/2012	14	<dl	16	<dl	13.5	714	0.00	100
9/15/2012	27	<dl	<dl	22	14.5	1,480	0.00	19
11/1/2012	79	21	1.4	<dl	17.1	5,106	0.00	100
11/4/2012	27	14	29	<dl	15.4	1,572	0.05	100
Average dry (<0.1 inch of rain)	89	25	24	19	17.4	8,418	0.01	79 (calc. from averages)
Average wet	33	30	19	18	24	2,866	1.00	45 (calc. from averages)

* insufficient sample volume for analyses

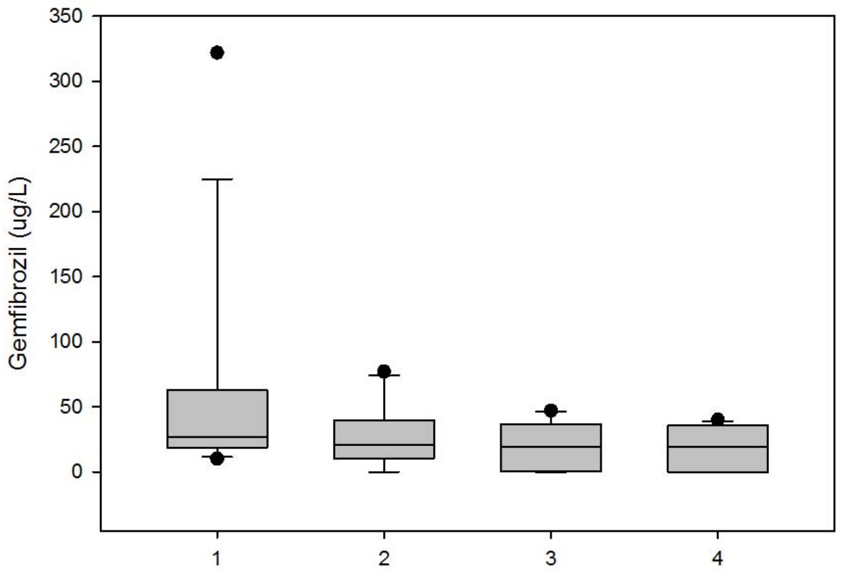

Probability Plot of Gemfibrozil
Normal - 95% CI
Percent
Influent3
Primary3
Secondary3
Final3
99
90
50
10
1
-200
0
200
400
-50
0
50
100
-50
0
50
Influent3
Mean 53.67
StDev 86.95
N 12
AD 2.252
P-Value <0.005
Primary3
Mean 26.75
StDev 27.03
N 12
AD 0.632
P-Value 0.075
Secondary3
Mean 19.17
StDev 15.85
N 12
AD 0.469
P-Value 0.202
Final3
Mean 17.83
StDev 15.35


Gemfibrozil
conc (µg/L)
1000
100
10
1
0.1
Influent
Primary
Secondary
Final
01/16/10 (w)
03/02/10 (w)
04/24/10 (w)
06/25/10 (w)
11/02/10 (w)
03/09/11 (w)
05/11/11 (d)
05/14/11 (d)
09/20/11 (w)
03/20/12 (d)
06/16/12 (d)
09/15/12 (d)
11/01/12 (d)
11/04/12 (d)
11/08/12 (d)
11/12/12 (w)
MDL (upper)
MDL (lower)

Column	Size	Missing	Mean	Std Dev	Std. Error	C-I. of Mean
Influent	15	2	59.000	82.000	22.743	49.552
after primary	15	2	27.000	24.187	6.708	14.616
after secondary	15	2	21.338	17.627	4.889	10.652
final effluent	15	2	18.385	16.810	4.662	10.158
FlowMGD	10	0	22.900	8.462	2.676	6.053
mass	9	1	7178.456	12293.197	4346.301	10277.369
rain depth	15	0	0.476	0.710	0.183	0.393

Column	Range	Max	Min	Median	25%	75%
Influent	312.000	322.000	10.000	27.000	19.250	61.500
after primary	77.000	77.000	0.000	21.000	11.250	39.250
after secondary	47.000	47.000	0.000	19.000	1.050	35.750
final effluent	40.000	40.000	0.000	19.000	0.000	35.250
FlowMGD	28.700	42.200	13.500	20.600	16.900	26.500
mass	36678.852	37366.812	687.960	2759.211	1897.938	5029.290
rain depth	2.670	2.670	0.000	0.0700	0.000	0.670

Column	Skewness	Kurtosis	K-S Dist.	K-S ProB-	SWilk W	SWilk Prob
Influent	3.171	10.720	0.327	<0.001	0.554	<0.001
after primary	1.086	0.497	0.181	0.278	0.884	0.080
after secondary	0.0310	-1.550	0.179	0.295	0.897	0.123
final effluent	0.00268	-1.927	0.248	0.028	0.817	0.011
FlowMGD	1.438	2.213	0.203	0.279	0.881	0.134
mass	2.743	7.631	0.432	<0.001	0.536	<0.001
rain depth	2.305	6.466	0.251	0.012	0.696	<0.001



1: Influent; 2: after primary; 3: after secondary; 4: final effluent

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Kruskal-Wallis One Way Analysis of Variance on Ranks

Group	N	Missing	Median	25%	75%
Influent	15	2	27.000	18.500	63.000
after primary	15	2	21.000	10.500	39.500
after secondary	15	2	19.000	0.700	36.500
final effluent	15	2	19.000	0.000	35.500

H = 5.408 with 3 degrees of freedom. (P = 0.144)

The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.144)

Mann-Whitney Rank Sum Test

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Influent	15	2	27.000	18.500	63.000
after primary	15	2	21.000	10.500	39.500

Mann-Whitney U Statistic= 55.500

T = 204.500 n(small)= 13 n(big)= 13 (P = 0.144)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.144)

```
Mann-Whitney Rank Sum Test

Normality Test (Shapiro-Wilk)   Passed        (P = 0.096)

Equal Variance Test:      Passed        (P = 0.618)

Group            N   Missing   Median      25%        75%
after primary    15       2       21.000     10.500     39.500
after secondary15       2       19.000      0.700     36.500

Mann-Whitney U Statistic= 78.000

T = 182.000  n(small)= 13  n(big)= 13  (P = 0.757)

The difference in the median values between the two groups is not great enough to
exclude the possibility that the difference is due to random sampling variability; there is
not a statistically significant difference  (P = 0.757)
```

```
Mann-Whitney Rank Sum Test

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

Group            N   Missing   Median      25%        75%
after secondary15       2       19.000      0.700     36.500
final effluent   15       2       19.000      0.000     35.500

Mann-Whitney U Statistic= 76.000

T = 184.000  n(small)= 13  n(big)= 13  (P = 0.677)

The difference in the median values between the two groups is not great enough to
exclude the possibility that the difference is due to random sampling variability; there is
not a statistically significant difference  (P = 0.677)
```

Mann-Whitney Rank Sum Test

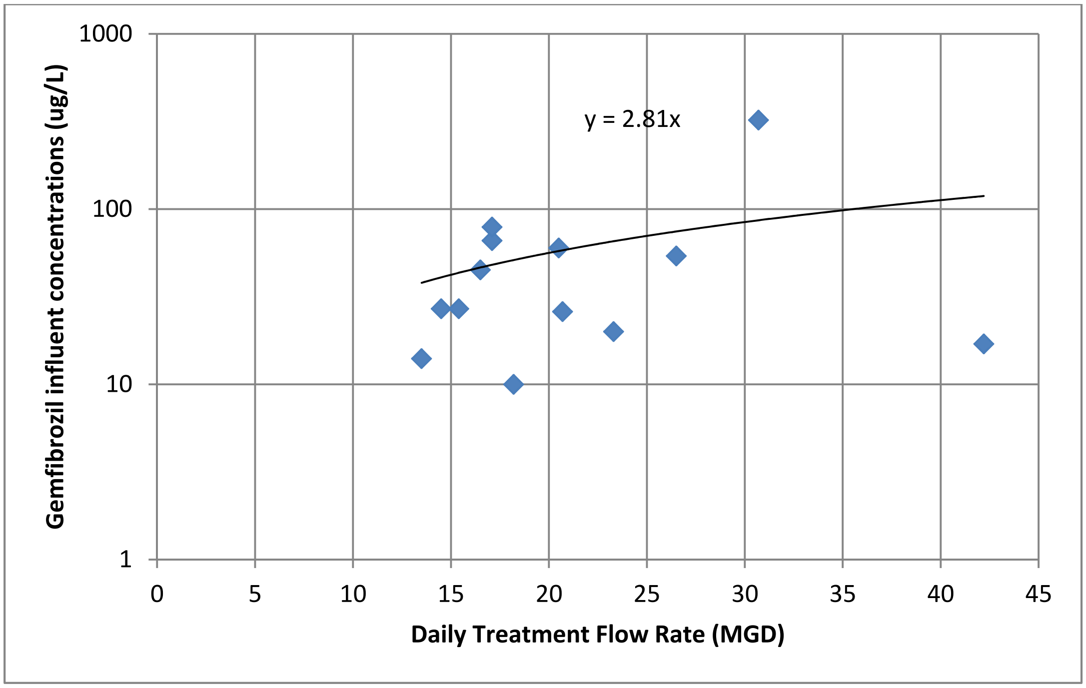
Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Influent	15	2	27.000	18.500	63.000
final effluent	15	2	19.000	0.000	35.500

Mann-Whitney U Statistic= 44.000

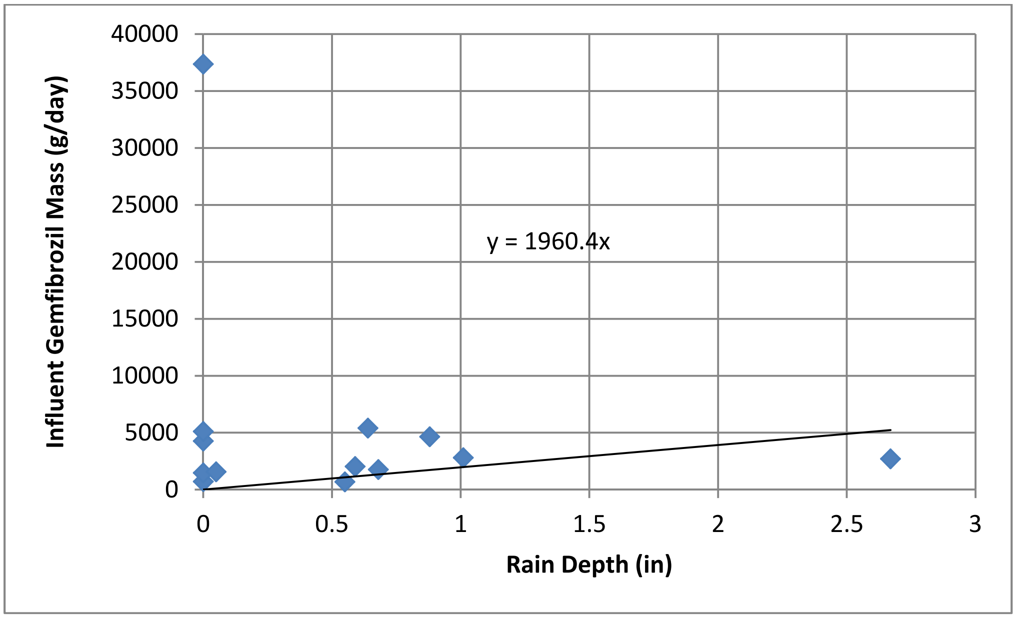
T = 216.000 n(small)= 13 n(big)= 13 (P = 0.039)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.039)



R^2	0.42					
Standard Error	78					
Observations	13					
ANOVA						
	df	SS	MS	F	Significance F	
Regression	1	52,524	52,524	8.59	0.013*	
Residual	12	73,417	6,118			
Total	13	125,941				
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Slope term	2.81	0.96	2.93	0.013*	0.72	4.95

*overall regression and slope terms are significant



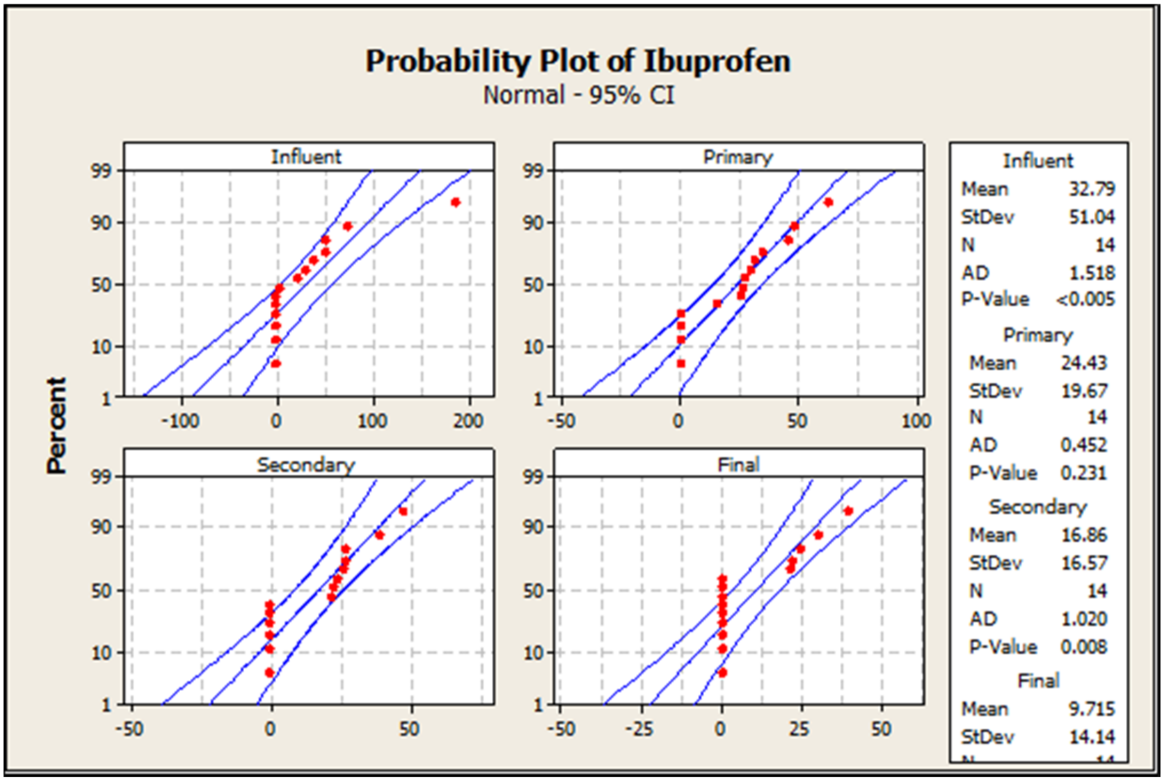
R^2	0.026					
Standard Error	11,103					
Observations	13					
ANOVA						
	df	SS	MS	F	Significance F	
Regression	1	40,156,596	40,156,596	0.33	0.58*	
Residual	12	1,479,389,797	1.23E+08			
Total	13	1,519,546,393				
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Slope term	1,960	3,435	0.57,	0.58*	-5,524	9,445

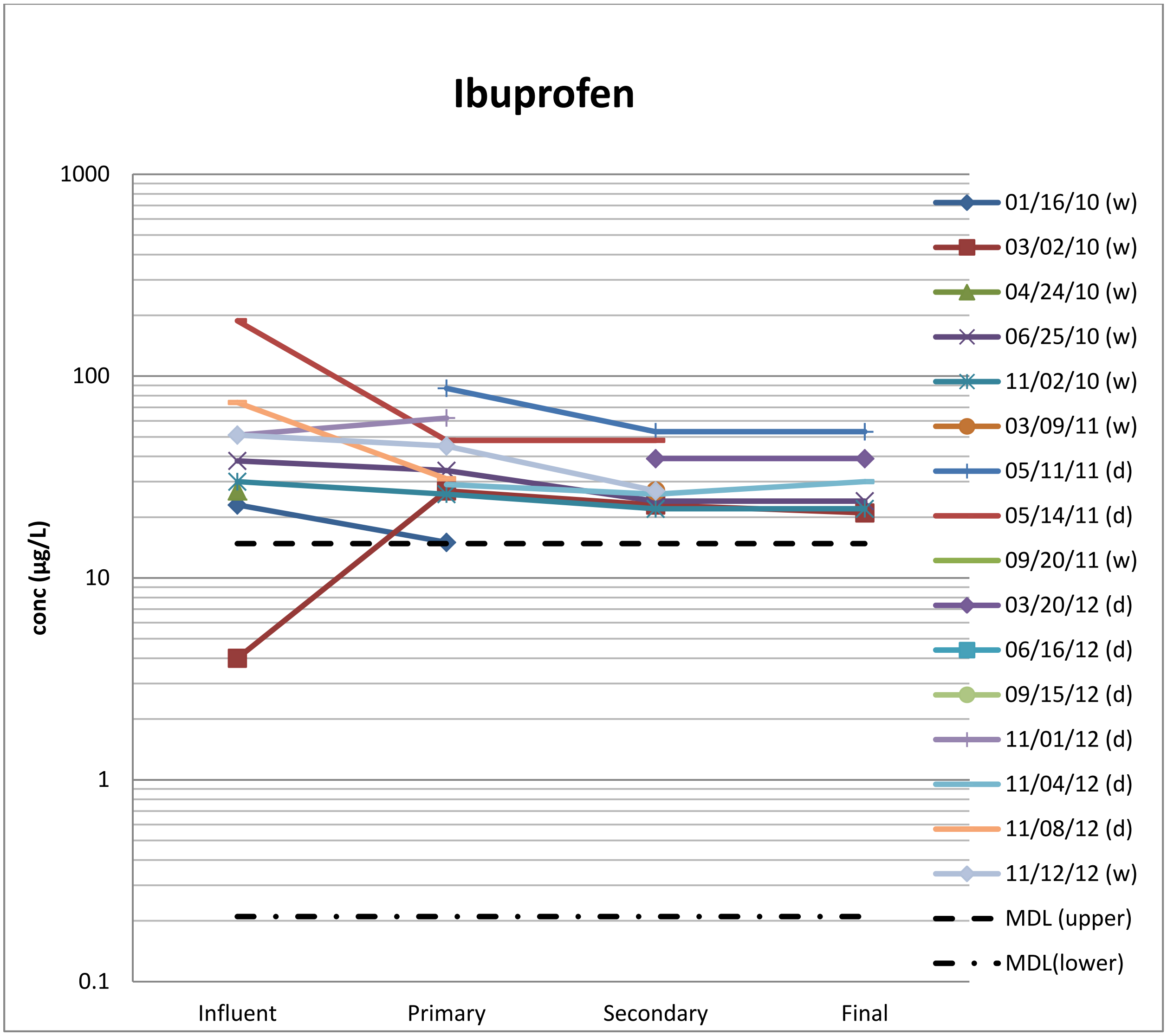
*overall regression and slope terms are not significant

Ibuprofen

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	23	15	<dl	<dl	18.2	1,582	0.55	100
3/2/2010	4.0	27	23	21	23.3	352	0.68	-425
4/24/2010	27	n/a*	n/a	n/a	16.5	1,684	1.01	n/a
6/25/2010	38	34	24	24	20.7	2,973	0.59	37
11/2/2010	30	26	22	22	20.5	2,325	0.88	27
3/9/2011	<dl	<dl	27	<dl	42.2	<dl	2.67	Increase from <dl
5/11/2011	n/a	87	53	53	13.5	n/a	0.00	Increase from <dl
5/14/2011	188	48	48	<dl	30.7	21,817	0.00	100
9/20/2011	<dl	<dl	<dl	<dl	26.5	<dl	0.64	n/a
3/20/2012	<dl	<dl	39	39	17.1	0	0.00	Increase from <dl
6/16/2012	<dl	25	<dl	<dl	13.5	0	0.00	n/a
9/15/2012	<dl	<dl	<dl	<dl	14.5	0	0.00	n/a
11/1/2012	51	62	<dl	<dl	17.1	3,297	0.00	100
11/4/2012	<dl	29	26	30	15.4	0	0.05	Increase from <dl
Average dry (<0.1 inch of rain)	40	36	24	17	17.4	4,186	0.01	58 (calc. from averages)
Average wet	17	17	16	11	24.0	1,274	1.00	35 (calc. from averages)

* insufficient sample volume for analyses

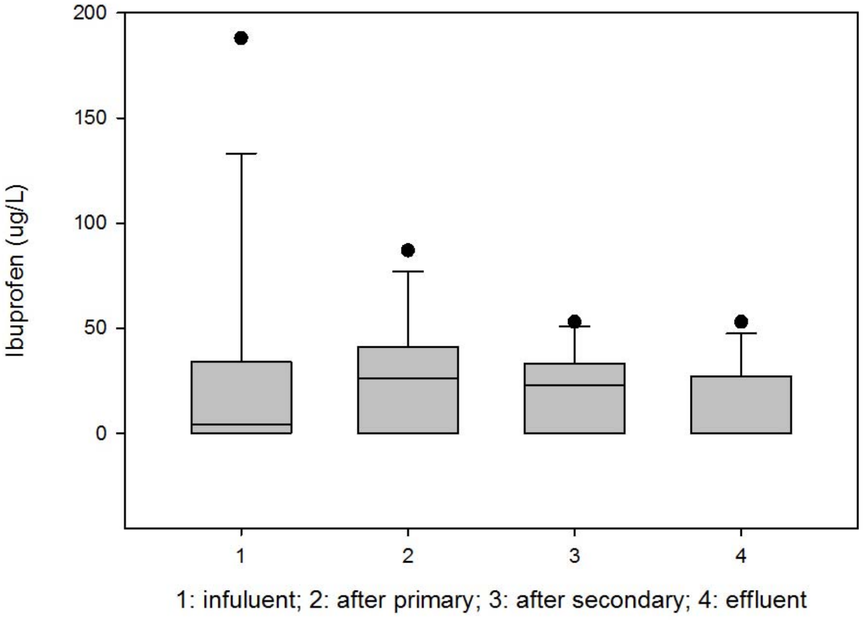

Probability Plot of Ibuprofen
Normal - 95% CI
Percent
Influent
Primary
Secondary
Final
99
90
50
10
1
-100
0
100
200
-50
0
50
100
-50
0
50
-50
-25
0
25
50
Influent
Mean 32.79
StDev 51.04
N 14
AD 1.518
P-Value <0.005
Primary
Mean 24.43
StDev 19.67
N 14
AD 0.452
P-Value 0.231
Secondary
Mean 16.86
StDev 16.57
N 14
AD 1.020
P-Value 0.008
Final
Mean 9.715
StDev 14.14


Ibuprofen
conc (µg/L)
1000
100
10
1
0.1
Influent
Primary
Secondary
Final
01/16/10 (w)
03/02/10 (w)
04/24/10 (w)
06/25/10 (w)
11/02/10 (w)
03/09/11 (w)
05/11/11 (d)
05/14/11 (d)
09/20/11 (w)
03/20/12 (d)
06/16/12 (d)
09/15/12 (d)
11/01/12 (d)
11/04/12 (d)
11/08/12 (d)
11/12/12 (w)
MDL (upper)
MDL(lower)

Column	Size	Missing	Mean	Std Dev	Std. Error	C-I. of Mean
influent	15	2	27.769	51.266	14.219	30.980
after primary	15	2	27.154	26.432	7.331	15.973
after secondary	15	2	20.154	19.034	5.279	11.502
effluent	15	2	14.538	18.219	5.053	11.010
flowMGD	10	0	22.900	8.462	2.676	6.053
rain depth	15	0	0.476	0.710	0.183	0.393
mass	9	1	3841.661	7344.657	2596.728	6140.287

Column	Range	Max	Min	Median	25%	75%
influent	188.000	188.000	0.000	4.000	0.000	32.000
after primary	87.000	87.000	0.000	26.000	0.000	37.500
after secondary	53.000	53.000	0.000	23.000	0.000	30.000
effluent	53.000	53.000	0.000	0.000	0.000	25.500
flowMGD	28.700	42.200	13.500	20.600	16.900	26.500
rain depth	2.670	2.670	0.000	0.0700	0.000	0.670
mass	21816.648	21816.648	0.000	1633.149	176.148	2649.024

Column	Skewness	Kurtosis	K-S Dist.	K-S ProB-	SWilk W	SWilk Prob
influent	2.913	9.314	0.294	0.003	0.588	<0.001
after primary	0.982	0.787	0.167	0.385	0.888	0.090
after secondary	0.334	-1.070	0.240	0.040	0.866	0.046
effluent	0.900	-0.262	0.326	<0.001	0.794	0.006
flowMGD	1.438	2.213	0.203	0.279	0.881	0.134
rain depth	2.305	6.466	0.251	0.012	0.696	<0.001
mass	2.705	7.475	0.422	<0.001	0.556	<0.001



Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Kruskal-Wallis One Way Analysis of Variance on Ranks

Group	**N**	**Missing**	**Median**	**25%**	**75%**
influent	15	2	4.000	0.000	34.000
after primary	15	2	26.000	0.000	41.000
after secondary	15	2	23.000	0.000	33.000
effluent	15	2	0.000	0.000	27.000

H = 1.955 with 3 degrees of freedom. (P = 0.582)

The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.582)

Mann-Whitney Rank Sum Test

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
influent	15	2	4.000	0.000	34.000
after primary	15	2	26.000	0.000	41.000

Mann-Whitney U Statistic= 71.500

T = 162.500 n(small)= 13 n(big)= 13 (P = 0.509)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.509)

Mann-Whitney Rank Sum Test

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
after primary	15	2	26.000	0.000	41.000
after secondary	15	2	23.000	0.000	33.000

Mann-Whitney U Statistic= 70.500

T = 189.500 n(small)= 13 n(big)= 13 (P = 0.479)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.479)

Mann-Whitney Rank Sum Test

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
after secondary	15	2	23.000	0.000	33.000
effluent	15	2	0.000	0.000	27.000

Mann-Whitney U Statistic= 68.500

T = 191.500 n(small)= 13 n(big)= 13 (P = 0.402)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.402)

Mann-Whitney Rank Sum Test

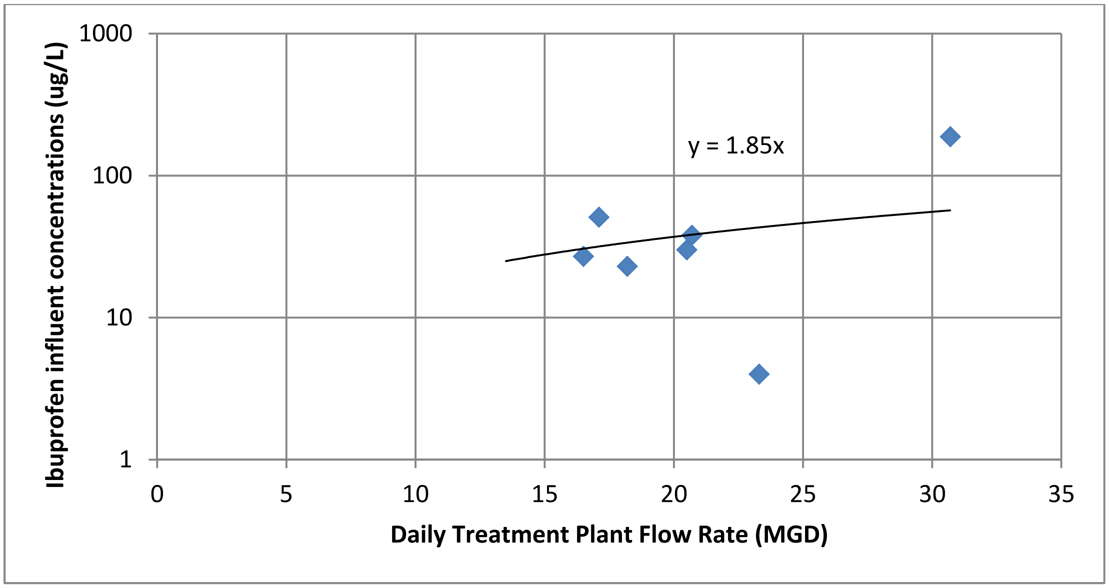
Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
influent	15	2	4.000	0.000	34.000
effluent	15	2	0.000	0.000	27.000

Mann-Whitney U Statistic= 75.500

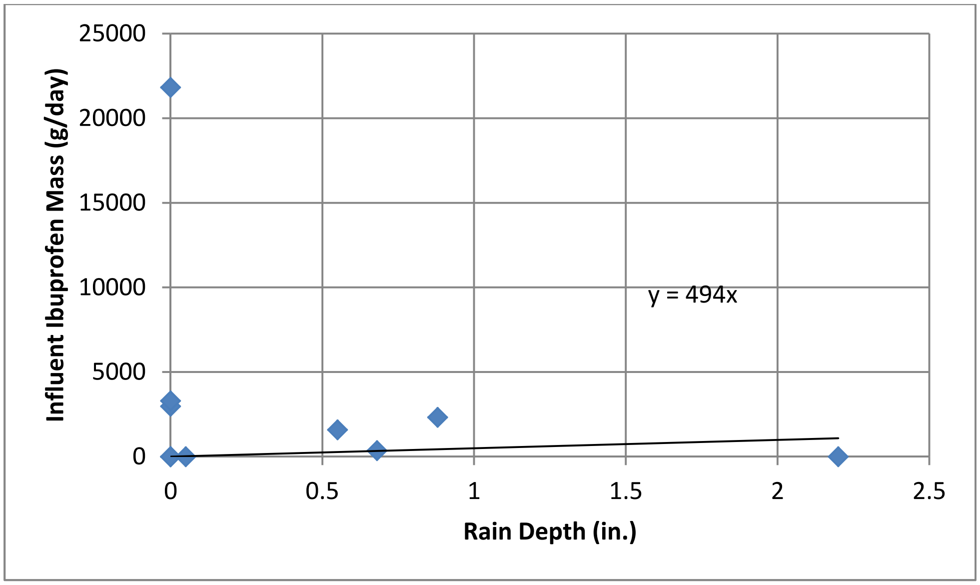
T = 184.500 n(small)= 13 n(big)= 13 (P = 0.641)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.641)



R^2	0.43					
Standard Error	41.8					
Observations	12					
ANOVA						
	df	SS	MS	F	Significance F	
Regression	1	13,228	13,228	7.57	0.020*	
Residual	10	17,475	1,748			
Total	11	30,703				
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Slope term	6.74	2.45	2.75	0.020*	1.28	12.2

*overall regression and slope terms are significant

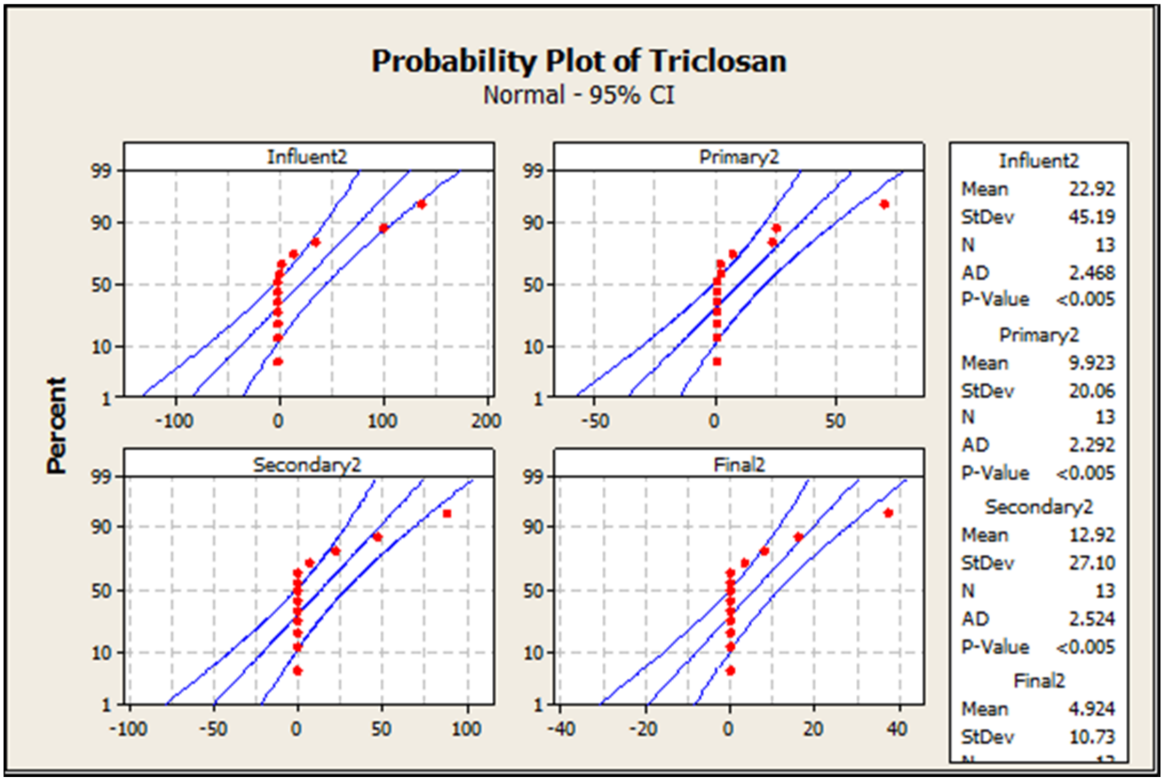


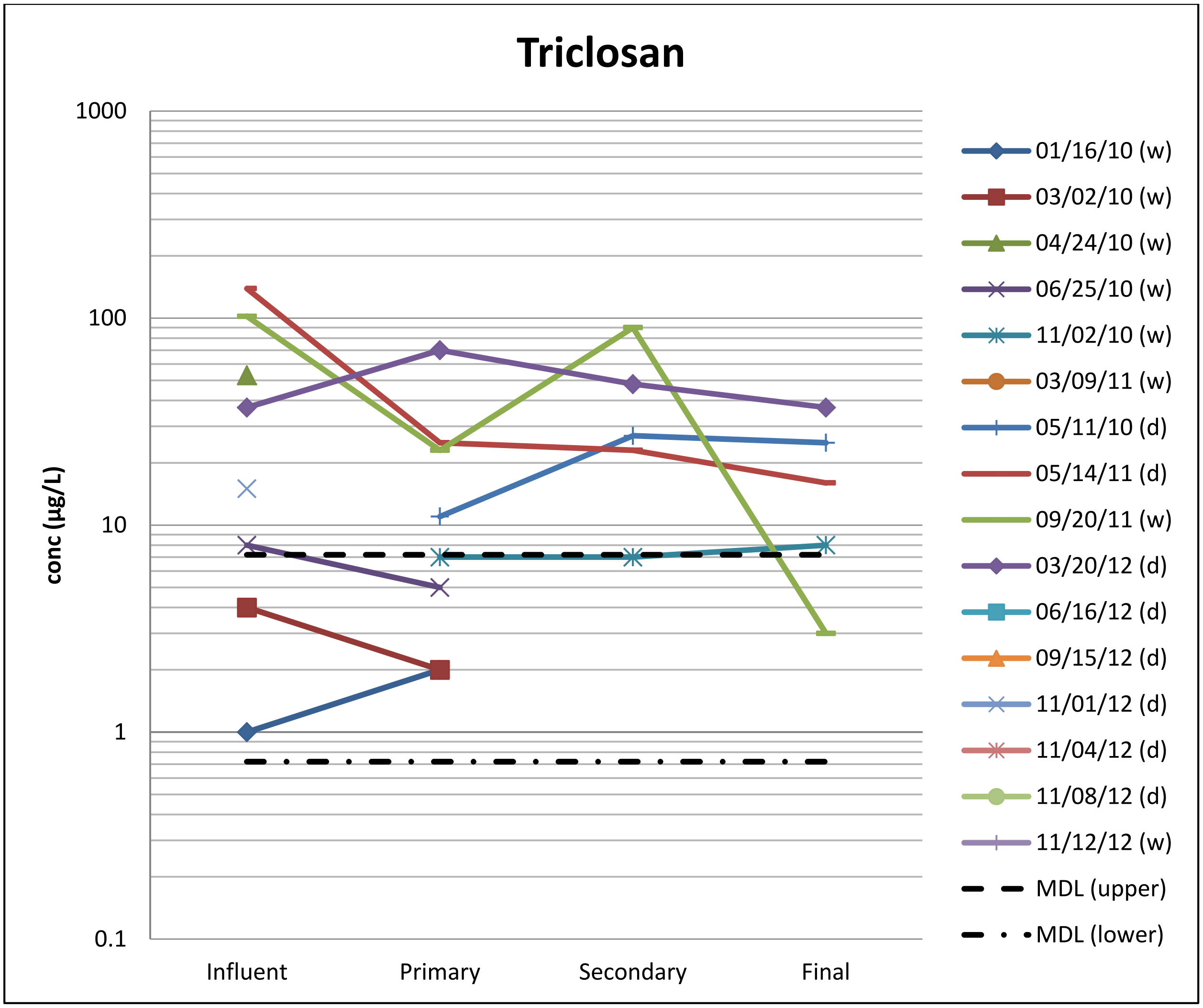
R^2	0.003					
Standard Error	7,086					
Observations	11					
ANOVA						
	df	SS	MS	F	Significance F	
Regression	1	1,560,312	1,560,312	0.031	0.86*	
Residual	10	502,145,820	50,214,582			
Total	11	503,706,132				
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Slope term	494	2,805	0.17	0.86*	-5,756	6,745

*overall regression and slope terms are not significant

Triclosan

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	1.0	2.0	0.0	0.0	18.2	69	0.55	100
3/2/2010	4.0	2.0	0.0	0.0	23.3	352	0.68	100
4/24/2010	53	n/a	n/a	n/a	16.5	3,306	1.01	n/a
6/25/2010	8	5	<dl	<dl	20.7	626	0.59	100
11/2/2010	<dl	7	7	8	20.5	n/a	0.88	n/a
3/9/2011	<dl	<dl	<dl	<dl	42.2	n/a	2.67	n/a
5/11/2011	n/a	11	27	25	13.5	n/a	0.00	n/a
5/14/2011	139	25	23	16	30.7	16,130	0.00	89
9/20/2011	102	23	90	3.0	26.5	10,217	0.64	97
3/20/2012	37	70	48	37	17.1	2,392	0.00	0
6/16/2012	<dl	<dl	<dl	<dl	13.5	0	0.00	n/a
9/15/2012	<dl	<dl	<dl	<dl	14.5	0	0.00	n/a
11/1/2012	15	<dl	<dl	<dl	17.1	970	0.00	100
11/4/2012	<dl	<dl	<dl	<dl	15.4	0	0.05	n/a
Average dry (<0.1 inch of rain)	32	15	14	11	17.4	3,249	0.01	66 (calc. from averages)
Average wet	24	6.5	16	1.8	21	2,428	1.00	93 (calc. from averages)

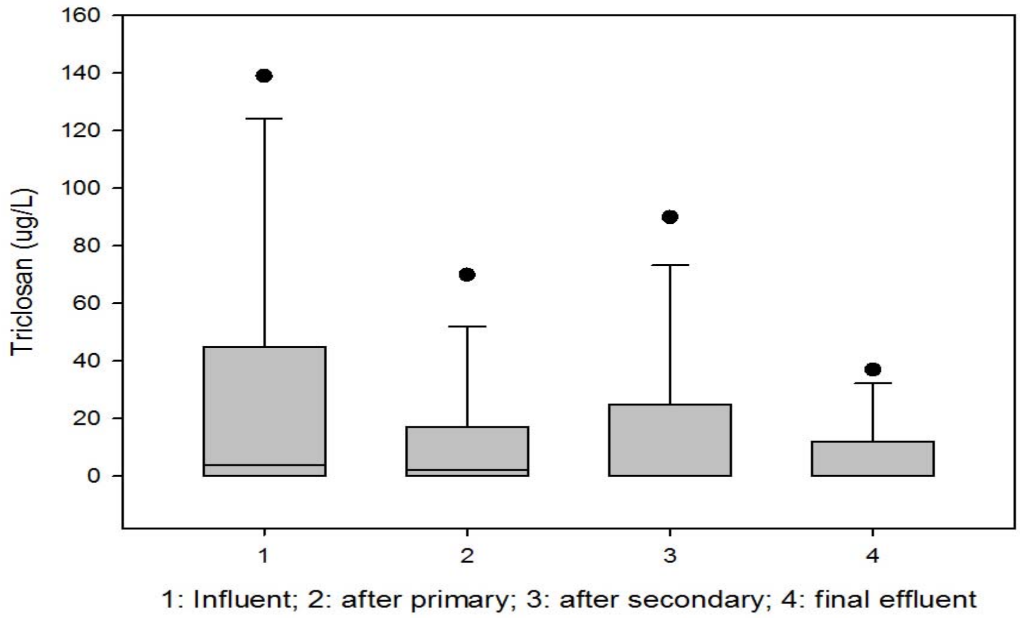

Probability Plot of Triclosan
Normal - 95% CI
Percent
Influent2
Primary2
Secondary2
Final2
99
90
50
10
1
-100
0
100
200
-50
0
50
-100
-50
0
50
100
-40
-20
0
20
40
Influent2
Mean 22.92
StDev 45.19
N 13
AD 2.468
P-Value <0.005
Primary2
Mean 9.923
StDev 20.06
N 13
AD 2.292
P-Value <0.005
Secondary2
Mean 12.92
StDev 27.10
N 13
AD 2.524
P-Value <0.005
Final2
Mean 4.924
StDev 10.73



Column	Size	Missing	Mean	Std Dev	Std. Error	C-I. of Mean
influent	14	1	27.616	44.995	12.479	27.190
after primary	14	1	11.154	19.663	5.454	11.882
after secondary	14	1	15.000	27.058	7.505	16.351
final effluent	14	1	6.846	11.950	3.314	7.221
flow MGD	9	0	23.567	8.692	2.897	6.682
influent mass	9	1	3837.580	6073.540	2147.321	5077.606
rain depth	14	0	0.505	0.727	0.194	0.420

Column	Range	Max	Min	Median	25%	75%
influent	139.000	139.000	0.000	4.000	0.000750	41.000
after primary	70.000	70.000	0.000	2.000	0.000	14.000
after secondary	90.000	90.000	0.000	0.001000	0.000	24.000
final effluent	37.000	37.000	0.000	0.001000	0.000	10.000
flow MGD	28.700	42.200	13.500	20.700	17.775	27.550
influent mass	16130.317	16130.394	0.0775	489.132	34.478	6761.475
rain depth	2.670	2.670	0.000	0.300	0.000	0.680

Column	Skewness	Kurtosis	K-S Dist.	K-S ProB-	SWilk W	SWilk Prob
influent	1.799	2.425	0.303	0.002	0.691	<0.001
after primary	2.582	7.271	0.285	0.005	0.633	<0.001
after secondary	2.150	4.628	0.326	<0.001	0.647	<0.001
final effluent	1.820	2.564	0.332	<0.001	0.662	<0.001
flow MGD	1.291	1.855	0.185	0.456	0.907	0.293
influent mass	1.594	1.495	0.327	0.012	0.714	0.003
rain depth	2.209	5.991	0.244	0.024	0.710	<0.001



```
Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

Kruskal-Wallis One Way Analysis of Variance on Ranks

Group            N   Missing   Median      25%        75%
influent         14      1     4.000      0.000500  45.000
after primary    14      1     2.000      0.000     17.000
after secondary14        1     0.001000 0.000       25.000
final effluent   14      1     0.001000 0.000       12.000

H = 1.361 with 3 degrees of freedom. (P = 0.715)

The differences in the median values among the treatment groups are not great enough
to exclude the possibility that the difference is due to random sampling variability; there
is not a statistically significant difference    (P = 0.715)


Mann-Whitney Rank Sum Test

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

Group          N   Missing   Median      25%        75%
influent       14      1       4.000    0.000500  45.000
after primary  14      1       2.000    0.000     17.000

Mann-Whitney U Statistic= 73.000

T = 187.000  n(small)= 13  n(big)= 13  (P = 0.569)

The difference in the median values between the two groups is not great enough to
exclude the possibility that the difference is due to random sampling variability; there is
not a statistically significant difference  (P = 0.569)


Mann-Whitney Rank Sum Test

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

Group            N   Missing   Median       25%        75%
after primary    14      1     2.000        0.000     17.000
after secondary14        1     0.001000     0.000     25.000

Mann-Whitney U Statistic= 82.000

T = 178.000  n(small)= 13  n(big)= 13  (P = 0.917)
```

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.917)

Mann-Whitney Rank Sum Test

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
after secondary	14	1	0.001000	0.000	25.000
final effluent	14	1	0.001000	0.000	12.000

Mann-Whitney U Statistic= 79.000

T = 181.000 n(small)= 13 n(big)= 13 (P = 0.792)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.792)

Mann-Whitney Rank Sum Test

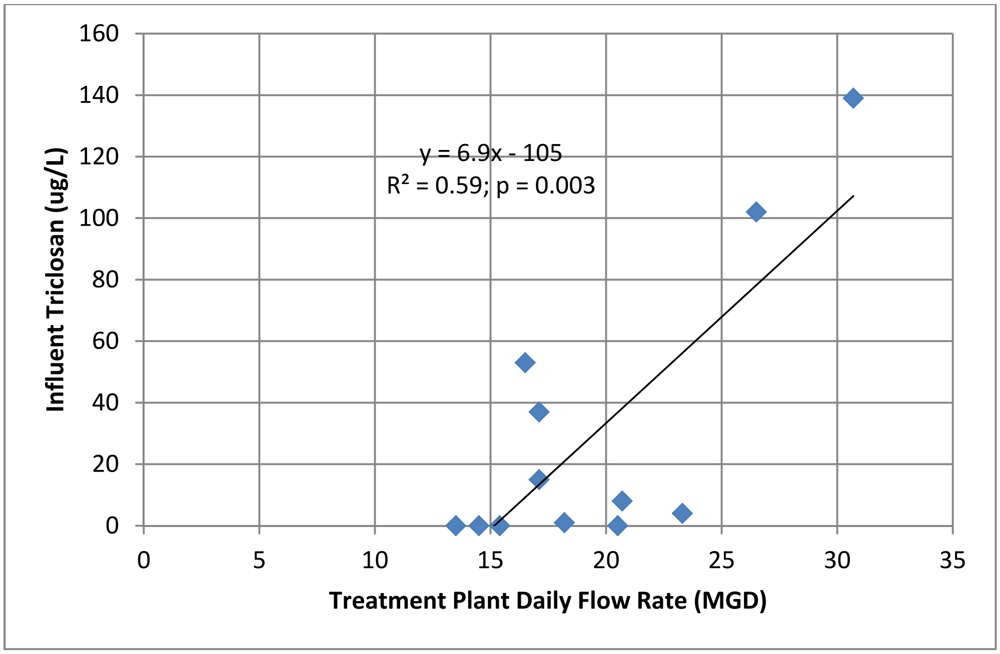
Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
influent	14	1	4.000	0.000500	45.000
final effluent	14	1	0.001000	0.000	12.000

Mann-Whitney U Statistic= 63.000

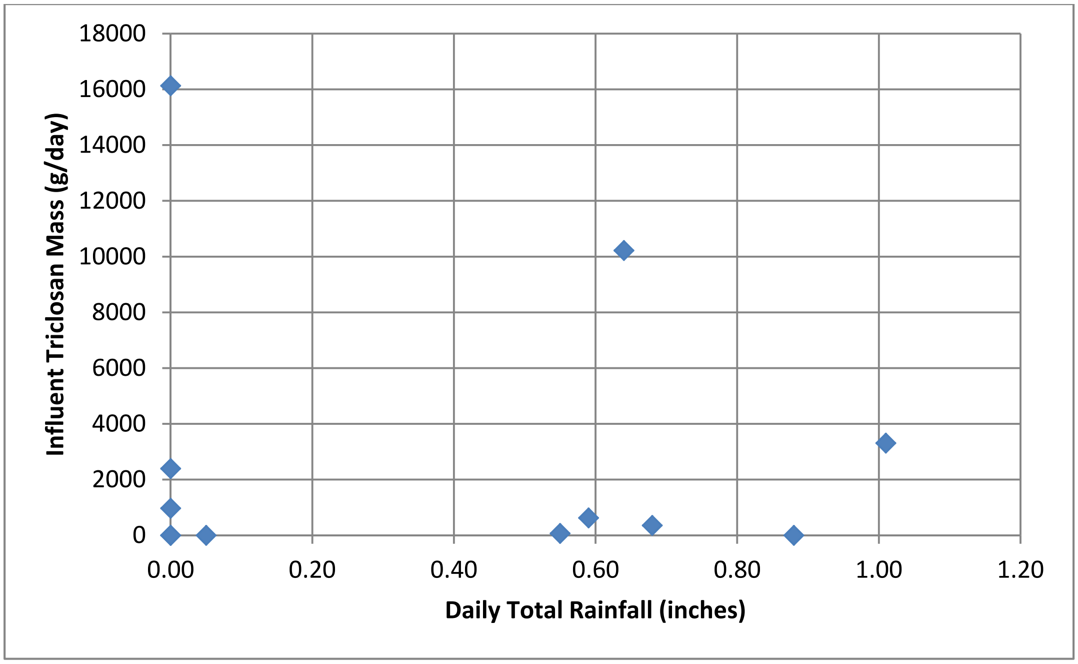
T = 197.000 n(small)= 13 n(big)= 13 (P = 0.274)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.274)



R^2	0.59					
Standard Error	30.9					
Observations	12					
ANOVA						
	df	SS	MS	F	Significance F	
Regression	1	13,874	13,874	14.57	0.0035*	
Residual	10	9,595	959			
Total	11	234,697				
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-105	36.5	-2.87	0.017*	-1867	-23.37
Slope term	6.90	1.81	3.80	0.0035*	2.86	10.9

*overall regression, intercept, and slope terms are significant

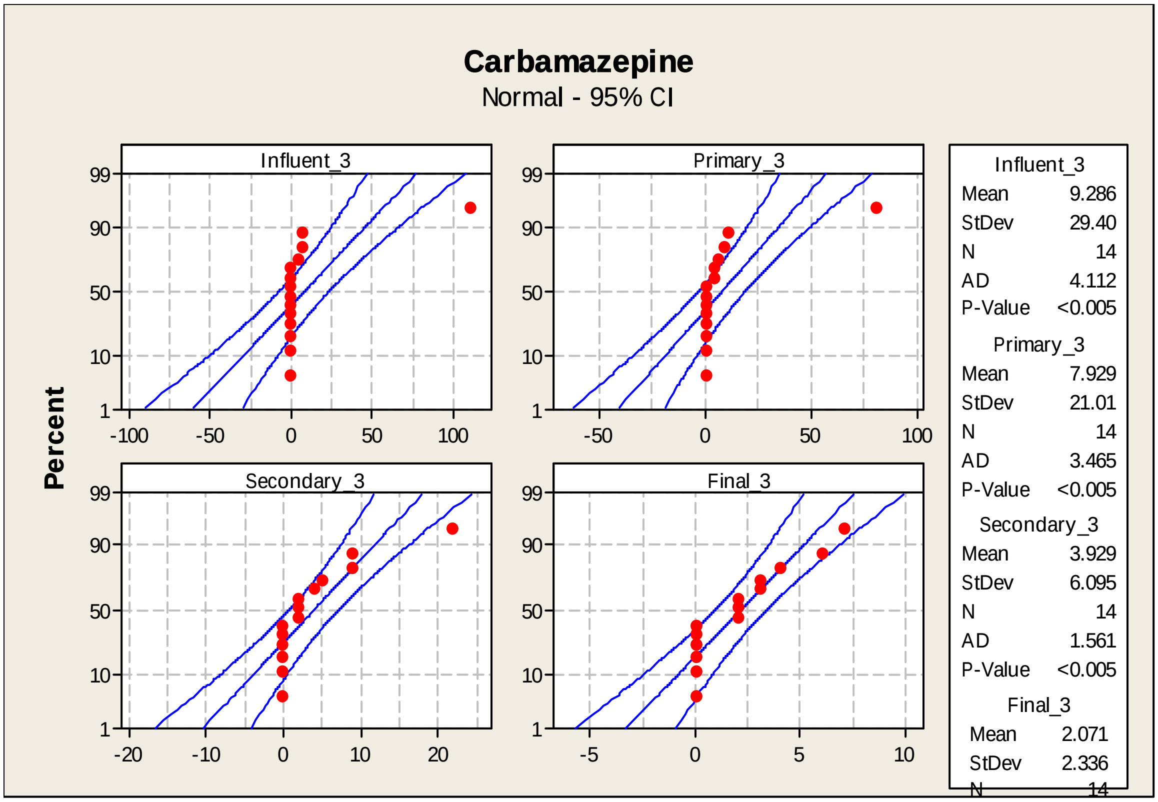


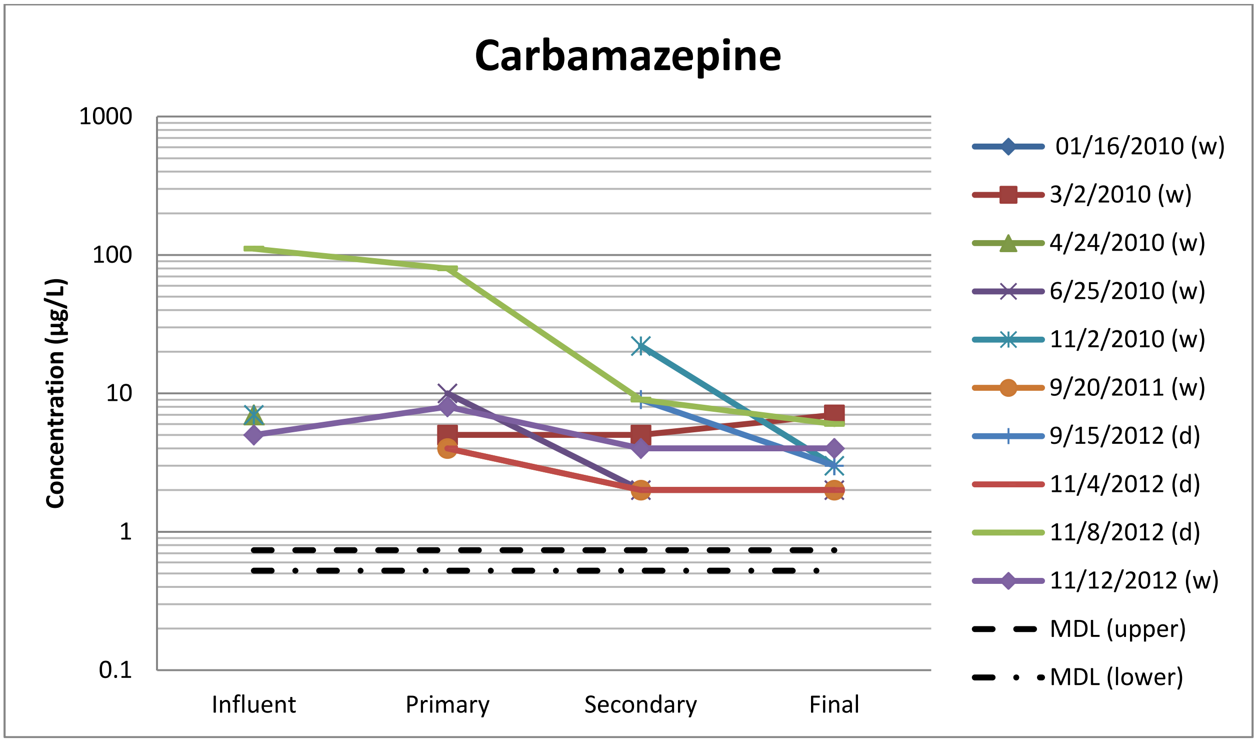
R^2	0.09					
Standard Error	5,635					
Observations	12					
ANOVA						
	df	SS	MS	F	Significance F	
Regression	1	33,367,332	33,367,332	1.05	0.33*	
Residual	11	349,323,899	31,756,718			
Total	12	382,691,231				
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Slope term	3,170	3,093	1.03	0.33*	-3,637	9,978

*overall regression and slope terms are not significant

Carbamazepine

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	0.0	8.0	0.0	0.0	18.2	0	0.55	0
3/2/2010	0.0	5.0	5.0	7.0	23.3	0	0.68	0
4/24/2010	7.0	n/a	n/a	n/a	16.5	437	1.01	0
6/25/2010	0	10	**2**	2	20.7	0	0.59	0.0
11/2/2010	7	0	22	3	20.5	542	0.88	57.1
3/9/2011	0	0	0	0	42.2	0	2.67	0.0
5/11/2011	n/a	0.0	0.0	0.0	13.5	n/a	0.00	0.0
5/14/2011	0.0	0.0	0.0	0.0	30.7	0	0.00	0.0
9/20/2011	0.00	4.00	2.0	2.0	26.5	0	0.64	0.0
3/20/2012	0.0	0	0.0	0.0	17.1	0	0.00	0.0
6/16/2012	0.00	0.00	0.00	0.00	13.5	0	0.00	0.0
9/15/2012	0.00	0.00	9.0	3.0	14.5	0	0.00	0.0
11/1/2012	0.00	0.00	0.00	0.00	17.1	0	0.00	0.0
11/4/2012	0.00	4.0	2.0	2.0	15.4	0	0.05	0.0
11/8/2012	111.00	80.0	9.0	6.0	15.9	6,671	0.00	94.6
11/12/2012	5.00	8.0	4.0	4.0	16	302	0.44	20.0
Average dry (<0.1 inch of rain)	15.86	10.50	2.50	1.38	17.21	953.05	0.01	12 (calc. from averages)
Average wet	2.38	5.00	5.00	2.57	22.99	160.18	0.93	9.6 (calc. from averages)


Carbamazepine
Normal - 95% CI
Percent
Influent_3
Primary_3
Secondary_3
Final_3
99
90
50
10
1
-100
-50
0
50
100
-20
-10
20
-5
5
10
Influent_3
Mean 9.286
StDev 29.40
N 14
AD 4.112
P-Value <0.005
Primary_3
Mean 7.929
StDev 21.01
N 14
AD 3.465
P-Value <0.005
Secondary_3
Mean 3.929
StDev 6.095
N 14
AD 1.561
P-Value <0.005
Final_3
Mean 2.071
StDev 2.336
N 14

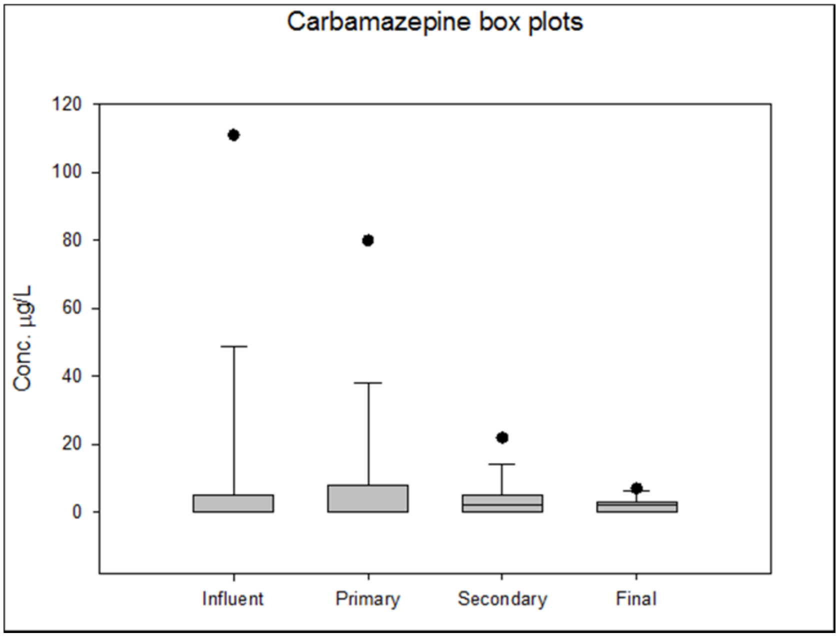

Carbamazepine
Concentration (µg/L)
1000
100
10
1
0.1
Influent
Primary
Secondary
Final
01/16/2010 (w)
3/2/2010 (w)
4/24/2010 (w)
6/25/2010 (w)
11/2/2010 (w)
9/20/2011 (w)
9/15/2012 (d)
11/4/2012 (d)
11/8/2012 (d)
11/12/2012 (w)
MDL (upper)
MDL (lower)

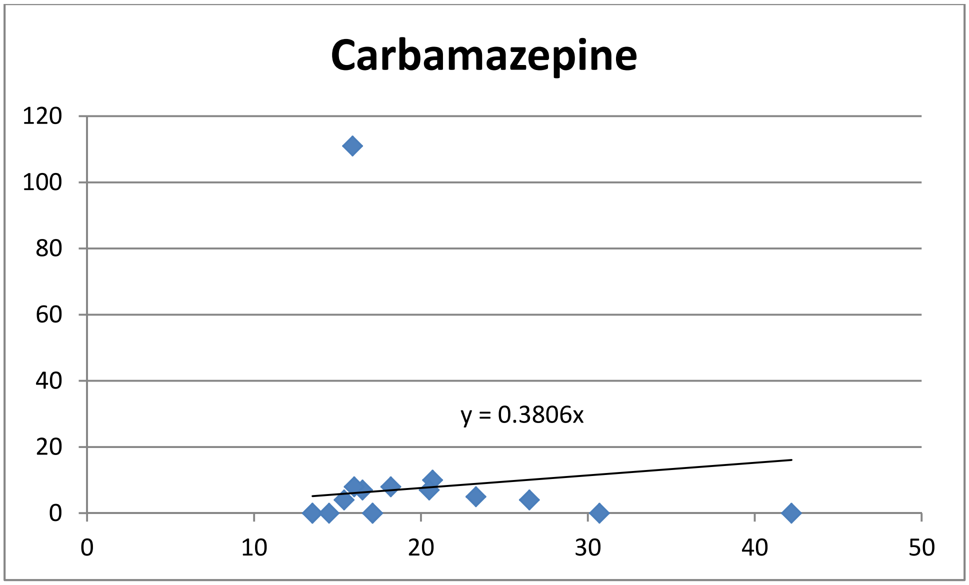
Column	Size	Missing	Mean	Std Dev	Std. Error	C-I. of Mean
Influent	16	1	8.667	28.432	7.341	15.745
After primary	16	1	7.933	20.250	5.229	11.214
After secondary	16	1	3.667	5.960	1.539	3.301
After final	16	1	1.933	2.314	0.597	1.281

Column	Range	Max	Min	Median	25%	75%
Carbamazepine-Inf	111.000	111.000	0.000	0.000	0.000	3.750
Carbamazepine-Prim	80.000	80.000	0.000	0.000	0.000	7.250
Carbamazepine-Sec	22.000	22.000	0.000	2.000	0.000	4.750
Carbamazepine-Fin	7.000	7.000	0.000	2.000	0.000	3.000

Column	Skewness	Kurtosis	K-S Dist.	K-S ProB-	SWilk W	SWilk Prob
Carbamazepine-Inf	3.817	14.683	0.457	<0.001	0.341	<0.001
Carbamazepine-Prim	3.674	13.879	0.393	<0.001	0.422	<0.001
Carbamazepine-Sec	2.378	6.322	0.277	0.003	0.673	<0.001
Carbamazepine-Fin	1.052	0.263	0.265	0.006	0.816	0.006

Column	Sum	Sum of Squares
Carbamazepine-Inf	130.000	12444.000
Carbamazepine-Prim	119.000	6685.000
Carbamazepine-Sec	55.000	699.000
Carbamazepine-Fin	29.000	131.000





Regression and coefficients are not significant based on the ANOVA analysis:

SUMMARY OUTPUT

Regression Statistics	
Adjusted R Square	0.016884
Standard Error	27.85985
Observations	16

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1061.43	1061.43	1.36752	0.261764
Residual	15	11642.57	776.1713		
Total	16	12704			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Slope term	0.380632	0.32549	1.16941	0.260486	-0.31313	1.074398

```
One Way Analysis of Variance

Data source: Data 1 in Notebook1

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)


Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source: Data 1 in Notebook1

Group N   Missing   Median     25%       75%
Col 1  16       1       0.000     0.000     5.000
Col 2  16       1       0.000     0.000     8.000
Col 3  16       1       2.000     0.000     5.000
Col 4  16       1       2.000     0.000     3.000

H = 1.574 with 3 degrees of freedom. (P = 0.665)

The differences in the median values among the treatment groups are not great enough
to exclude the possibility that the difference is due to random sampling variability; there
is not a statistically significant difference    (P = 0.665)


Mann-Whitney Rank Sum Test

Data source: Data 1 in Notebook1

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

Group N   Missing   Median     25%       75%
Col 1  16       1       0.000     0.000     5.000
Col 2  16       1       0.000     0.000     8.000

Mann-Whitney U Statistic= 91.500

T = 211.500  n(small)= 15  n(big)= 15  (P = 0.325)

The difference in the median values between the two groups is not great enough to
exclude the possibility that the difference is due to random sampling variability; there is
not a statistically significant difference  (P = 0.325)
```

Mann-Whitney Rank Sum Test

Data source: Data 1 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Col 2	16	1	0.000	0.000	8.000
Col 3	16	1	2.000	0.000	5.000

Mann-Whitney U Statistic= 111.500

T = 233.500 n(small)= 15 n(big)= 15 (P = 0.982)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.982**)

Mann-Whitney Rank Sum Test

Data source: Data 1 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Col 3	16	1	2.000	0.000	5.000
Col 4	16	1	2.000	0.000	3.000

Mann-Whitney U Statistic= 104.500

T = 240.500 n(small)= 15 n(big)= 15 (P = 0.742)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.742**)

Mann-Whitney Rank Sum Test

Data source: Data 1 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Col 1	16	1	0.000	0.000	5.000
Col 4	16	1	2.000	0.000	3.000

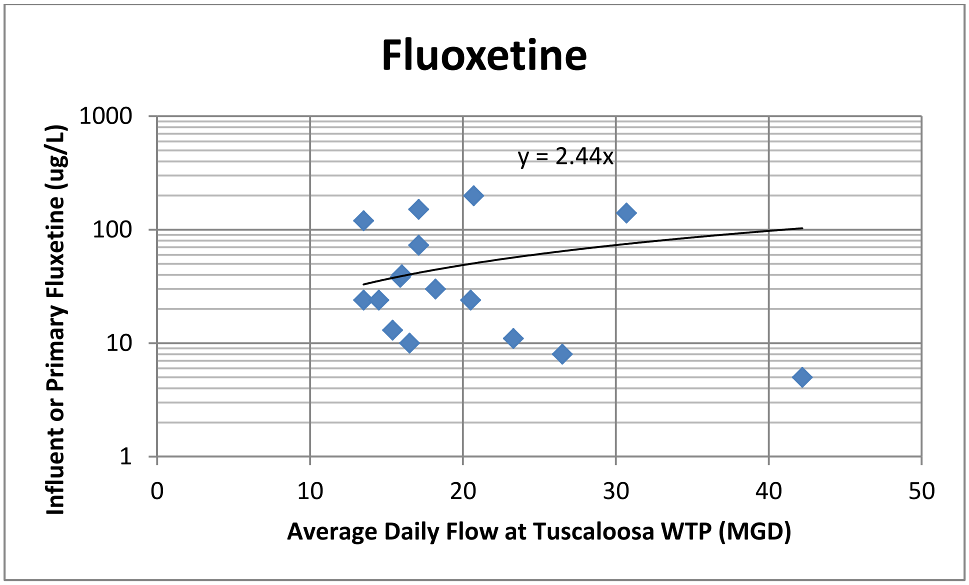
Mann-Whitney U Statistic= 95.500

T = 215.500 n(small)= 15 n(big)= 15 (P = 0.439)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.439**)

Fluoxetine

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	30.0	18.0	0.0	0.0	18.2	2,064	0.55	100.0
3/2/2010	11.0	0.0	9.0	0.0	23.3	969	0.68	100.0
4/24/2010	10.0	n/a	n/a	n/a	16.5	624	1.01	0.0
6/25/2010	8	199	7	7	20.7	626	0.59	12.5
11/2/2010	18	24	0	0	20.5	1,395	0.88	100.0
3/9/2011	0	5	7	6	42.2	0	2.67	0.0
5/11/2011	n/a	120.0	13.0	0.0	13.5	0	0.00	0.0
5/14/2011	140.0	0.0	26.0	0.0	30.7	16,246	0.00	100.0
9/20/2011	8.00	6.00	0.0	0.0	26.5	801	0.64	100.0
3/20/2012	73.0	48	9.0	19.0	17.1	4,719	0.00	74.0
6/16/2012	17.00	24.0	5.0	12.0	13.5	868	0.00	29.4
9/15/2012	12.00	24.0	14.0	19.0	14.5	658	0.00	-58.3
11/1/2012	151.00	47.0	12.0	14.0	17.1	9,760	0.00	90.7
11/4/2012	1.00	13.0	5.0	5.0	15.4	58	0.05	-400.0
11/8/2012	38.00	18.0	9.0	8.0	15.9	2,284	0.00	78.9
11/12/2012	28.00	40.0	0.0	0.0	16	1,693	0.44	100.0
Average dry (<0.1 inch of rain)	61.71	36.75	11.63	9.63	17.21	4,941.81	0.01	-11 (calc. from averages)
Average wet	14.13	41.71	3.29	1.86	22.99	4,046.11	0.93	64 (calc. from averages)



Overall equation and slope term are both significant (p = 0.006) based on ANOVA:

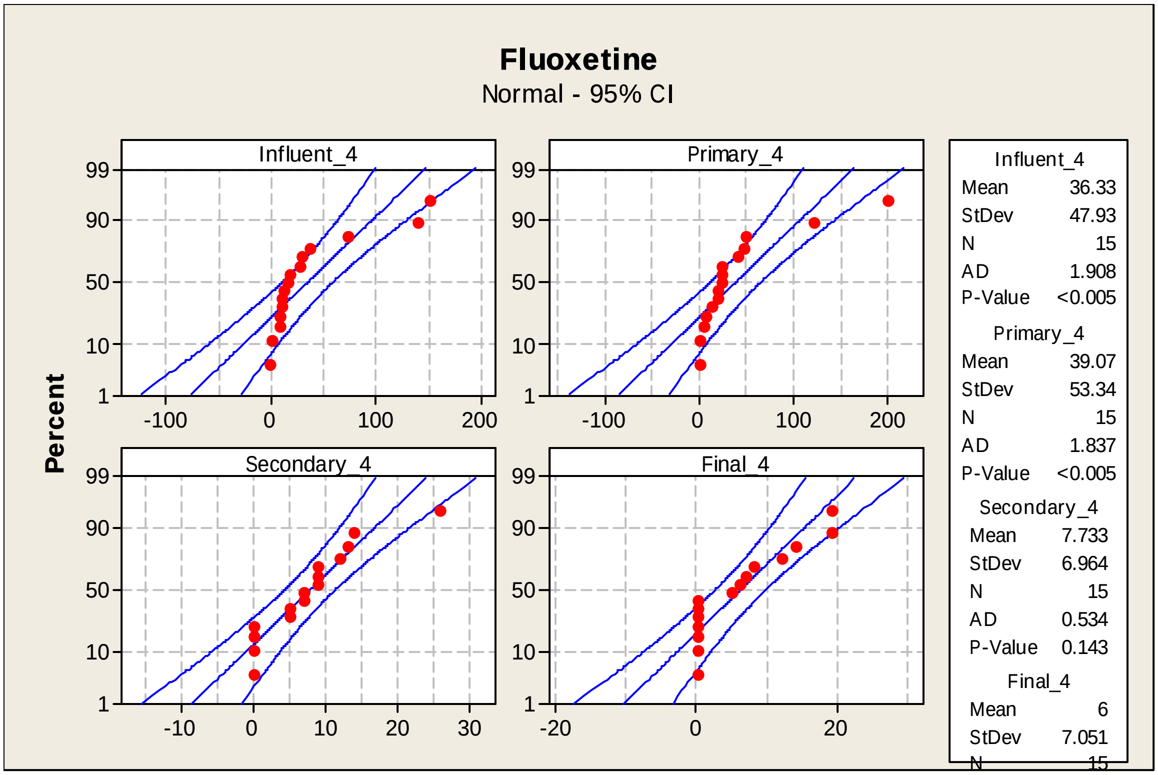
SUMMARY OUTPUT

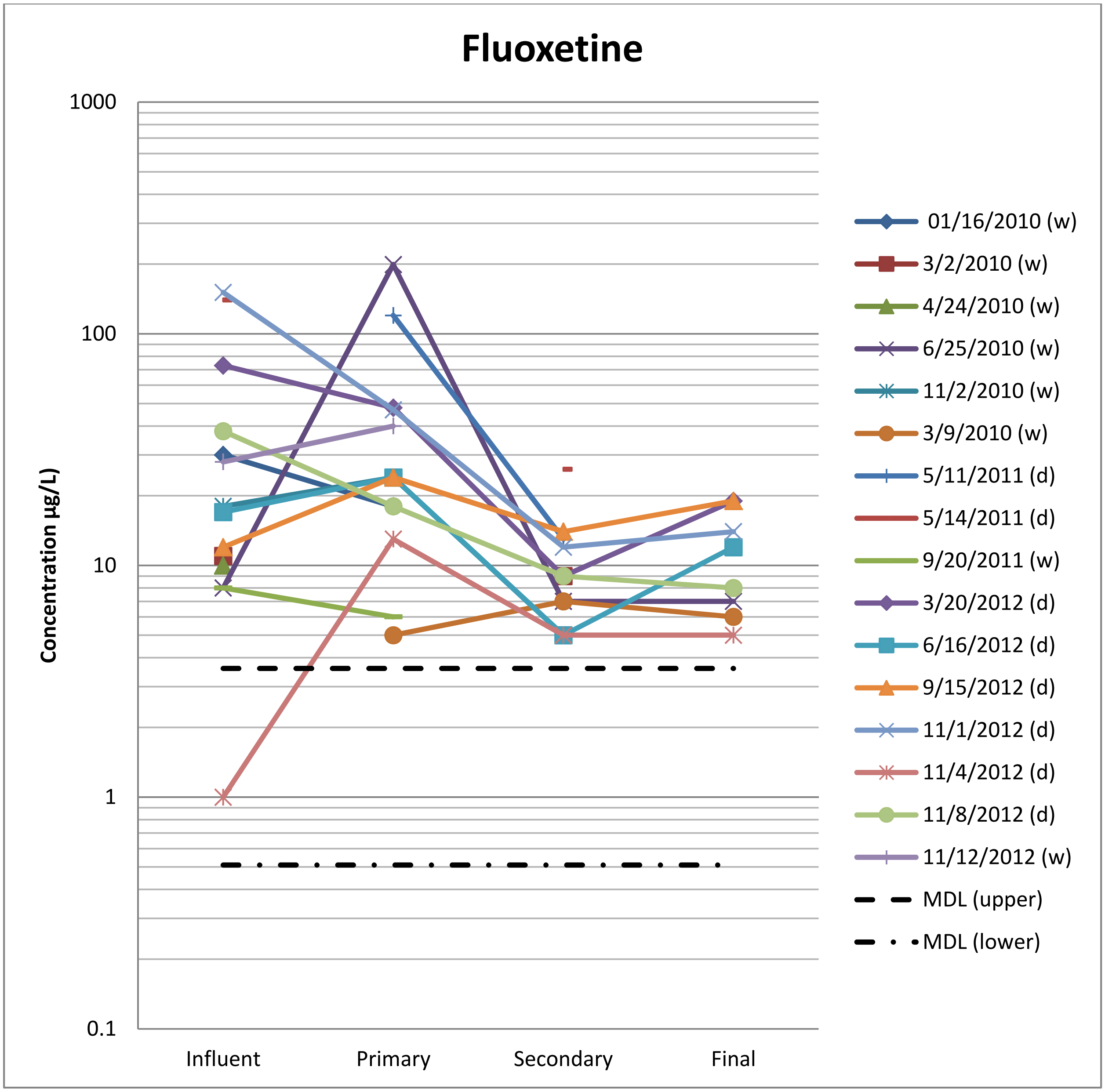
Regression Statistics	
Adjusted R Square	0.337206
Standard Error	65.47847
Observations	16

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	43570.54	43570.54	10.16239	0.006578
Residual	15	64311.46	4287.431		
Total	16	107882			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Slope term	2.438686	0.764994	3.18785	0.006114	0.80814	4.069232


Fluoxetine
Normal - 95% CI
Percent
Influent_4
Primary_4
Secondary_4
Final_4
99
90
50
10
1
-100
0
100
200
-10
10
20
30
-20
Influent_4
Mean 36.33
StDev 47.93
N 15
AD 1.908
P-Value <0.005
Primary_4
Mean 39.07
StDev 53.34
N 15
AD 1.837
P-Value <0.005
Secondary_4
Mean 7.733
StDev 6.964
N 15
AD 0.534
P-Value 0.143
Final_4
Mean 6
StDev 7.051
N 15



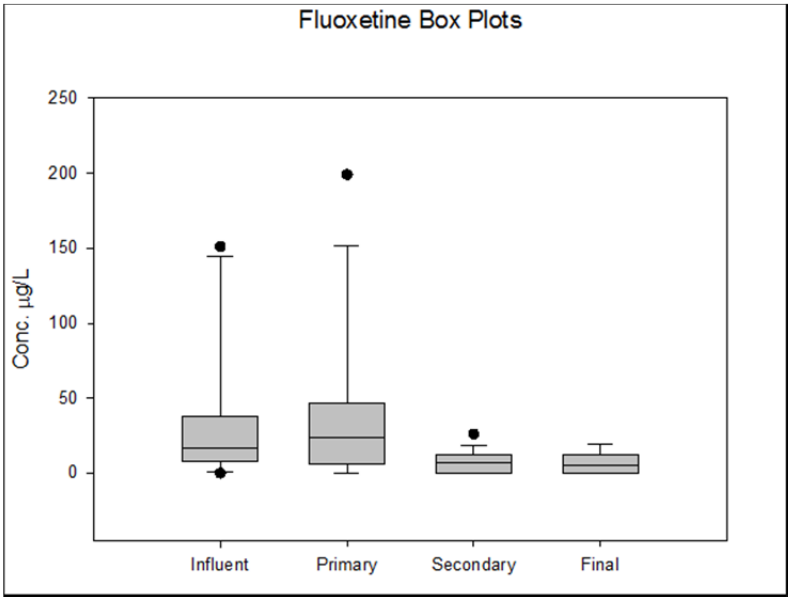
Column	Size	Missing	Mean	Std Dev	Std. Error	C-I. of Mean
Fluoxetine-Inf	16	1	36.333	47.931	12.376	26.543
Fluoxetine-Prim	16	1	39.067	53.336	13.771	29.537
Fluoxetine-Sec	16	1	7.733	6.964	1.798	3.856
Fluoxetine-Final	16	1	6.000	7.051	1.821	3.905

Column	Range	Max	Min	Median	25%	75%
Fluoxetine-Inf	151.000	151.000	0.000	17.000	8.500	36.000
Fluoxetine-Prim	199.000	199.000	0.000	24.000	7.750	45.250
Fluoxetine-Sec	26.000	26.000	0.000	7.000	1.250	11.250

Fluoxetine-Final	19.000	19.000	0.000	5.000	0.000	11.000

Column	**Skewness**	**Kurtosis**	**K-S Dist.**	**K-S ProB-**	**SWilk W**	**SWilk Prob**
Fluoxetine-Inf	1.849	2.399	0.286	0.002	0.700	<0.001
Fluoxetine-Prim	2.379	5.809	0.300	<0.001	0.684	<0.001
Fluoxetine-Sec	1.142	2.231	0.161	0.348	0.884	0.054
Fluoxetine-Final	0.851	-0.586	0.269	0.005	0.812	0.005

Column	**Sum**	**Sum of Squares**
Fluoxetine-Inf	545.000	51965.000
Fluoxetine-Prim	586.000	62720.000
Fluoxetine-Sec	116.000	1576.000
Fluoxetine-Final	90.000	1236.000



One Way Analysis of Variance

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source: PHRM 2 in Notebook1

```
Group N   Missing   Median     25%      75%
Col 6  16      1      17.000    8.000    38.000
Col 7  16      1      24.000    6.000    47.000
Col 8  16      1       7.000    0.000    12.000
Col 9  16      1       5.000    0.000    12.000
```

H = 15.108 with 3 degrees of freedom. (P = 0.002)

The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (**P = 0.002**)

To isolate the group or groups that differ from the others use a multiple comparison procedure.

All Pairwise Multiple Comparison Procedures (Tukey Test):

```
Comparison Diff of Ranks     q       P<0.05
Col 7 vs Col 9    292.500      4.324          Yes
Col 7 vs Col 8    237.500      3.511           No
Col 7 vs Col 6     14.000      0.207Do Not Test
Col 6 vs Col 9    278.500      4.117          Yes
Col 6 vs Col 8    223.500      3.304Do Not Test
Col 8 vs Col 9     55.000      0.813           No
```

Mann-Whitney Rank Sum Test

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

```
Group N   Missing   Median     25%      75%
Col 6  16      1      17.000    8.000    38.000
Col 7  16      1      24.000    6.000    47.000
```

Mann-Whitney U Statistic= 105.000

T = 225.000 n(small)= 15 n(big)= 15 (P = 0.771)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.771**)

Mann-Whitney Rank Sum Test

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Col 7	16	1	24.000	6.000	47.000
Col 8	16	1	7.000	0.000	12.000

Mann-Whitney U Statistic= 52.500

T = 292.500 n(small)= 15 n(big)= 15 (P = 0.013)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (**P = 0.013**)

Mann-Whitney Rank Sum Test

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Col 8	16	1	7.000	0.000	12.000
Col 9	16	1	5.000	0.000	12.000

Mann-Whitney U Statistic= 93.000

T = 252.000 n(small)= 15 n(big)= 15 (P = 0.418)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.418**)

Mann-Whitney Rank Sum Test

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

```
Group N   Missing   Median     25%       75%
Col 6  16     1      17.000    8.000    38.000
Col 9  16     1       5.000    0.000    12.000
```

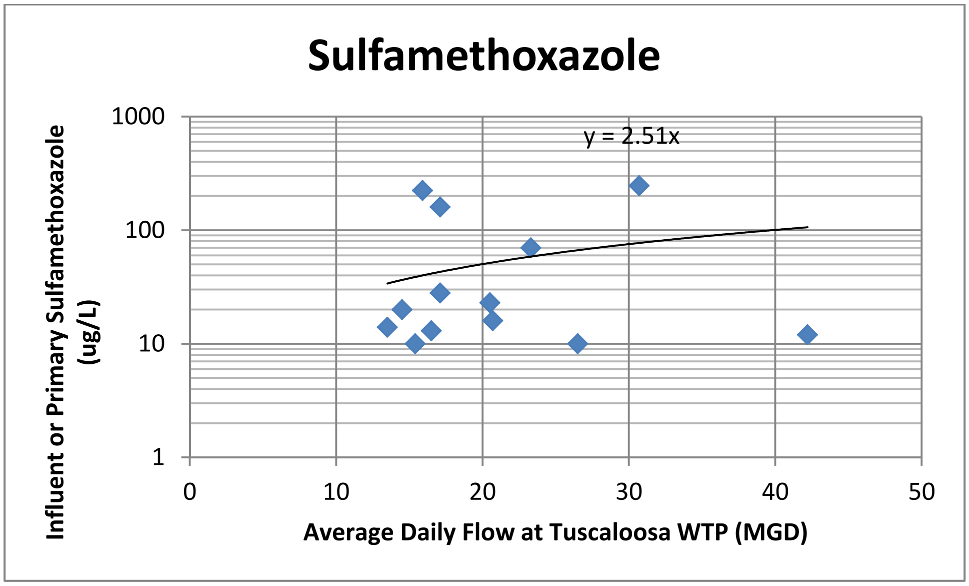
Mann-Whitney U Statistic= 44.000

T = 301.000 n(small)= 15 n(big)= 15 (P = 0.004)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (**P = 0.004**)

Sulfamethoxazole

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	0.0	0.0	14.0	12.0	18.2	0	0.55	0.0
3/2/2010	26.0	70.0	22.0	24.0	23.3	2,290	0.68	7.7
4/24/2010	13.0	n/a	n/a	n/a	16.5	811	1.01	0.0
6/25/2010	10	16	9	10	20.7	782	0.59	0.0
11/2/2010	23	21	10	10	20.5	1,782	0.88	56.5
3/9/2011	11	12	12	10	42.2	1,755	2.67	9.1
5/11/2011	n/a	0.0	57.0	0.0	13.5		0.00	0.0
5/14/2011	247.0	46.0	0.0	42.0	30.7	28,663	0.00	83.0
9/20/2011	0.00	10.00	24.0	13.0	26.5	0	0.64	0.0
3/20/2012	0.0	28	50.0	31.0	17.1	0	0.00	0.0
6/16/2012	0.00	14.0	9.0	19.0	13.5	0	0.00	0.0
9/15/2012	10.00	20.0	34.0	25.0	14.5	548	0.00	-150.0
11/1/2012	0.00	160.0	22.0	0.0	17.1	0	0.00	0.0
11/4/2012	0.00	10.0	24.0	13.0	15.4	0	0.05	0.0
11/8/2012	224.00	63.0	53.0	65.0	15.9	13,463	0.00	71.0
11/12/2012	0.00	0.0	12.0	13.0	16	0	0.44	0.0
Average dry (<0.1 inch of rain)	68.71	42.63	31.13	24.38	17.21	6,096.33	0.01	0.50 (from average)
Average wet	10.38	18.43	14.71	13.14	22.99	927.52	0.93	9.16 (from average)



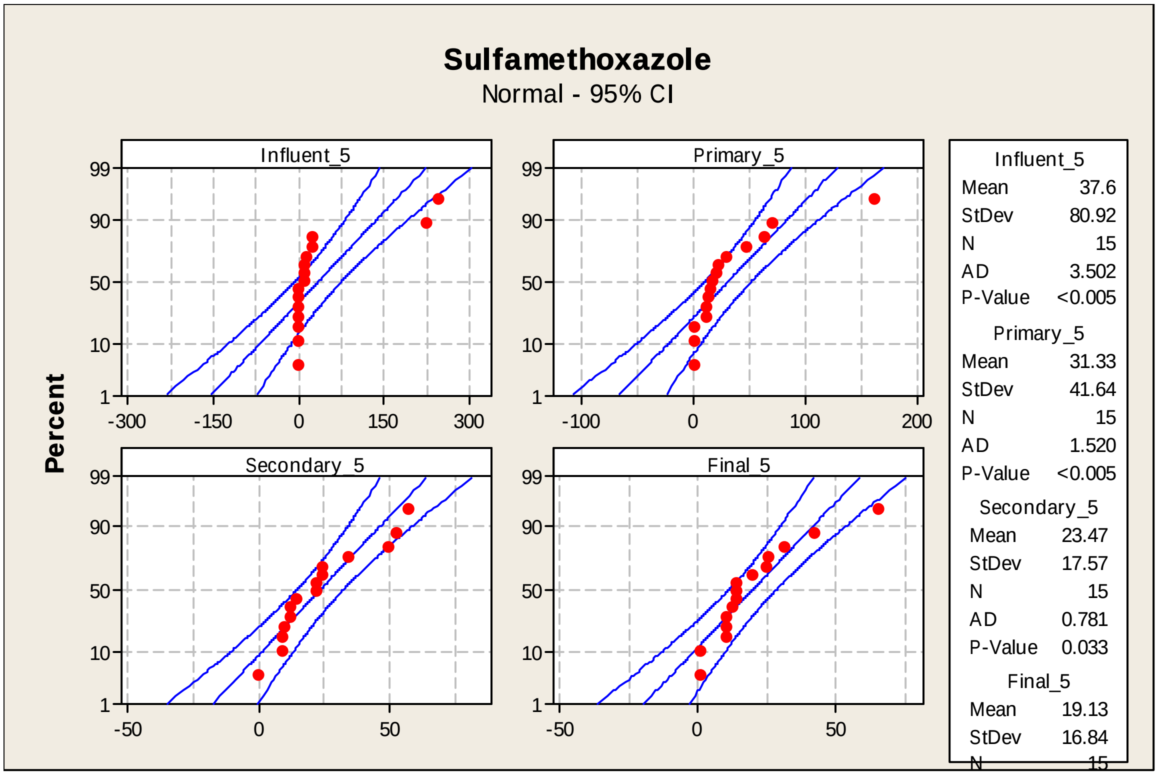
Equation and slope term both significant (p = 0.02) based on ANOVA:

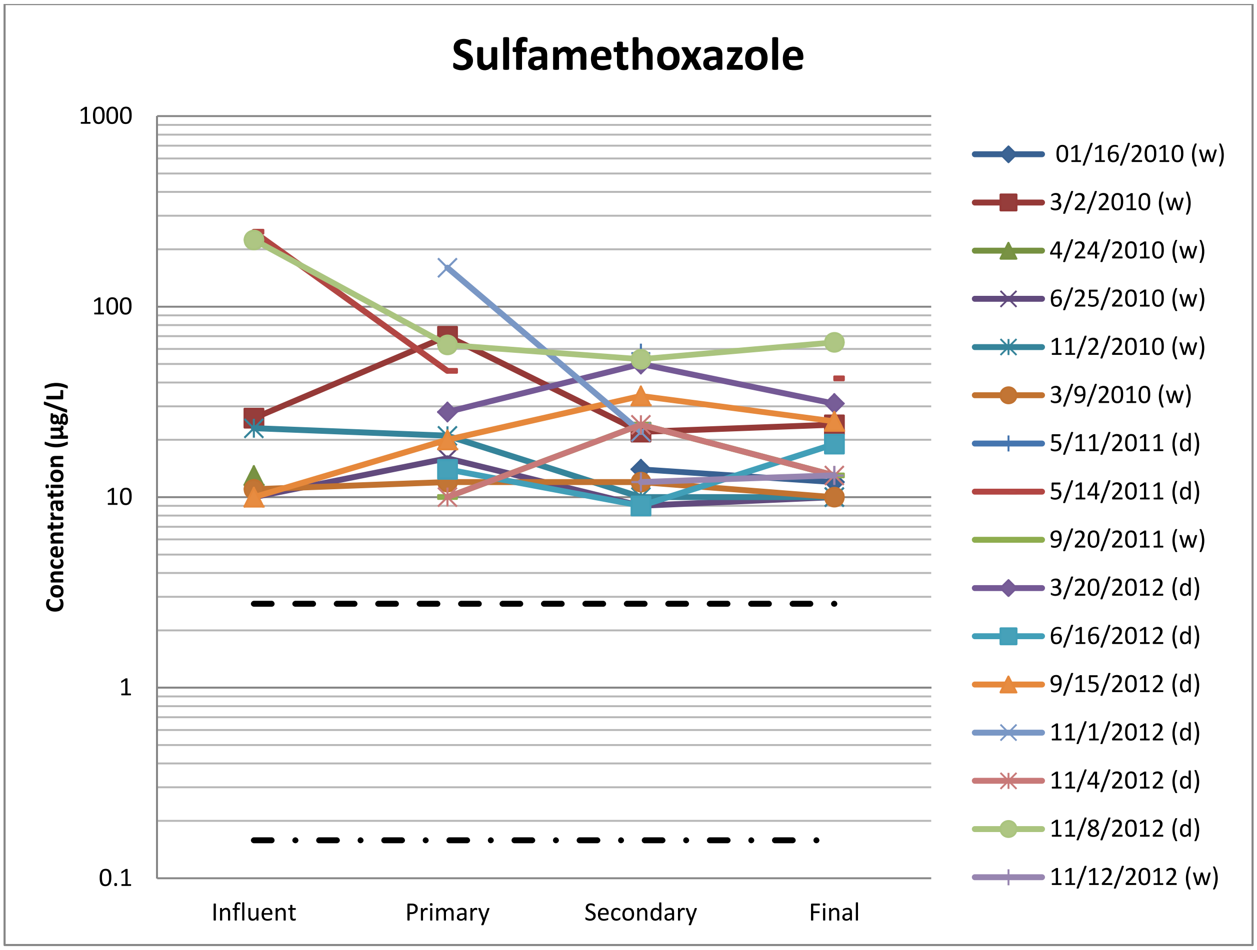
Regression Statistics	
Adjusted R Square	0.253857
Standard Error	80.86665
Observations	16

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	46271.77	46271.77	7.075826	0.01866
Residual	15	98091.23	6539.416		
Total	16	144363			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Slope term	2.513145	0.944776	2.660042	0.01783	0.499402	4.526887


Sulfamethoxazole
Normal - 95% CI
Percent
Influent_5
Primary_5
Secondary_5
Final_5
99
90
50
10
1
-300
-150
0
150
300
-100
0
100
200
-50
0
50
Influent_5
Mean 37.6
StDev 80.92
N 15
AD 3.502
P-Value <0.005
Primary_5
Mean 31.33
StDev 41.64
N 15
AD 1.520
P-Value <0.005
Secondary_5
Mean 23.47
StDev 17.57
N 15
AD 0.781
P-Value 0.033
Final_5
Mean 19.13
StDev 16.84
N 15

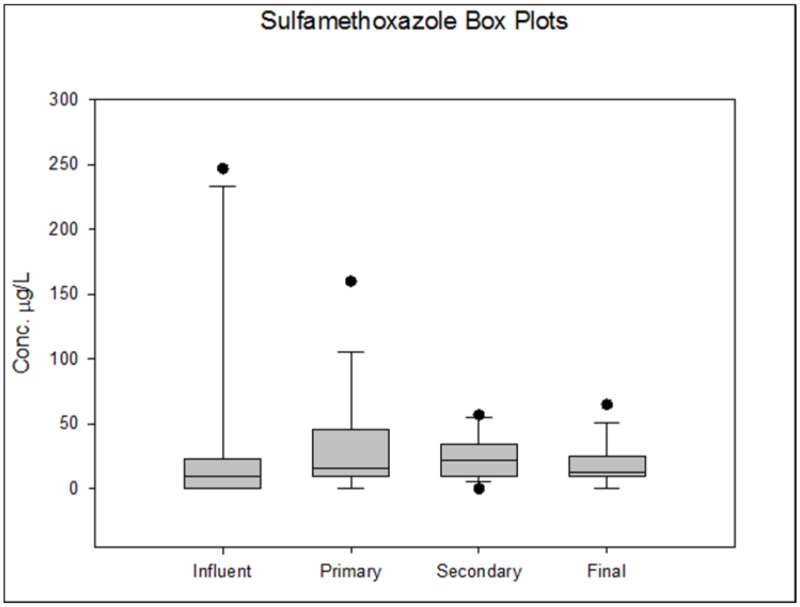


Column	Size	Missing	Mean	Std Dev	Std. Error	C-I. of Mean
SMX-I	16	1	37.600	80.920	20.894	44.812
SMX-P	16	1	31.333	41.644	10.752	23.062
SMX-S	16	1	23.467	17.566	4.535	9.728
SMX-F	16	1	19.133	16.843	4.349	9.327

Column	Range	Max	Min	Median	25%	75%
SMX-I	247.000	247.000	0.000	10.000	0.000	20.500
SMX-P	160.000	160.000	0.000	16.000	10.000	41.500
SMX-S	57.000	57.000	0.000	22.000	10.500	31.500
SMX-F	65.000	65.000	0.000	13.000	10.000	24.750

Column	Skewness	Kurtosis	K-S Dist.	K-S ProB-	SWilk W	SWilk Prob
SMX-I	2.365	4.293	0.424	<0.001	0.506	<0.001
SMX-P	2.388	6.497	0.265	0.006	0.712	<0.001
SMX-S	0.882	-0.307	0.221	0.047	0.880	0.048
SMX-F	1.606	3.080	0.242	0.018	0.845	0.015

Column	Sum	Sum of Squares
SMX-I	564.000	112880.000
SMX-P	470.000	39006.000
SMX-S	352.000	12580.000
SMX-F	287.000	9463.000



One Way Analysis of Variance

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk) Failed ($P < 0.050$)

Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source: PHRM 2 in Notebook1

Group	N	Missing	Median	25%	75%
Col 11	16	1	10.000	0.000	23.000
Col 12	16	1	16.000	10.000	46.000
Col 13	16	1	22.000	10.000	34.000
Col 14	16	1	13.000	10.000	25.000

H = 3.754 with 3 degrees of freedom. ($P = 0.289$)

The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.289**)

Mann-Whitney Rank Sum Test

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Col 11	16	1	10.000	0.000	23.000
Col 12	16	1	16.000	10.000	46.000

Mann-Whitney U Statistic= 79.500

T = 199.500 n(small)= 15 n(big)= 15 (P = 0.169)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.169**)

Mann-Whitney Rank Sum Test

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Col 12	16	1	16.000	10.000	46.000
Col 13	16	1	22.000	10.000	34.000

Mann-Whitney U Statistic= 109.000

T = 229.000 n(small)= 15 n(big)= 15 (P = 0.901)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.901**)

Mann-Whitney Rank Sum Test

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Col 13	16	1	22.000	10.000	34.000
Col 14	16	1	13.000	10.000	25.000

Mann-Whitney U Statistic= 100.500

T = 244.500 n(small)= 15 n(big)= 15 (P = 0.632)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.632**)

Mann-Whitney Rank Sum Test

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Col 11	16	1	10.000	0.000	23.000
Col 14	16	1	13.000	10.000	25.000

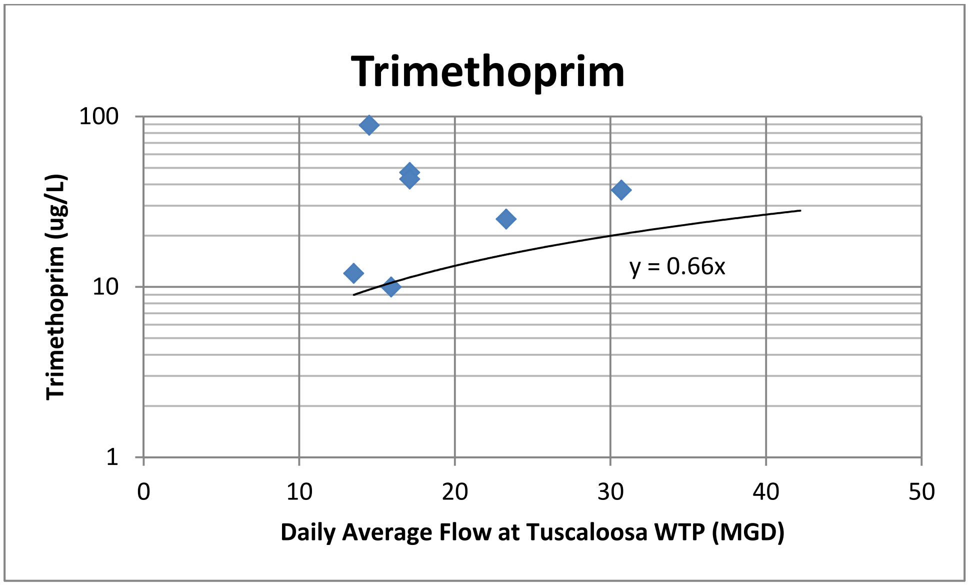
Mann-Whitney U Statistic= 78.500

T = 198.500 n(small)= 15 n(big)= 15 (P = 0.158)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.158**)

Trimethoprim

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	0.0	0.0	16.0	14.0	18.2	0	0.55	0.0
3/2/2010	25.0	22.0	0.0	0.0	23.3	2,202	0.68	100.0
4/24/2010	0.0	n/a	n/a	n/a	16.5	0	1.01	0.0
6/25/2010	0	0	0	0	20.7	0	0.59	0.0
11/2/2010	0	0	0	0	20.5	0	0.88	0.0
3/9/2011	0	0	0	0	42.2	0	2.67	0.0
5/11/2011	n/a	0.0	38.0	34.0	13.5	0	0.00	0.0
5/14/2011	0.0	37.0	0.0	28.0	30.7	0	0.00	0.0
9/20/2011	0.00	0.00	11.0	0.0	26.5	0	0.64	0.0
3/20/2012	43.0	47	23.0	29.0	17.1	2,779	0.00	32.6
6/16/2012	12.00	0.0	0.0	0.0	13.5	612	0.00	100.0
9/15/2012	22.00	89.0	63.0	63.0	14.5	1,206	0.00	-186.4
11/1/2012	37.00	43.0	0.0	0.0	17.1	2,392	0.00	100.0
11/4/2012	0.00	0.0	14.0	0.0	15.4	0	0.05	0.0
11/8/2012	0.00	10.0	31.0	14.0	15.9	0	0.00	0.0
11/12/2012	0.00	0.00	0.00	0.00	16	0	0.44	0.0
Average dry (<0.1 inch of rain)	16.29	28.25	21.13	21.00	17.21	998.46	0.01	5.77 (calc from avg)
Average wet	3.13	3.14	3.86	2.00	22.99	275.23	0.93	11.11 (calc from avg)



Both equation and slope term are marginally significant (p = 0.054), based on ANOVA (zero values are not plotted on the log scale):

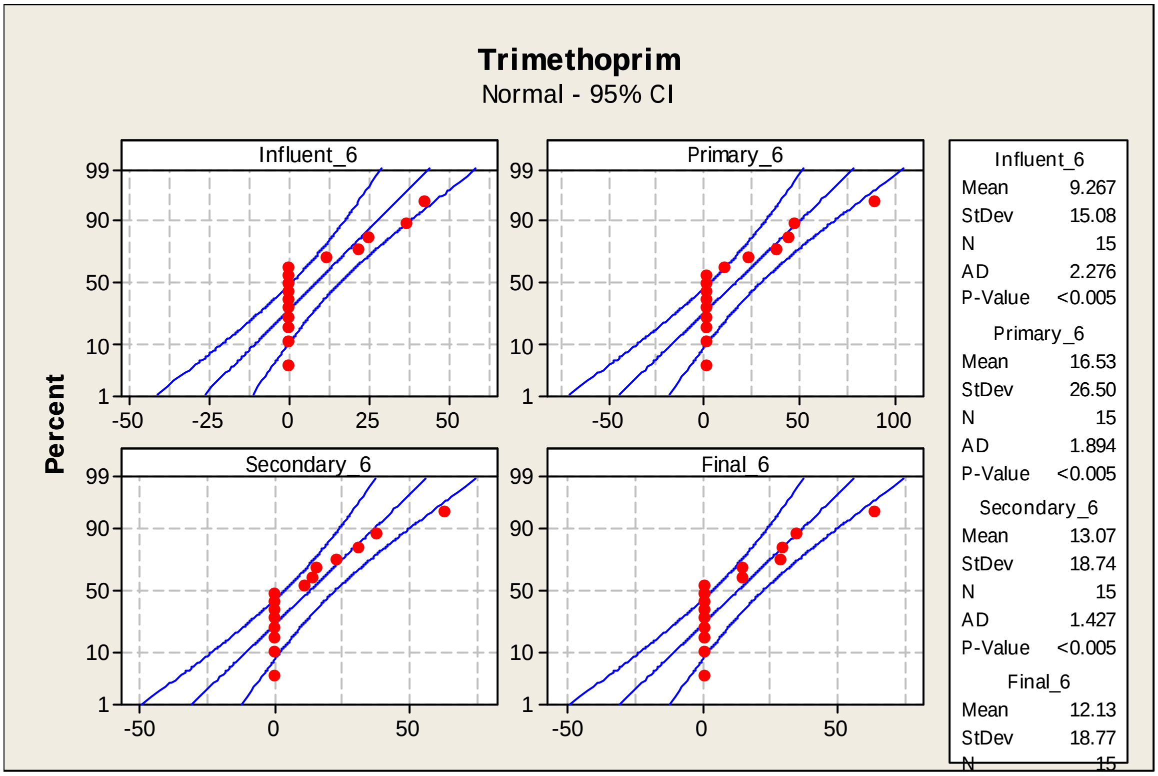
SUMMARY OUTPUT

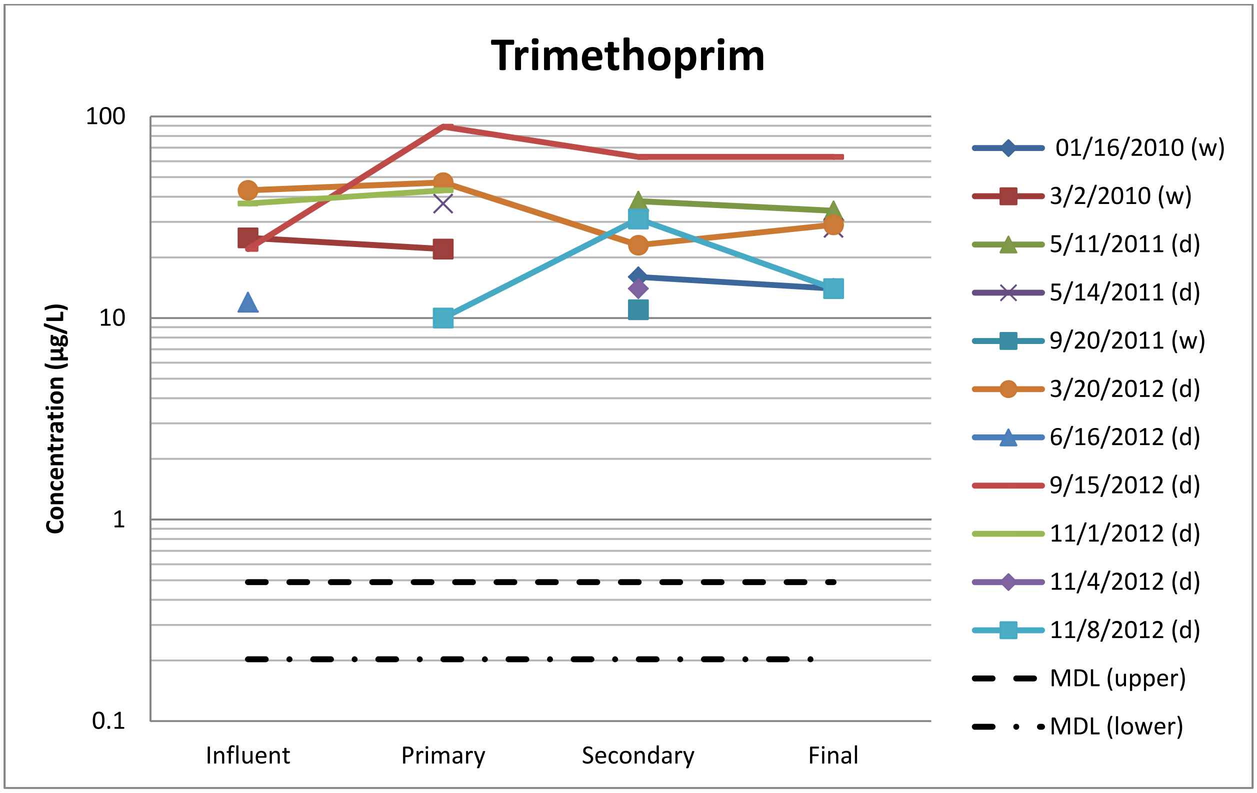
Regression Statistics	
Adjusted R Square	0.160934
Standard Error	27.05699
Observations	16

ANOVA

	df	SS	MS	F	Significance F
Regression	1	3235.792	3235.792	4.419994	0.054095
Residual	15	10981.21	732.0805		
Total	16	14217			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
X Variable 1	0.664584	0.31611	2.102378	0.052818	-0.00919	1.338357



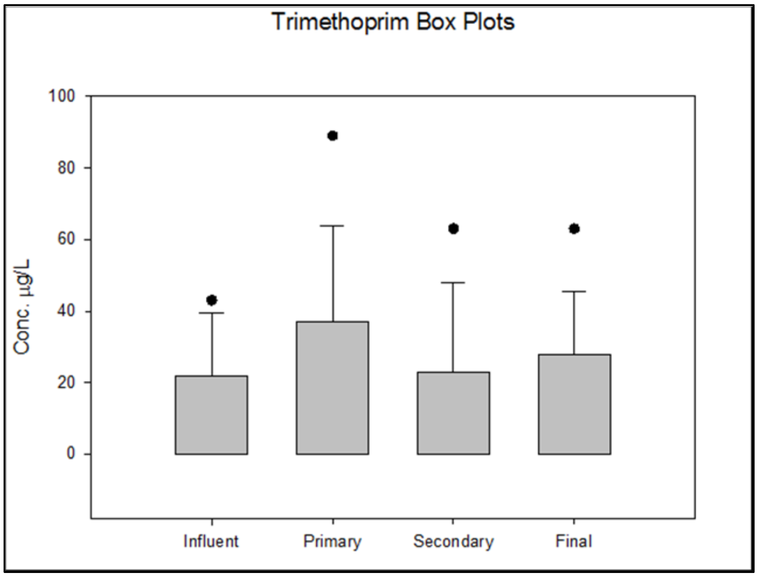


Column	Size	Missing	Mean	Std Dev	Std. Error	C-I. of Mean
TRM-I	16	1	9.267	15.078	3.893	8.350
TRM-P	16	1	16.533	26.500	6.842	14.675
TRM-S	16	1	13.067	18.737	4.838	10.376
TRM-F	16	1	12.133	18.773	4.847	10.396

Column	Range	Max	Min	Median	25%	75%
TRM-I	43.000	43.000	0.000	0.000	0.000	19.500
TRM-P	89.000	89.000	0.000	0.000	0.000	33.250
TRM-S	63.000	63.000	0.000	0.000	0.000	21.250
TRM-F	63.000	63.000	0.000	0.000	0.000	24.500

Column	Skewness	Kurtosis	K-S Dist.	K-S ProB-	SWilk W	SWilk Prob
TRM-I	1.388	0.584	0.397	<0.001	0.676	<0.001
TRM-P	1.750	2.866	0.334	<0.001	0.699	<0.001
TRM-S	1.615	2.427	0.291	0.001	0.756	0.001
TRM-F	1.679	2.657	0.341	<0.001	0.713	<0.001

Column	Sum	Sum of Squares
TRM-I	139.000	4471.000
TRM-P	248.000	13932.000
TRM-S	196.000	7476.000
TRM-F	182.000	7142.000



One Way Analysis of Variance

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk) Failed ($P < 0.050$)

Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source: PHRM 2 in Notebook1

Group	N	Missing	Median	25%	75%
Col 16	16	1	0.000	0.000	22.000
Col 17	16	1	0.000	0.000	37.000
Col 18	16	1	0.000	0.000	23.000
Col 19	16	1	0.000	0.000	28.000

H = 0.514 with 3 degrees of freedom. ($P = 0.916$)

The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.916**)

Mann-Whitney Rank Sum Test

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Col 16	16	1	0.000	0.000	22.000
Col 17	16	1	0.000	0.000	37.000

Mann-Whitney U Statistic= 100.500

T = 220.500 n(small)= 15 n(big)= 15 (P = 0.581)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.581**)

Mann-Whitney Rank Sum Test

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Col 17	16	1	0.000	0.000	37.000
Col 18	16	1	0.000	0.000	23.000

Mann-Whitney U Statistic= 111.000

T = 231.000 n(small)= 15 n(big)= 15 (P = 0.963)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.963**)

Mann-Whitney Rank Sum Test

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

```
Group  N   Missing   Median    25%      75%
Col 18 16     1       0.000    0.000   23.000
Col 19 16     1       0.000    0.000   28.000
```

Mann-Whitney U Statistic= 106.500

T = 238.500 n(small)= 15 n(big)= 15 (P = 0.801)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.801**)

Mann-Whitney Rank Sum Test

Data source: PHRM 2 in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

```
Group  N   Missing   Median    25%      75%
Col 16 16     1       0.000    0.000   22.000
Col 19 16     1       0.000    0.000   28.000
```

Mann-Whitney U Statistic= 104.000

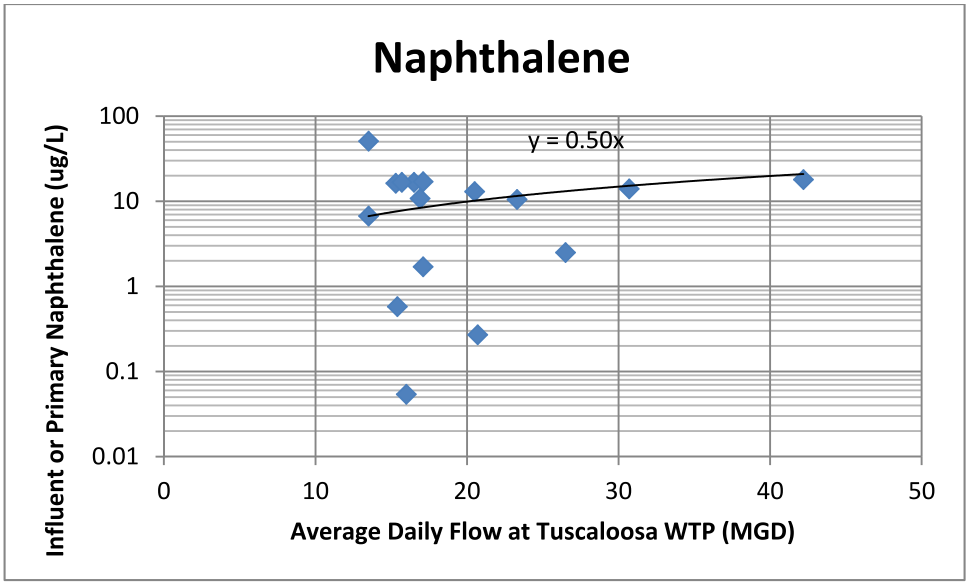
T = 224.000 n(small)= 15 n(big)= 15 (P = 0.701)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.701**)

Polycyclic Aromatic Hydrocarbons (PAHs)

Naphthalene

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	57.0	350.0	190	160	18.2	3,921	0.55	-180.7
3/2/2010	1.7	10.5	5.6	4.7	23.3	151	0.68	-175.1
4/24/2010	20.7	16.7	0.4	4.7	16.5	1,289	1.01	77.2
6/25/2010	0.33	0.25	0.27	0.33	20.7	26	0.59	0.4
10/17/2010	14	16.3	0.072	2.7	15.3	805	0.00	80.8
10.24/2010	20.7	16.7	0.4	4.7	15.7	1,227	0.10	77.2
11/2/2010	2.5	13	0.73	0.049	20.5	196	0.88	98.1
3/9/2011	7.7	18	BQ	n/a	42.2	1,231	2.67	0.0
5/11/2011	30.4	50.9	8.0	0.0	13.5	1,552	0.00	100.0
5/14/2011	17.0	14.0	11.3	1.5	30.7	1,971	0.00	91.2
9/20/2011	0.86	0.84	2.5	7.3	26.5	86	0.64	-745.0
10/10/2011	0.18	4.33	10.8	4.6	16.9	11	0.00	-2477.4
3/20/2012	7.1	17	5.4	2.7	17.1	456	0.00	62.0
6/16/2012	0.62	6.7	2.4	BDL	13.5	32	0.00	100.0
9/15/2012	0.0	0.0	0.0	0.0	14.5	0	0.00	0.0
11/1/2012	1.1	1.7	0.0	0.0	17.1	72	0.00	100.0
11/4/2012	0.14	0.58	0.0	0.0	15.4	8	0.05	100.0
11/8/2012	0.14	0	0.0	0.0	15.9	8	0.00	100.0
11/12/2012	26	0.054	0.0	0.0	16.0	1,571	0.44	100.0
Average dry (<0.1 inch of rain)	7.058	11.143	3.811	1.273	16.990	491.692	0.005	-174 (calc from avg)
Average wet	15.27	47.24	24.99	22.72	22.18	1,077.57	0.84	-83.10 (calc from avg)



Regression equation and slope coefficient are both significant (p = 0.003) based on ANOVA (removed very large single value):

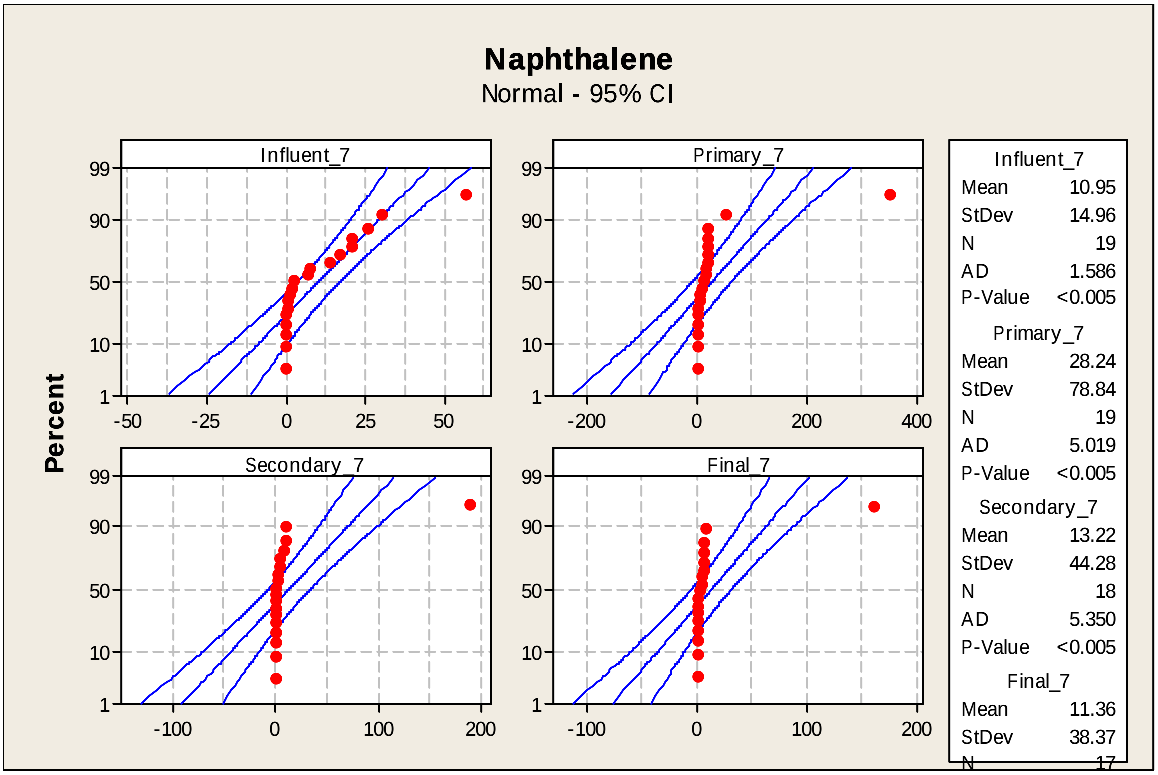
SUMMARY OUTPUT

Regression Statistics	
Adjusted R Square	0.349647
Standard Error	12.75234
Observations	18

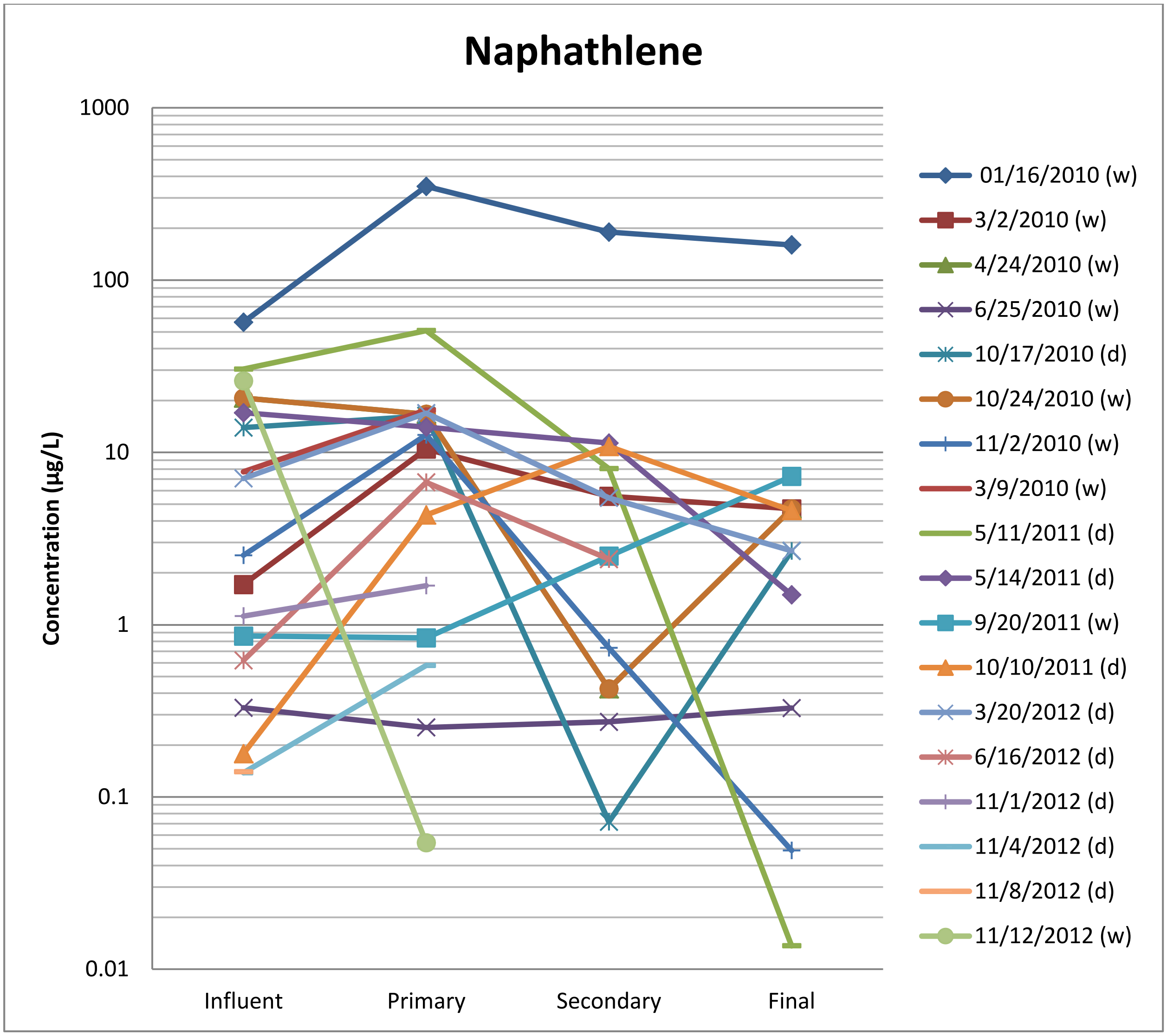
ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1909.034	1909.034	11.73908	0.003463
Residual	17	2764.578	162.6222		
Total	18	4673.612			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Slope term	0.495956	0.144752	3.426233	0.00322	0.190555	0.801356



Naphthalene
Normal - 95% CI
Percent
Influent_7
Primary_7
Secondary_7
Final_7
99
90
50
10
1
-50
-25
0
25
50
-200
0
200
400
-100
0
100
200
Influent_7
Mean 10.95
StDev 14.96
N 19
AD 1.586
P-Value <0.005
Primary_7
Mean 28.24
StDev 78.84
N 19
AD 5.019
P-Value <0.005
Secondary_7
Mean 13.22
StDev 44.28
N 18
AD 5.350
P-Value <0.005
Final_7
Mean 11.36
StDev 38.37
N 17


Naphathlene
Concentration (µg/L)
1000
100
10
1
0.1
0.01
Influent
Primary
Secondary
Final
01/16/2010 (w)
3/2/2010 (w)
4/24/2010 (w)
6/25/2010 (w)
10/17/2010 (d)
10/24/2010 (w)
11/2/2010 (w)
3/9/2010 (w)
5/11/2011 (d)
5/14/2011 (d)
9/20/2011 (w)
10/10/2011 (d)
3/20/2012 (d)
6/16/2012 (d)
11/1/2012 (d)
11/4/2012 (d)
11/8/2012 (d)
11/12/2012 (w)

Descriptive Statistics:

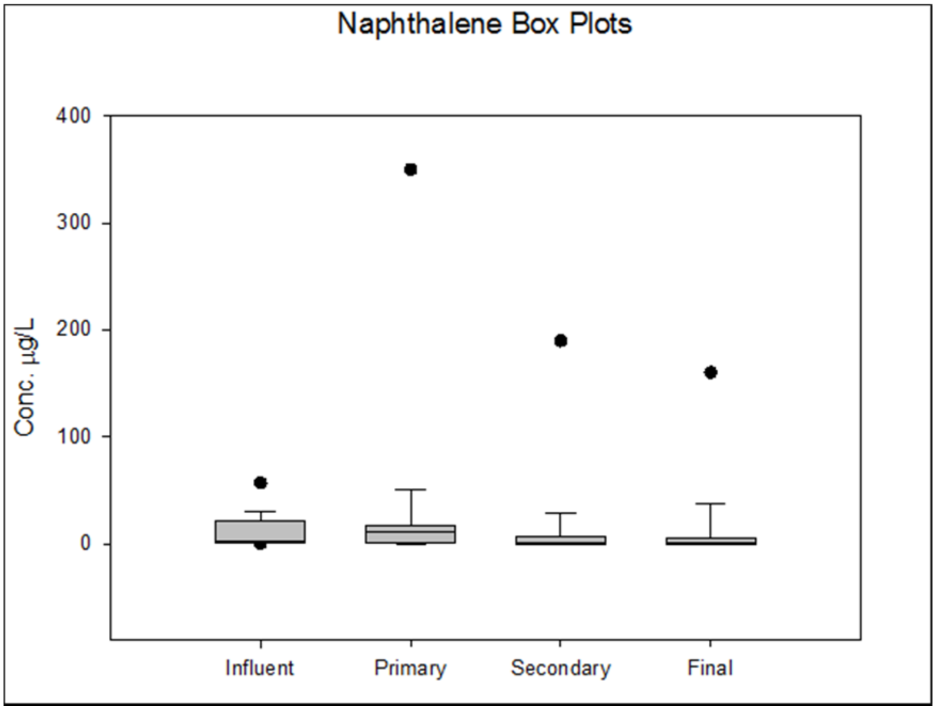
Data source: PAH in PAH 2010-2012

```
Column        Size  Missing   Mean   Std Dev  Std. Error  C-I. of Mean
Naphthalene-I 19        0     10.950   14.962      3.432          7.211
Naphthalene-P19         0     28.241   78.841     18.087         38.000
Naphthalene-S19         1     13.224   44.283     10.437         22.021
Naphthalene-F19         2     11.365   38.374      9.307         19.730

Column        Range      Max     Min    Median    25%     75%
Naphthalene-I56.996   56.996  0.000     2.528   0.402  19.751
Naphthalene-P350.000350.000  0.000    10.458   0.644  16.666
Naphthalene-S190.000190.000  0.000     0.579   0.000   5.567
Naphthalene-F160.000160.000  0.000     1.490   0.000   4.704

Column      Skewness Kurtosis  K-S Dist.  K-S ProB- SWilk W SWilk Prob
Naphthalene-I  1.847     3.894     0.240      0.005   0.757     <0.001
Naphthalene-P 4.197     17.967     0.448     <0.001   0.355     <0.001
Naphthalene-S 4.190     17.682     0.462     <0.001   0.316     <0.001
Naphthalene-F 4.097     16.848     0.484     <0.001   0.310     <0.001

Column          Sum   Sum of Squares
Naphthalene-I208.053     6307.469
Naphthalene-P536.588 127040.994
Naphthalene-S238.032   36483.767
Naphthalene-F193.205   25756.844
```



One Way Analysis of Variance

Data source: PAH in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source: PAH in Notebook1

Group	N	Missing	Median	25%	75%
Col 1	19	0	2.528	0.329	20.673
Col 2	19	0	10.458	0.580	16.666
Col 3	19	1	0.579	0.000	6.187
Col 4	19	2	1.490	0.000	4.704

H = 7.681 with 3 degrees of freedom. (P = 0.053)

The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.053**)

```
Mann-Whitney Rank Sum Test

Data source: PAH in Notebook1

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

Group N   Missing   Median     25%       75%
Col 1  19      0       2.528    0.329    20.673
Col 2  19      0      10.458    0.580    16.666

Mann-Whitney U Statistic= 176.000

T = 366.000  n(small)= 19  n(big)= 19  (P = 0.907)

The difference in the median values between the two groups is not great enough to
exclude the possibility that the difference is due to random sampling variability; there is
not a statistically significant difference  (P = 0.907)
```

```
Mann-Whitney Rank Sum Test

Data source: PAH in Notebook1

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

Group N   Missing   Median     25%       75%
Col 2  19      0      10.458    0.580    16.666
Col 3  19      1       0.579    0.000     6.187

Mann-Whitney U Statistic= 102.000

T = 273.000  n(small)= 18  n(big)= 19  (P = 0.037)

The difference in the median values between the two groups is greater than would be
expected by chance; there is a statistically significant difference  (P = 0.037)
```

Mann-Whitney Rank Sum Test

Data source: PAH in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Col 3	19	1	0.579	0.000	6.187
Col 4	19	2	1.490	0.000	4.704

Mann-Whitney U Statistic= 142.500

T = 295.500 n(small)= 17 n(big)= 18 (P = 0.738)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.738**)

Mann-Whitney Rank Sum Test Sunday, January 13, 2013, 2:09:25 PM

Data source: PAH in Notebook1

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Col 1	19	0	2.528	0.329	20.673
Col 4	19	2	1.490	0.000	4.704

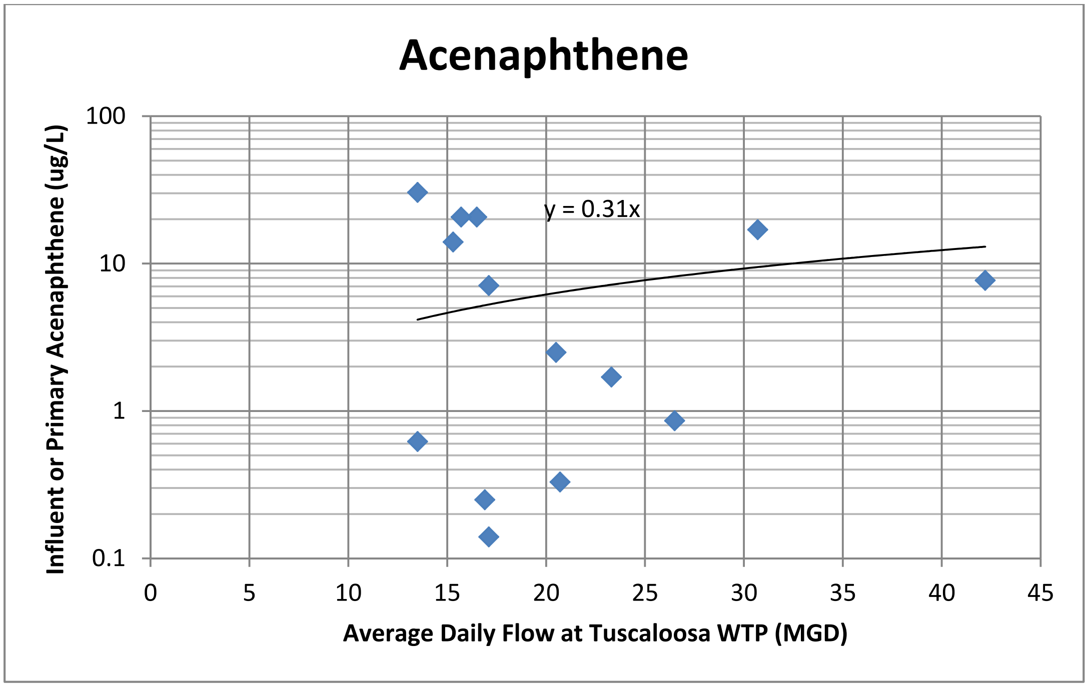
Mann-Whitney U Statistic= 106.500

T = 259.500 n(small)= 17 n(big)= 19 (P = 0.083)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.083**)

Acenaphthene

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	57.0	21.4	0.0	0.0	18.2	3921.1	0.55	100.0
3/2/2010	1.7	0.6	0.0	0.0	23.3	150.6	0.68	100.0
4/24/2010	20.7	3.1	2.5	4.2	16.5	1289.3	1.01	79.8
6/25/2010	0.33	0.099	0.036	0.022	20.7	25.8	0.59	93.3
10/17/2010	14	3.4	BDL	0.051	15.3	805.0	0.00	99.6
10.24/2010	20.7	4.8	0.2	0.2	15.7	1226.8	0.10	99.2
11/2/2010	2.5	0.97	BDL	BQ	20.5	195.9	0.88	100.0
3/9/2011	7.7	2.3	BQ	n/a	42.2	1231.1	2.67	100.0
5/11/2011	30.4	0.9	0.0	0.0	13.5	1552.4	0.00	100.0
5/14/2011	17.0	0.7	BQ	BQ	30.7	1971.3	0.00	100.0
9/20/2011	0.86	0.29	0.00	0.085	26.5	86.0	0.64	90.0
10/10/2011	0.18	0.25	0.63	0.018	16.9	11.4	0.00	90.1
3/20/2012	7.1	2.4	0.16	0.088	17.1	456.2	0.00	98.8
6/16/2012	0.62	0.35	0.01	BDL	13.5	31.6	0.00	100.0
9/15/2012	0.00	0.00	0.00	0.0	14.5	0.0	0.00	0.0
11/1/2012	0.14	0.14	0.00	0.0	17.1	9.1	0.00	100.0
11/4/2012	0.00	0.00	0.00	0.00	15.4	0.0	0.05	0.0
11/8/2012	BQ	0.00	0.00	0.00	15.9	0.0	0.00	0.0
11/12/2012	BQ	BQ	0.01	0.00	16.0	0.0	0.44	0.0
Average dry (<0.1 inch of rain)	7.70	0.82	0.10	0.02	16.99	483.71	0.01	68 (calc from avg)
Average wet	16.87	5.07	0.39	0.64	19.56	957.09	0.57	80. (calc from avg)



Regression equation and slope coefficient are both significant (p = 0.01) based on ANOVA (removed very large single value):

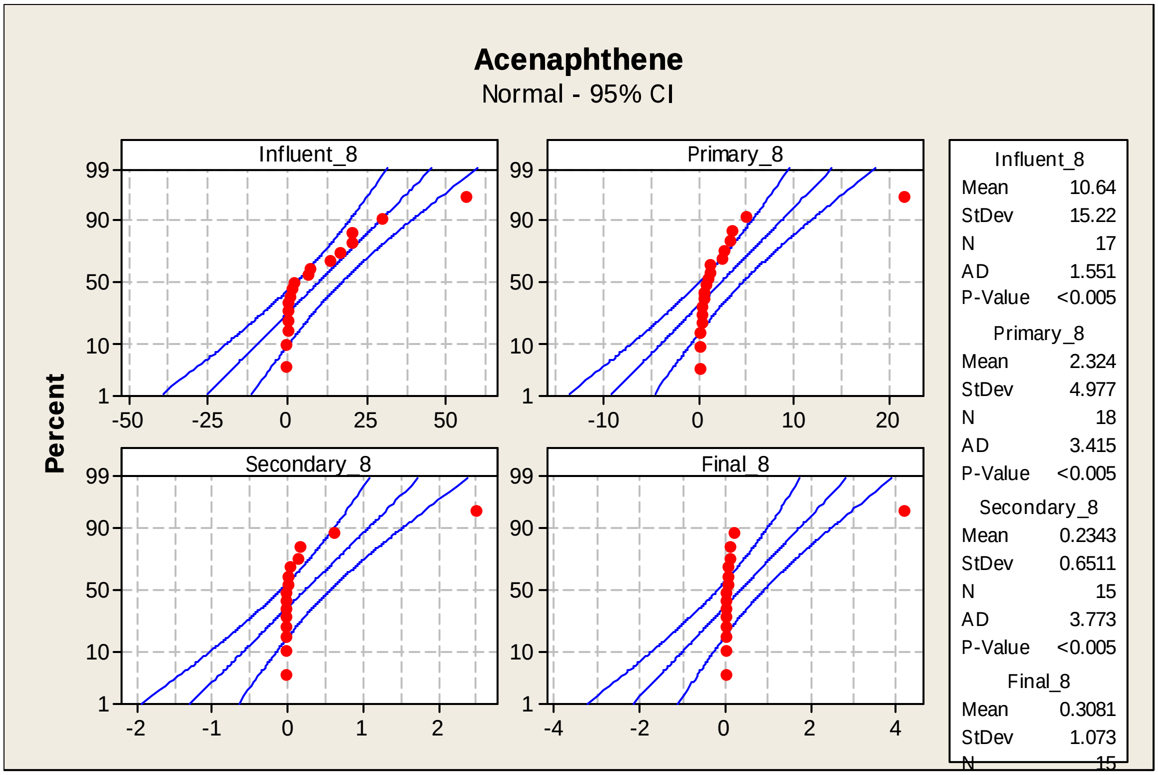
SUMMARY OUTPUT

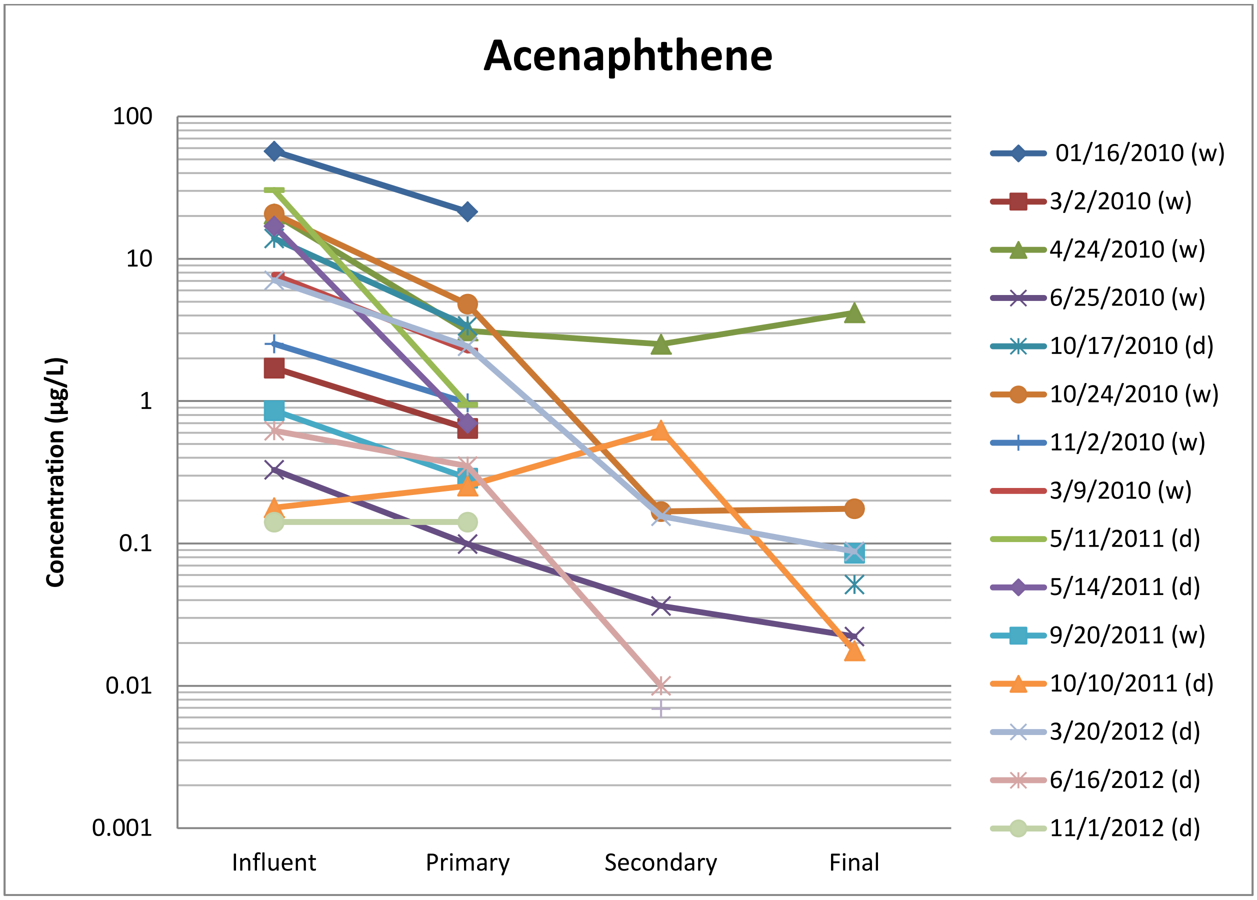
Regression Statistics	
Adjusted R Square	0.250853
Standard Error	9.843828
Observations	18

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	738.9787	738.9787	7.626124	0.013900119
Residual	17	1647.316	96.90096		
Total	18	2386.295			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Slope term	0.308569	0.111738	2.761544	0.013341	0.072822641	0.544315


Acenaphthene
Normal - 95% CI
Percent
Influent_8
Primary_8
Secondary_8
Final_8
99
90
50
10
1
-50
-25
0
25
50
-10
0
10
20
-2
-1
0
1
2
-4
-2
0
2
4
Influent_8
Mean 10.64
StDev 15.22
N 17
AD 1.551
P-Value <0.005
Primary_8
Mean 2.324
StDev 4.977
N 18
AD 3.415
P-Value <0.005
Secondary_8
Mean 0.2343
StDev 0.6511
N 15
AD 3.773
P-Value <0.005
Final_8
Mean 0.3081
StDev 1.073
N 15

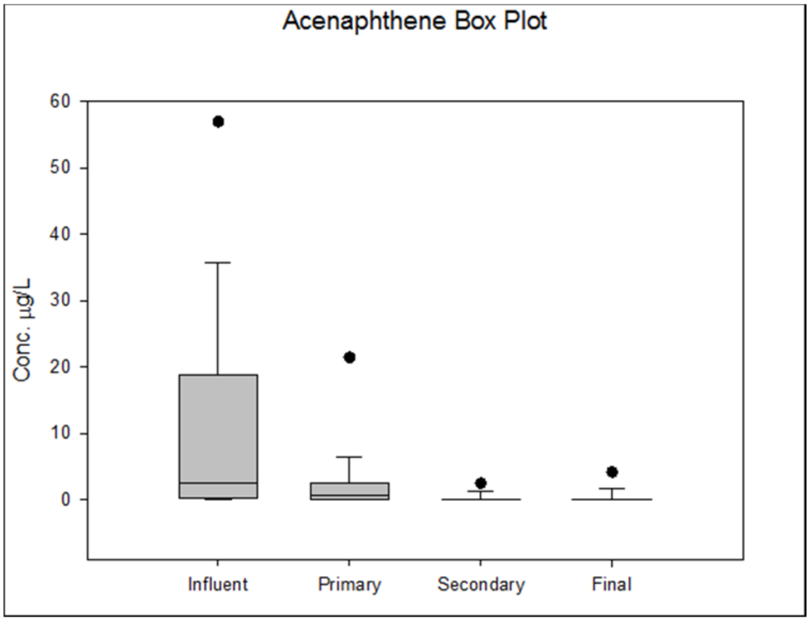

Acenaphthene
Concentration (µg/L)
100
10
1
0.1
0.01
0.001
Influent
Primary
Secondary
Final
01/16/2010 (w)
3/2/2010 (w)
4/24/2010 (w)
6/25/2010 (w)
10/17/2010 (d)
10/24/2010 (w)
11/2/2010 (w)
3/9/2010 (w)
5/11/2011 (d)
5/14/2011 (d)
9/20/2011 (w)
10/10/2011 (d)
3/20/2012 (d)
6/16/2012 (d)
11/1/2012 (d)

Column	Size	Missing	Mean	Std Dev	Std. Error	C-I. of Mean
Acenaphthene-I	19	2	10.636	15.223	3.692	7.827
Acenaphthene-P	19	1	2.324	4.977	1.173	2.475
Acenaphthene-S	19	4	0.234	0.651	0.168	0.361
Acenaphthene-F	19	4	0.308	1.073	0.277	0.594

Column	Range	Max	Min	Median	25%	75%
Acenaphthene-I	56.996	56.996	0.000	2.528	0.292	17.909
Acenaphthene-P	21.447	21.447	0.000	0.672	0.141	2.428
Acenaphthene-S	2.513	2.513	0.000	0.000	0.000	0.126
Acenaphthene-F	4.182	4.182	0.000	0.000	0.000	0.0770

Column	Skewness	Kurtosis	K-S Dist.	K-S ProB-	SWilk W	SWilk Prob
Acenaphthene-I	2.021	4.628	0.242	0.009	0.737	<0.001
Acenaphthene-P	3.711	14.694	0.320	<0.001	0.479	<0.001
Acenaphthene-S	3.509	12.737	0.407	<0.001	0.420	<0.001
Acenaphthene-F	3.858	14.919	0.483	<0.001	0.317	<0.001

Column	Sum	Sum of Squares
Acenaphthene-I	180.811	5631.046
Acenaphthene-P	41.837	518.294
Acenaphthene-S	3.515	6.759
Acenaphthene-F	4.622	17.535



```
One Way Analysis of Variance

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)


Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source: PAH in PAH 2010-2012

Group           N   Missing   Median      25%        75%
Acenaphthene-I19      2         2.528      0.254     18.830
Acenaphthene-P19      1         0.672      0.131      2.602
Acenaphthene-S19      4         0.000      0.000      0.156
Acenaphthene-F19      4         0.000      0.000      0.0855

H = 24.614 with 3 degrees of freedom. (P = <0.001)

The differences in the median values among the treatment groups are greater than
would be expected by chance; there is a statistically significant difference (P = <0.001)

To isolate the group or groups that differ from the others use a multiple comparison
procedure.


All Pairwise Multiple Comparison Procedures (Dunn's Method) :

Comparison                    Diff of Ranks      Q      P<0.05
Acenaphthene- vs Acenaphthene-26.355       3.935     Yes
Acenaphthene- vs Acenaphthene-25.822       3.855     Yes
Acenaphthene- vs Acenaphthene- 7.394       1.156      No
Acenaphthene- vs Acenaphthene-18.961       2.868     Yes
Acenaphthene- vs Acenaphthene-18.428       2.788     Yes
Acenaphthene- vs Acenaphthene- 0.533       0.0772    No
```

```
Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

Group           N   Missing   Median      25%        75%
Acenaphthene-I19      2          2.528       0.254     18.830
Acenaphthene-P19      1          0.672       0.131      2.602

Mann-Whitney U Statistic= 104.500

T = 354.500  n(small)= 17  n(big)= 18  (P = 0.113)

The difference in the median values between the two groups is not great enough to
exclude the possibility that the difference is due to random sampling variability; there is
not a statistically significant difference  (P = 0.113)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

Group           N   Missing   Median      25%        75%
Acenaphthene-P19      1          0.672       0.131      2.602
Acenaphthene-S19      4          0.000       0.000      0.156

Mann-Whitney U Statistic= 53.000

T = 173.000  n(small)= 15  n(big)= 18  (P = 0.003)

The difference in the median values between the two groups is greater than would be
expected by chance; there is a statistically significant difference (P = 0.003)
```

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Acenaphthene-S19	4		0.000	0.000	0.156
Acenaphthene-F19	4		0.000	0.000	0.0855

Mann-Whitney U Statistic= 112.000

T = 232.000 n(small)= 15 n(big)= 15 (P = 1.000)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 1.000**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Acenaphthene-I19	2		2.528	0.254	18.830
Acenaphthene-F19	4		0.000	0.000	0.0855

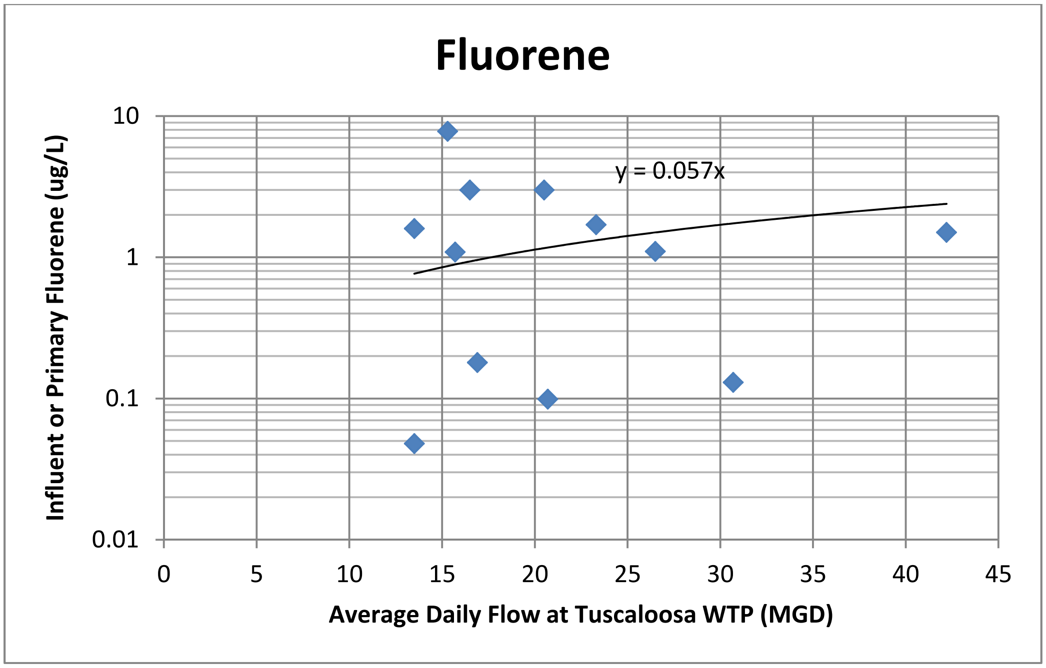
Mann-Whitney U Statistic= 30.000

T = 150.000 n(small)= 15 n(big)= 17 (P = <0.001)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (**P = <0.001**)

Fluorene

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	56.7	0.0	0.0	0.0	18.2	3816.1	0.55	100.0
3/2/2010	1.7	0.0	0.0	0.0	23.3	146.6	0.68	100.0
4/24/2010	3.0	2.9	3.3	3.3	16.5	185.0	1.01	100.0
6/25/2010	0.094	0.099	0.073	0.044	20.7	7.2	0.59	-8.3
10/17/2010	1.7	7.8	BQ	0.14	15.3	98.3	0.00	53.6
11/2/2010	BQ	1.09	BQ	BQ	20.5	0.0	0.88	0.0
3/9/2011	0.060	3.0	BQ	n/a	42.2	9.3	2.67	0.0
5/11/2011	1.5	1.4	0.0	0.0	13.5	73.4	0.00	100.0
5/14/2011	1.6	1.3	BQ	BQ	30.7	185.4	0.00	100.0
9/20/2011	0.03	0.13	0.011	0.11	26.5	2.6	0.64	-320.8
3/20/2012	0.46	1.1	0.3	0.14	17.1	29.1	0.00	69.3
6/16/2012	BDL	0.18	BDL	BDL	13.5	0.0	0.00	0.0
9/15/2012	0.00	0.00	0.00	0.0	14.5	0.0	0.00	0.0
11/1/2012	0.0021	0.048	0.0	0.0	17.1	0.1	0.00	100.0
11/4/2012	0.00	0.00	0.00	0.00	15.4	0.0	0.05	0.0
11/8/2012	BQ	0.00	0.00	0.00	15.9	0.0	0.00	0.0
11/12/2012	BQ	BQ	0.00	0.00	16.0	0.0	0.44	0.0
Average dry (<0.1 inch of rain)	0.67	1.19	0.04	0.05	17.95	38.89	0.01	42.3 (calc from avg)
Average wet	10.26	1.03	0.56	0.57	22.18	462.98	0.84	-3.63 (calc from avg)



Regression equation and slope coefficient are both significant (p = 0.02) based on ANOVA (removed very large single value):

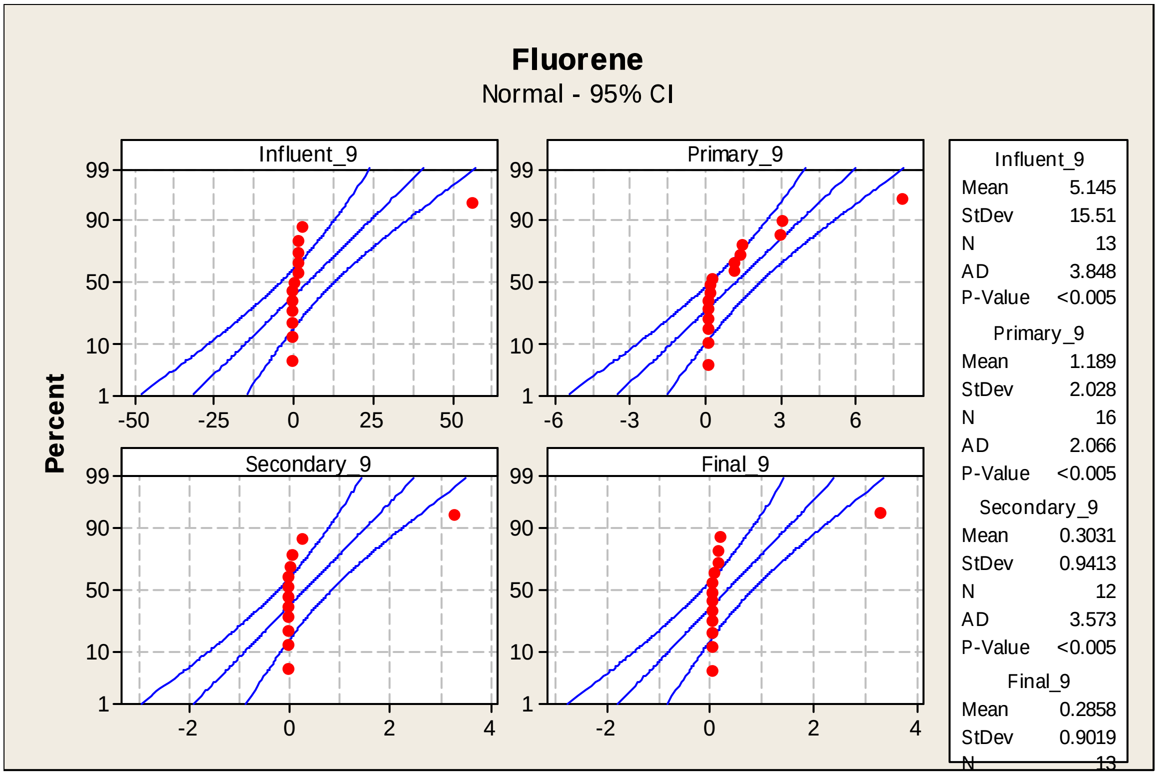
SUMMARY OUTPUT

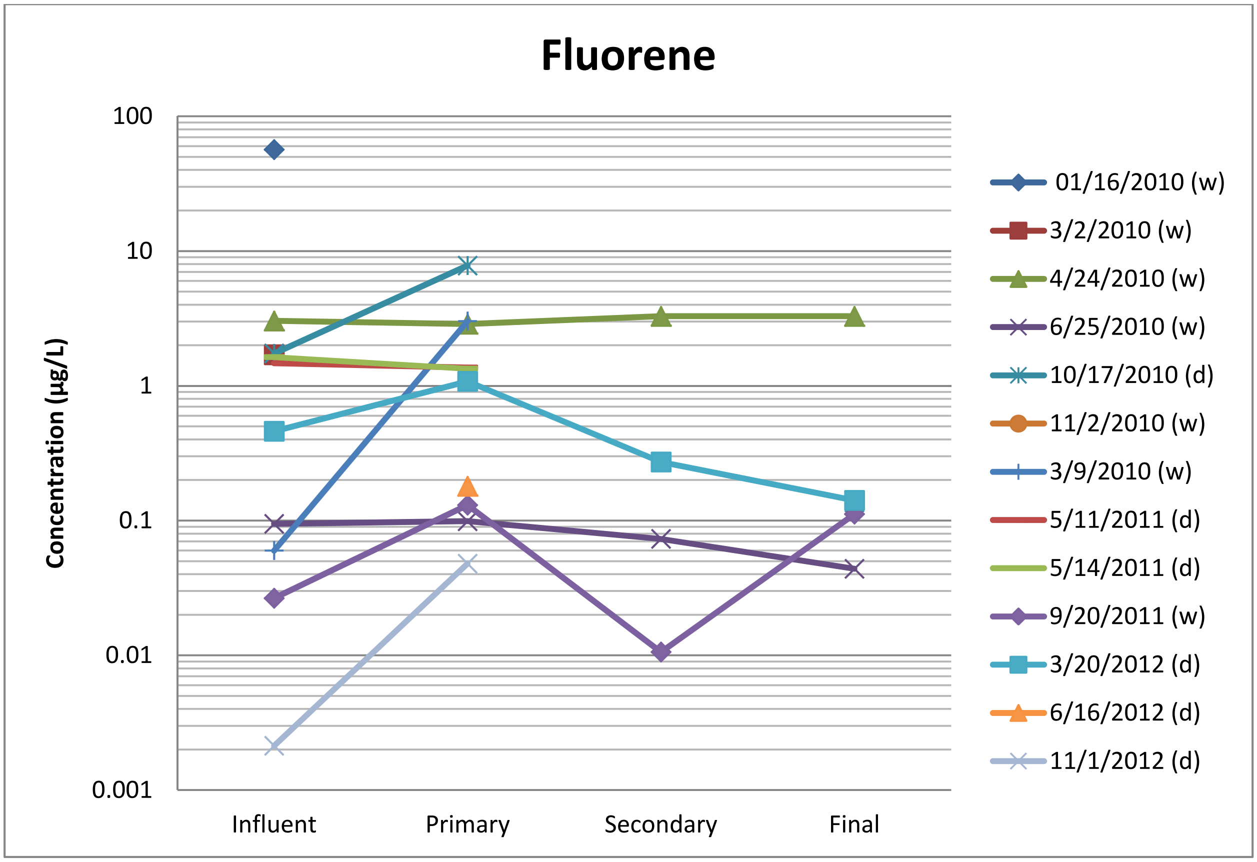
Regression Statistics	
Adjusted R Square	0.254138
Standard Error	2.007454
Observations	16

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	28.55146	28.55145678	7.084957	0.018597
Residual	15	60.44805	4.029869881		
Total	16	88.99951			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Slope term	0.062875	0.023622	2.661758345	0.017769	0.012527	0.113223


Fluorene
Normal - 95% CI
Percent
Influent_9
Primary_9
Secondary_9
Final_9
99
90
50
10
1
-50
-25
0
25
50
-6
-3
0
3
6
-2
0
2
4
Influent_9
Mean 5.145
StDev 15.51
N 13
AD 3.848
P-Value <0.005
Primary_9
Mean 1.189
StDev 2.028
N 16
AD 2.066
P-Value <0.005
Secondary_9
Mean 0.3031
StDev 0.9413
N 12
AD 3.573
P-Value <0.005
Final_9
Mean 0.2858
StDev 0.9019
N 13

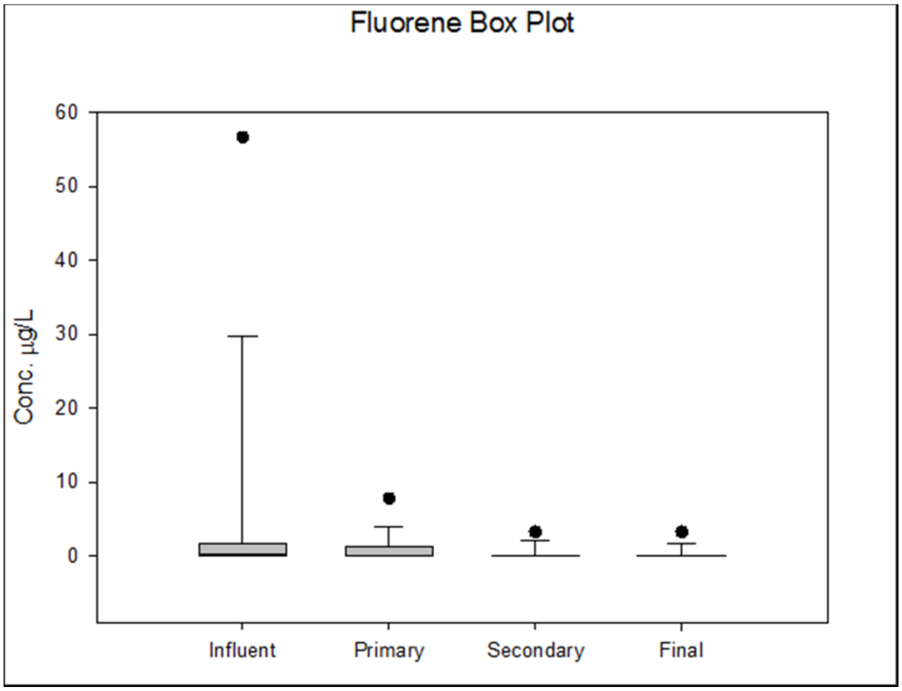

Fluorene
Concentration (µg/L)
100
10
1
0.1
0.01
0.001
Influent
Primary
Secondary
Final
01/16/2010 (w)
3/2/2010 (w)
4/24/2010 (w)
6/25/2010 (w)
10/17/2010 (d)
11/2/2010 (w)
3/9/2010 (w)
5/11/2011 (d)
5/14/2011 (d)
9/20/2011 (w)
3/20/2012 (d)
6/16/2012 (d)
11/1/2012 (d)

Column	Size	Missing	Mean	Std Dev	Std. Error	C-I. of Mean
Fluorene-I	19	5	4.779	14.966	4.000	8.641
Fluorene-P	19	2	1.127	1.980	0.480	1.018
Fluorene-S	19	6	0.281	0.905	0.251	0.547
Fluorene-F	19	5	0.273	0.868	0.232	0.501

Column	Range	Max	Min	Median	25%	75%
Fluorene-I	56.669	56.669	0.000	0.277	0.0265	1.700
Fluorene-P	7.803	7.803	0.000	0.130	0.000	1.346
Fluorene-S	3.282	3.282	0.000	0.000	0.000	0.0262
Fluorene-F	3.282	3.282	0.000	0.000	0.000	0.112

Column	Skewness	Kurtosis	K-S Dist.	K-S ProB-	SWilk W	SWilk Prob
Fluorene-I	3.715	13.855	0.475	<0.001	0.347	<0.001
Fluorene-P	2.712	8.316	0.285	<0.001	0.624	<0.001
Fluorene-S	3.563	12.768	0.437	<0.001	0.356	<0.001
Fluorene-F	3.713	13.848	0.489	<0.001	0.346	<0.001

Column	Sum	Sum of Squares
Fluorene-I	66.907	3231.537
Fluorene-P	19.154	84.330
Fluorene-S	3.648	10.850
Fluorene-F	3.826	10.835



One Way Analysis of Variance

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed ($P < 0.050$)

Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source: PAH in PAH 2010-2012

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Fluorene-I	19	5	0.277	0.0204	1.709
Fluorene-P	19	2	0.130	0.000	1.353
Fluorene-S	19	6	0.000	0.000	0.0418
Fluorene-F	19	5	0.000	0.000	0.118

H = 9.668 with 3 degrees of freedom. ($P = 0.022$)

The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (**$P = 0.022$**)

To isolate the group or groups that differ from the others use a multiple comparison procedure.

All Pairwise Multiple Comparison Procedures (Dunn's Method) :

Comparison	**Diff of Ranks**	**Q**	**P<0.05**
Fluorene-I vs Fluorene-S	15.874	2.441	No
Fluorene-I vs Fluorene-F	13.536	2.121	Do Not Test
Fluorene-I vs Fluorene-P	2.790	0.458	Do Not Test
Fluorene-P vs Fluorene-S	13.084	2.103	Do Not Test
Fluorene-P vs Fluorene-F	10.746	1.763	Do Not Test
Fluorene-F vs Fluorene-S	2.338	0.359	Do Not Test

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed ($P < 0.050$)

Group	N	Missing	Median	25%	75%
Fluorene-I	19	5	0.277	0.0204	1.709
Fluorene-P	19	2	0.130	0.000	1.353

Mann-Whitney U Statistic= 107.000

T = 236.000 n(small)= 14 n(big)= 17 (P = 0.646)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.646**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Fluorene-P	19	2	0.130	0.000	1.353
Fluorene-S	19	6	0.000	0.000	0.0418

Mann-Whitney U Statistic= 62.000

T = 153.000 n(small)= 13 n(big)= 17 (P = 0.036)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (**P = 0.036**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Fluorene-S	19	6	0.000	0.000	0.0418
Fluorene-F	19	5	0.000	0.000	0.118

Mann-Whitney U Statistic= 83.500

T = 174.500 n(small)= 13 n(big)= 14 (P = 0.703)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.703**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Fluorene-I	19	5	0.277	0.0204	1.709
Fluorene-F	19	5	0.000	0.000	0.118

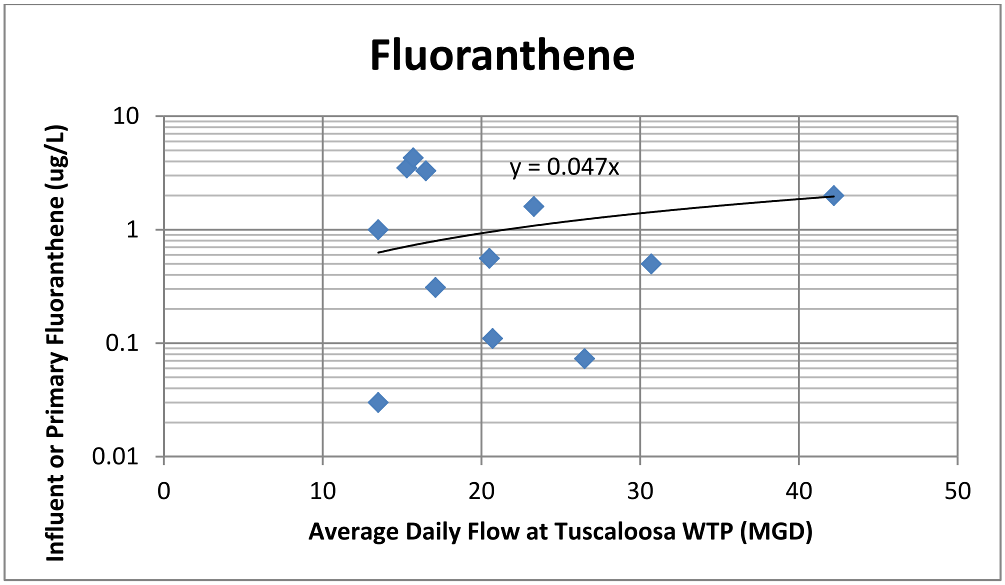
Mann-Whitney U Statistic= 54.000

T = 247.000 n(small)= 14 n(big)= 14 (P = 0.041)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (**P = 0.041**)

Fluoranthene

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	53.4	22.8	0.0	0.0	18.2	3596.9	0.55	100.0
3/2/2010	1.6	0.7	0.0	0.0	23.3	138.1	0.68	100.0
4/24/2010	3.3	3.3	3.3	3.6	16.5	199.9	1.01	-10.4
6/25/2010	0.11	0.10	0.074	0.041	20.7	8.2	0.59	62.0
10/17/2010	1.4	3.5	0.11	0.20	15.3	80.6	0.00	86.0
10.24/2010	3.3	4.3	0.4	0.0	15.7	190.8	0.10	98.6
11/2/2010	BQ	0.56	BQ	BQ	20.5	0.0	0.88	0.0
3/9/2011	BQ	2.0	BQ	n/a	42.2	0.0	2.67	0.0
5/11/2011	0.7	1.0	0.0	0.0	13.5	35.4	0.00	96.8
5/14/2011	0.5	0.5	BQ	BQ	30.7	59.9	0.00	100.0
9/20/2011	0.046	0.073	0.000	0.0064	26.5	4.5	0.64	85.9
3/20/2012	0.091	0.31	n/a	0.12	17.1	5.8	0.00	-29.9
6/16/2012	0	0.03	0	0	13.5	0.0	0.00	0.0
9/15/2012	0	0	0	0.0	14.5	0.0	0.00	0.0
11/1/2012	0	0.000	0.0	0.0	17.1	0.0	0.00	0.0
11/4/2012	0	0	0	0	15.4	0.0	0.05	0.0
11/8/2012	BQ	0	0	0	15.9	0.0	0.00	0.0
11/12/2012	BQ	BQ	0	0	16.0	0.0	0.44	0.0
Average dry (<0.1 inch of rain)	0.31	0.53	0.02	0.04	17.95	18.61	0.01	28 (calc from avg)
Average wet	10.29	4.23	0.54	0.53	22.18	459.82	0.84	48.46 (calc from avg)



Regression equation and slope coefficient are both significant (p = 0.01) based on ANOVA (removed very large single value):

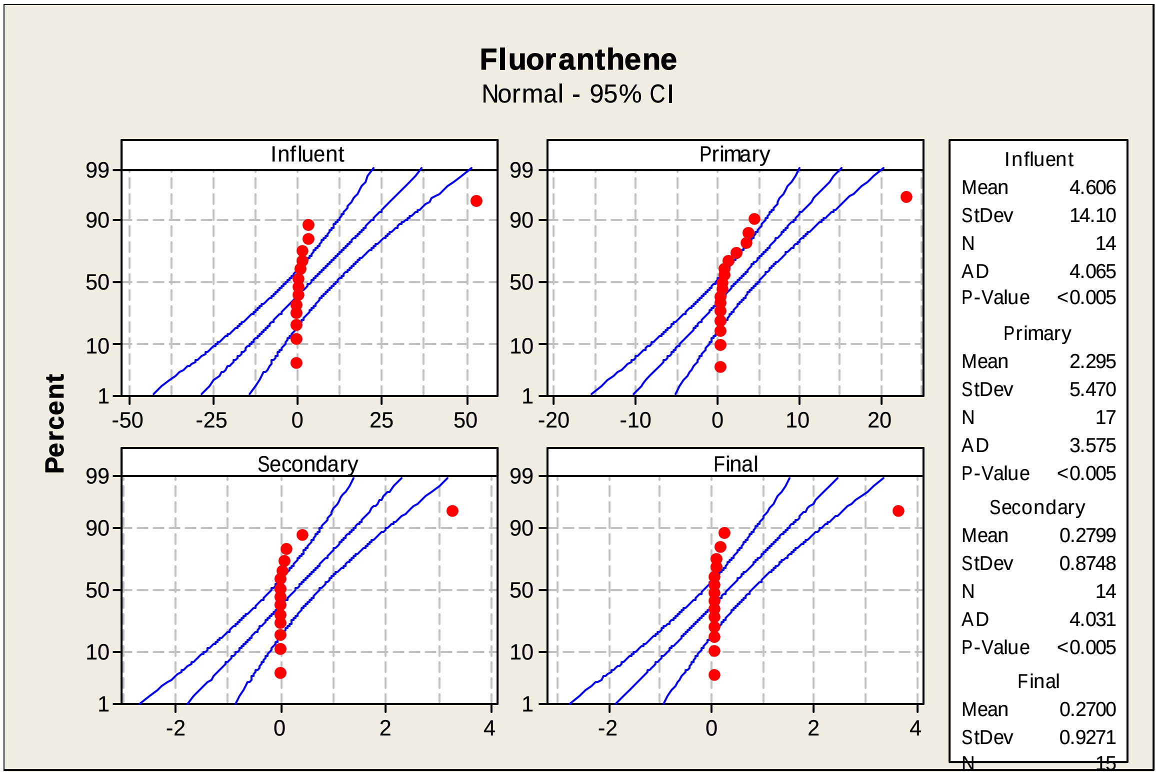
SUMMARY OUTPUT

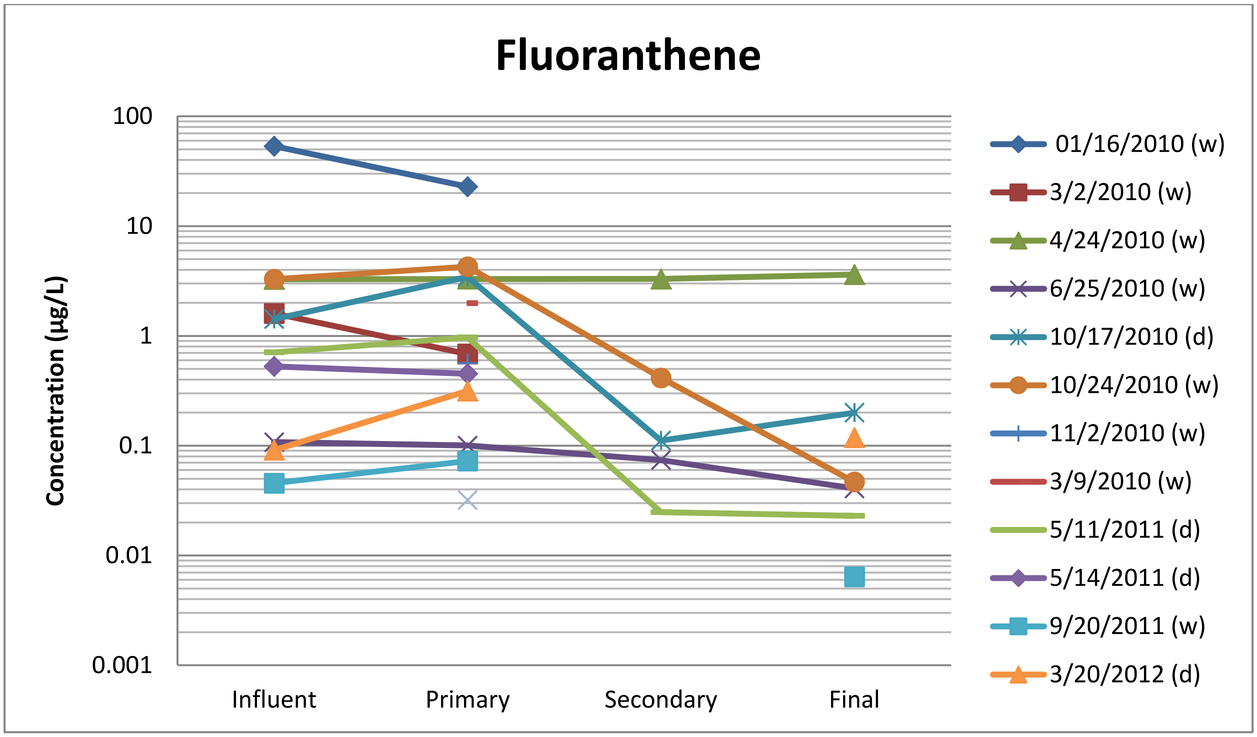
Regression Statistics	
Adjusted R Square	0.261307039
Standard Error	1.451731943
Observations	17

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	16.14762	16.14762	7.661885	0.014356
Residual	16	33.72041	2.107526		
Total	17	49.86803			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Slope term	0.046476327	0.016791	2.768011	0.013716	0.010882	0.082071


Fluoranthene
Normal - 95% CI
Percent
Influent
Primary
Secondary
Final
99
90
50
10
1
-50
-25
0
25
50
-20
-10
0
10
20
-2
0
2
4
Influent
Mean 4.606
StDev 14.10
N 14
AD 4.065
P-Value <0.005
Primary
Mean 2.295
StDev 5.470
N 17
AD 3.575
P-Value <0.005
Secondary
Mean 0.2799
StDev 0.8748
N 14
AD 4.031
P-Value <0.005
Final
Mean 0.2700
StDev 0.9271
N 15

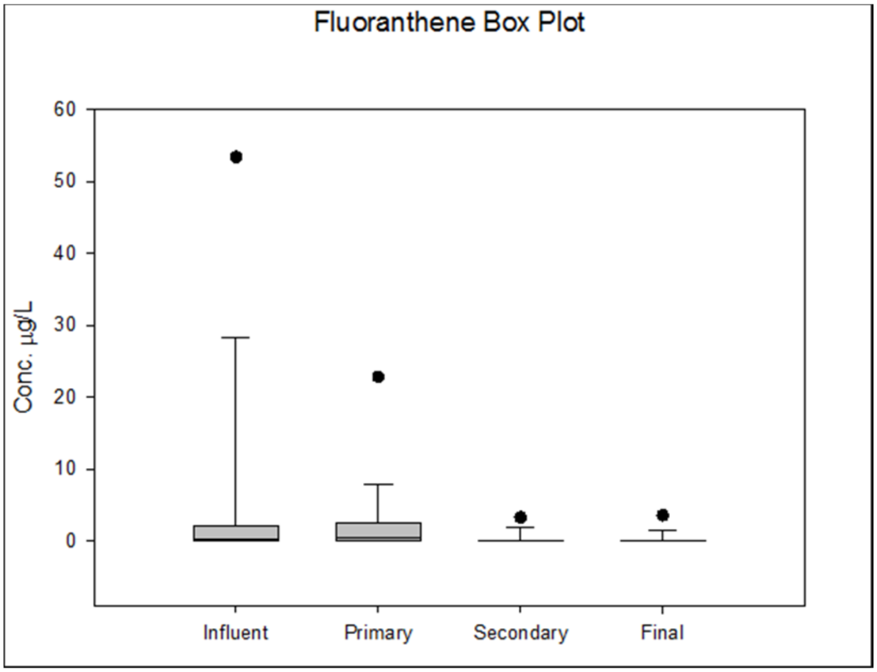

Fluoranthene
Concentration (µg/L)
100
10
1
0.1
0.01
0.001
Influent
Primary
Secondary
Final
01/16/2010 (w)
3/2/2010 (w)
4/24/2010 (w)
6/25/2010 (w)
10/17/2010 (d)
10/24/2010 (w)
11/2/2010 (w)
3/9/2010 (w)
5/11/2011 (d)
5/14/2011 (d)
9/20/2011 (w)
3/20/2012 (d)

Column	Size	Missing	Mean	Std Dev	Std. Error	C-I. of Mean
Fluoranthene-I	19	5	4.606	14.096	3.767	8.139
Fluoranthene-P	19	2	2.295	5.470	1.327	2.813
Fluoranthene-S	19	5	0.280	0.875	0.234	0.505
Fluoranthene-F	19	4	0.270	0.927	0.239	0.513

Column	Range	Max	Min	Median	25%	75%
Fluoranthene-I	53.414	53.414	0.000	0.317	0.000	1.602
Fluoranthene-P	22.834	22.834	0.000	0.452	0.0240	2.312
Fluoranthene-S	3.295	3.295	0.000	0.000	0.000	0.0740
Fluoranthene-F	3.615	3.615	0.000	0.000	0.000	0.0452

Column	Skewness	Kurtosis	K-S Dist.	K-S ProB-	SWilk W	SWilk Prob
Fluoranthene-I	3.698	13.763	0.466	<0.001	0.359	<0.001
Fluoranthene-P	3.707	14.466	0.337	<0.001	0.453	<0.001
Fluoranthene-S	3.643	13.435	0.434	<0.001	0.367	<0.001
Fluoranthene-F	3.849	14.862	0.464	<0.001	0.324	<0.001

Column	Sum	Sum of Squares
Fluoranthene-I	64.478	2879.911
Fluoranthene-P	39.021	568.334
Fluoranthene-S	3.919	11.045
Fluoranthene-F	4.050	13.127



One Way Analysis of Variance

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source: PAH in PAH 2010-2012

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Fluoranthene-I19		5	0.317	0.000	2.020
Fluoranthene-P19		2	0.452	0.0160	2.638
Fluoranthene-S19		5	0.000	0.000	0.0834
Fluoranthene-F19		4	0.000	0.000	0.0467

H = 11.087 with 3 degrees of freedom. (P = 0.011)

The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (**P = 0.011**)

To isolate the group or groups that differ from the others use a multiple comparison procedure.

All Pairwise Multiple Comparison Procedures (Dunn's Method) :

Comparison	**Diff of Ranks**	**Q**	**P<0.05**
Fluoranthene- vs Fluoranthene-	15.866	2.517	No
Fluoranthene- vs Fluoranthene-	14.627	2.364	Do Not Test
Fluoranthene- vs Fluoranthene-	1.866	0.296	Do Not Test

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Fluoranthene-I19		5	0.317	0.000	2.020
Fluoranthene-P19		2	0.452	0.0160	2.638

Mann-Whitney U Statistic= 113.000

T = 218.000 n(small)= 14 n(big)= 17 (P = 0.826)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.826**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Fluoranthene-P19		2	0.452	0.0160	2.638
Fluoranthene-S19		5	0.000	0.000	0.0834

Mann-Whitney U Statistic= 57.000

T = 162.000 n(small)= 14 n(big)= 17 (P = 0.011)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (**P = 0.011**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Fluoranthene-S19		5	0.000	0.000	0.0834
Fluoranthene-F19		4	0.000	0.000	0.0467

Mann-Whitney U Statistic= 98.000

T = 203.000 n(small)= 14 n(big)= 15 (P = 0.751)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.751**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Fluoranthene-I	19	5	0.317	0.000	2.020
Fluoranthene-F	19	4	0.000	0.000	0.0467

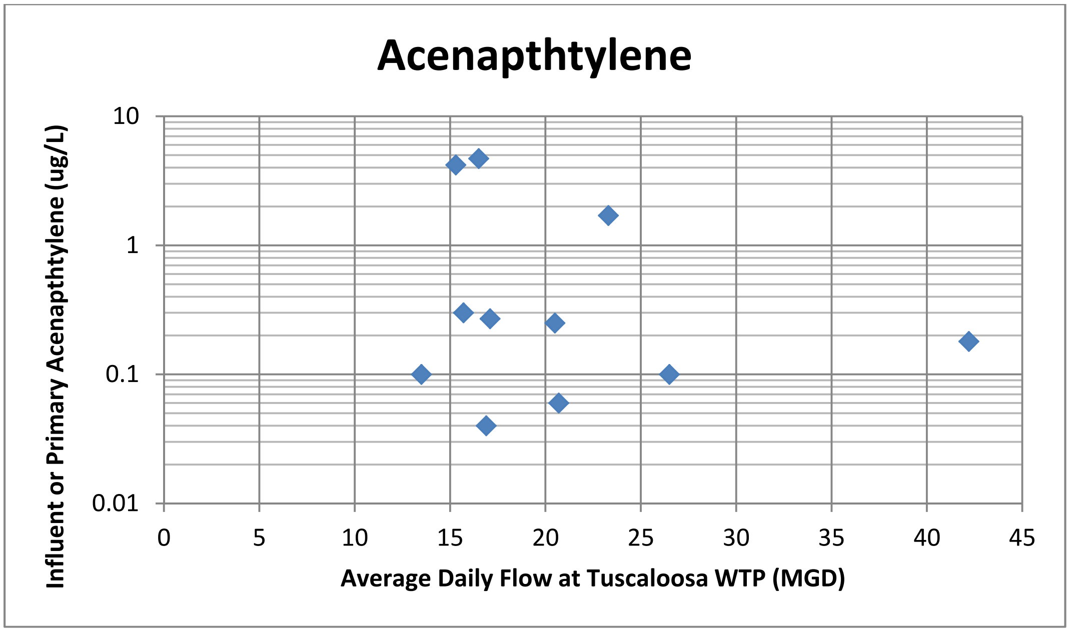
Mann-Whitney U Statistic= 60.000

T = 255.000 n(small)= 14 n(big)= 15 (P = 0.044)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (**P = 0.044**)

Acenaphthylene

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	56.6	0.0	0.0	0.0	18.2	3,895	0.55	100.0
3/2/2010	1.7	0.0	0.0	0.0	23.3	150	0.68	100.0
4/24/2010	4.7	3.9	4.0	4.6	16.5	292	1.01	1.9
6/25/2010	0.056	0.060	0.055	0.029	20.7	4	0.59	48.8
10/17/2010	0.29	4.2	0.0024	0.030	15.3	17	0.00	89.5
10.24/2010	0.2	0.3	0.2	0.0	15.7	9	0.10	81.4
11/2/2010	BQ	0.25	BQ	BQ	20.5	0	0.88	0.0
3/9/2011	BQ	0.18	BQ	x	42.2	0	2.67	0.0
5/11/2011	0.1	0.1	0.1	0.1	13.5	3	0.00	-50.5
9/20/2011	0.10	0.057	0.000	0.0042	26.5	10	0.64	95.8
10/10/2011	0.00	0.04	0.015	0.067	16.9	0		0.0
3/20/2012	0.12	0.27	0.050	0.057	17.1	8	0.00	50.7
6/16/2012	BDL	BDL	BDL	BDL	13.5	0	0.00	0.0
9/15/2012	0.00	0.00	0.00	0.0	14.5	0	0.00	0.0
11/1/2012	0.00	0.00	0.00	0.0	17.1	0	0.00	0.0
11/4/2012	0.00	0.00	0.00	0.00	15.4	0	0.05	0.0
11/8/2012	BQ	0.00	0.00	0.00	15.9	0	0.00	0.0
11/12/2012	BQ	BQ	0.00	0.00	16.0	0	0.44	0.0
Average dry (<0.1 inch of rain)	0.08	0.58	0.01	0.02	17.95	3.74	0.01	8.98 (calc from avg)
Average wet	10.55	0.60	0.61	0.67	22.18	484.49	0.84	47.54 (calc from avg)



Regression equation and coefficients are all insignificant (p = 0.11) based on ANOVA (even with removal of single very large value):

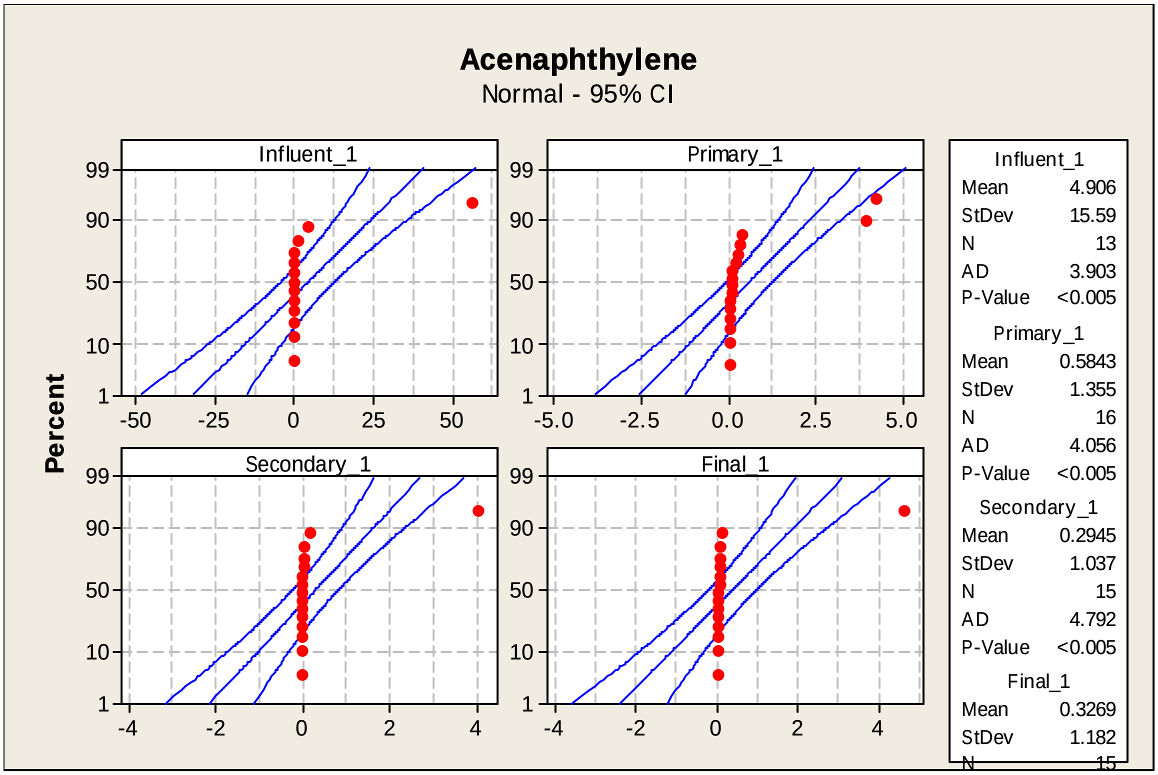
SUMMARY OUTPUT

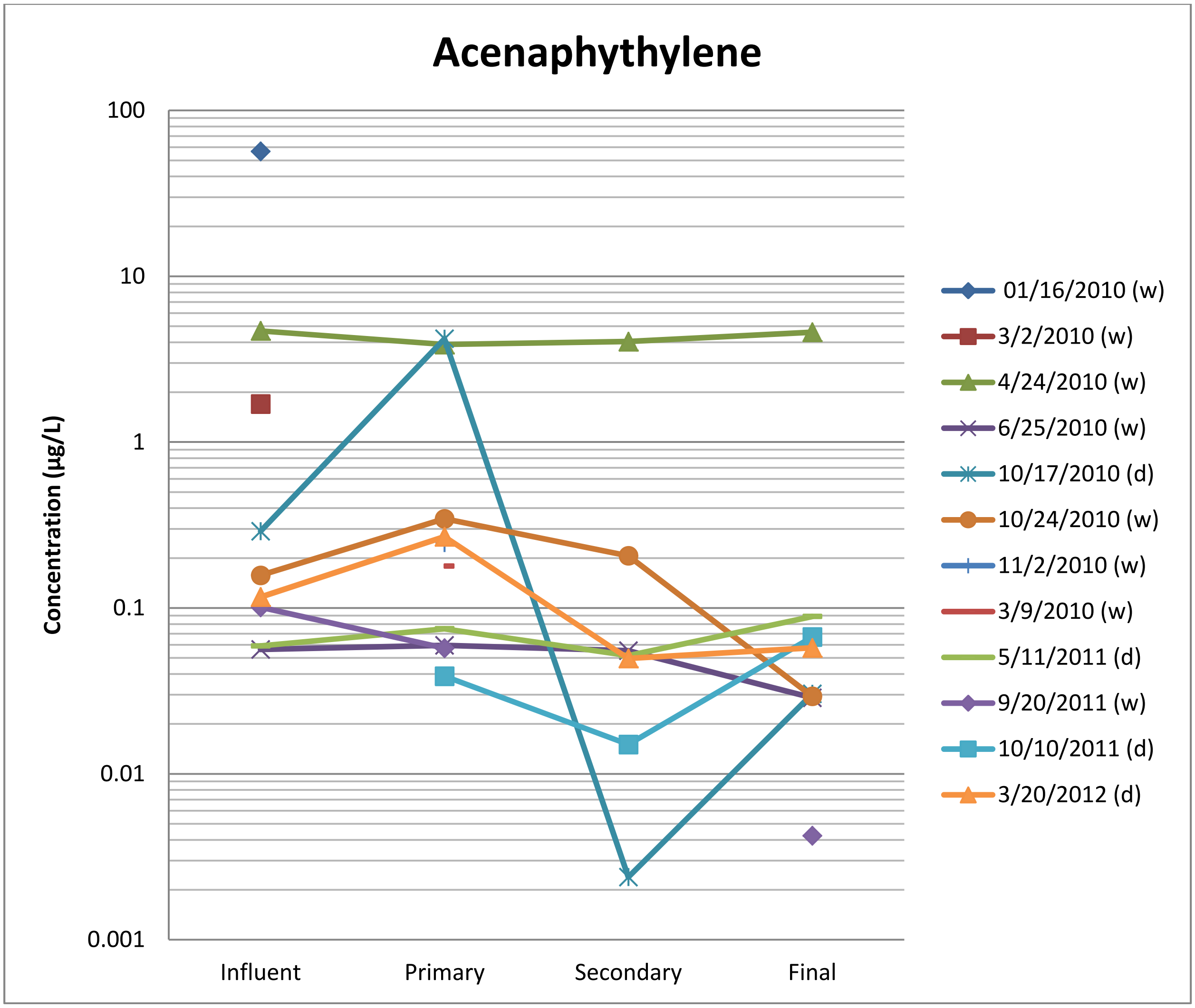
Regression Statistics	
Adjusted R Square	0.087367
Standard Error	1.509827
Observations	17

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	6.429744	6.429744	2.820585	0.11376513
Residual	16	36.47326	2.279578		
Total	17	42.903			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Slope term	0.030708	0.018284	1.67946	0.11248	-0.00805	0.069468


Acenaphthylene
Normal - 95% CI
Percent
Influent_1
Primary_1
Secondary_1
Final_1
99
90
50
10
1
-50
-25
0
25
50
-5.0
-2.5
0.0
2.5
5.0
-4
-2
0
2
4
Influent_1
Mean 4.906
StDev 15.59
N 13
AD 3.903
P-Value <0.005
Primary_1
Mean 0.5843
StDev 1.355
N 16
AD 4.056
P-Value <0.005
Secondary_1
Mean 0.2945
StDev 1.037
N 15
AD 4.792
P-Value <0.005
Final_1
Mean 0.3269
StDev 1.182
N 15



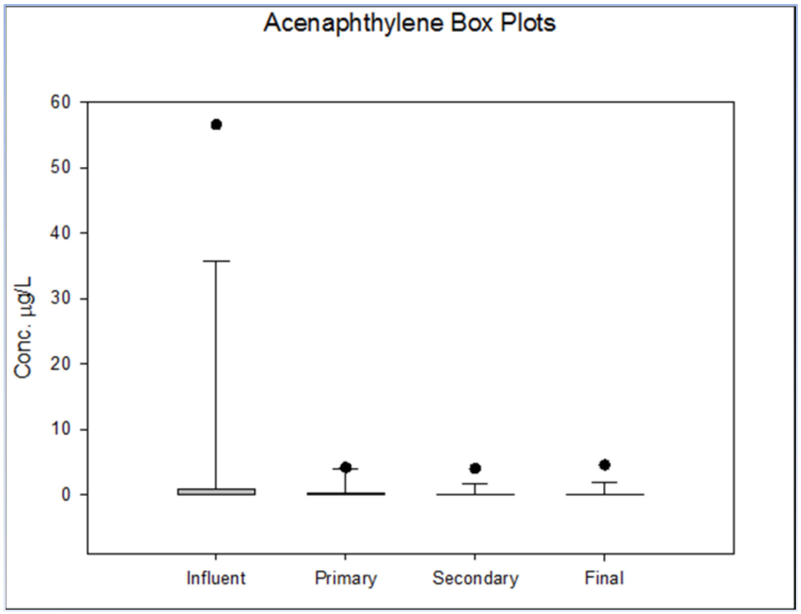
Column	Size	Missing	Mean	Std Dev	Std. Error	C-I. of Mean
Acenaphthylene-I	19	6	4.906	15.591	4.324	9.422
Acenaphthylene-P	19	3	0.584	1.355	0.339	0.722
Acenaphthylene-S	19	4	0.294	1.037	0.268	0.574
Acenaphthylene-F	19	4	0.327	1.182	0.305	0.655

Column	Range	Max	Min	Median	25%	75%
Acenaphthylene-I	56.612	56.612	0.000	0.101	0.000	0.642
Acenaphthylene-P	4.200	4.200	0.000	0.0584	0.000	0.257
Acenaphthylene-S	4.037	4.037	0.000	0.000	0.000	0.0511
Acenaphthylene-F	4.598	4.598	0.000	0.00423	0.000	0.0507

Column	Skewness	Kurtosis	K-S Dist.	K-S ProB-	SWilk W	SWilk Prob
Acenaphthylene-I	3.562	12.764	0.429	<0.001	0.359	<0.001
Acenaphthylene-P	2.486	4.868	0.445	<0.001	0.470	<0.001

Acenaphthylene-S	3.855	14.900	0.467	<0.001	0.315	<0.001
Acenaphthylene-F	3.869	14.978	0.513	<0.001	0.303	<0.001

Column	**Sum**	**Sum of Squares**
Acenaphthylene-I	63.778	3229.911
Acenaphthylene-P	9.349	32.987
Acenaphthylene-S	4.417	16.348
Acenaphthylene-F	4.904	21.162



One Way Analysis of Variance

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks Wednesday, January 16, 2013, 12:30:57 PM

Data source: PAH in PAH 2010-2012

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Acenaphthylene-I19	6		0.101	0.000	0.994
Acenaphthylene-P19	3		0.0584	0.000	0.263
Acenaphthylene-S19	4		0.000	0.000	0.0516
Acenaphthylene-F19	4		0.00423	0.000	0.0575

H = 6.008 with 3 degrees of freedom. (P = 0.111)

The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.111**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Acenaphthylene-I19	6		0.101	0.000	0.994
Acenaphthylene-P19	3		0.0584	0.000	0.263

Mann-Whitney U Statistic= 92.000

T = 207.000 n(small)= 13 n(big)= 16 (P = 0.607)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.607**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Acenaphthylene-P19		3	0.0584	0.000	0.263
Acenaphthylene-S19		4	0.000	0.000	0.0516

Mann-Whitney U Statistic= 83.000

T = 203.000 n(small)= 15 n(big)= 16 (P = 0.130)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.130**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Acenaphthylene-S19		4	0.000	0.000	0.0516
Acenaphthylene-F19		4	0.00423	0.000	0.0575

Mann-Whitney U Statistic= 104.000

T = 224.000 n(small)= 15 n(big)= 15 (P = 0.723)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.723**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed ($P < 0.050$)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Acenaphthylene-I	19	6	0.101	0.000	0.994
Acenaphthylene-F	19	4	0.00423	0.000	0.0575

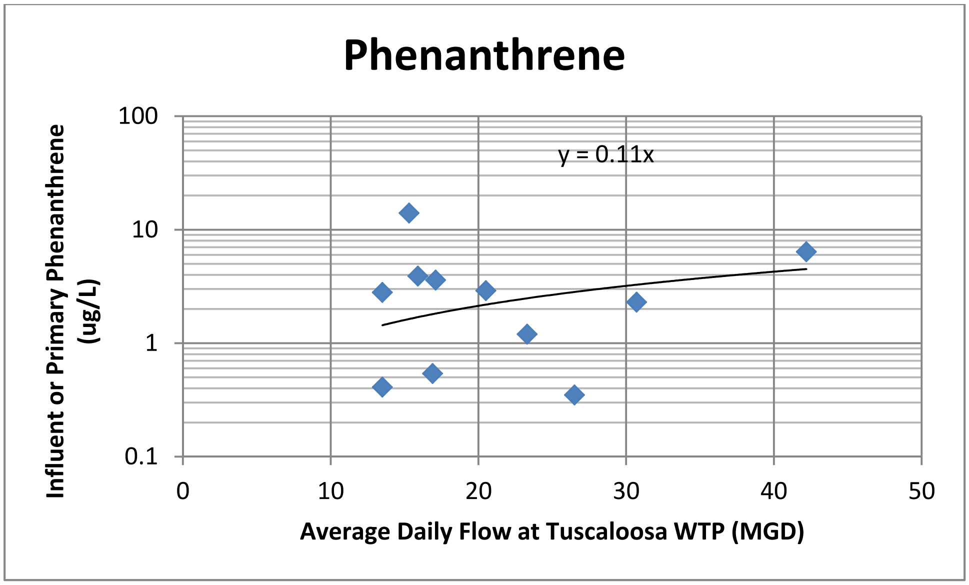
Mann-Whitney U Statistic= 58.000

T = 228.000 n(small)= 13 n(big)= 15 (P = 0.064)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.064**)

Phenanthrene

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	40.9	20.2	0.0	0.0	18.2	2752.4	0.55	100.0
3/2/2010	1.2	0.6	0.0	0.0	23.3	105.7	0.68	100.0
4/24/2010	0.0	0.0	0.0	0.0	16.5	0.0	1.01	0.0
6/25/2010	BQ	BQ	BQ	BQ	20.7	0.0	0.59	0.0
10/17/2010	4.9	14	0.043	0.61	15.3	280.1	0.00	87.7
10.24/2010	0.0	0.0	0.0	0.0	15.7	0.0	0.10	0.0
11/2/2010	0.40	2.9	0.19	0.24	20.5	30.0	0.88	38.5
3/9/2011	0.30	6.4	BQ	n/a	42.2	46.1	2.67	100.0
5/11/2011	2.8	2.8	0.0	0.0	13.5	137.5	0.00	100.0
5/14/2011	2.3	1.8	BQ	BQ	30.7	258.6	0.00	100.0
9/20/2011	0.19	0.35	0.000	0.019	26.5	18.5	0.64	89.9
10/10/2011	0.14	0.54	0.045	0.043	16.9	8.5	0.00	68.0
3/20/2012	1.4	3.6	1.1	0.69	17.1	88.2	0.00	50.8
6/16/2012	0.09	0.41	0.065	BDL	13.5	4.4	0.00	100.0
9/15/2012	0.00	0.00	0.00	0.0	14.5	0.0	0.00	0.0
11/1/2012	0.00	0.000	0.000	0.0	17.1	0.0	0.00	0.0
11/4/2012	0.00	0.00	0.00	0.00	15.4	0.0	0.05	0.0
11/8/2012	3.9	0.00	0.00	0.00	15.9	231.3	0.00	100.0
11/12/2012	BQ	BQ	0.00	0.00	16.0	0.0	0.44	0.0
Average dry (<0.1 inch of rain)	1.56	0.77	0.16	0.12	18.84	75.13	0.01	53.55 (calc from avg)
Average wet	6.14	4.36	0.05	0.15	20.10	62.77	0.84	47.60 (calc from avg)



Regression equation and slope coefficient are both significant (p = 0.01) based on ANOVA (removed very large single value):

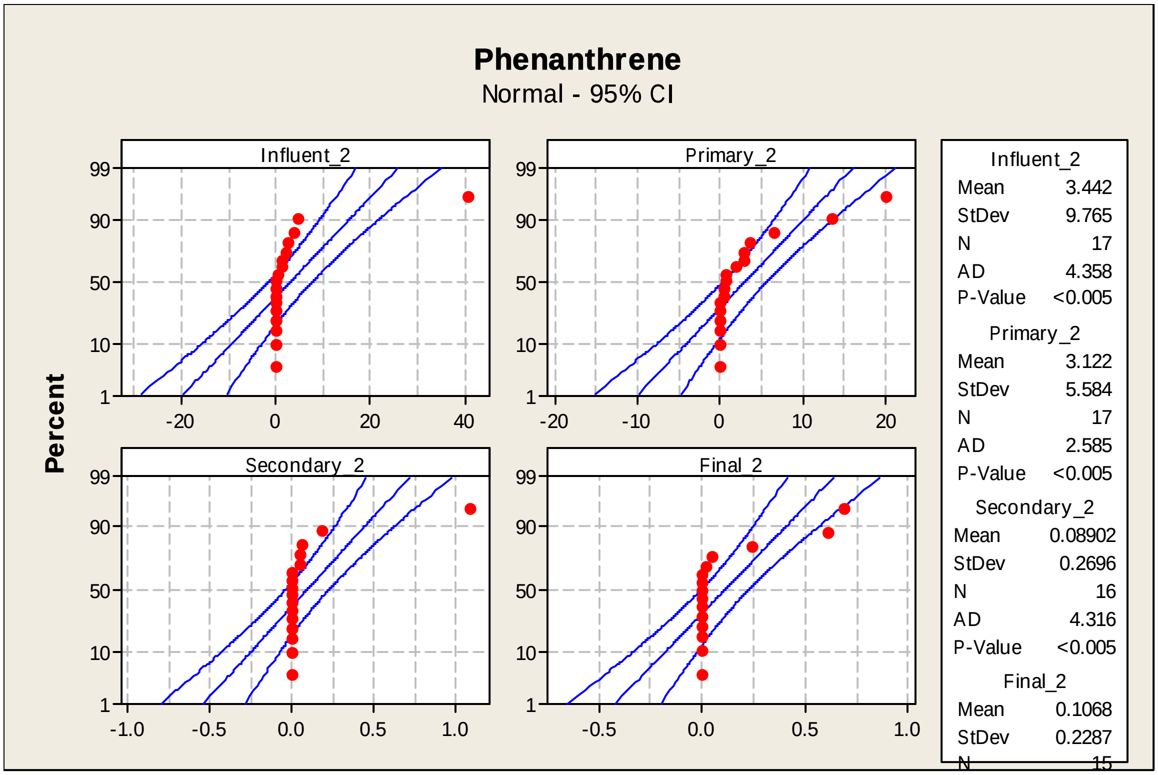
SUMMARY OUTPUT

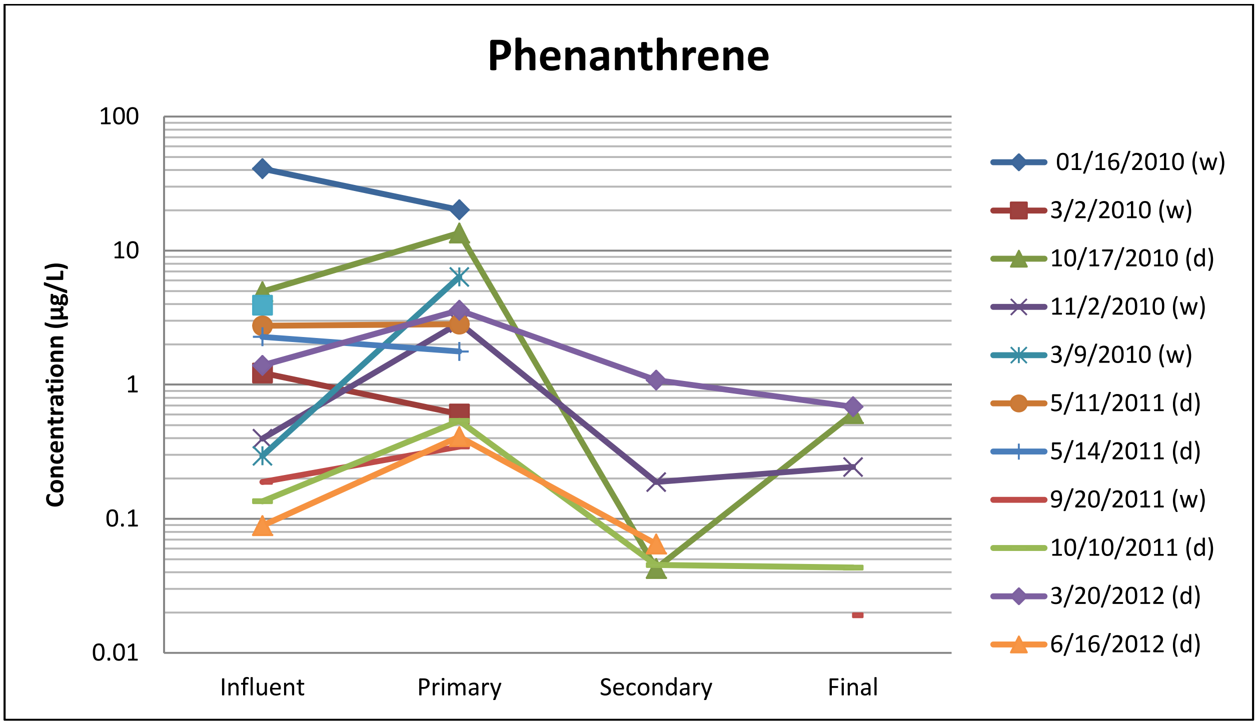
Regression Statistics	
Adjusted R Square	0.246868
Standard Error	3.433754
Observations	18

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	88.25086	88.25086	7.484806	0.014654
Residual	17	200.4413	11.79067		
Total	18	288.6922			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Slope term	0.106634	0.038977	2.735837	0.01408	0.0244	0.188868


Phenanthrene
Normal - 95% CI
Percent
Influent_2
Primary_2
Secondary_2
Final_2
99
90
50
10
1
-20
0
20
40
-20
-10
0
10
20
-1.0
-0.5
0.0
0.5
1.0
-0.5
0.0
0.5
1.0
Influent_2
Mean 3.442
StDev 9.765
N 17
AD 4.358
P-Value <0.005
Primary_2
Mean 3.122
StDev 5.584
N 17
AD 2.585
P-Value <0.005
Secondary_2
Mean 0.08902
StDev 0.2696
N 16
AD 4.316
P-Value <0.005
Final_2
Mean 0.1068
StDev 0.2287
N 15


Phenanthrene
Concentrationn (µg/L)
100
10
1
0.1
0.01
Influent
Primary
Secondary
Final
01/16/2010 (w)
3/2/2010 (w)
10/17/2010 (d)
11/2/2010 (w)
3/9/2010 (w)
5/11/2011 (d)
5/14/2011 (d)
9/20/2011 (w)
10/10/2011 (d)
3/20/2012 (d)
6/16/2012 (d)

```
Column         Size  Missing   Mean    Std Dev  Std. Error  C-I. of Mean
Phenanthrene-I19        2      3.442    9.765     2.368           5.021
Phenanthrene-P19        2      3.122    5.584     1.354           2.871
Phenanthrene-S19        3      0.0890   0.270     0.0674          0.144
Phenanthrene-F19        4      0.107    0.229     0.0591          0.127
```

```
Column        Range    Max      Min      Median    25%     75%
Phenanthrene-I40.873 40.873   0.000     0.295    0.000   2.396
Phenanthrene-P20.17920.179   0.000     0.538    0.000   3.064
Phenanthrene-S1.083   1.083   0.000     0.000    0.000   0.0439
Phenanthrene-F0.686   0.686   0.000     0.000    0.000   0.0372
```

```
Column       Skewness Kurtosis  K-S Dist.  K-S ProB- SWilk W SWilk Prob
Phenanthrene-I 3.960    16.018     0.380      <0.001    0.379     <0.001
Phenanthrene-P 2.388     5.460     0.290      <0.001    0.625     <0.001
Phenanthrene-S 3.795    14.739     0.411      <0.001    0.377     <0.001
Phenanthrene-F 2.140     3.378     0.409      <0.001    0.535     <0.001
```

```
Column          Sum  Sum of Squares
Phenanthrene-I58.507   1727.075
Phenanthrene-P53.075    664.664
Phenanthrene-S1.424       1.217
Phenanthrene-F1.601       0.904
```

One Way Analysis of Variance

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source: PAH in PAH 2010-2012

```
Group           N   Missing   Median      25%        75%
Phenanthrene-I19      2         0.295      0.000      2.515
Phenanthrene-P19      2         0.538      0.000      3.241
Phenanthrene-S19      3         0.000      0.000      0.0446
Phenanthrene-F19      4         0.000      0.000      0.0433
```

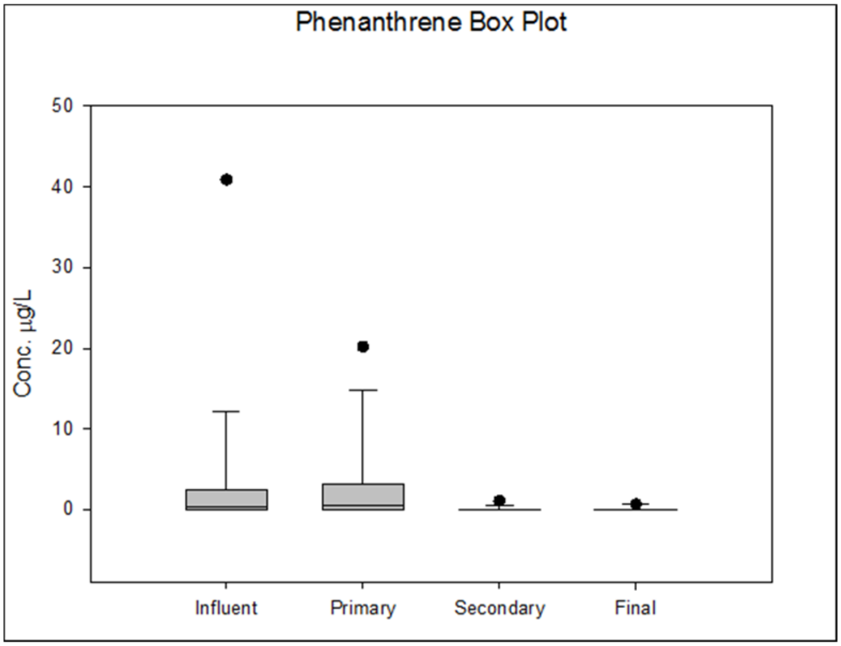
H = 14.272 with 3 degrees of freedom. (P = 0.003)

The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.003)

To isolate the group or groups that differ from the others use a multiple comparison procedure.

All Pairwise Multiple Comparison Procedures (Dunn's Method) :

Comparison	**Diff of Ranks**	**Q**	**P<0.05**
Phenanthrene- vs Phenanthrene-	17.517	2.660	Yes
Phenanthrene- vs Phenanthrene-	16.302	2.434	No
Phenanthrene- vs Phenanthrene-	0.618	0.0952	Do Not Test



Mann-Whitney Rank Sum Test
Data source: PAH in PAH 2010-2012
Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Phenanthrene-I	19	2	0.295	0.000	2.515
Phenanthrene-P	19	2	0.538	0.000	3.241

Mann-Whitney U Statistic= 133.000

T = 286.000 n(small)= 17 n(big)= 17 (P = 0.700)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.700**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Phenanthrene-P19		2	0.538	0.000	3.241
Phenanthrene-S19		3	0.000	0.000	0.0446

Mann-Whitney U Statistic= 67.000

T = 203.000 n(small)= 16 n(big)= 17 (P = 0.008)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = **0.008**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Phenanthrene-S19		3	0.000	0.000	0.0446
Phenanthrene-F19		4	0.000	0.000	0.0433

Mann-Whitney U Statistic= 117.000

T = 243.000 n(small)= 15 n(big)= 16 (P = 0.905)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.905**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Phenanthrene-I	19	2	0.295	0.000	2.515
Phenanthrene-F	19	4	0.000	0.000	0.0433

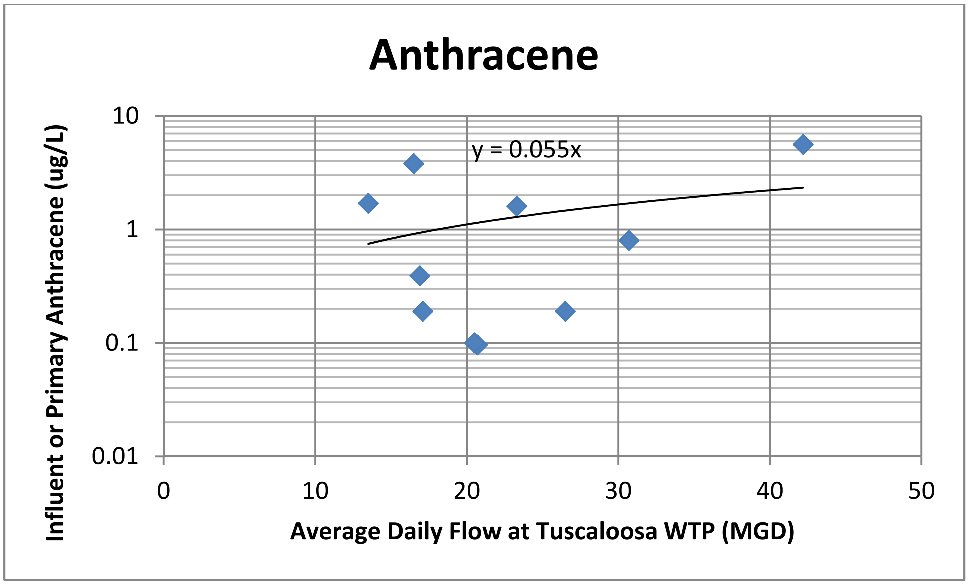
Mann-Whitney U Statistic= 63.000

T = 183.000 n(small)= 15 n(big)= 17 (P = 0.011)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (**P = 0.011**)

Anthracene

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	54.5	0.0	69.1	0.0	18.2	3669.2	0.55	100.0
3/2/2010	1.6	0.0	2.1	0.0	23.3	110.1	0.68	100.0
4/24/2010	3.8	2.7	4.1	4.1	16.5	255.2	1.01	-7.2
6/25/2010	0.096	0.087	0.11	0.049	20.7	6.5	0.59	48.8
10/17/2010	478	0.90	BQ	0.20	15.3	32166.9	0.00	100.0
10.24/2010	**1124.8**	9.5	2.2	1.5	15.7	75742.0	0.10	99.9
11/2/2010	BQ	0.10	0.11	BQ	20.5	0.0	0.88	0.0
3/9/2011	BQ	5.6	BQ	n/a	42.2	0.0	2.67	0.0
5/11/2011	1.7	0.0	1.0	0.9	13.5	117.6	0.00	47.2
5/14/2011	0.8	0.4	1.1	BQ	30.7	55.4	0.00	100.0
9/20/2011	0.10	0.19	0.000	0.13	26.5	6.6	0.64	-34.7
10/10/2011	0.01	0.39	0.061	0.18	16.9	0.8	0.00	-1345.8
3/20/2012	0.19	0.08	0.060	0.037	17.1	12.9	0.00	80.7
6/16/2012	BDL	BDL	0.0068	0.062	13.5	0.0	0.00	0.0
9/15/2012	0.00	0.00	0.00	0.000	14.5	0.0	0.00	0.0
11/1/2012	0.00	0.000	0.0000	0.000	17.1	0.0	0.00	0.0
11/4/2012	0.00	0.00	0.00	0.00	15.4	0.0	0.05	0.0
11/8/2012	BQ	0.00	0.00	0.00	15.9	0.0	0.00	0.0
11/12/2012	BQ	BQ	0.00	0.00	16.0	0.0	0.44	0.0
Average dry (<0.1 inch of rain)	60.07	0.18	0.24	0.15	17.95	3,235.94	0.01	-101.80 (calc from avg)
Average wet	197.48	2.27	9.70	0.81	22.18	8,865.52	0.84	34.09 (calc from avg)



Regression equation and slope coefficient are both significant (p = 0.004) based on ANOVA (removed very large single value):

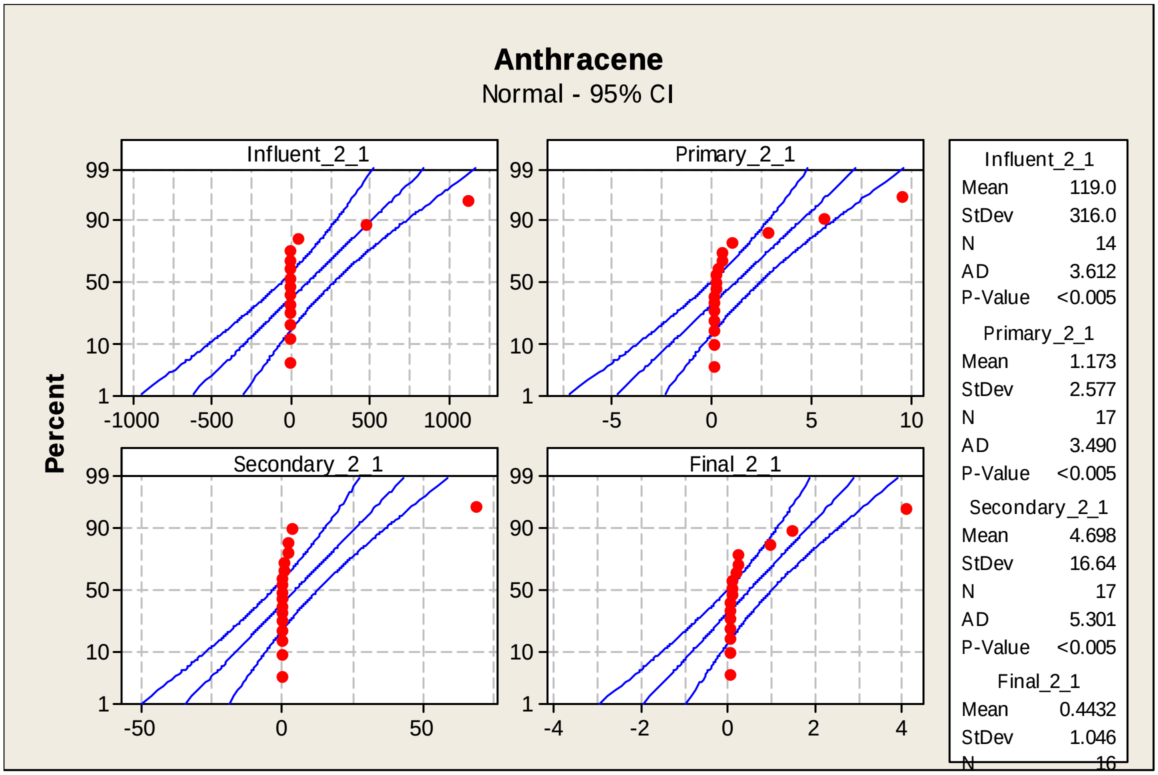
SUMMARY OUTPUT

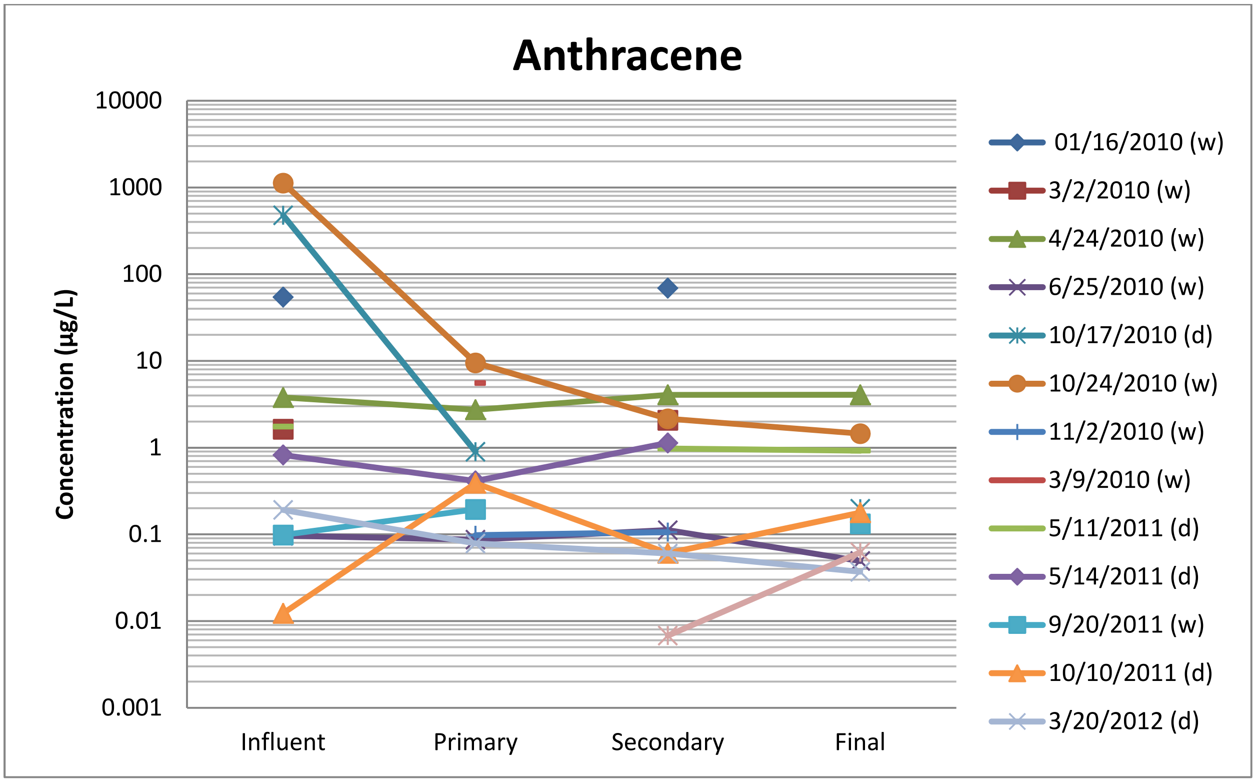
Regression Statistics	
Adjusted R Square	0.360627
Standard Error	1.410844
Observations	16

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	22.27632	22.27632	11.19143	0.004808
Residual	15	29.8572	1.99048		
Total	16	52.13352			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Slope term	0.055314	0.016535	3.345359	0.004427	0.020072	0.090557


Anthracene
Normal - 95% CI
Percent
Influent_2_1
Primary_2_1
Secondary_2_1
Final_2_1
99
90
50
10
1
-1000
-500
0
500
1000
-5
0
5
10
-50
0
50
-4
-2
0
2
4
Influent_2_1
Mean 119.0
StDev 316.0
N 14
AD 3.612
P-Value <0.005
Primary_2_1
Mean 1.173
StDev 2.577
N 17
AD 3.490
P-Value <0.005
Secondary_2_1
Mean 4.698
StDev 16.64
N 17
AD 5.301
P-Value <0.005
Final_2_1
Mean 0.4432
StDev 1.046
N 16

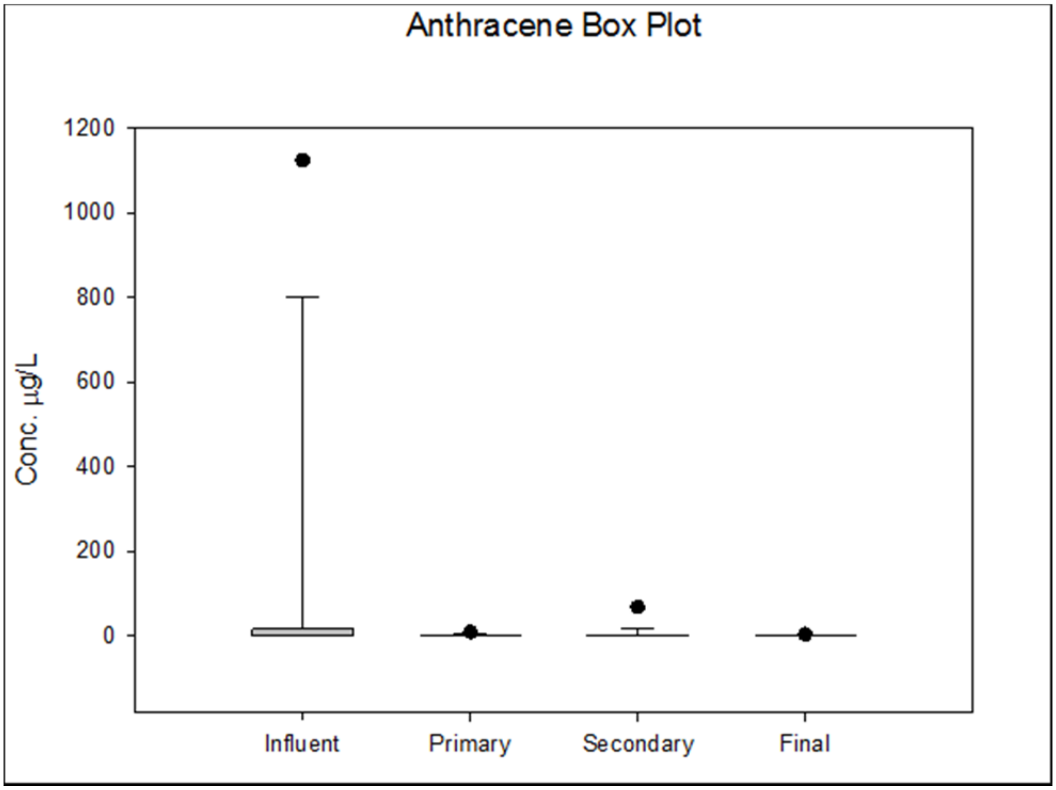

Anthracene
Concentration (µg/L)
10000
1000
100
10
1
0.1
0.01
0.001
Influent
Primary
Secondary
Final
01/16/2010 (w)
3/2/2010 (w)
4/24/2010 (w)
6/25/2010 (w)
10/17/2010 (d)
10/24/2010 (w)
11/2/2010 (w)
3/9/2010 (w)
5/11/2011 (d)
5/14/2011 (d)
9/20/2011 (w)
10/10/2011 (d)
3/20/2012 (d)

Column	Size	Missing	Mean	Std Dev	Std. Error	C-I. of Mean
Anthracene-I	19	5	118.952	316.006	84.456	182.457
Anthracene-P	19	2	1.173	2.577	0.625	1.325
Anthracene-S	19	2	4.698	16.641	4.036	8.556
Anthracene-F	19	3	0.443	1.046	0.261	0.557

Column	Range	Max	Min	Median	25%	75%
Anthracene-I	1124.770	1124.770	0.000	0.507	0.0123	3.790
Anthracene-P	9.490	9.490	0.000	0.0867	0.000	0.534
Anthracene-S	69.125	69.125	0.000	0.0605	0.000	1.368
Anthracene-F	4.062	4.062	0.000	0.0431	0.000	0.188

Column	Skewness	Kurtosis	K-S Dist.	K-S ProB-	SWilk W	SWilk Prob
Anthracene-I	2.973	8.949	0.438	<0.001	0.449	<0.001
Anthracene-P	2.676	7.042	0.381	<0.001	0.533	<0.001
Anthracene-S	4.091	16.811	0.456	<0.001	0.308	<0.001
Anthracene-F	3.174	10.691	0.405	<0.001	0.493	<0.001

Column	Sum	Sum of Squares
Anthracene-I	1665.329	1496274.755
Anthracene-P	19.942	129.638
Anthracene-S	79.869	4806.004
Anthracene-F	7.091	19.549



One Way Analysis of Variance

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source: PAH in PAH 2010-2012

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Anthracene-I19		5	0.507	0.00922	16.465
Anthracene-P19		2	0.0867	0.000	0.655
Anthracene-S19		2	0.0605	0.000	1.603
Anthracene-F19		3	0.0431	0.000	0.193

H = 3.737 with 3 degrees of freedom. (P = 0.291)

The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.291**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Anthracene-I19		5	0.507	0.00922	16.465
Anthracene-P19		2	0.0867	0.000	0.655

Mann-Whitney U Statistic= 84.500

T = 258.500 n(small)= 14 n(big)= 17 (P = 0.170)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.170**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

```
Group        N   Missing   Median      25%        75%
Anthracene-P19      2        0.0867      0.000       0.655
Anthracene-S19      2        0.0605      0.000       1.603
```

Mann-Whitney U Statistic= 139.000

T = 292.000 n(small)= 17 n(big)= 17 (P = 0.859)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.859**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

```
Group        N   Missing   Median      25%        75%
Anthracene-S19      2        0.0605      0.000       1.603
Anthracene-F19      3        0.0431      0.000       0.193
```

Mann-Whitney U Statistic= 116.000

T = 252.000 n(small)= 16 n(big)= 17 (P = 0.469)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.469**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Anthracene-I	19	5	0.507	0.00922	16.465
Anthracene-F	19	3	0.0431	0.000	0.193

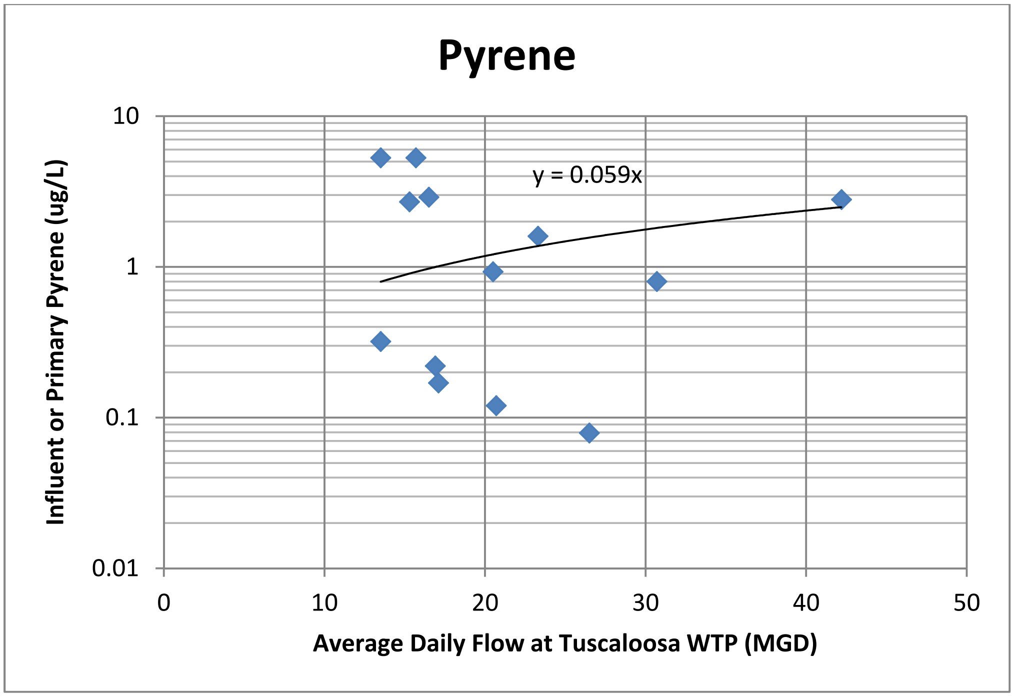
Mann-Whitney U Statistic= 68.500

T = 260.500 n(small)= 14 n(big)= 16 (P = 0.069)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.069**)

Pyrene

	Influent (µg/L)	After Primary (µg/L)	After Secondary (µg/L)	Final Effluent (µg/L)	Daily Flow (MGD)	Mass Influent (g/day)	Daily Rain Depth at Tuscaloosa airport (in)	Overall % Reduction
1/16/2010	53.7	19.9	0.0	0.0	18.2	3619.1	0.55	100.0
3/2/2010	1.6	0.6	0.0	0.0	23.3	139.0	0.68	100.0
4/24/2010	2.9	2.6	3.5	2.8	16.5	175.7	1.01	100.0
6/25/2010	0.12	0.12	n/a	0.045	20.7	9.3	0.59	2.9
10/17/2010	1.4	2.7	0.19	0.20	15.3	79.3	0.00	62.9
10.24/2010	3.0	5.3	0.8	0.7	15.7	174.6	0.10	85.5
11/2/2010	BQ	0.93	BQ	BQ	20.5	0.0	0.88	0.0
3/9/2011	BQ	2.8	BQ	n/a	42.2	0.0	2.67	0.0
5/11/2011	3.0	5.3	0.8	0.7	13.5	150.2	0.00	76.7
5/14/2011	0.6	0.8	BQ	BQ	30.7	69.9	0.00	100.0
9/20/2011	0.049	0.079	0.000	0.019	26.5	4.8	0.64	61.8
10/10/2011	0.03	0.22	0.021	0.032	16.9	1.6	0.00	-26.8
3/20/2012	0.17	0.30	0.10	0.081	17.1	11.0	0.00	53.7
6/16/2012	BDL	0.32	0.14	BDL	13.5	0.0	0.00	0.0
9/15/2012	0.00	0.00	0.00	0.0	14.5	0.0	0.00	0.0
11/1/2012	0.00	0.000	0.00	0.0	17.1	0.0	0.00	0.0
11/4/2012	0.00	0.00	0.00	0.00	15.4	0.0	0.05	0.0
11/8/2012	BQ	0.00	0.00	0.00	15.9	0.0	0.00	0.0
11/12/2012	BQ	BQ	0.00	0.00	16.0	0.0	0.44	0.0
Average dry (<0.1 inch of rain)	0.66	0.95	0.13	0.13	17.95	31.52	0.01	26.65 (calc from avg)
Average wet	10.24	4.04	0.72	0.51	22.18	458.06	0.84	50.02 (calc from avg)



Regression equation and slope coefficient are both significant (p = 0.01) based on ANOVA (removed very large single value):

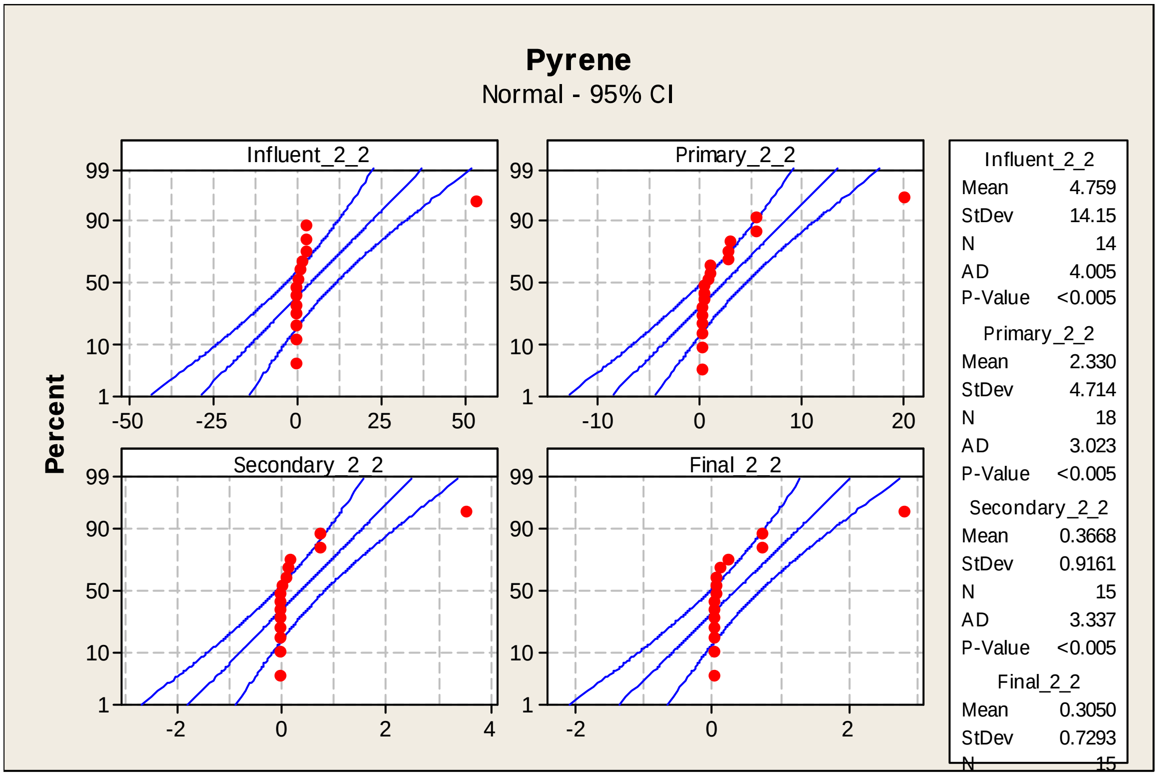
SUMMARY OUTPUT

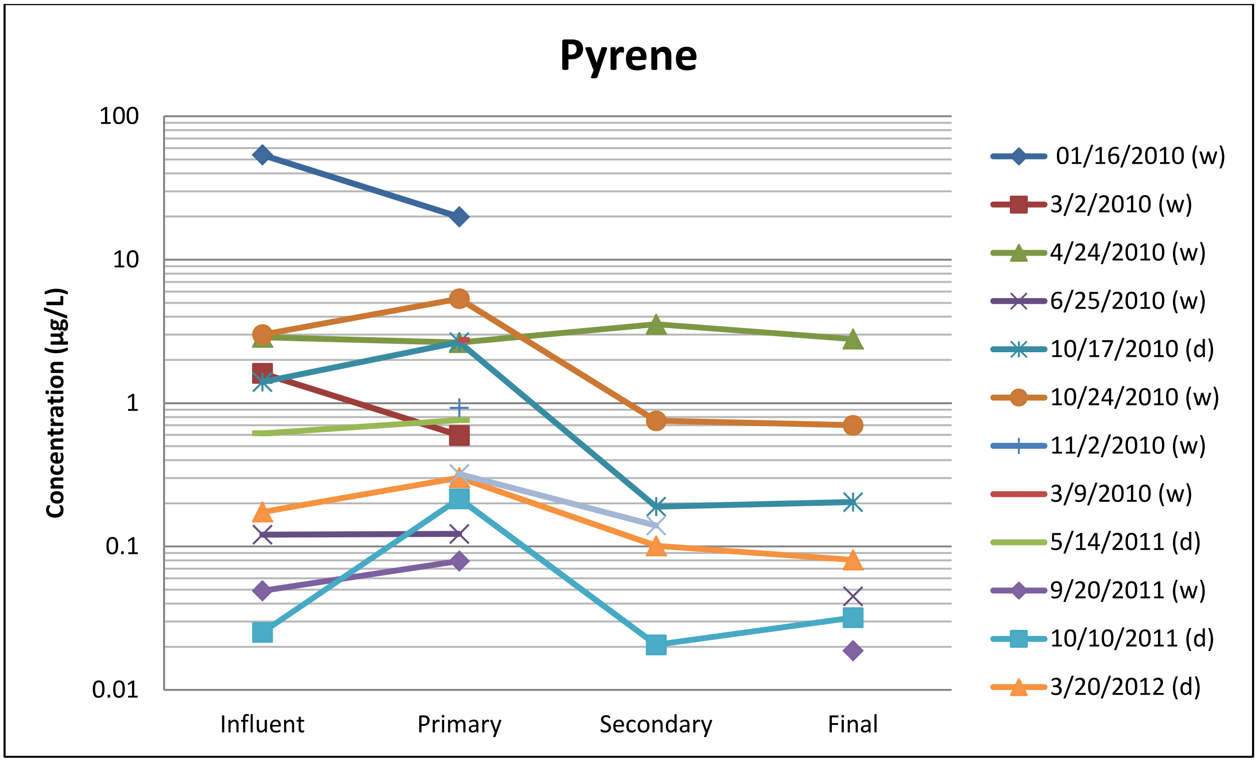
Regression Statistics	
Adjusted R Square	0.2637
Standard Error	1.829465
Observations	18

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	27.08723	27.08723	8.093128	0.011705
Residual	17	56.89801	3.346942		
Total	18	83.98524			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Slope term	0.059077	0.020766	2.844842	0.011196	0.015264	0.10289


Pyrene
Normal - 95% CI
Percent
Influent_2_2
Primary_2_2
Secondary_2_2
Final_2_2
99
90
50
10
1
-50
-25
0
25
50
-10
0
10
20
-2
0
2
4
-2
0
2
Influent_2_2
Mean 4.759
StDev 14.15
N 14
AD 4.005
P-Value <0.005
Primary_2_2
Mean 2.330
StDev 4.714
N 18
AD 3.023
P-Value <0.005
Secondary_2_2
Mean 0.3668
StDev 0.9161
N 15
AD 3.337
P-Value <0.005
Final_2_2
Mean 0.3050
StDev 0.7293
N 15

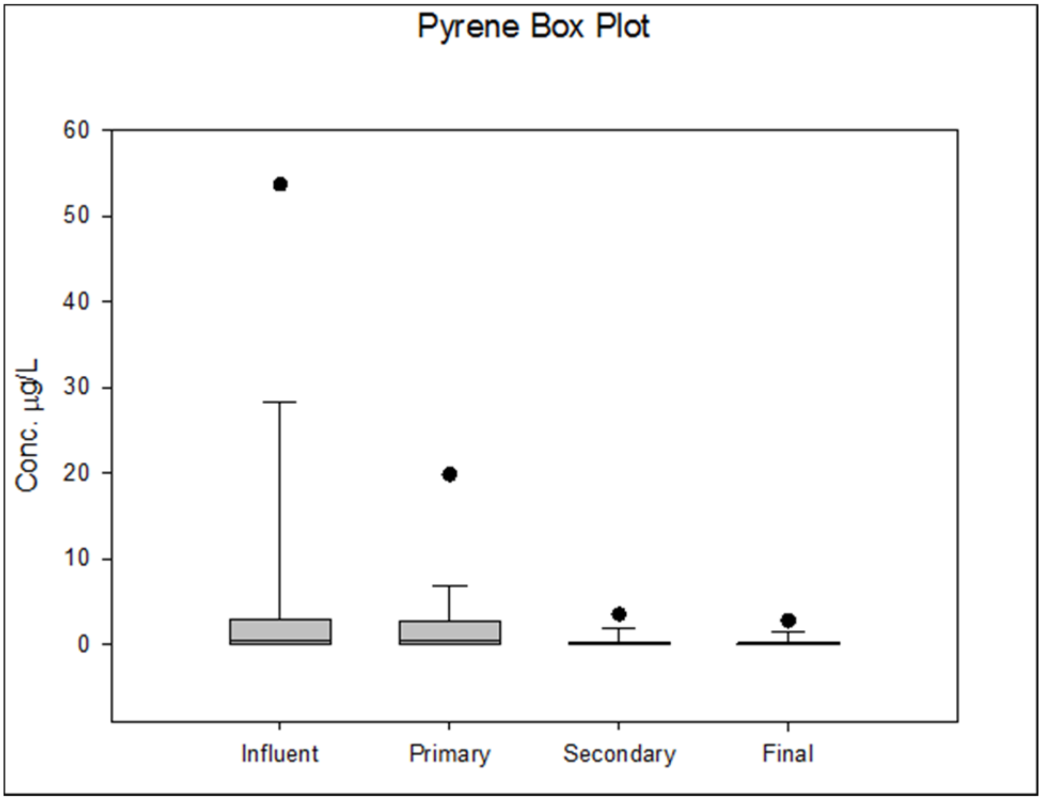

Pyrene
Concentration (µg/L)
100
10
1
0.1
0.01
Influent
Primary
Secondary
Final
01/16/2010 (w)
3/2/2010 (w)
4/24/2010 (w)
6/25/2010 (w)
10/17/2010 (d)
10/24/2010 (w)
11/2/2010 (w)
3/9/2010 (w)
5/14/2011 (d)
9/20/2011 (w)
10/10/2011 (d)
3/20/2012 (d)

Column	**Size**	**Missing**	**Mean**	**Std Dev**	**Std. Error**	**C-I. of Mean**
Pyrene-I	19	5	4.759	14.149	3.782	8.170
Pyrene-P	19	1	2.330	4.714	1.111	2.344
Pyrene-S	19	4	0.367	0.916	0.237	0.507
Pyrene-F	19	4	0.305	0.729	0.188	0.404

Column	**Range**	**Max**	**Min**	**Median**	**25%**	**75%**
Pyrene-I	53.744	53.744	0.000	0.395	0.0252	2.878
Pyrene-P	19.868	19.868	0.000	0.458	0.0791	2.663
Pyrene-S	3.545	3.545	0.000	0.000	0.000	0.177
Pyrene-F	2.794	2.794	0.000	0.0187	0.000	0.173

Column	**Skewness**	**Kurtosis**	**K-S Dist.**	**K-S ProB-**	**SWilk W**	**SWilk Prob**
Pyrene-I	3.696	13.751	0.478	<0.001	0.364	<0.001
Pyrene-P	3.371	12.508	0.311	<0.001	0.531	<0.001
Pyrene-S	3.404	12.186	0.377	<0.001	0.461	<0.001
Pyrene-F	3.247	11.204	0.355	<0.001	0.485	<0.001

Column	**Sum**	**Sum of Squares**
Pyrene-I	66.632	2919.771
Pyrene-P	41.939	475.567
Pyrene-S	5.502	13.769
Pyrene-F	4.575	8.841



One Way Analysis of Variance

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source: PAH in PAH 2010-2012

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Pyrene-I	19	5	0.395	0.0189	2.910
Pyrene-P	19	1	0.458	0.0593	2.687
Pyrene-S	19	4	0.000	0.000	0.189
Pyrene-F	19	4	0.0187	0.000	0.204

H = 9.592 with 3 degrees of freedom. (P = 0.022)

The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.022)

To isolate the group or groups that differ from the others use a multiple comparison procedure.

All Pairwise Multiple Comparison Procedures (Dunn's Method) :

Comparison	**Diff of Ranks**	**Q**	**P<0.05**
Pyrene-P vs Pyrene-F	14.422	2.287	No
Pyrene-P vs Pyrene-S	14.322	2.271	Do Not Test
Pyrene-P vs Pyrene-I	1.187	0.185	Do Not Test
Pyrene-I vs Pyrene-F	13.236	1.974	Do Not Test
Pyrene-I vs Pyrene-S	13.136	1.959	Do Not Test
Pyrene-S vs Pyrene-F	0.1000	0.0152	Do Not Test

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Pyrene-I	19	5	0.395	0.0189	2.910
Pyrene-P	19	1	0.458	0.0593	2.687

Mann-Whitney U Statistic= 122.000

T = 227.000 n(small)= 14 n(big)= 18 (P = 0.894)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 0.894**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk) Failed (P < 0.050)

Group	**N**	**Missing**	**Median**	**25%**	**75%**
Pyrene-P	19	1	0.458	0.0593	2.687
Pyrene-S	19	4	0.000	0.000	0.189

Mann-Whitney U Statistic= 72.000

T = 192.000 n(small)= 15 n(big)= 18 (P = 0.021)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.021)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Pyrene-S	19	4	0.000	0.000	0.189
Pyrene-F	19	4	0.0187	0.000	0.204

Mann-Whitney U Statistic= 112.000

T = 232.000 n(small)= 15 n(big)= 15 (P = 1.000)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (**P = 1.000**)

Mann-Whitney Rank Sum Test

Data source: PAH in PAH 2010-2012

Normality Test (Shapiro-Wilk)   Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Pyrene-I	19	5	0.395	0.0189	2.910
Pyrene-F	19	4	0.0187	0.000	0.204

Mann-Whitney U Statistic= 59.500

T = 255.500 n(small)= 14 n(big)= 15 (P = 0.045)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (**P = 0.045**)

Appendix B: Chromatographs for HPLC Treatment Facility Samples

The following are chromatographs of HPLC selected samples.

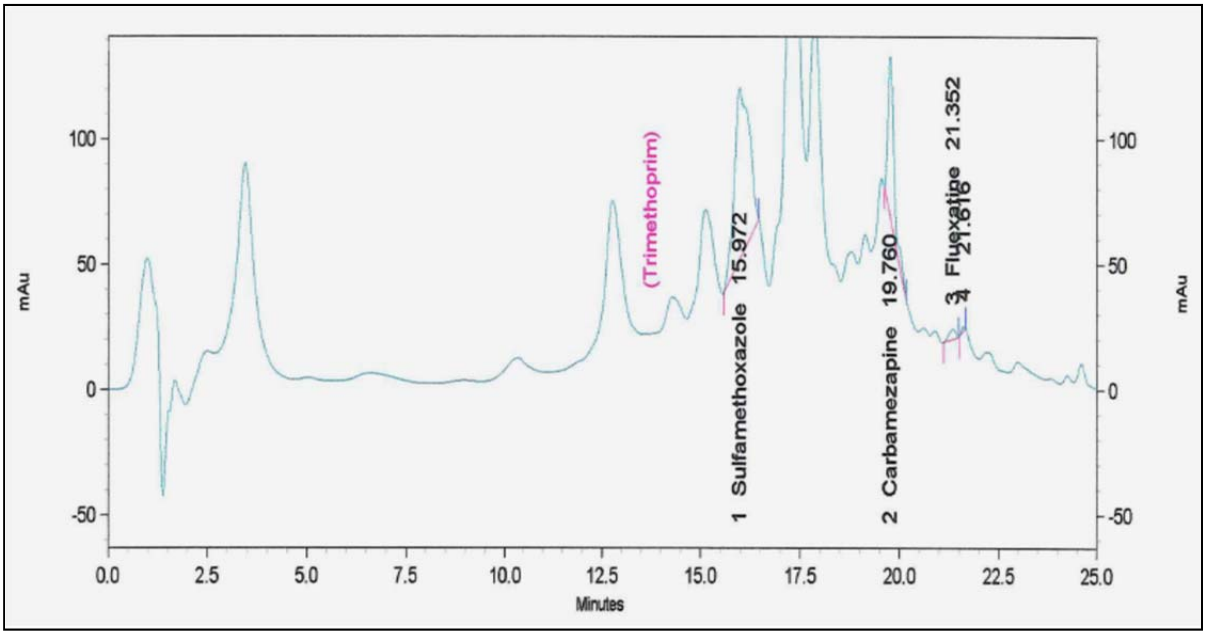


Figure B-1. Influent Sample for 11/08/12: Acid Group I

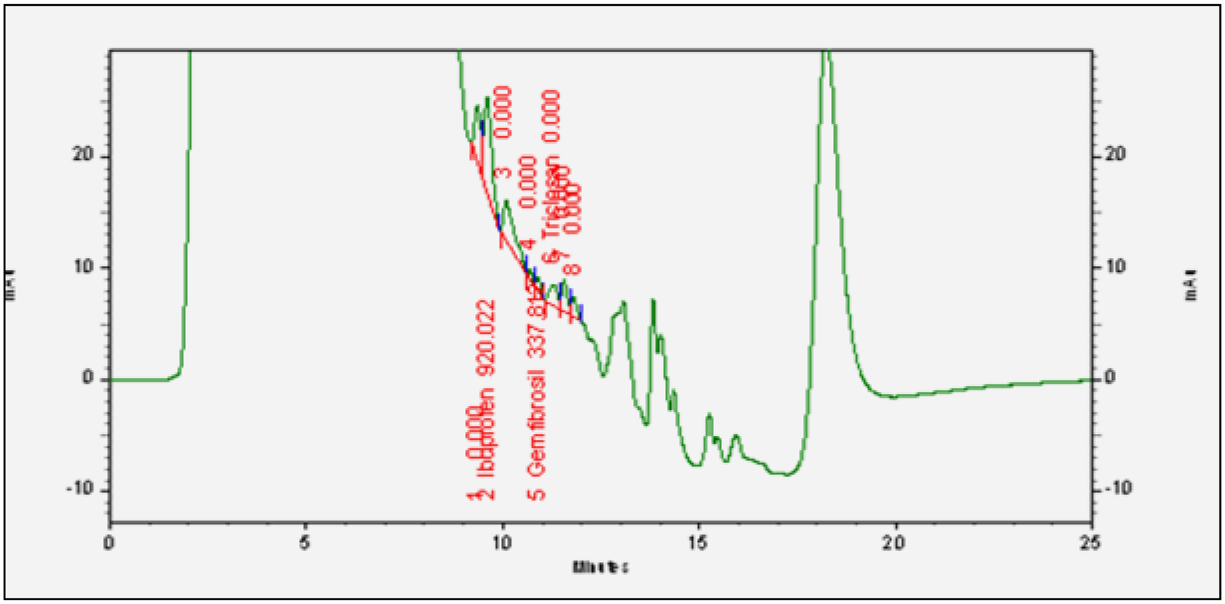


Figure B-2. Influent Sample for 11/08/12: Acid Group II

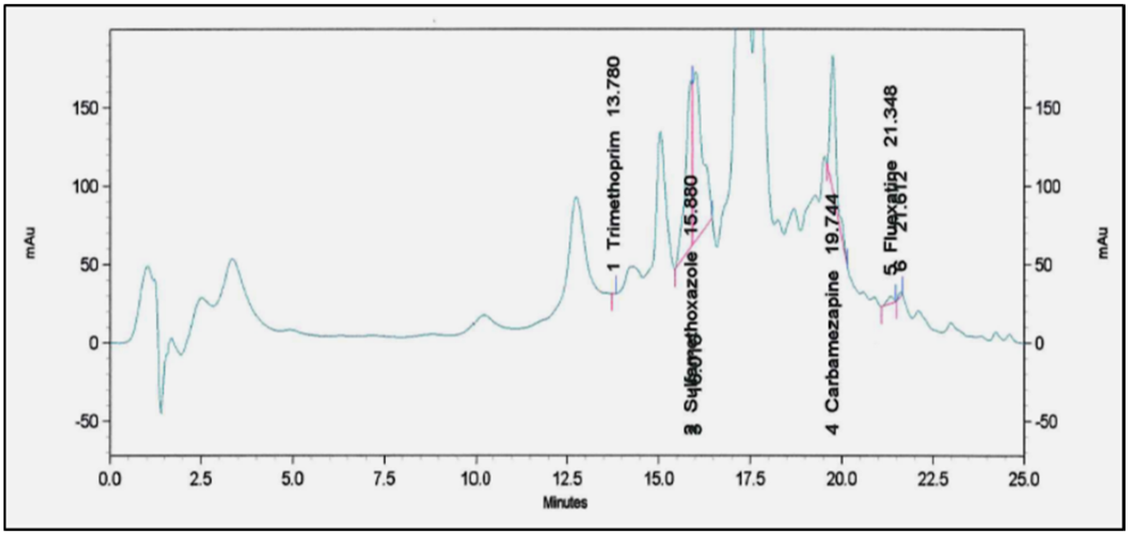


Figure B-3. Primary Effluent Sample for 11/08/12: Acid Group I

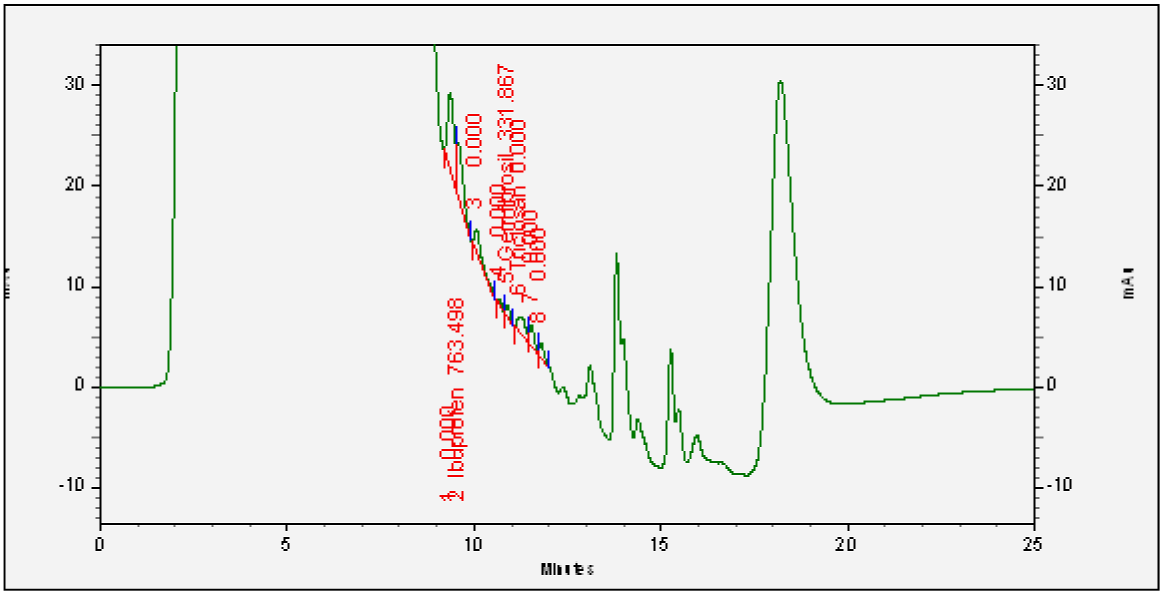


Figure B-4. Primary Effluent Sample for 11/08/12: Acid Group II

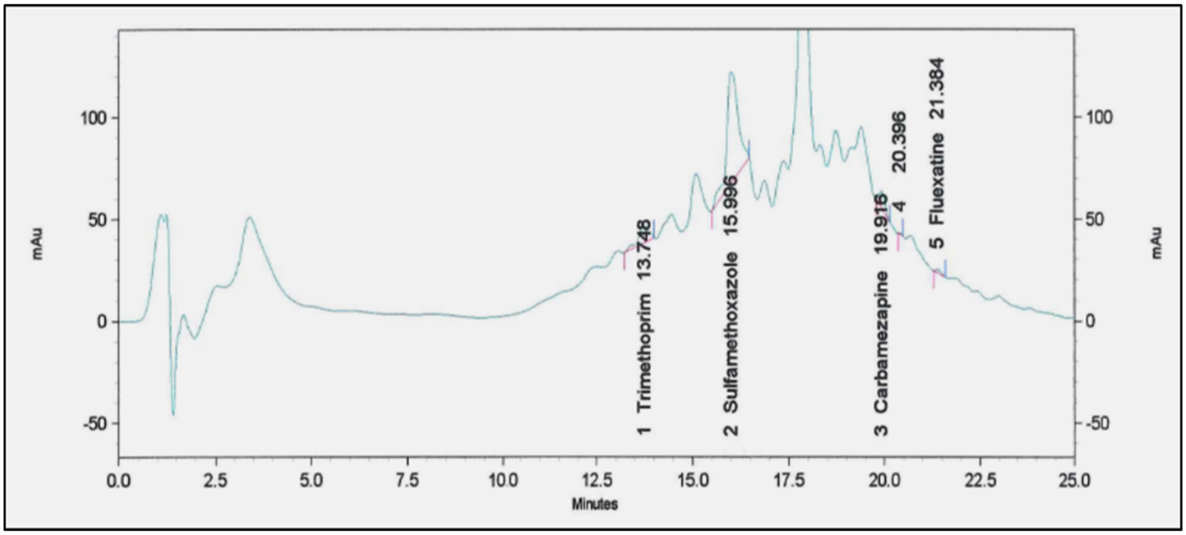


Figure B-5. Secondary Effluent Sample for 11/08/12: Acid Group I

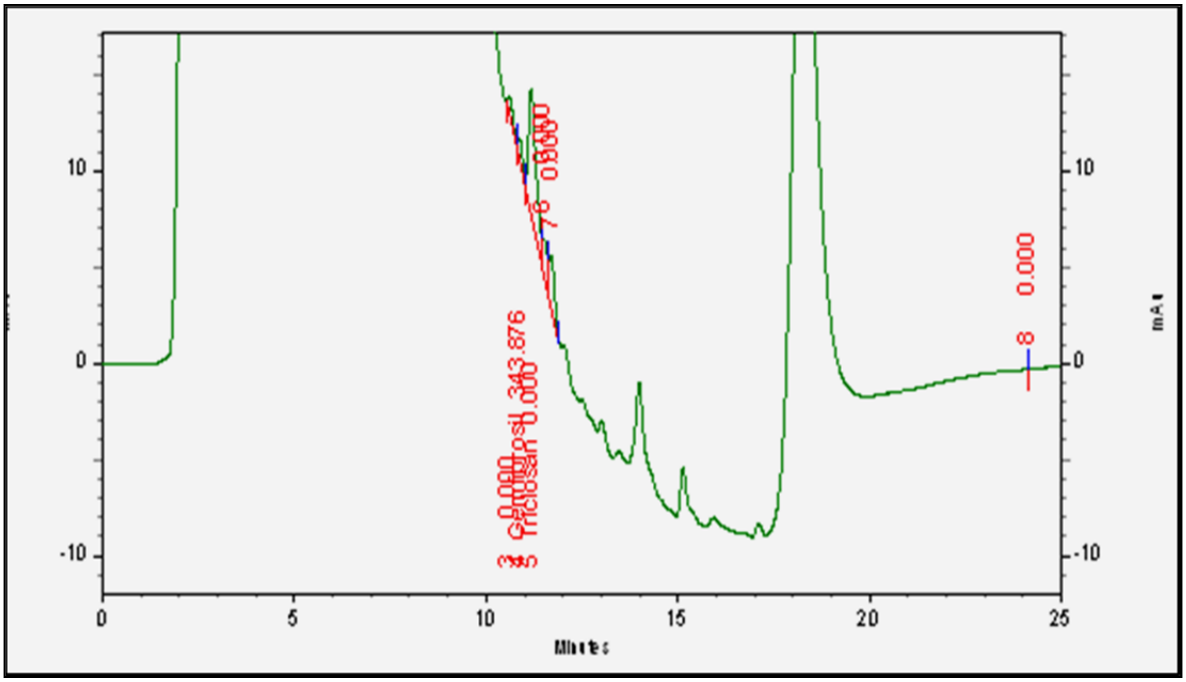


Figure B-6. Secondary Effluent Sample for 11/08/12: Acid Group II

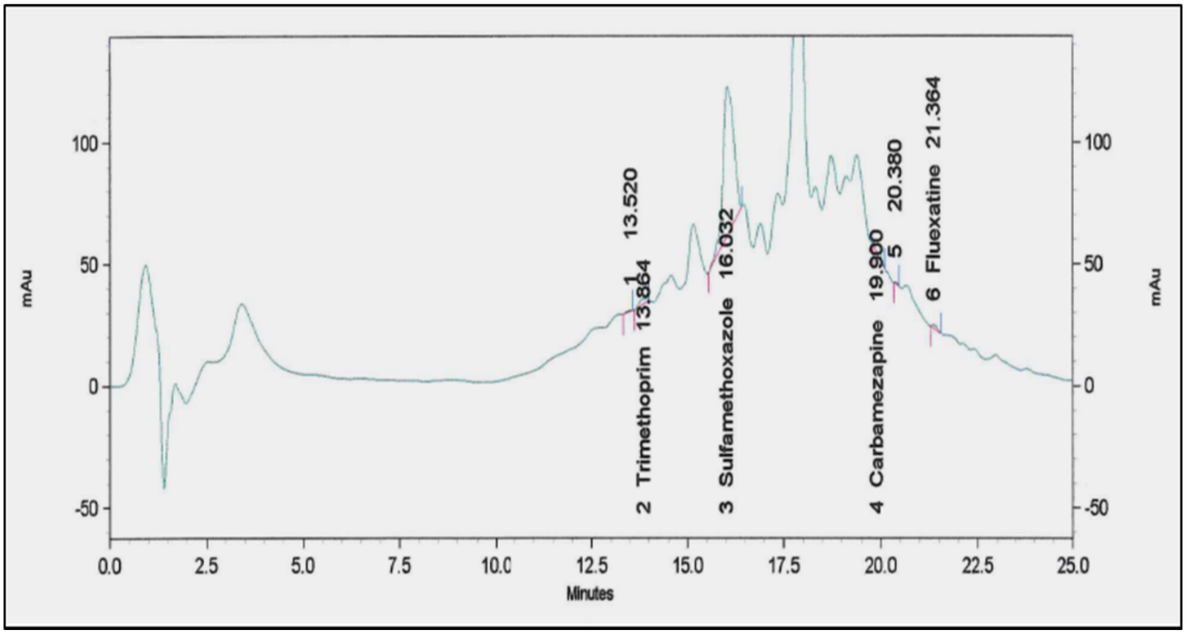


Figure B-7. Final Effluent Sample for 11/08/12: Acid Group I

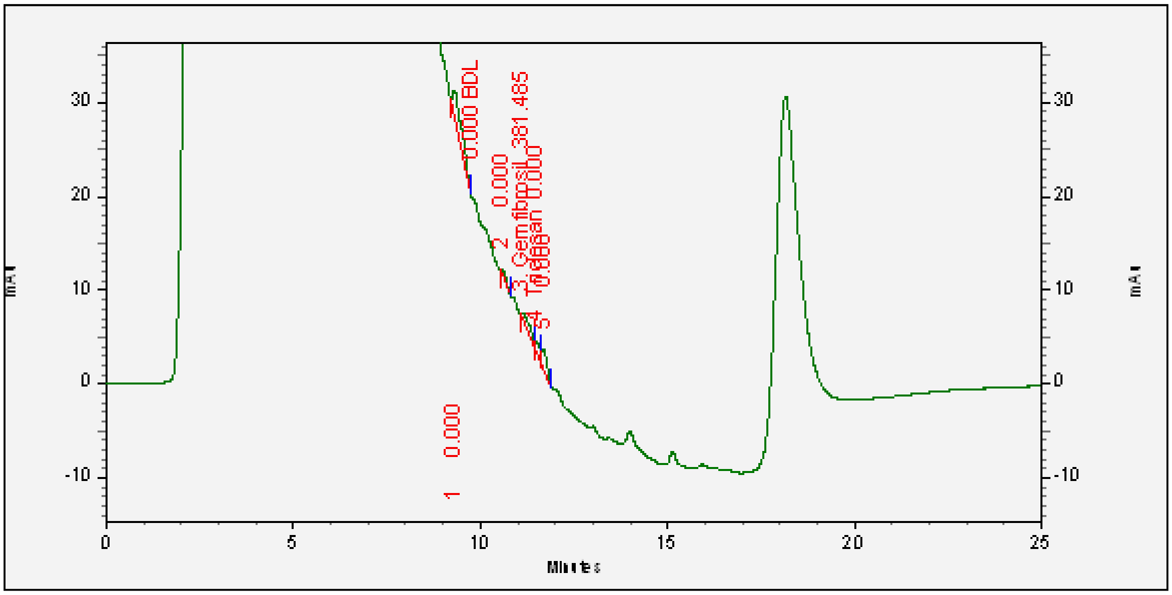


Figure B-8. Final Effluent Sample for 11/08/12: Acid Group II

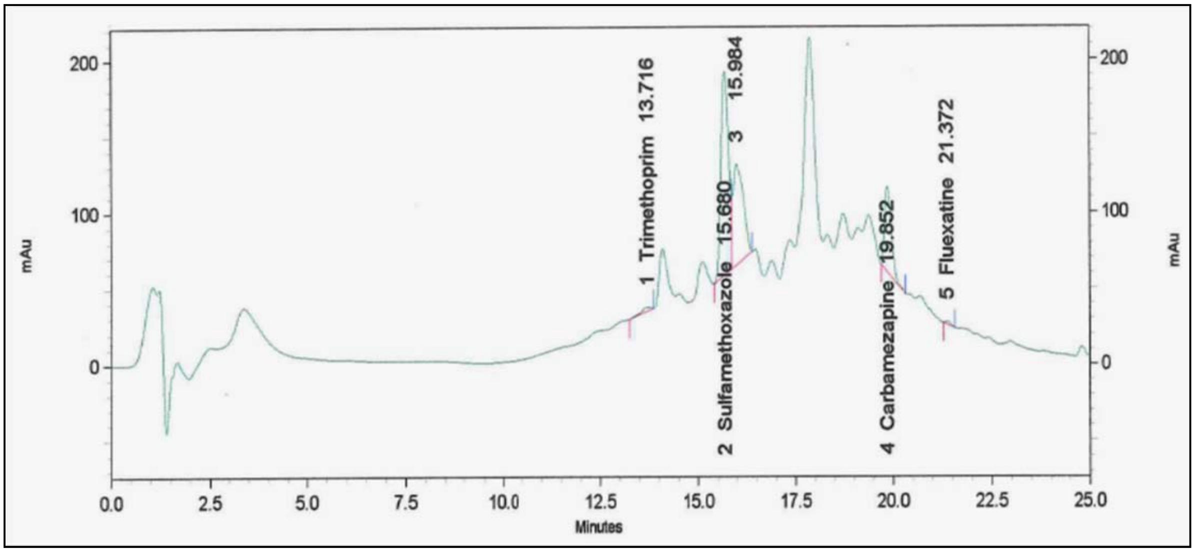


Figure B-9. Final Spiked Effluent Sample for 11/08/12: Acid Group I

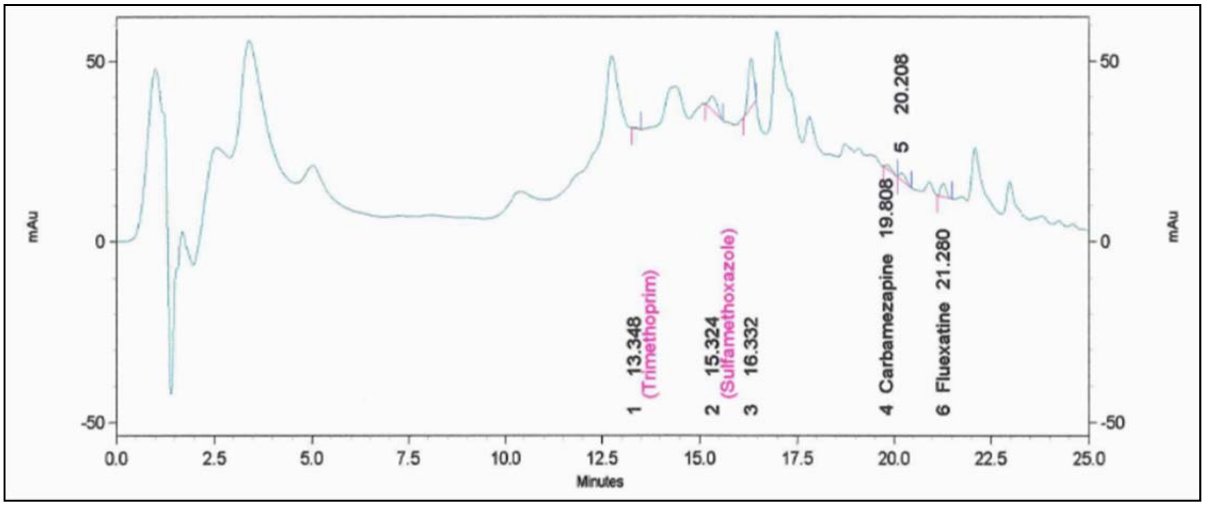


Figure B-10. Influent Sample for 11/12/12: Acid Group I

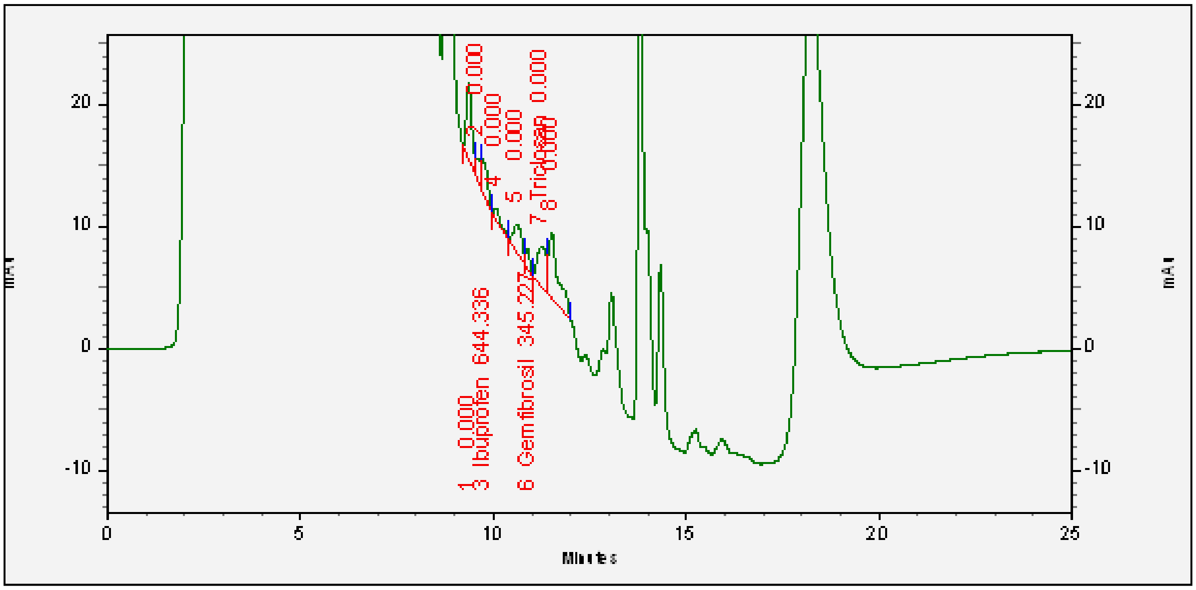


Figure B-11. Influent for 11/12/12: Acid Group II

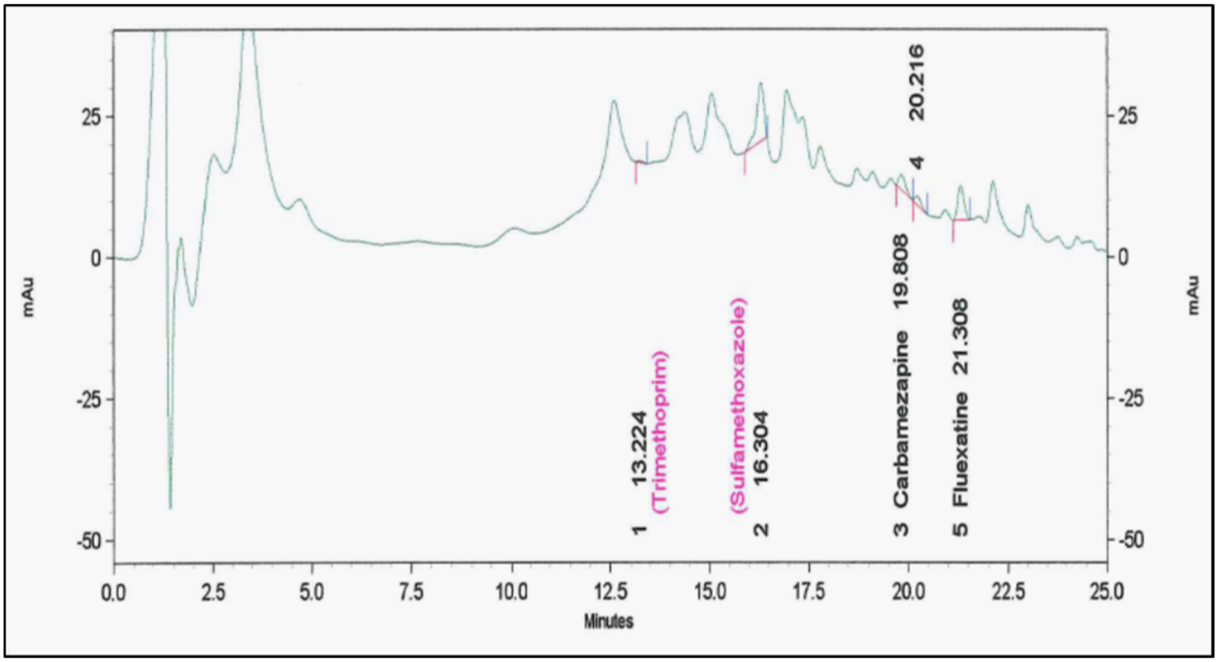


Figure B-12. Primary Effluent for 11/12/12: Acid Group I

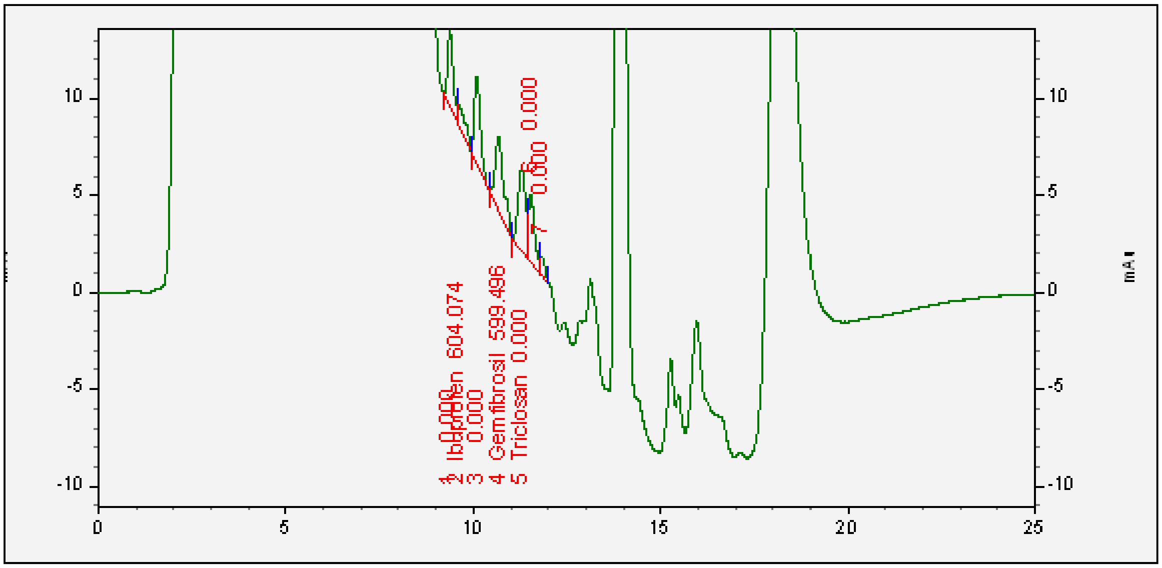


Figure B-13. Primary Effluent for 11/12/12: Acid Group II

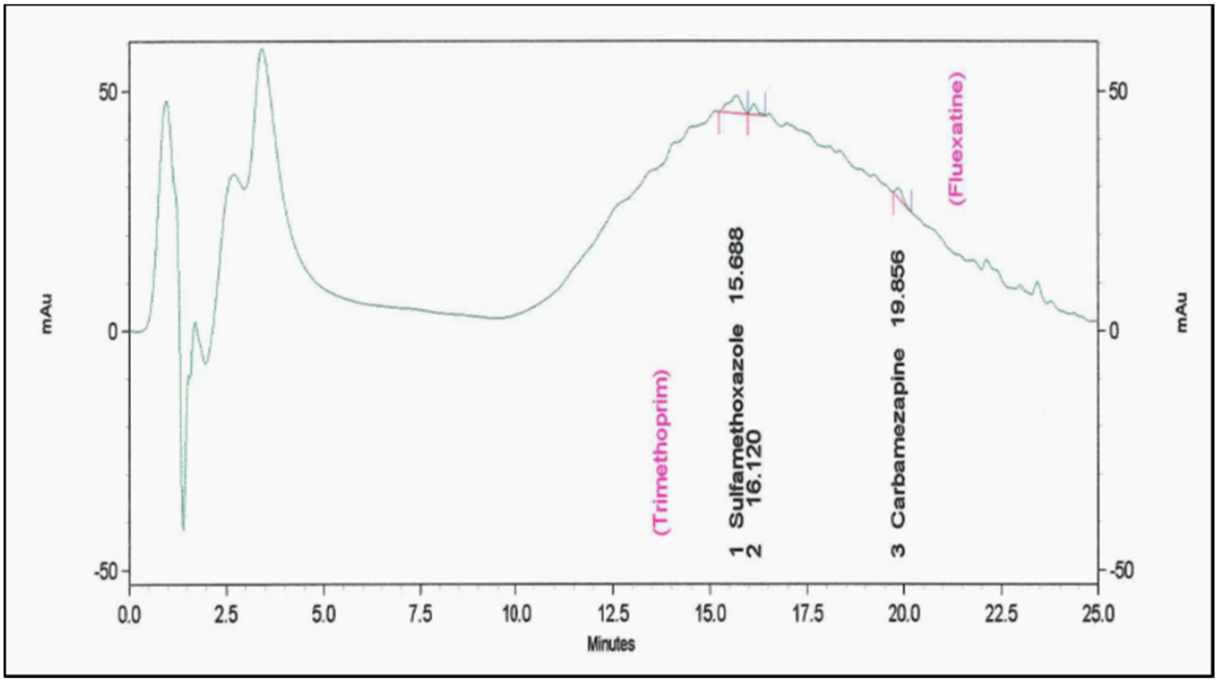


Figure B-14. Secondary Effluent for 11/12/12: Acid Group I

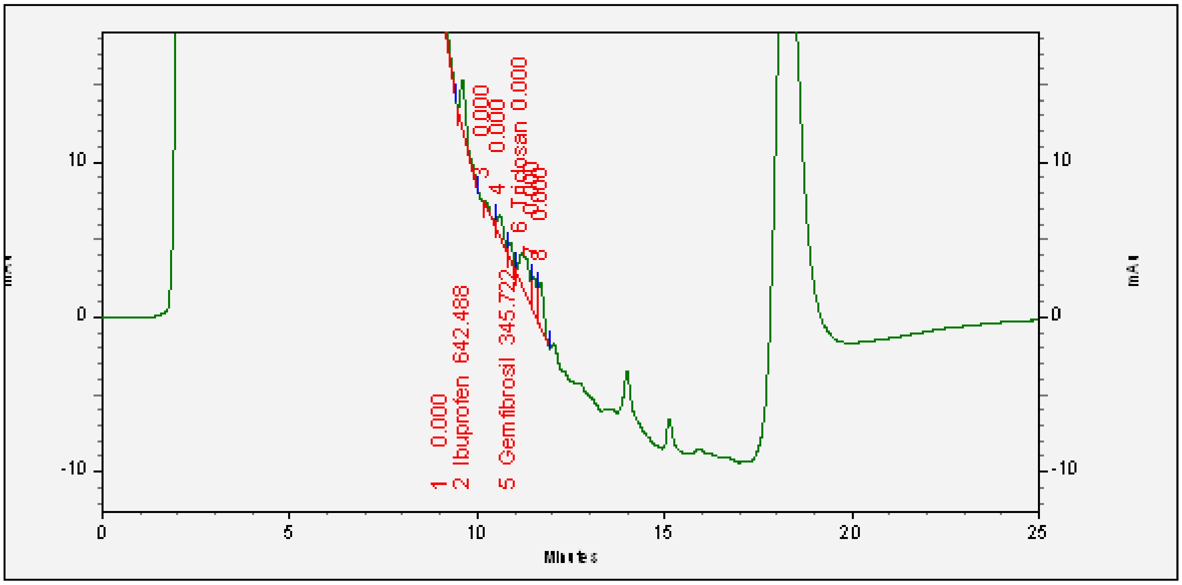


Figure B-15. Secondary Effluent from 11/12/12: Acid Group II

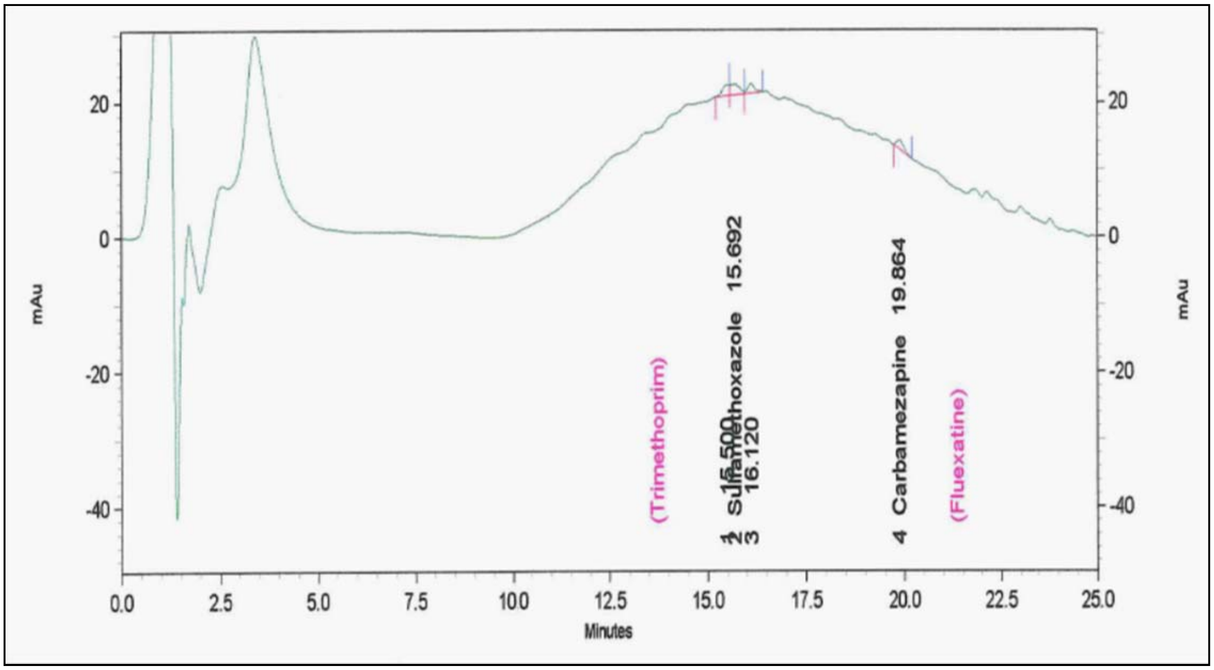


Figure B-16. Final Effluent for 11/12/12: Acid Group I

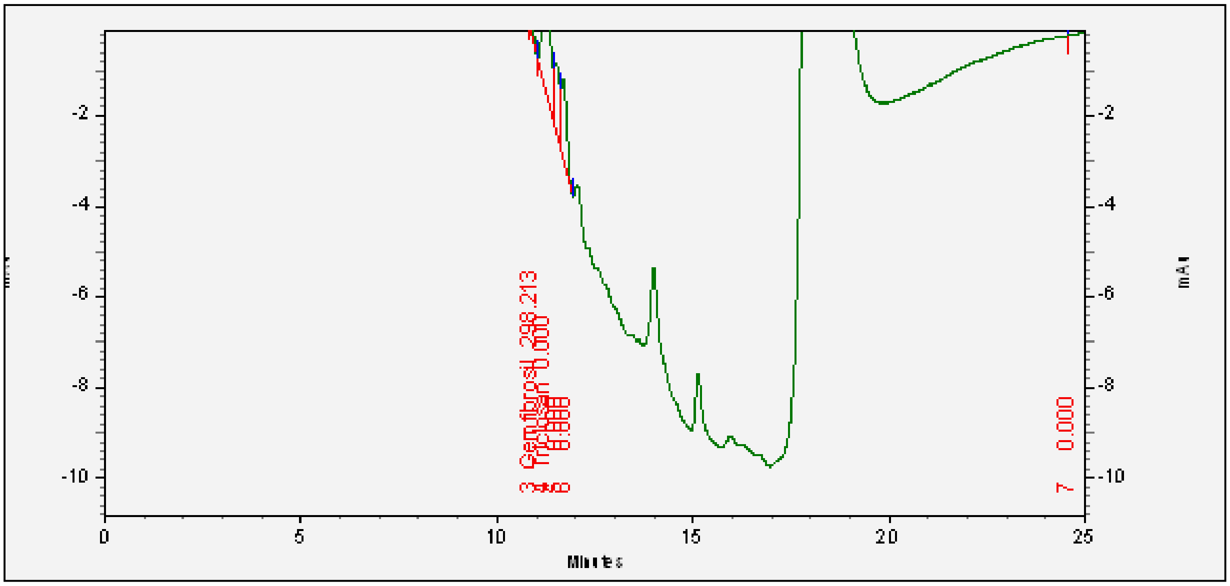


Figure B-17. Final Effluent from 11/12/12: Acid Group II

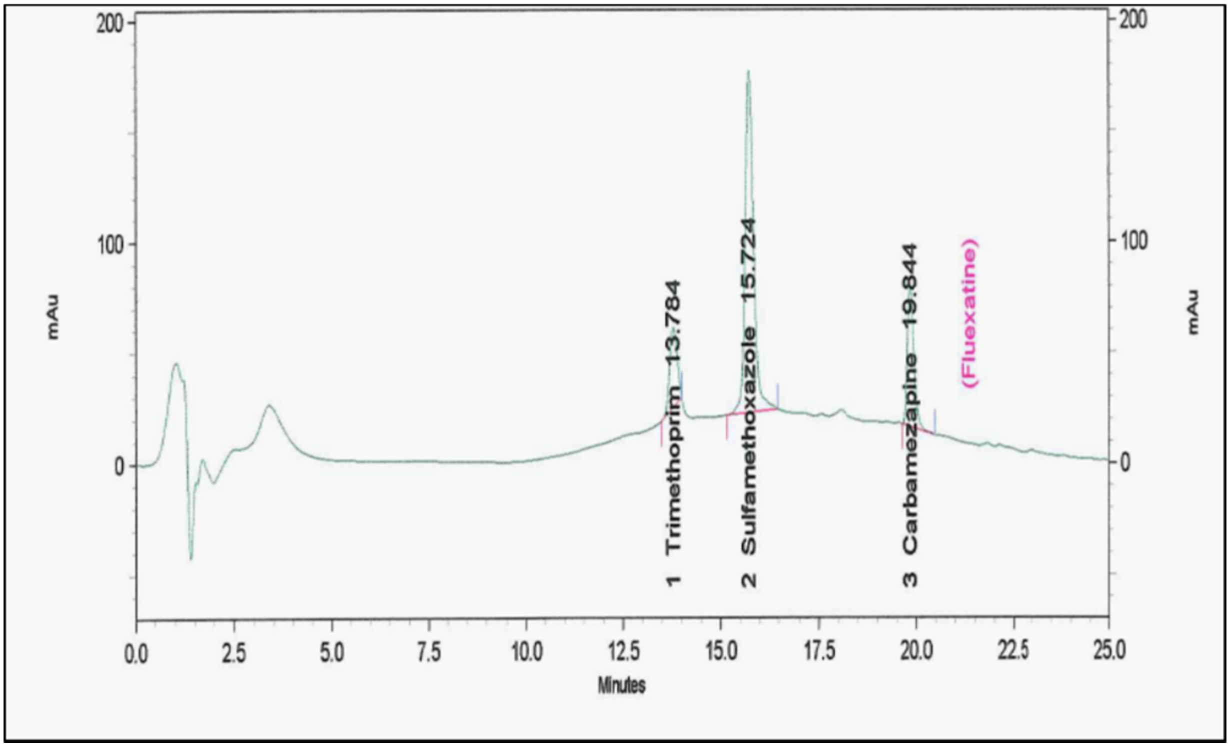


Figure B-18. Final Effluent (Spiked) for 11/12/12: Acid Group I

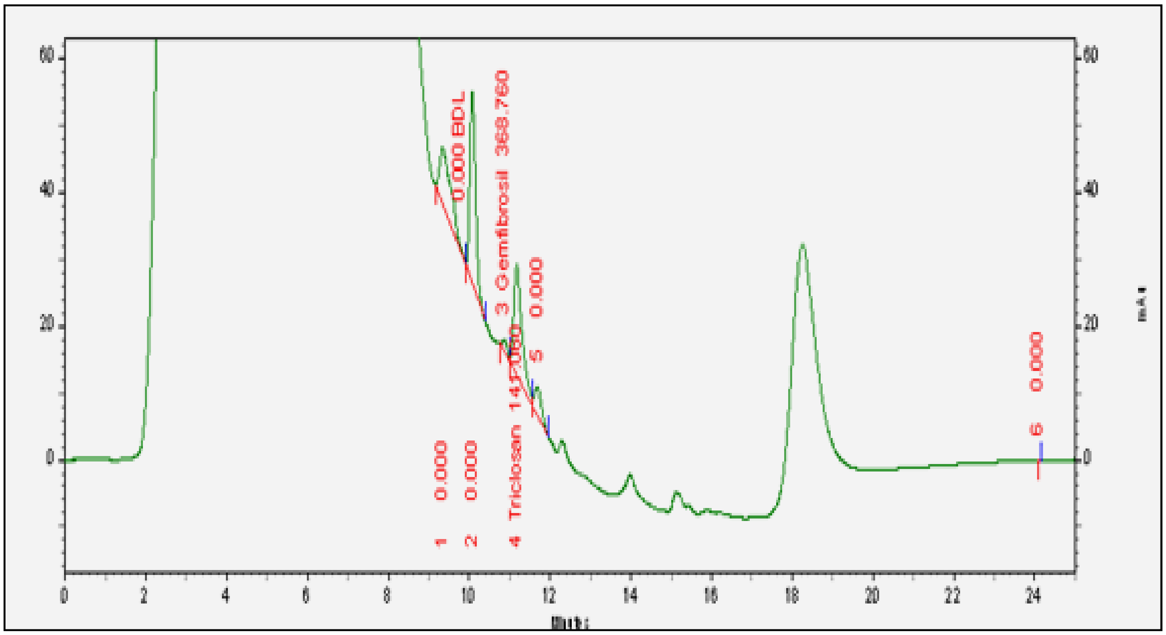


Figure B-19. Primary Effluent from 05/11/11: Acid Group II

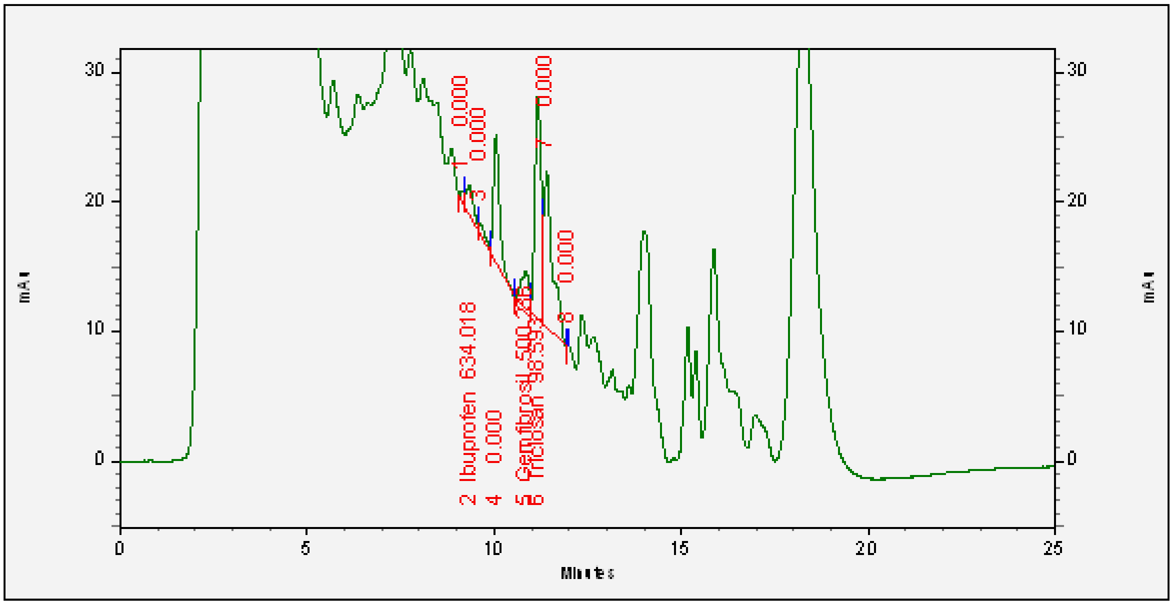


Figure B-20. Influent from 03/02/10: Acid Group II

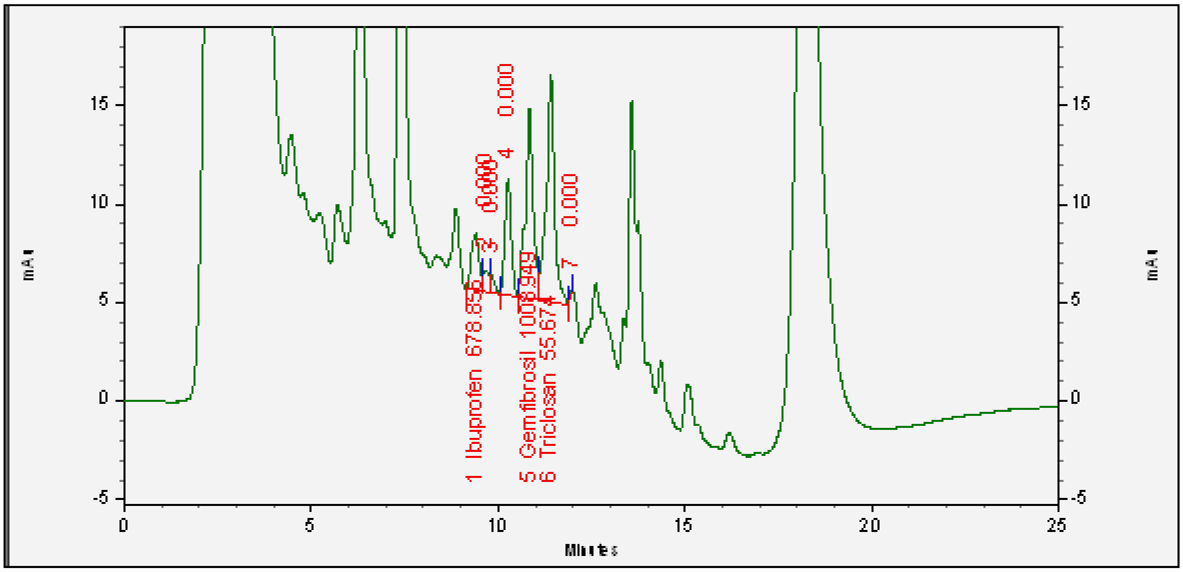


Figure B-21. Primary Effluent from 03/02/10: Acidic Group II

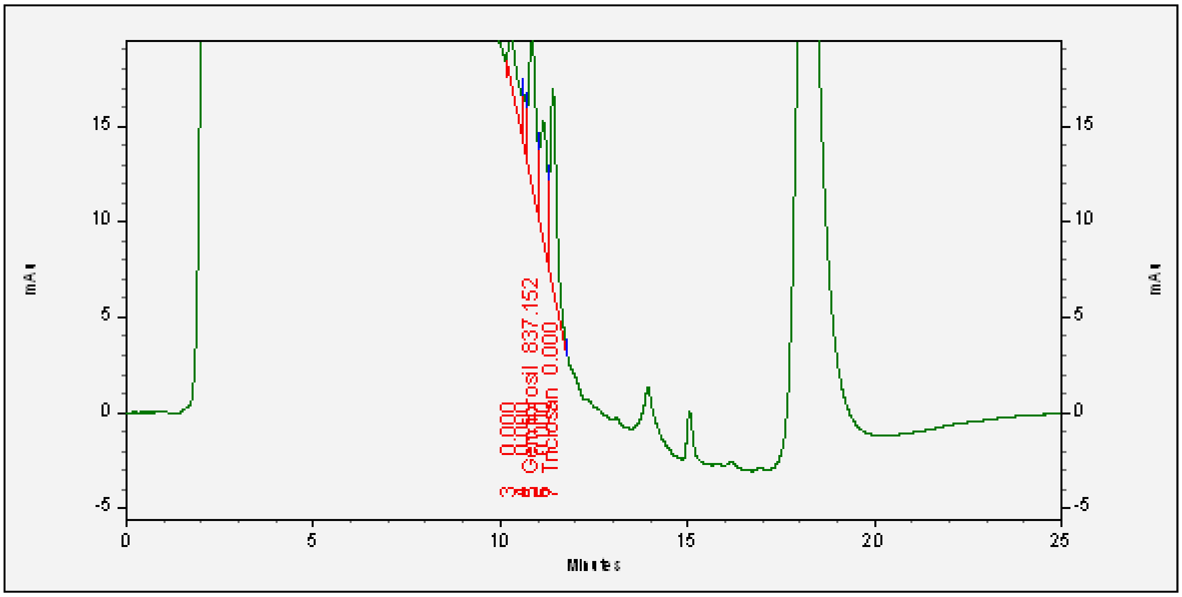


Figure B-22. Secondary Effluent from 03/02/10: Acid Group II

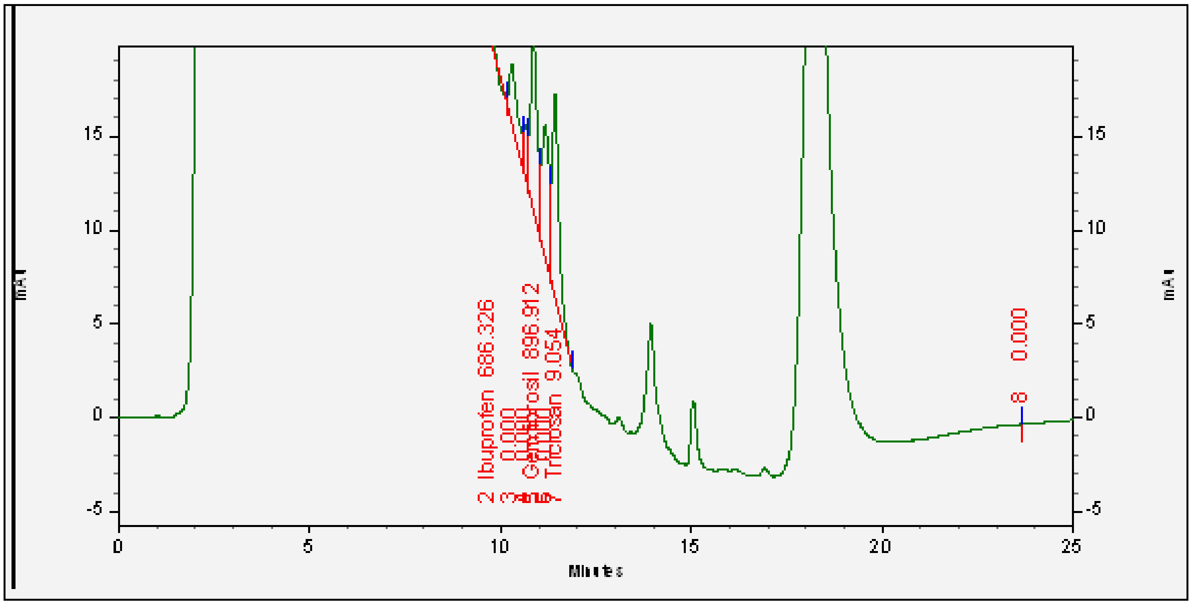


Figure B-23. Final Effluent from 03/02/10: Acid Group II

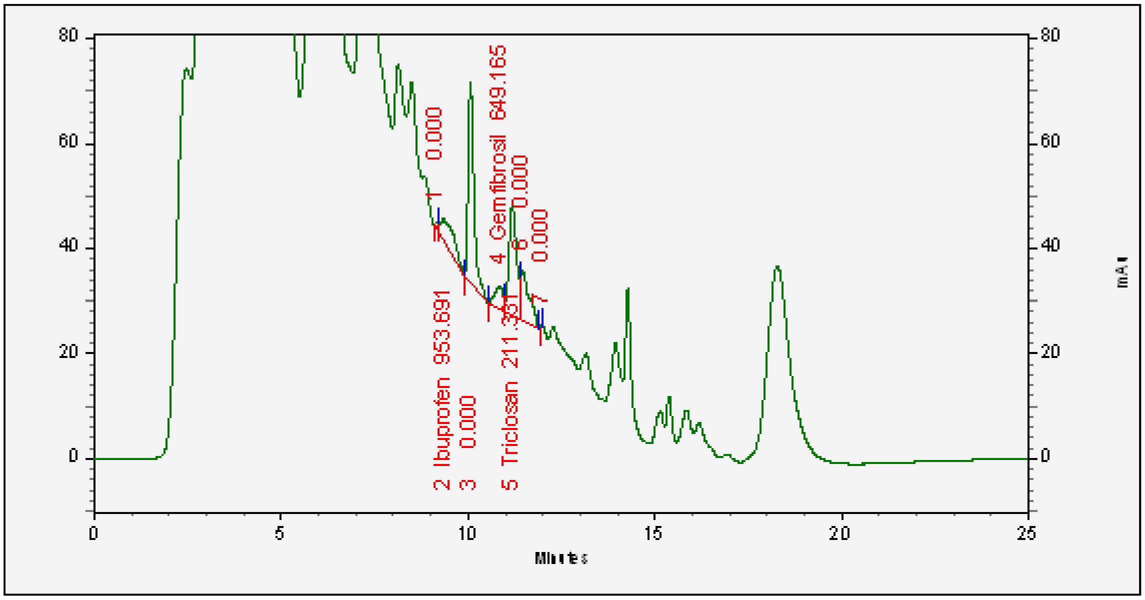


Figure B-24. Influent from 06/25/10: Acid Group II

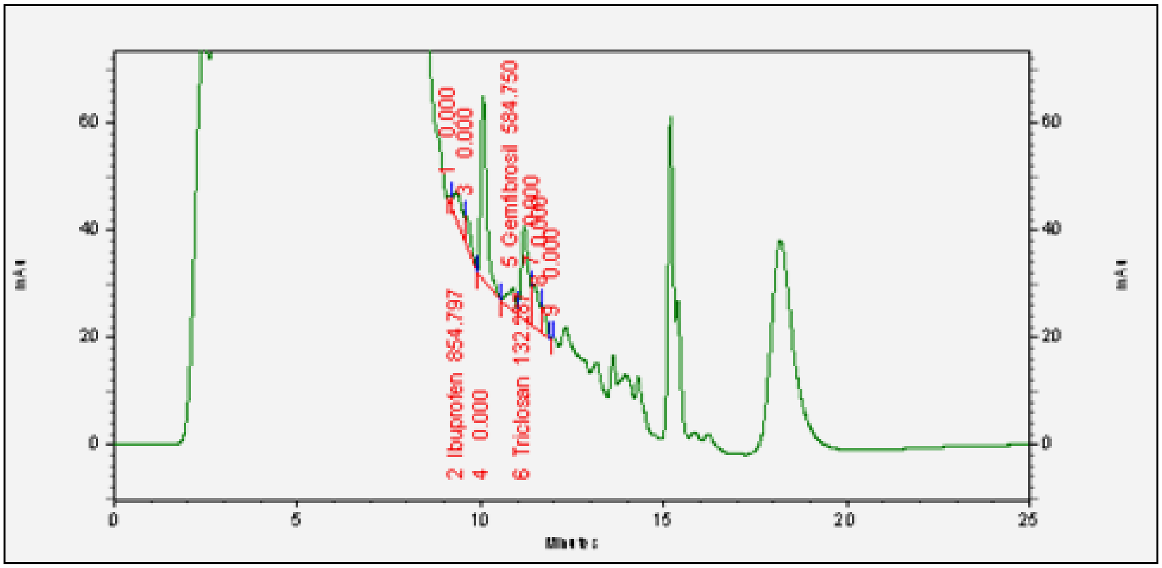


Figure B-25. Primary Effluent from 06/25/10: Acid Group II

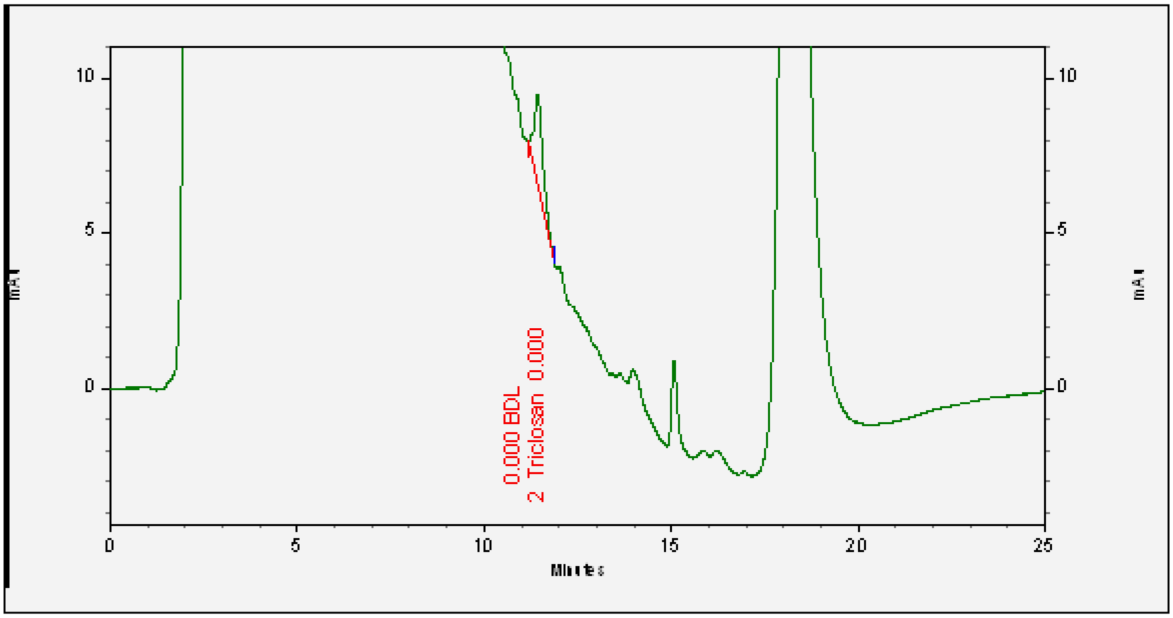


Figure B-26. Secondary Effluent from 06/25/10: Acid Group II

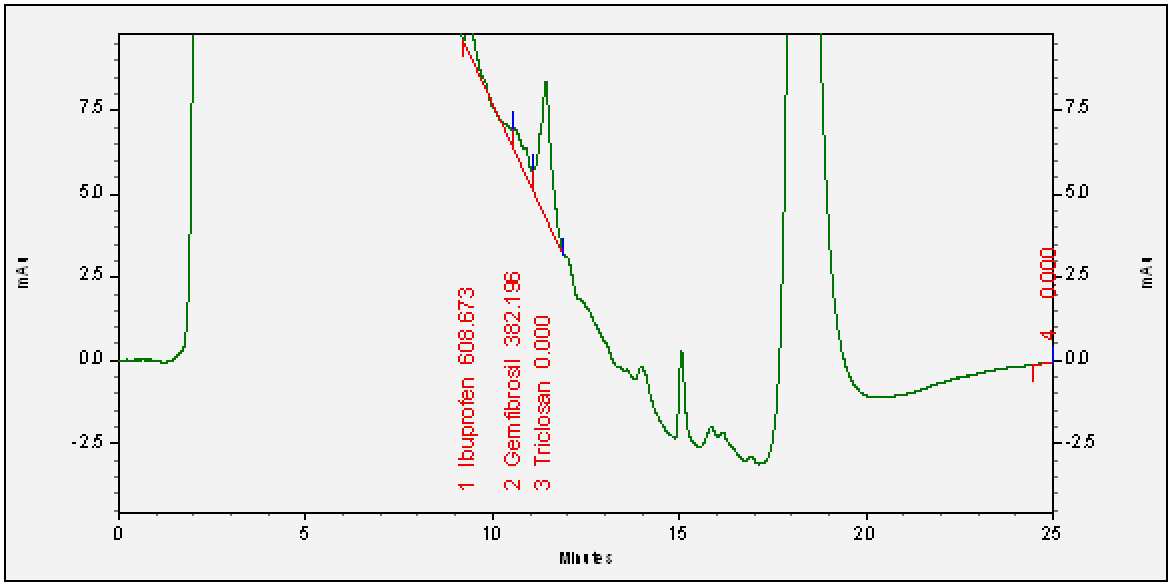


Figure B-27. Final Effluent from 06/25/10: Acid Group II

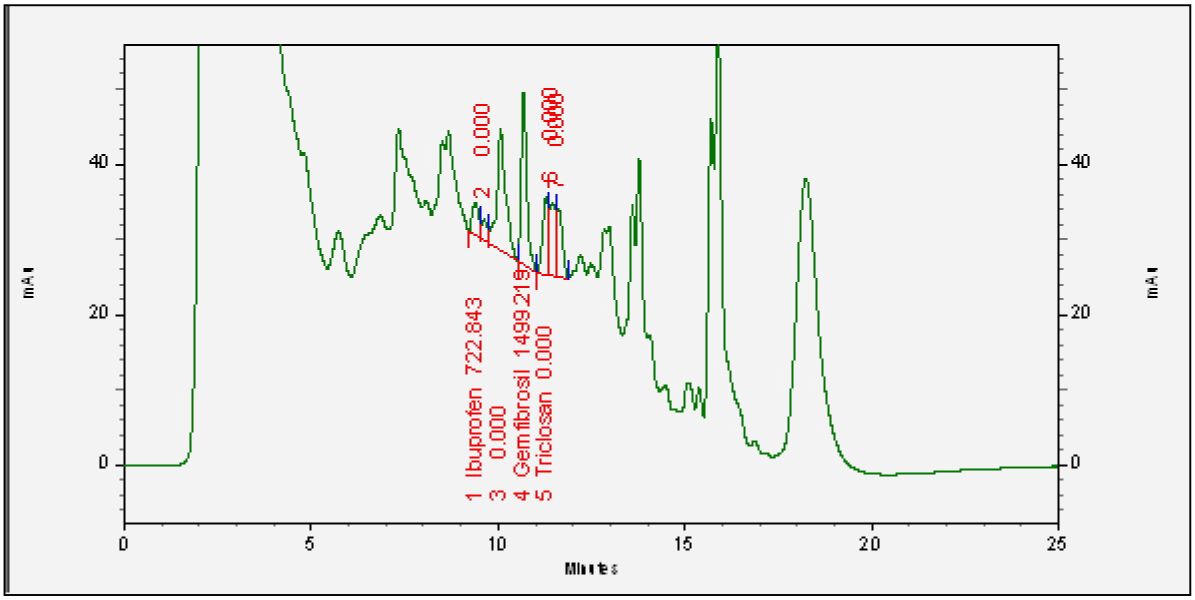


Figure B-28. Influent from 11/02/10: Acid Group II

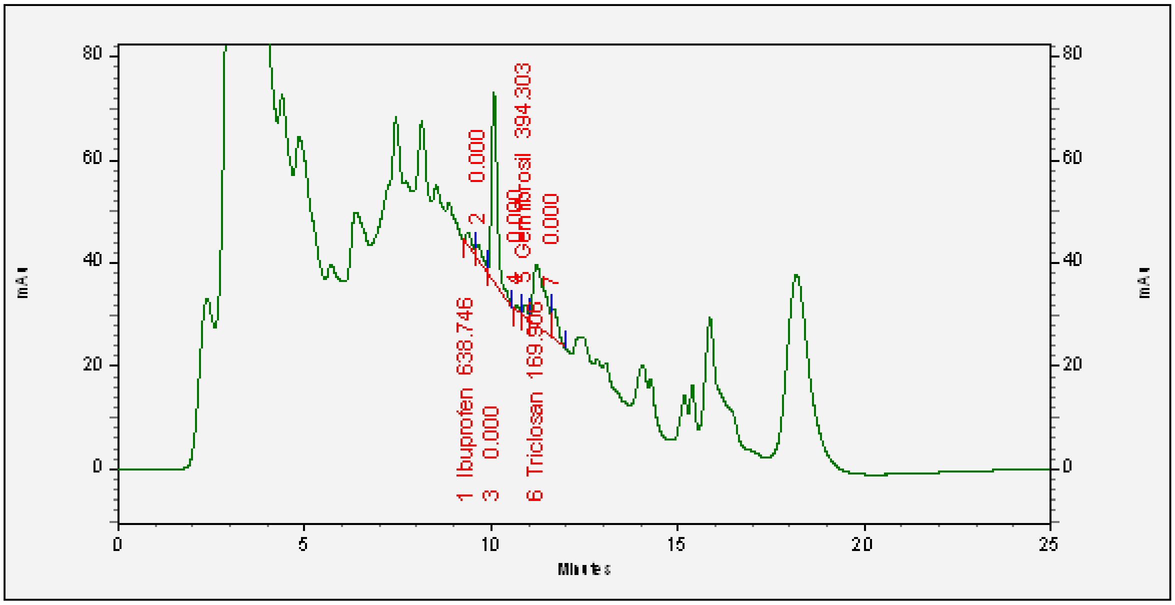


Figure B-29. Primary Effluent from 11/02/10: Acid Group II

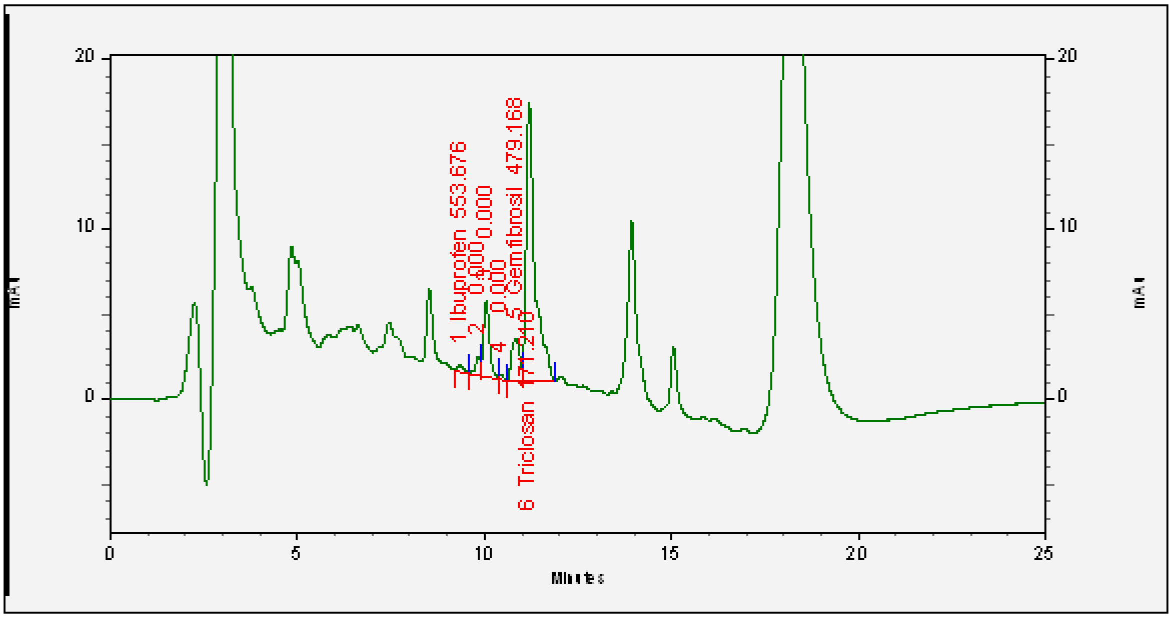


Figure B-30. Secondary Effluent from 11/02/10: Acid Group II

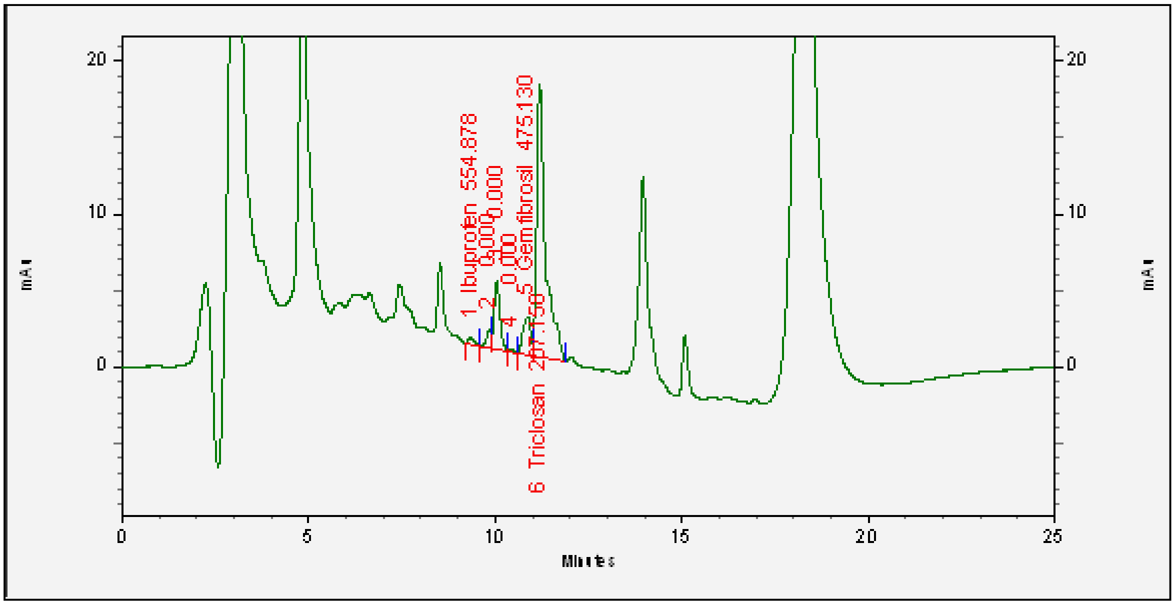


Figure B-31. Final Effluent from 11/02/10: Acid Group II

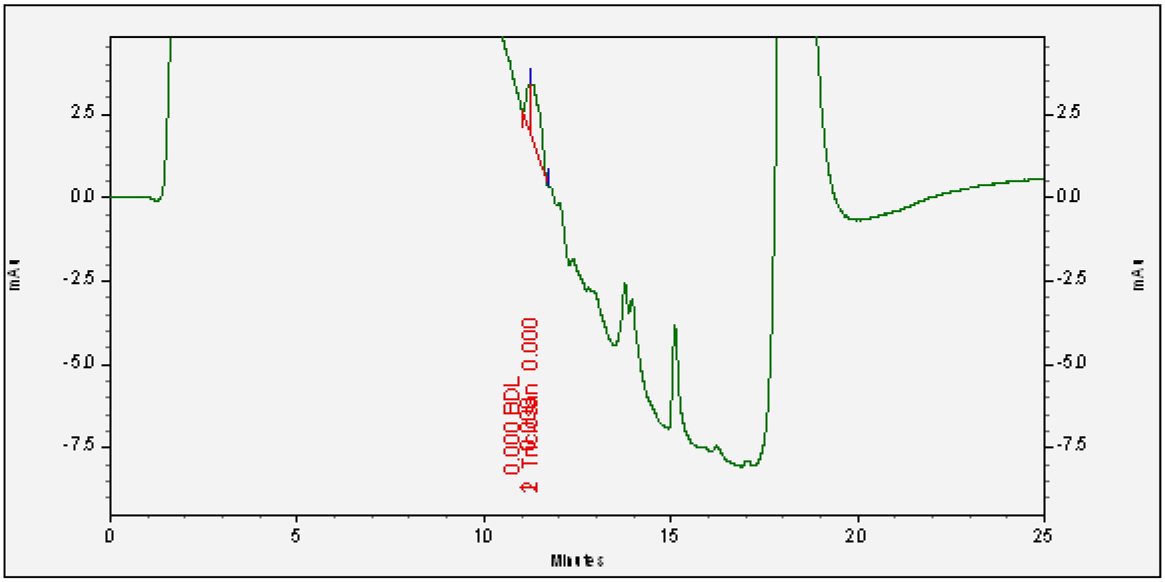


Figure B-32. Influent from 03/09/11: Acid Group II

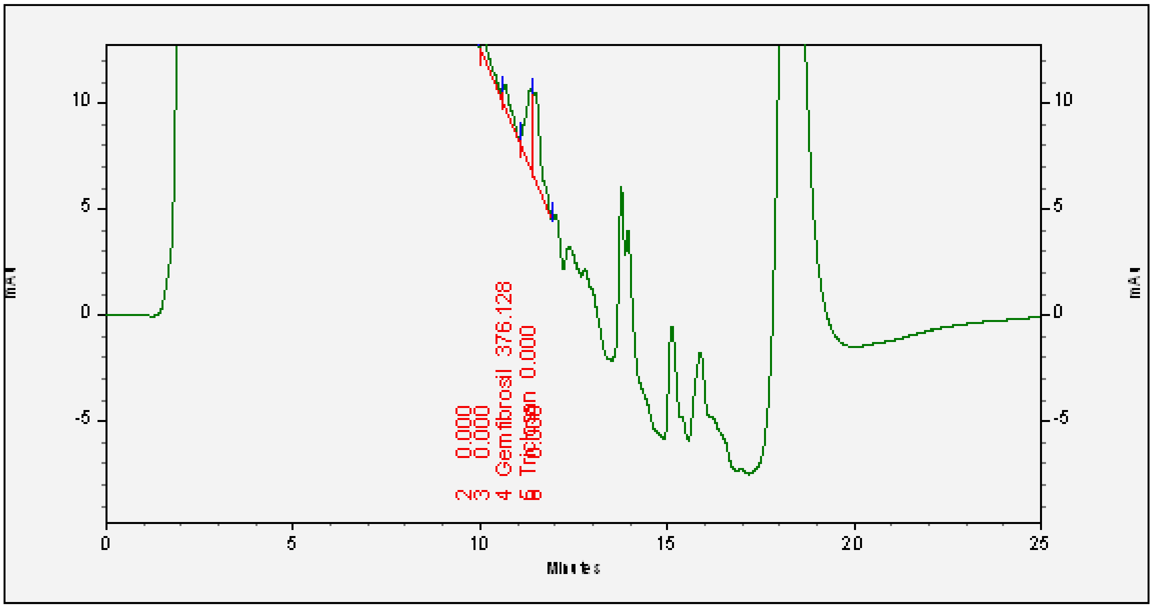


Figure B-33. Primary Effluent from 03/09/11: Acid Group II

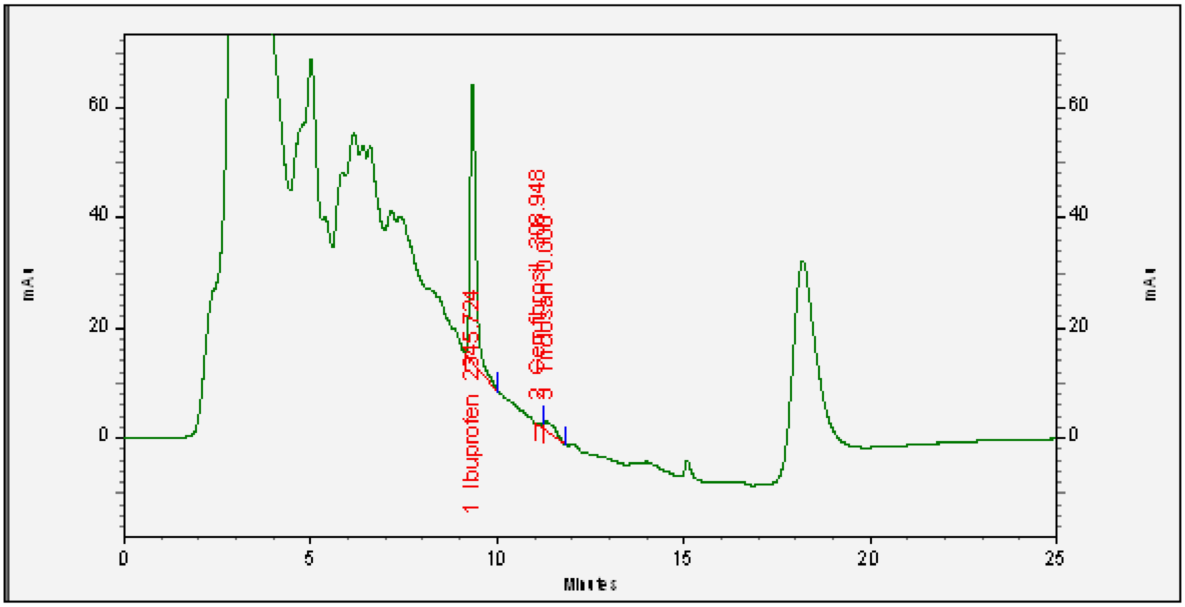


Figure B-34. Secondary Effluent from 03/09/11: Acid Group II

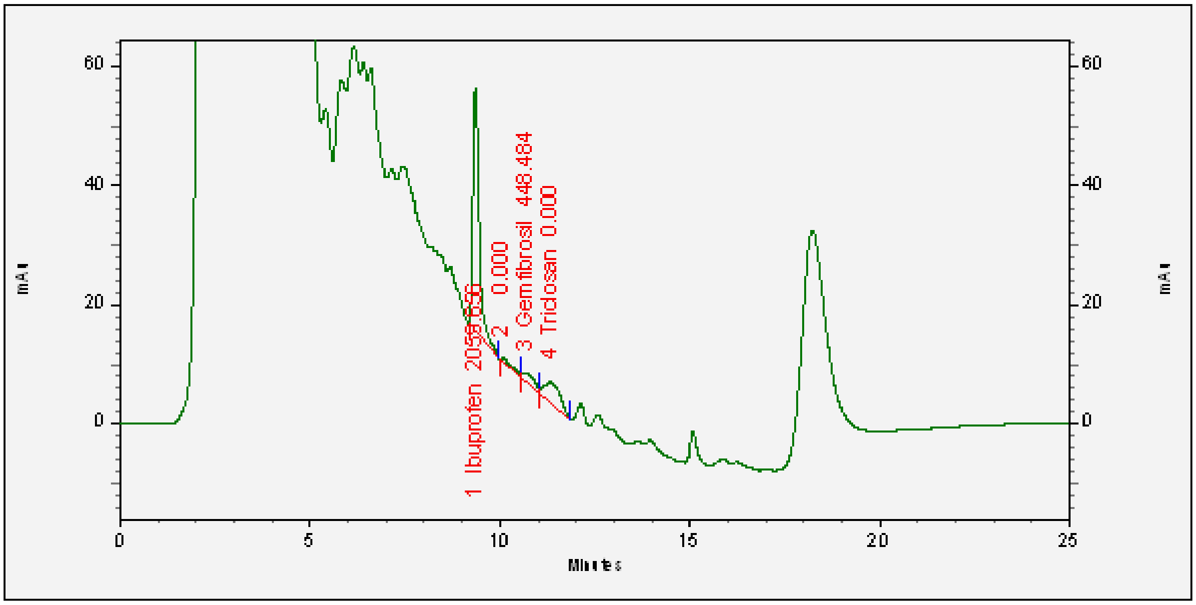


Figure B-35. Final Effluent from 03/09/11: Acid Group II

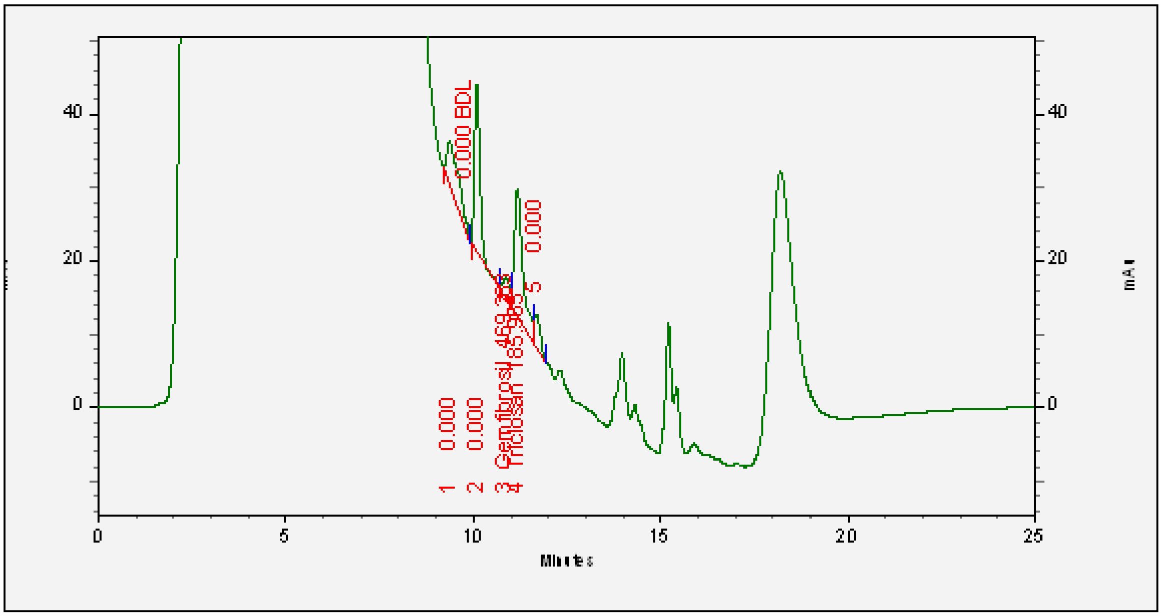


Figure B-36. Influent from 05/14/11: Acid Group II

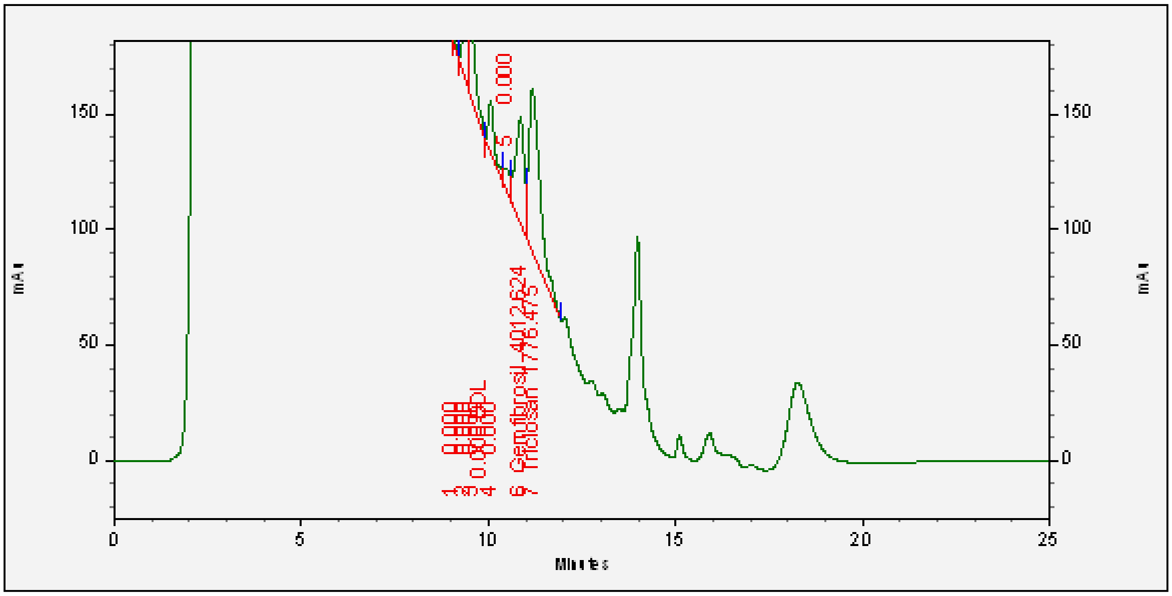


Figure B-37. Primary Effluent from 05/14/11: Acid Group II

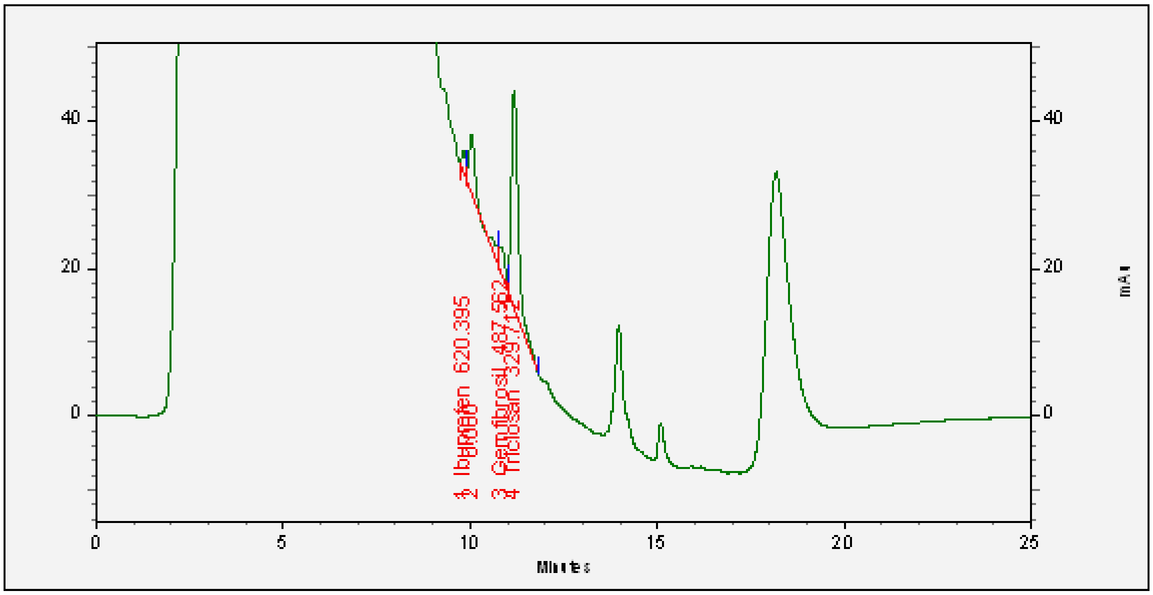


Figure B-38. Secondary Effluent from 05/14/11: Acid Group II

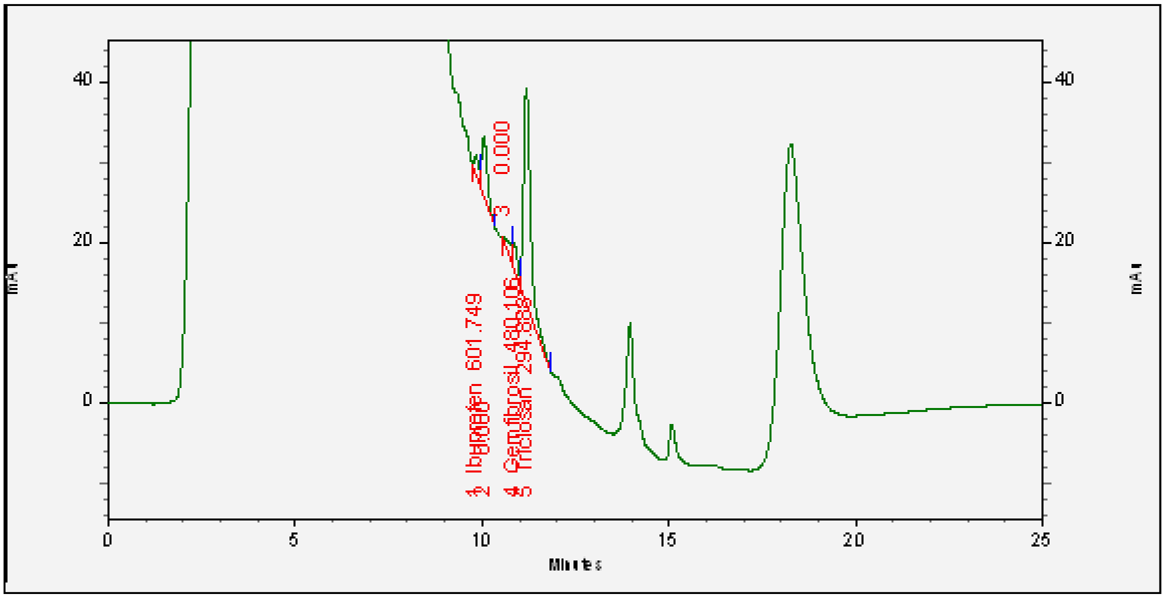


Figure B-39. Final Effluent from 05/14/11: Acid Group II

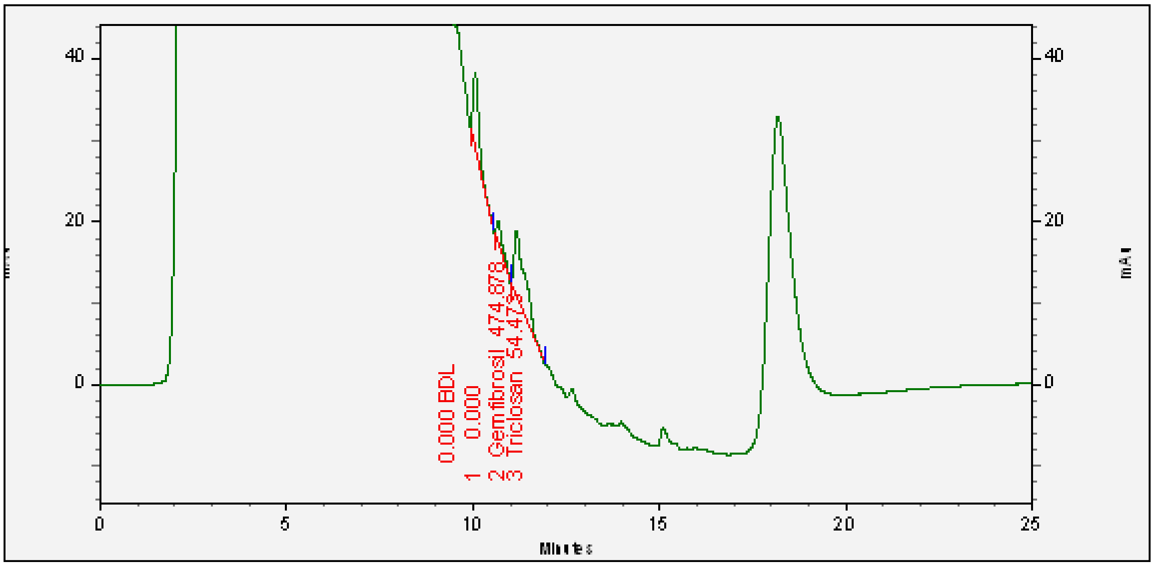


Figure B-40. Influent from 09/20/11: Acid Group II

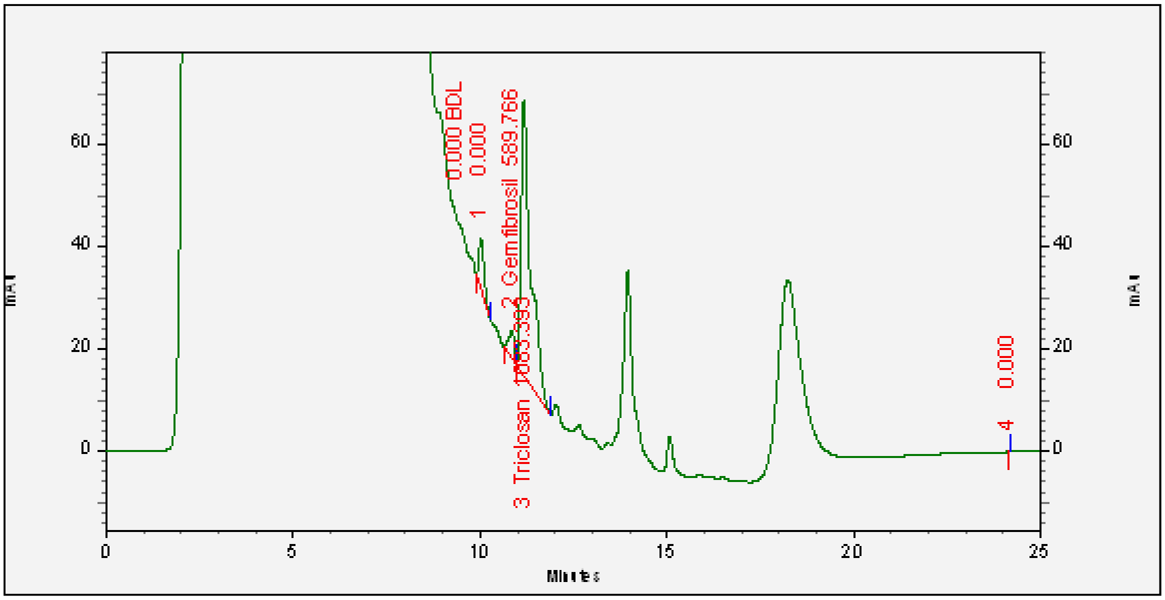


Figure B-41. Primary Effluent from 09/20/11: Acid Group II

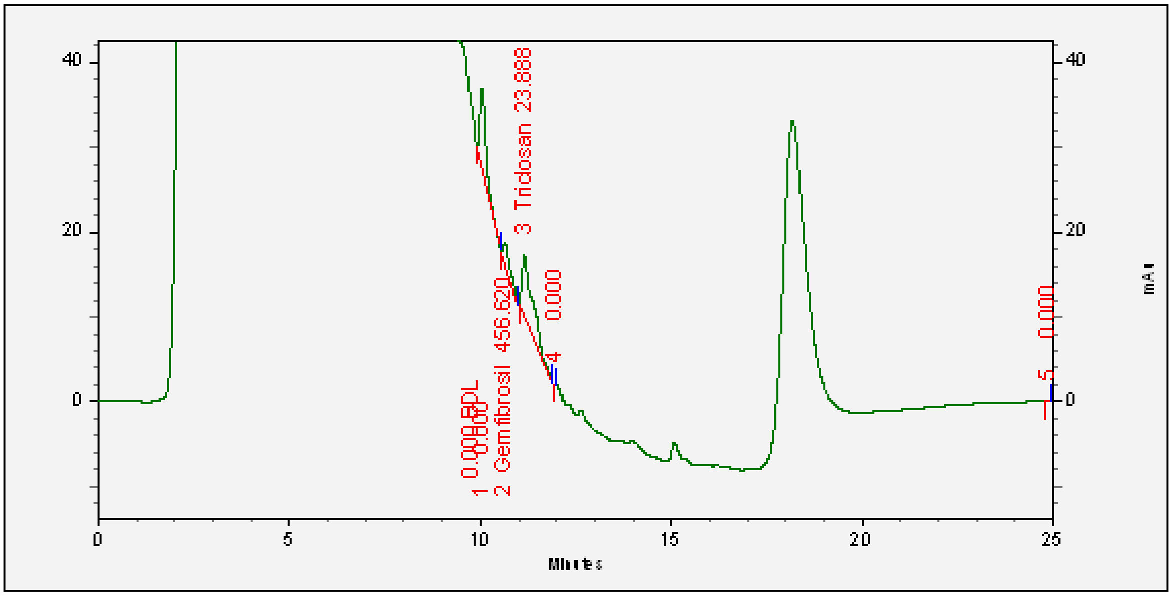


Figure B-42. Secondary Effluent from 09/20/11: Acid Group II

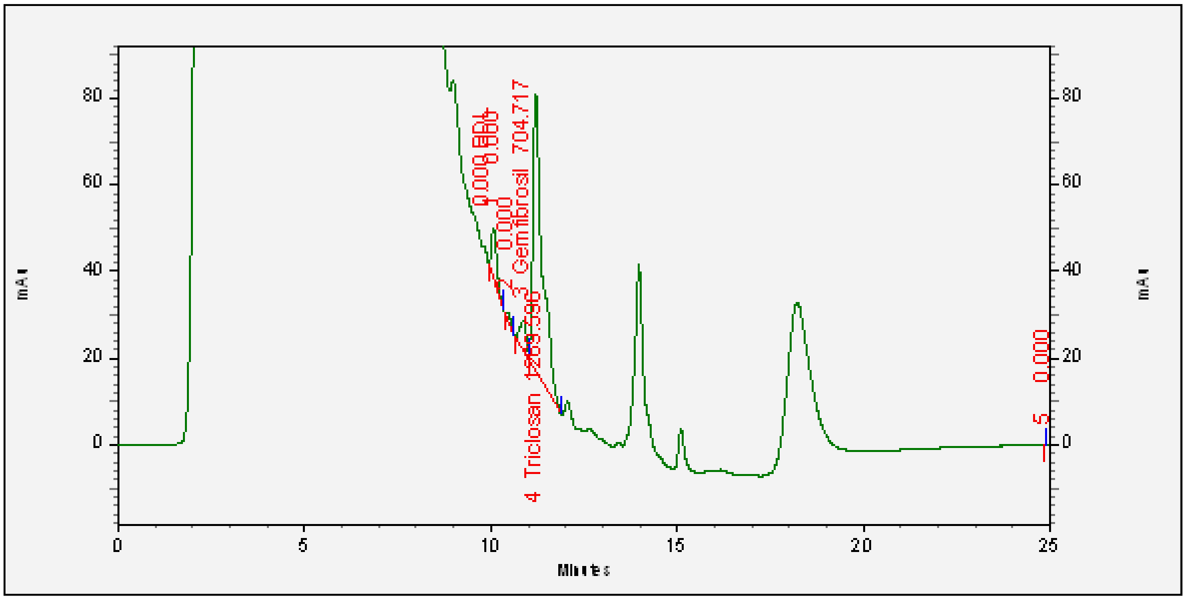


Figure B-43. Final Effluent from 09/20/11: Acid Group II

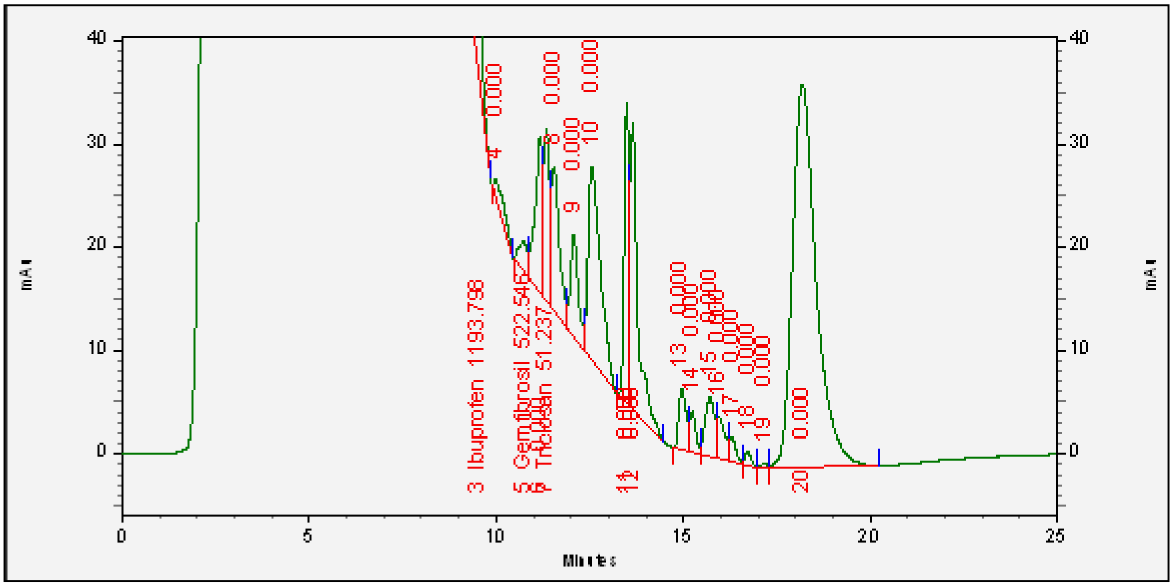


Figure B-44. Influent from 01/16/10: Acid Group II

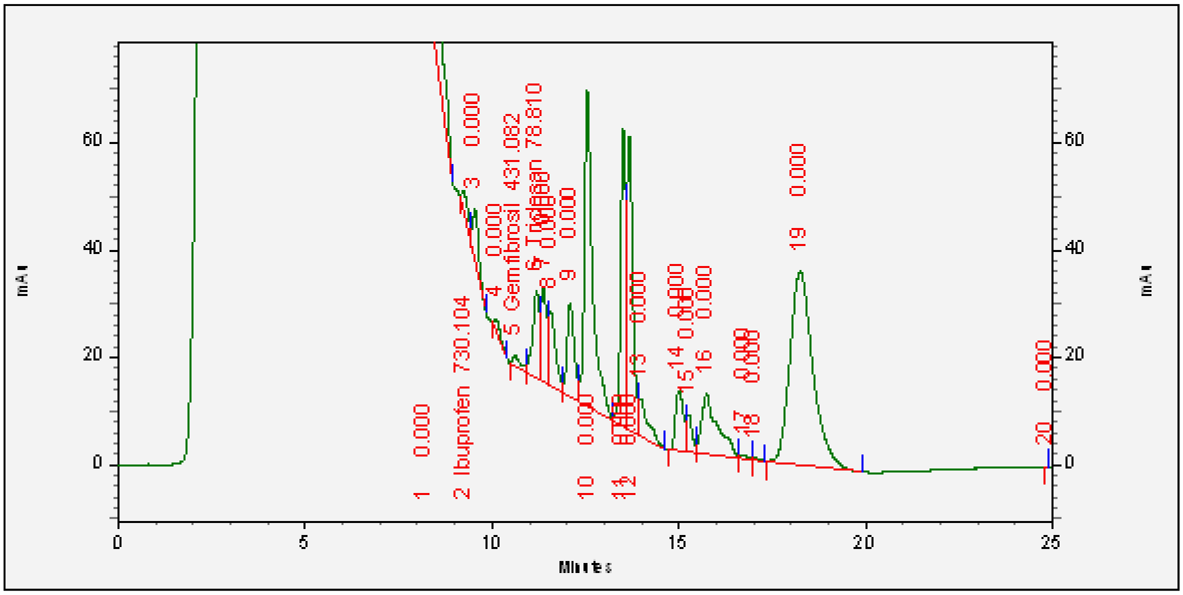


Figure B-45. Primary Effluent for 01/16/10: Acid Group II

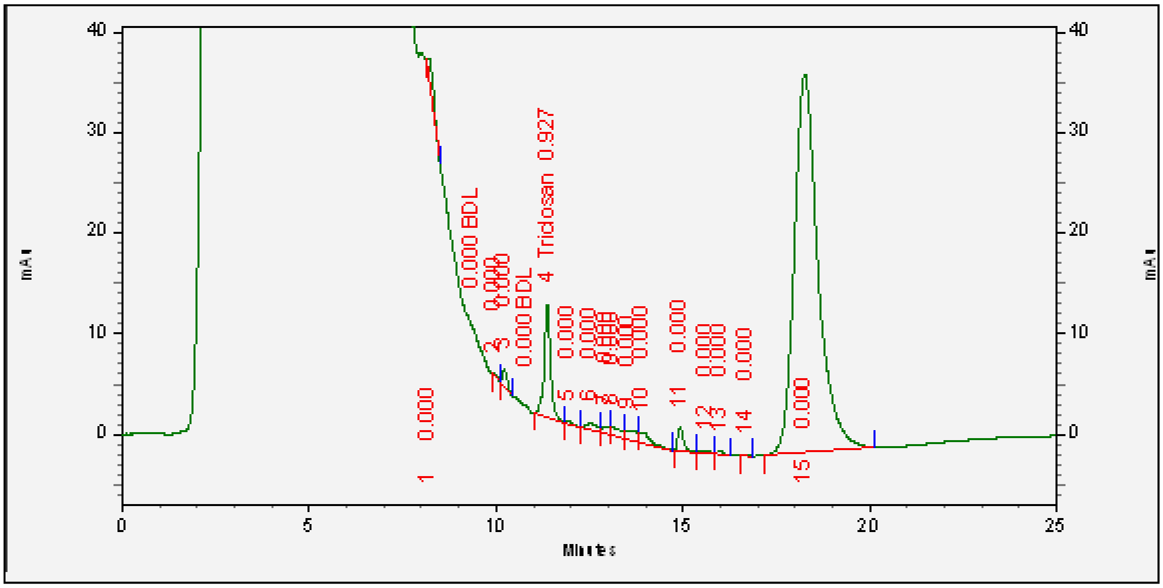


Figure B-46. Secondary Effluent for 01/16/10: Acid Group II

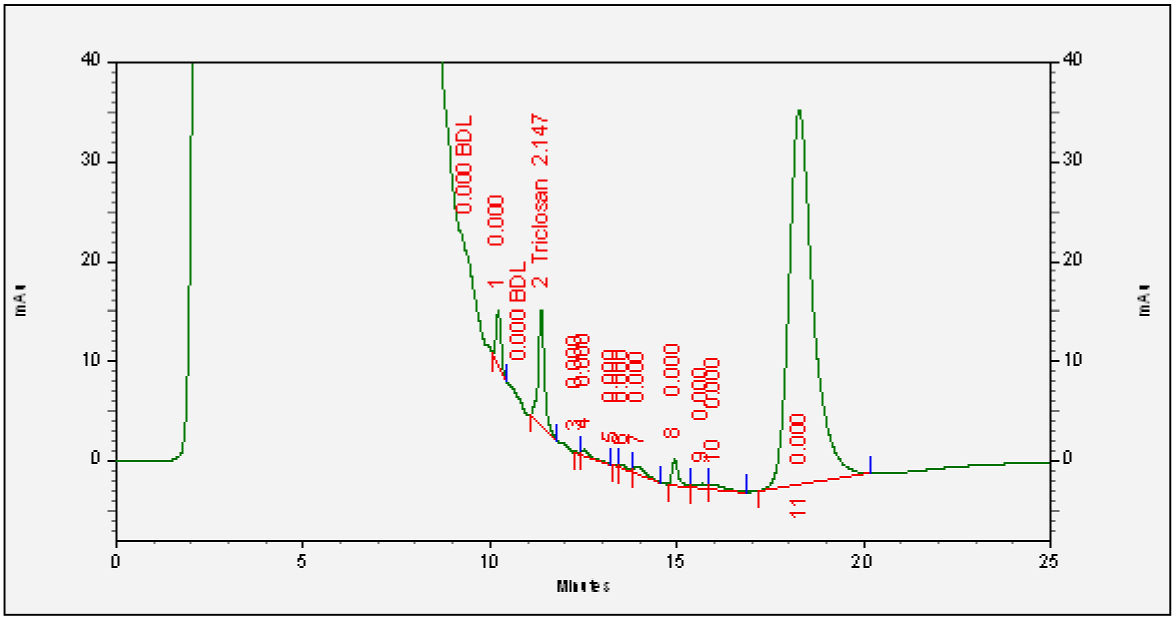


Figure B-47. Final Effluent for 01/16/10: Acid Group II

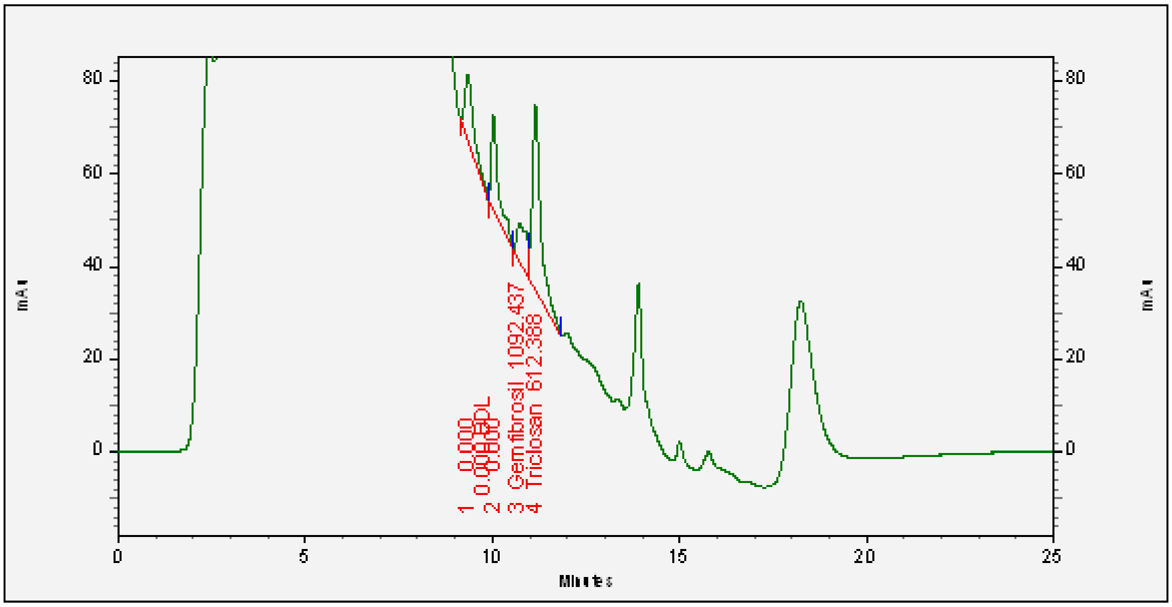


Figure B-48. Influent from 03/20/11: Acid Group II

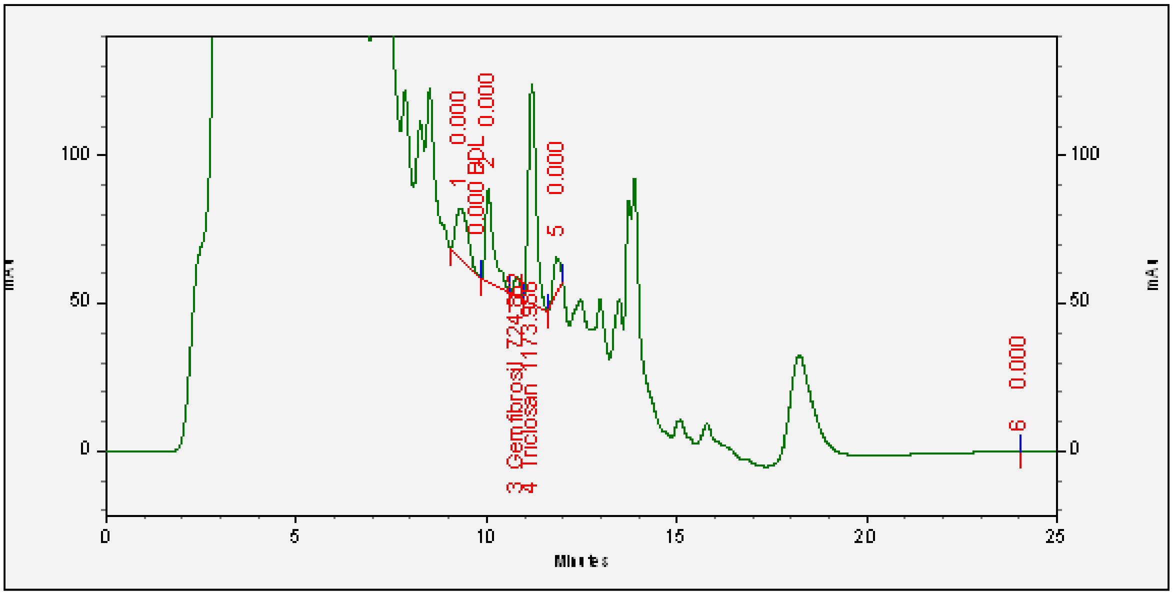


Figure B-49. Primary Effluent from 03/20/11: Acid Group II

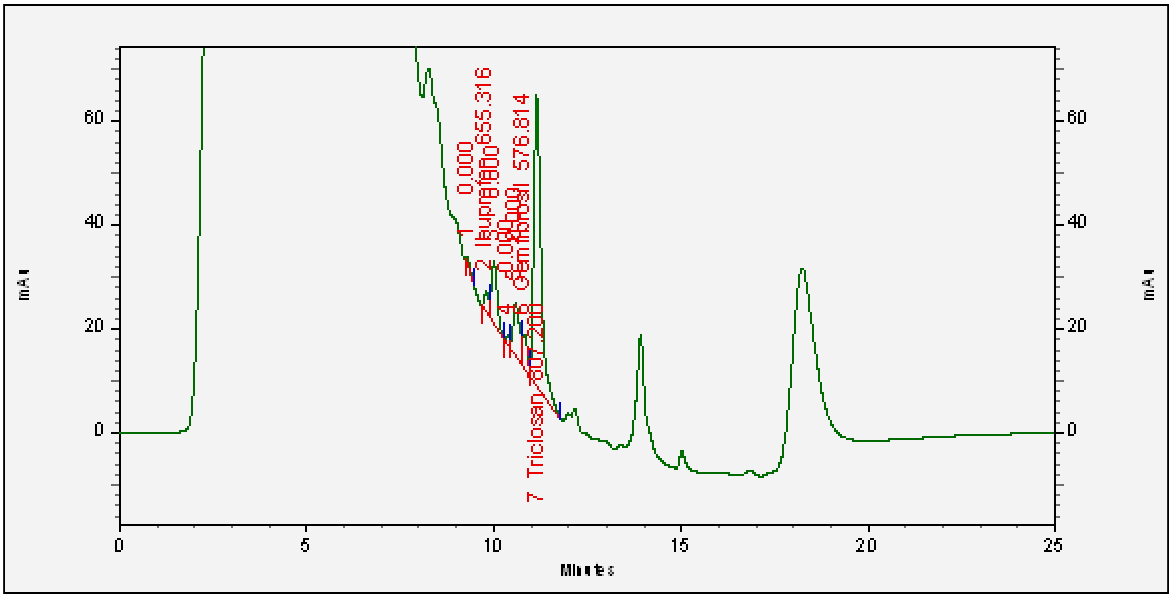


Figure B-50. Secondary Effluent for 03/20/12: Acid Group II

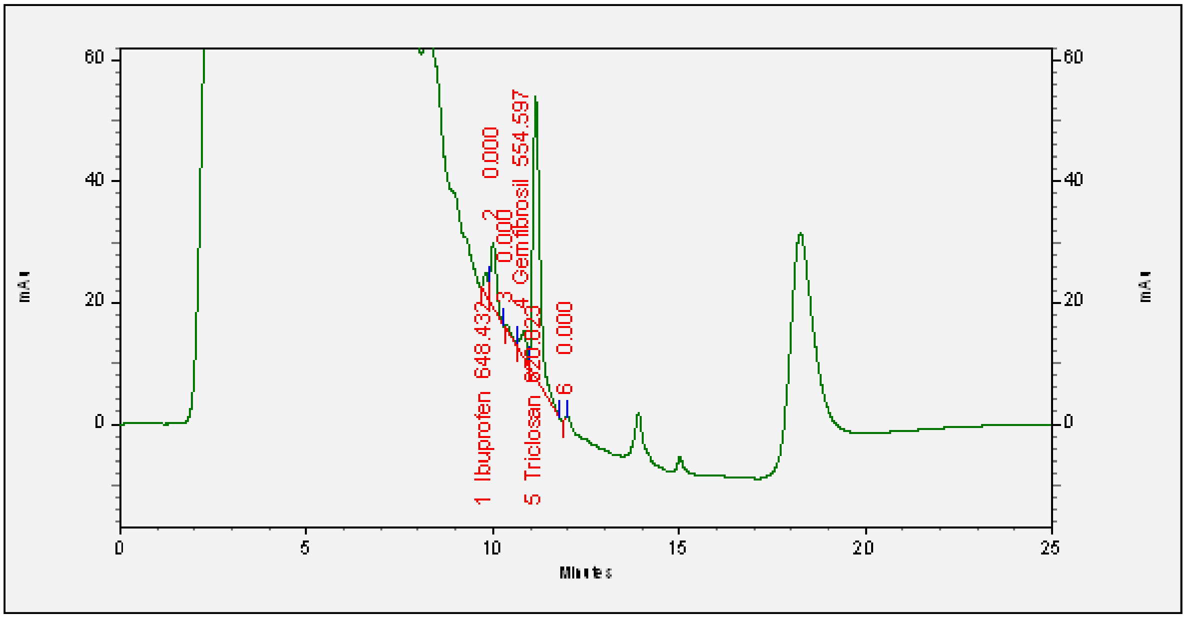


Figure B-51. Final Effluent for 03/20/12: Acid Group II

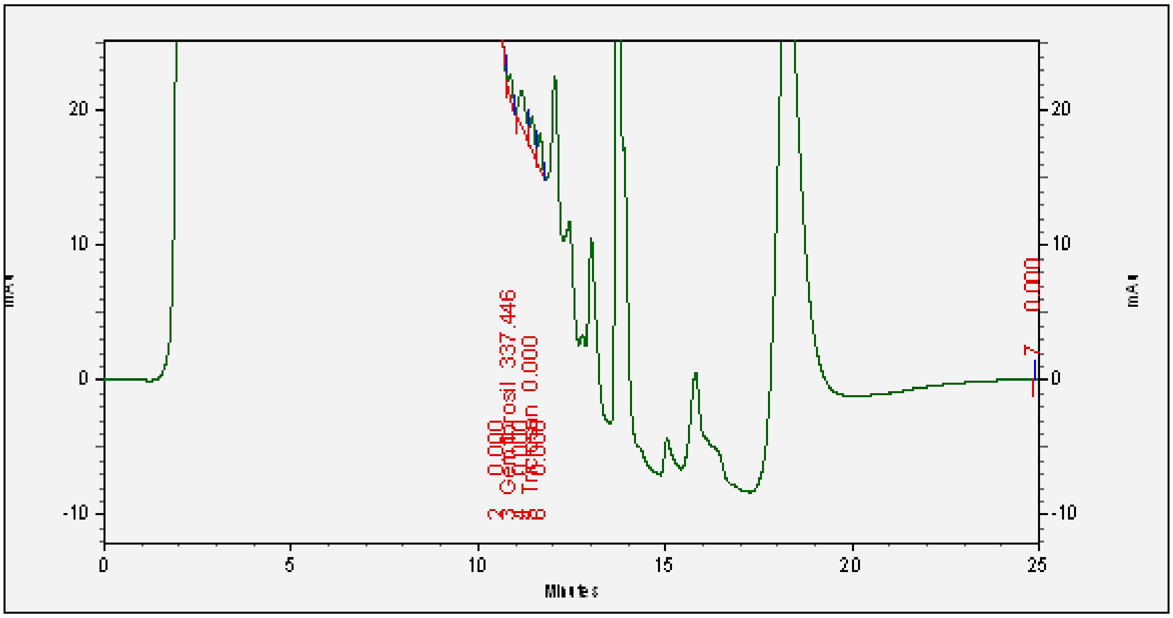


Figure B-52. Influent from 06/16/12: Acid Group II

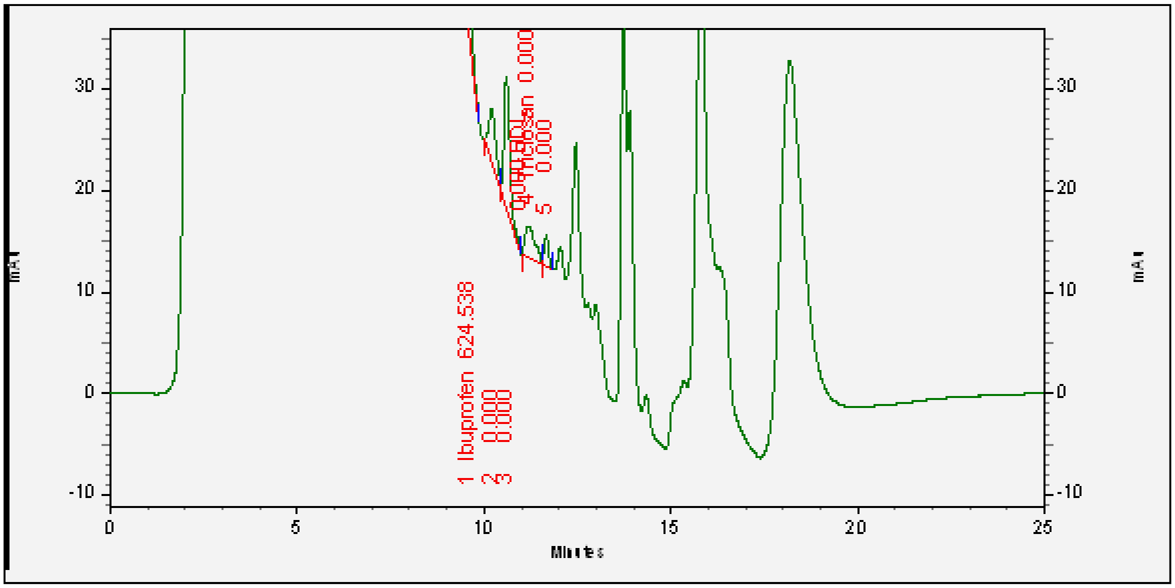


Figure B-53. Primary Effluent from 06/16/12: Acid Group II

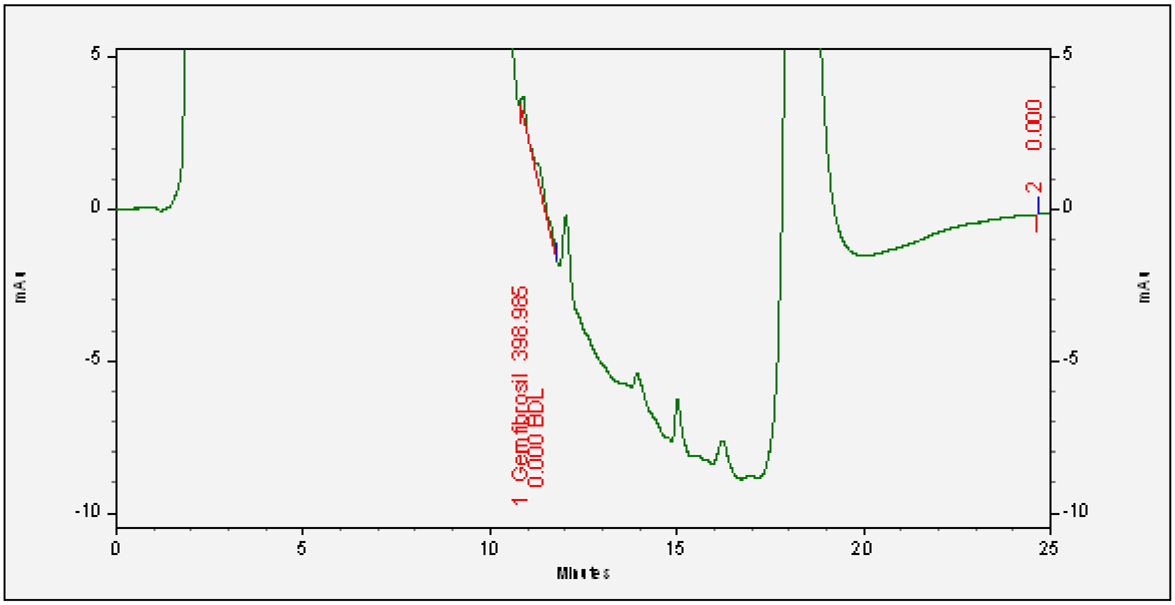


Figure B-54. Secondary Effluent from 06/16/12: Acid Group II

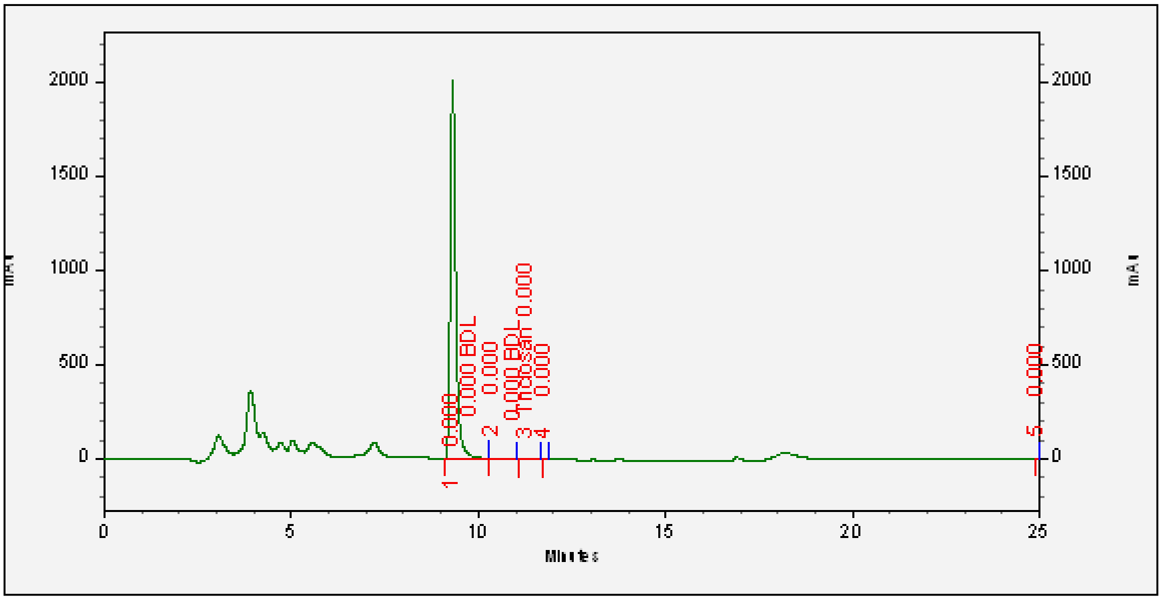


Figure B-55. Final Effluent for 06/16/12: Acid Group II

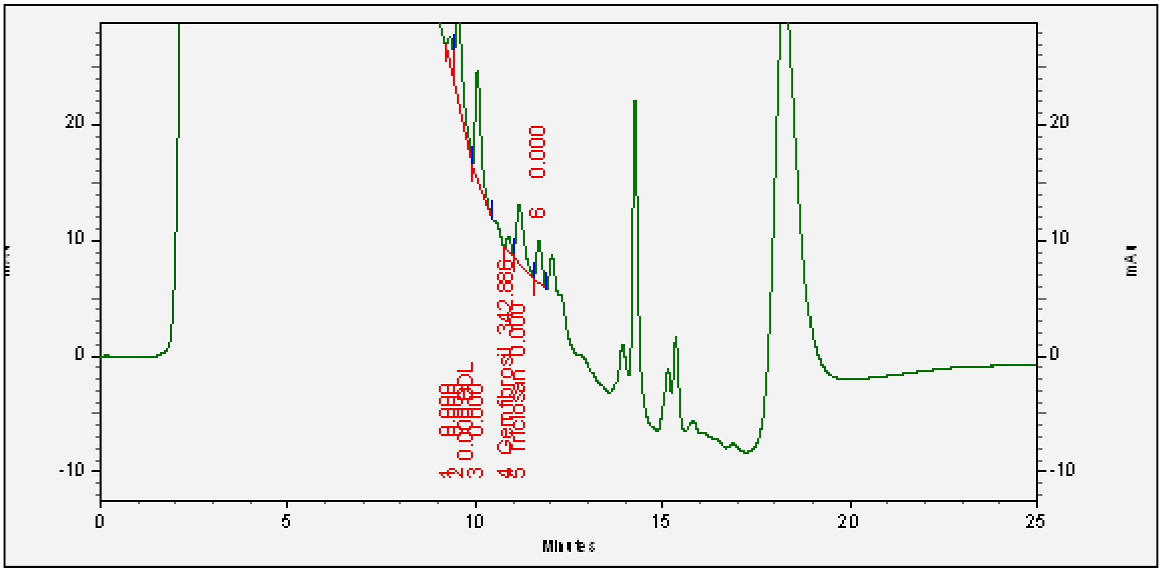


Figure B-56. Influent from 09/15/12: Acid Group II

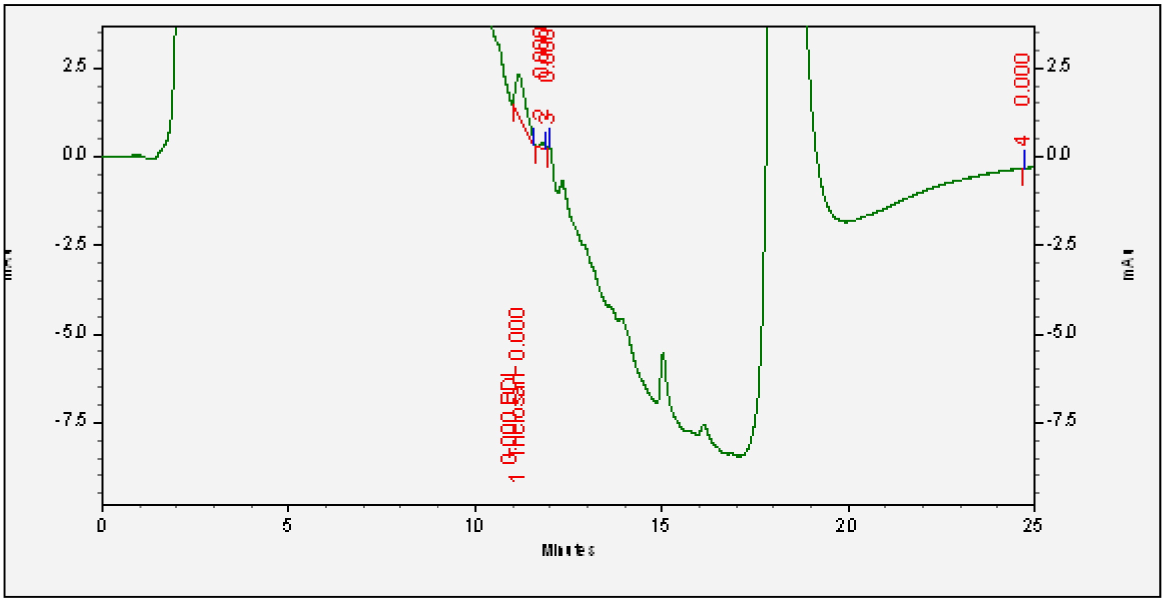


Figure B-57. Primary Effluent from 09/15/12: Acid Group II

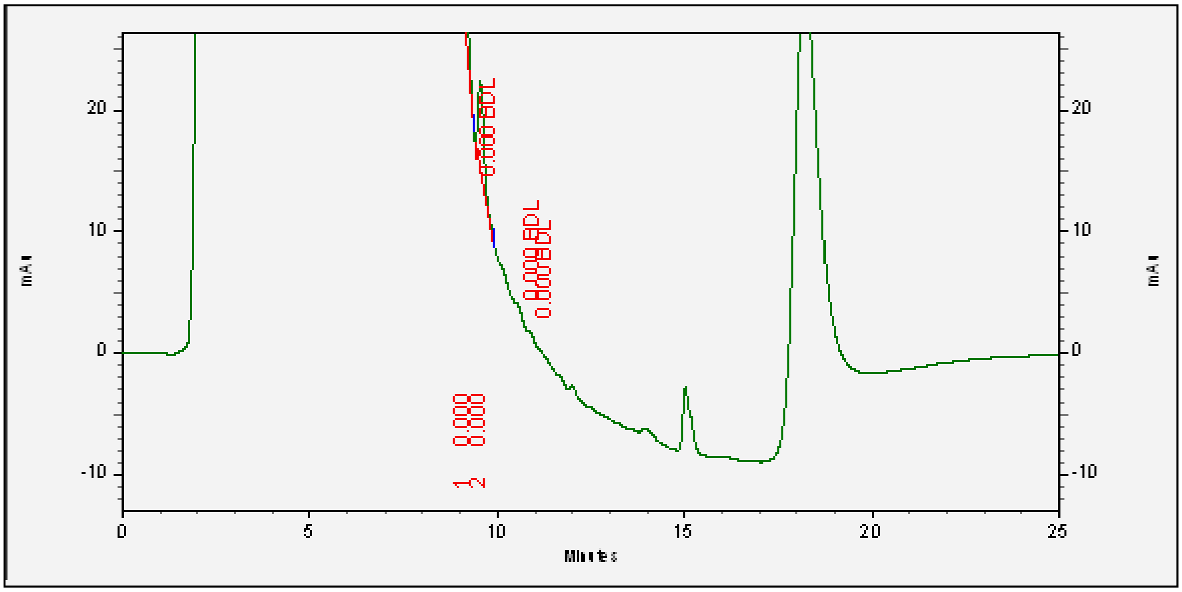


Figure B-58. Secondary Effluent from 09/15/12: Acid Group II

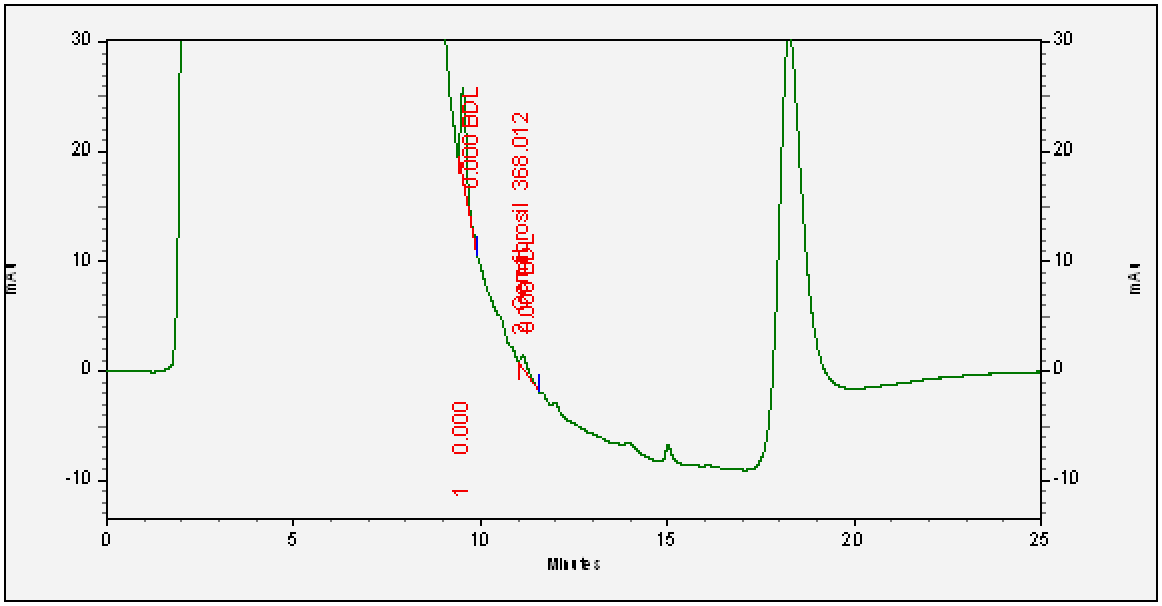


Figure B-59. Final Effluent from 09/15/12: Acid Group II

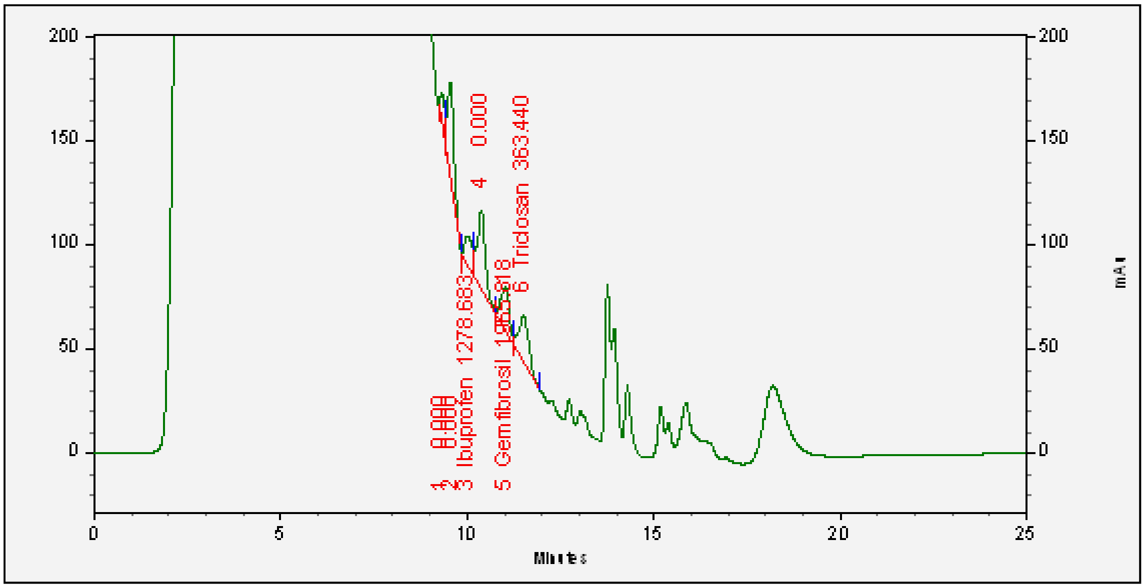


Figure B-60. Influent from 11/01/12: Acid Group II

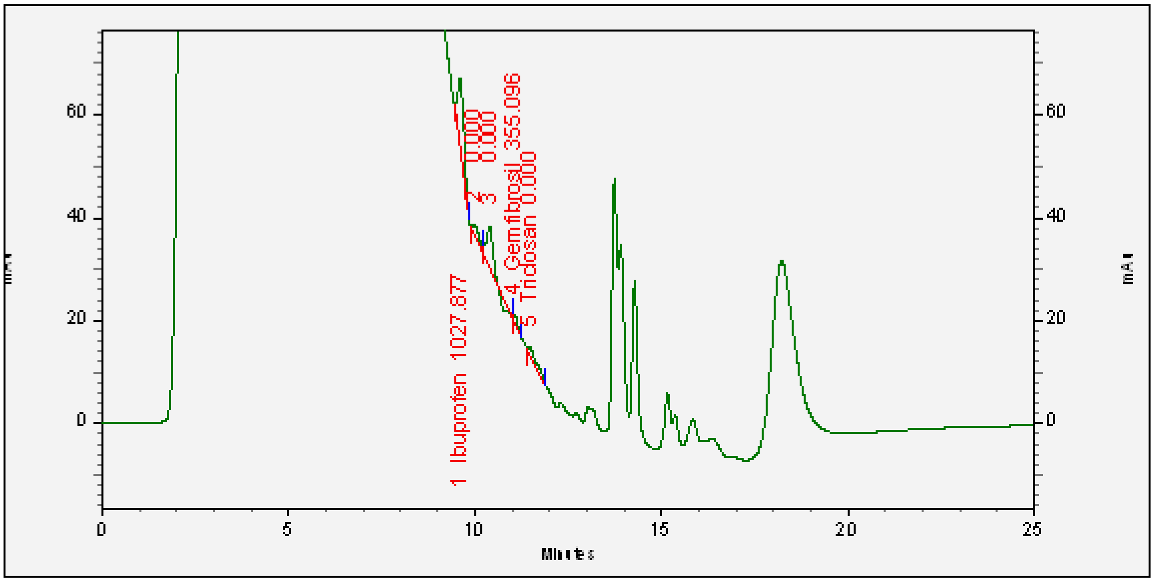


Figure B-61. Primary Effluent from 11/01/12: Acid Group II

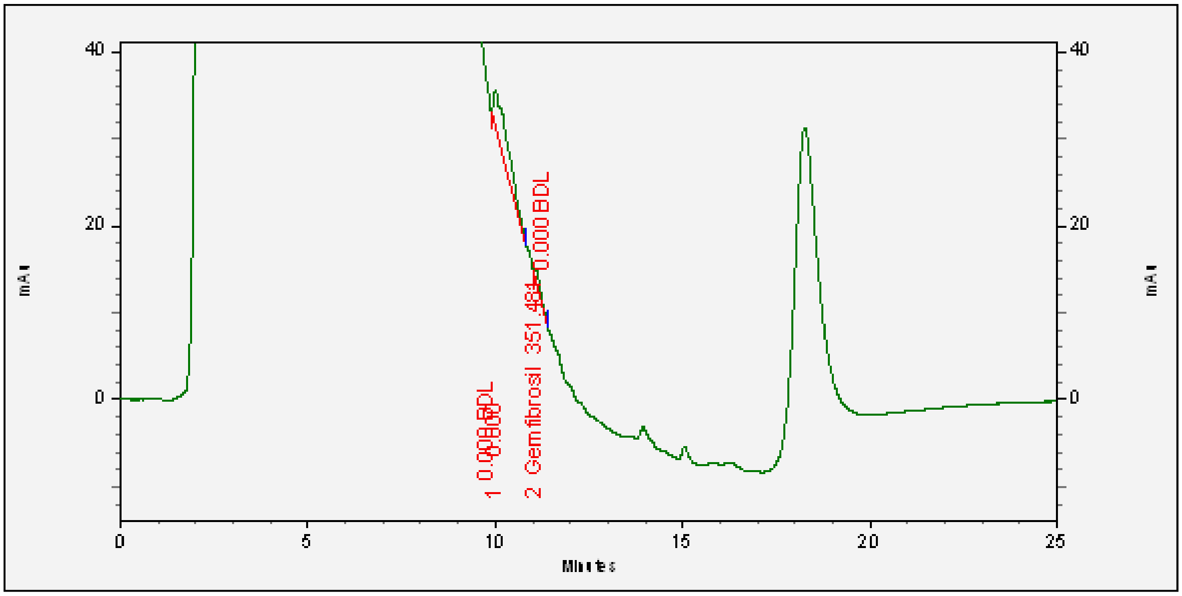


Figure B-62. Secondary Effluent from 11/01/12: Acid Group II

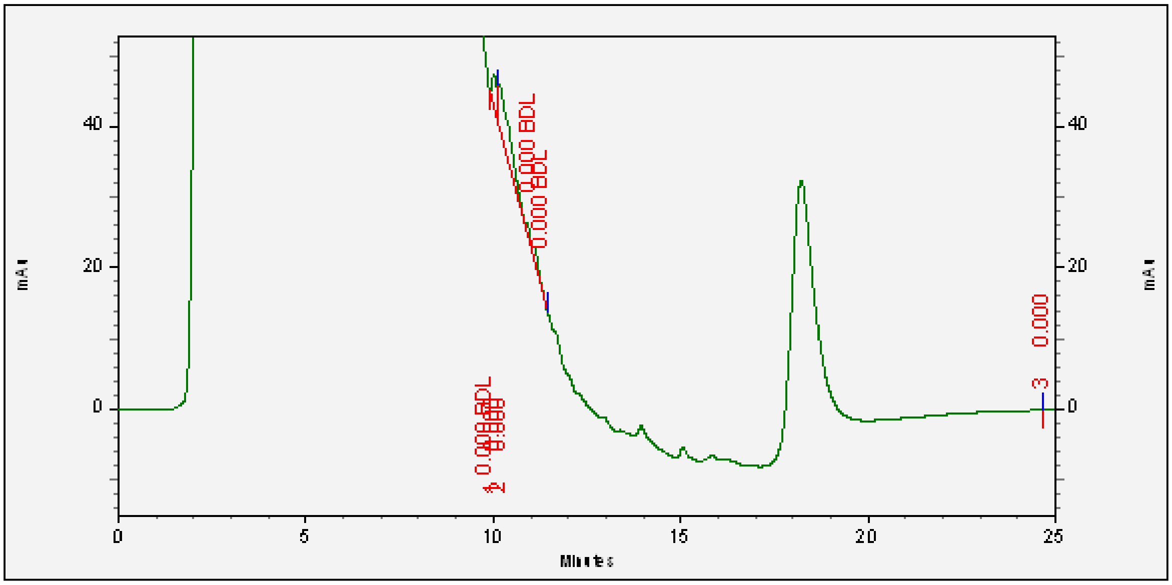


Figure B-63. Final Effluent from 11/01/12: Acid Group II

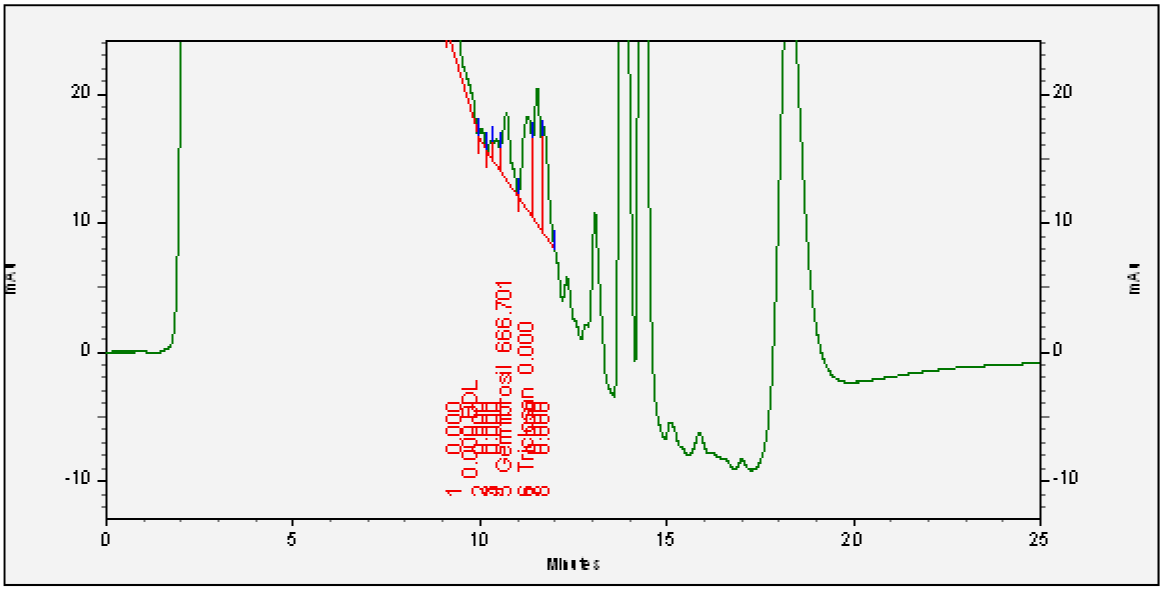


Figure B-64. Influent from 11/04/12: Acid Group II

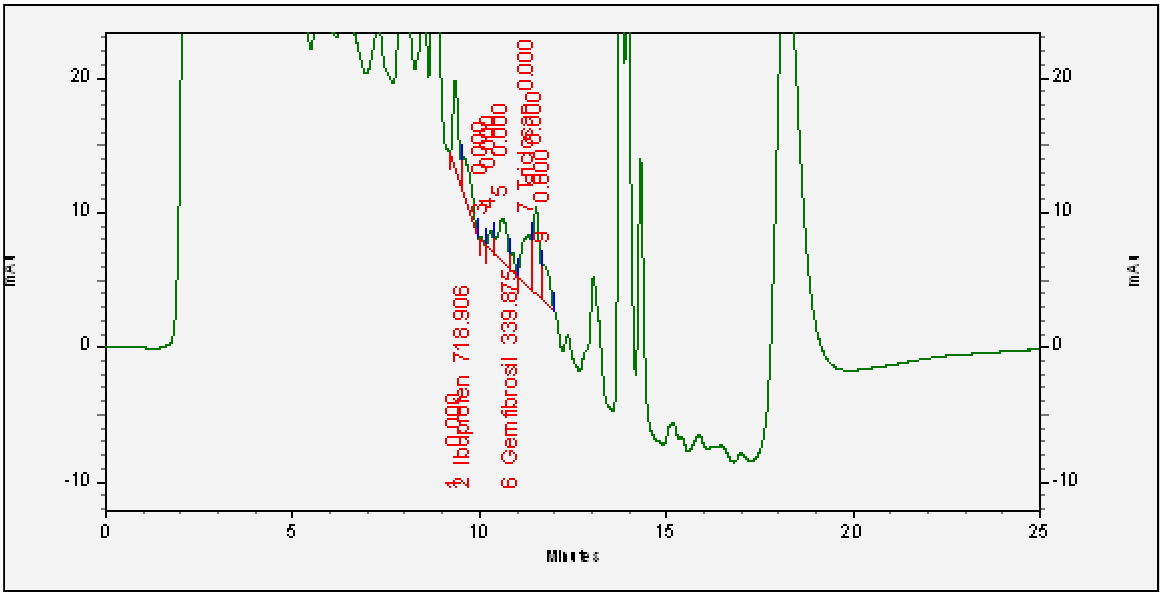


Figure B-65. Primary Effluent from 11/04/12: Acid Group II

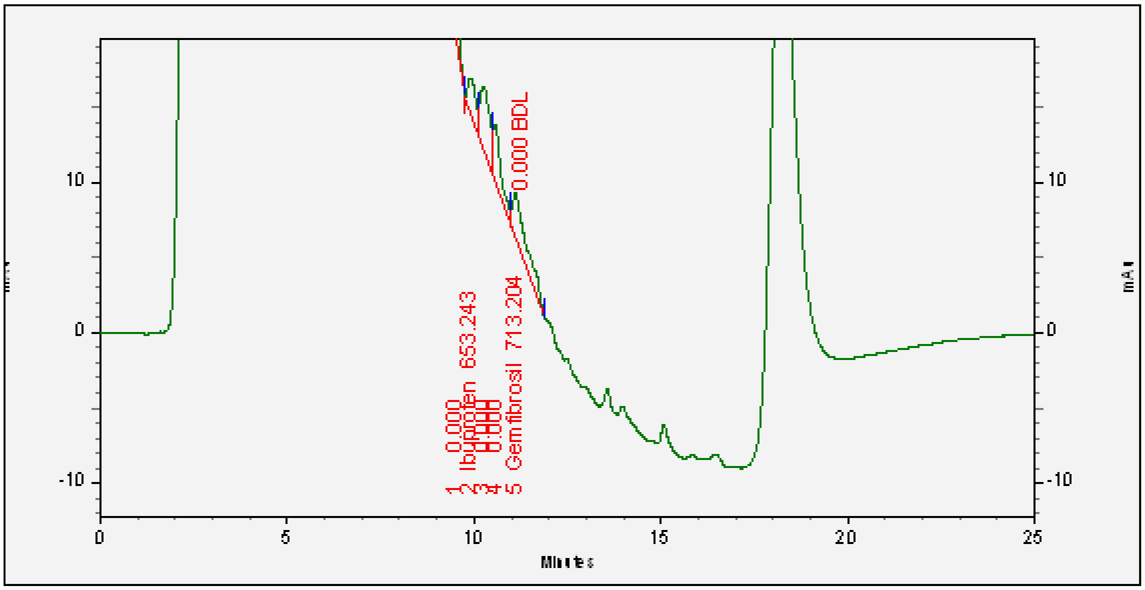


Figure B-66. Secondary Effluent from 11/04/12: Acid Group II

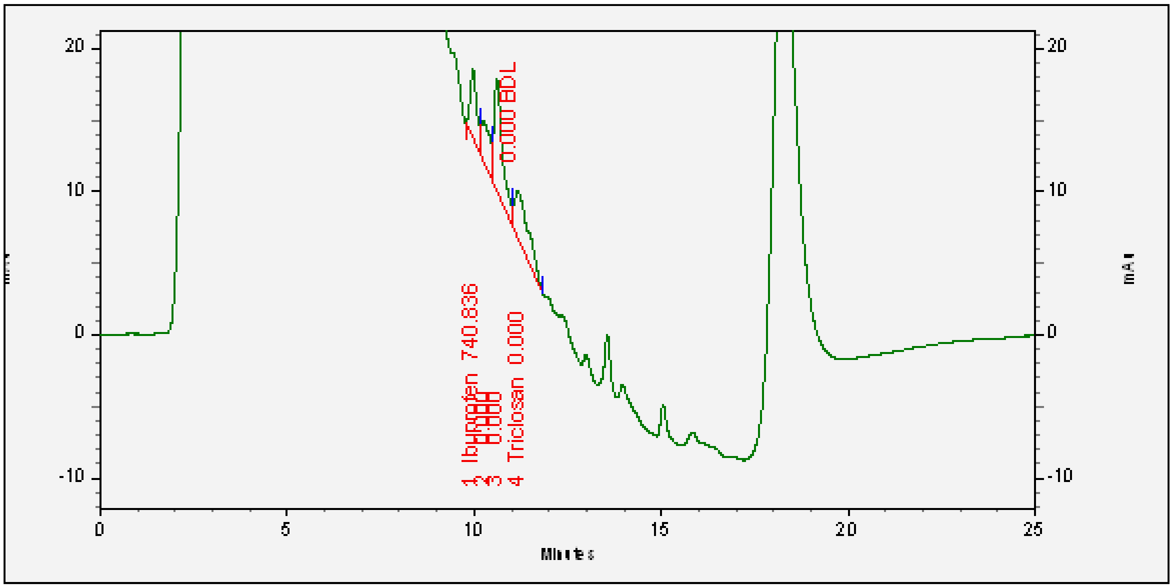


Figure B-67. Final Effluent from 11/04/12: Acid Group II

Appendix C: Quality Assurance and Quality Control Data

Standard Curves for PAHs

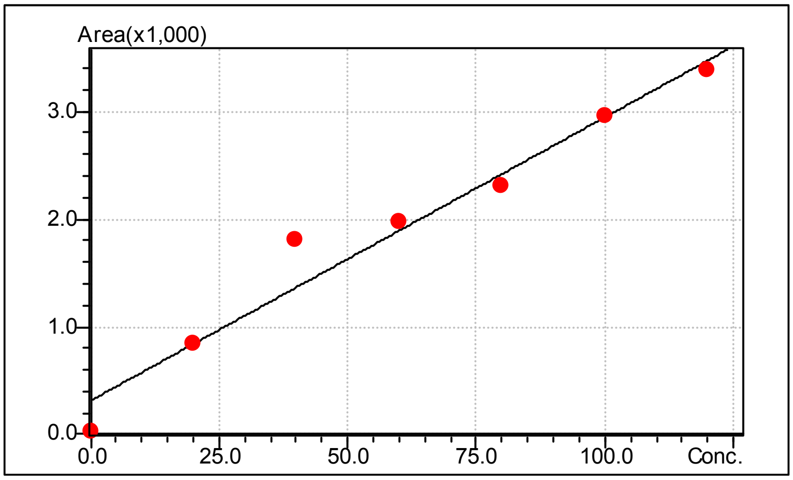


Figure C-1. Standard Curve for Naphthalene

Y = 26.29821X + 318.6786
R^2 = 0.9637912
R = 0.9817287
External Standard
Curve: Linear
Origin: Force Through(Polyline)
Mean RF : 29.49726
RF SD : 14.64758
RF %RSD : 49.65744

0, 20, 40, 60, 80, 100, and 120 ppb were used for calibration

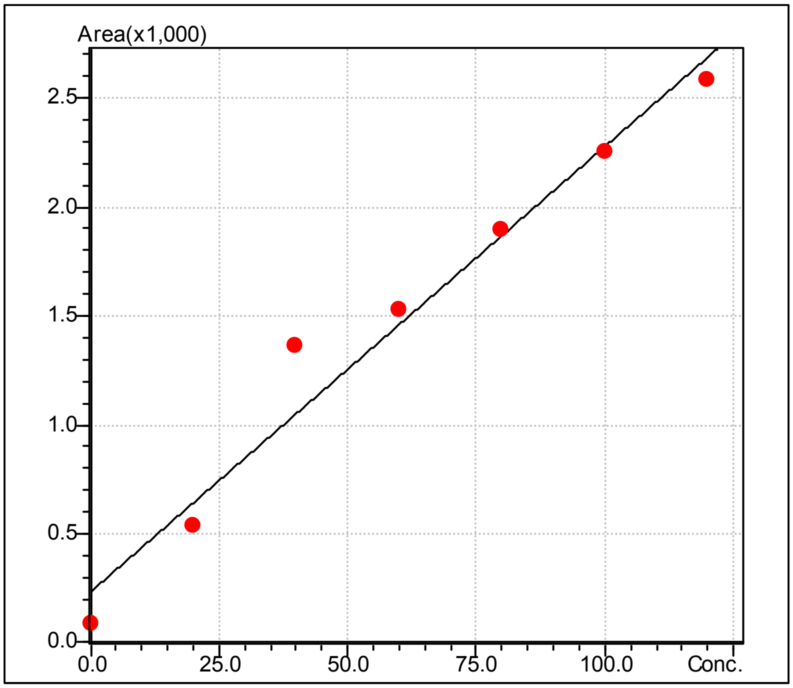


Figure C-2. Standard Curves for Acenaphthylene

Y = 20.44643X + 236.6429
R^2 = 0.9691085
R = 0.9844331
External Standard
Curve: Linear
Origin: Force Through(Polyline)
Weighting Method: None
External Standard
Mean RF: 22.03214
RF SD: 10.57422
RF %RSD : 47.99455

0, 20, 40, 60, 80, 100, 120 ppb used for calibration

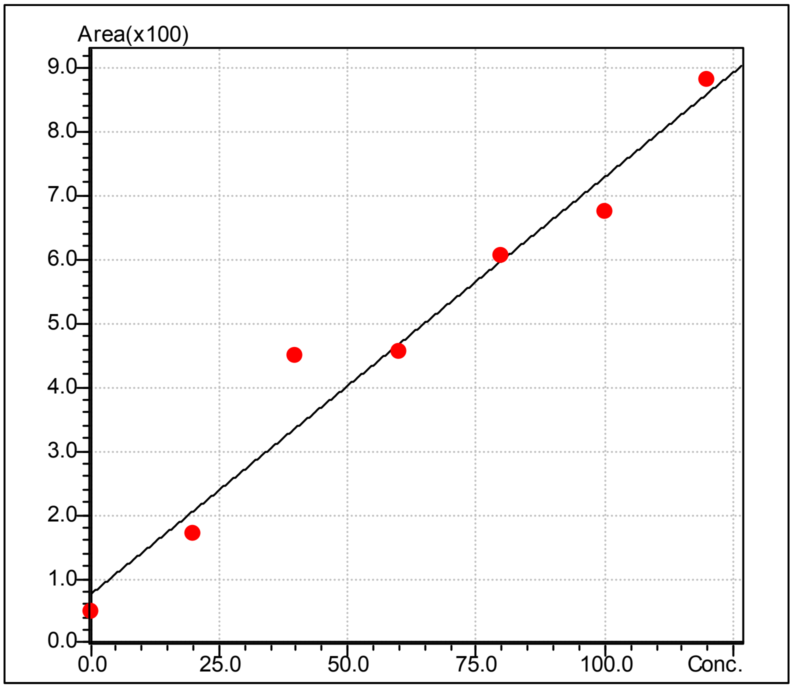


Figure C-3. Standard Curve for Acenaphthene

Y = 6.539286X + 76.5

R^2 = 0.9635812

R = 0.9816217

External Standard

Curve: Linear

Origin: Force Through(Polyline)

Weighting Method: None

Mean RF : 7.00119

RF SD : 3.417826

RF %RSD : 48.81778

0, 20, 40, 60, 80, 100, 120 ppb used for calibration

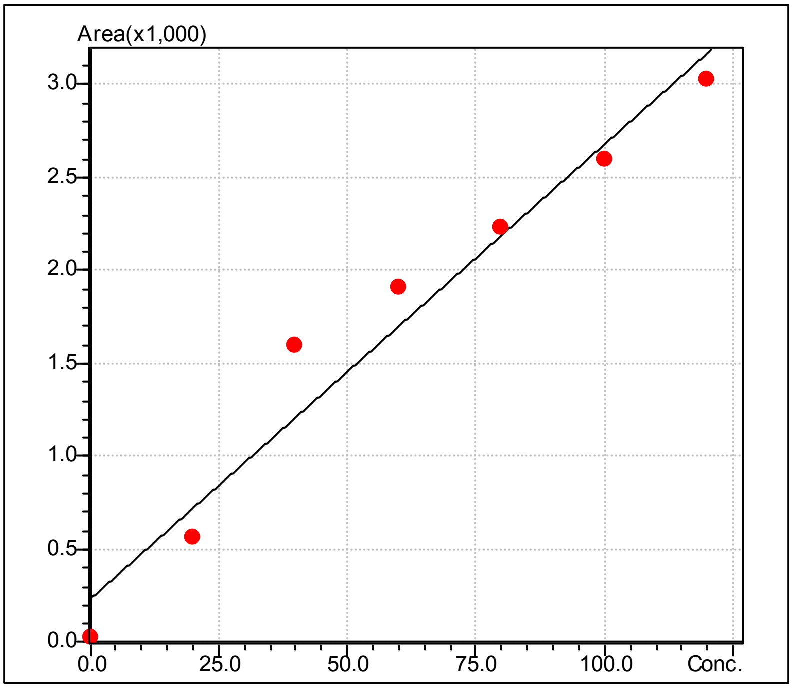


Figure C-4. Standard Curve for Fluorene

Y = 24.46786X + 237.7857
R^2 = 0.9584859
R = 0.9790229
External Standard
Curve: Linear
Origin: Force Through(Polyline)
Weighting Method: None
Mean RF : 25.56071
RF SD : 12.33030
RF %RSD : 48.23928

0, 20, 40, 60, 80, 100, 120 ppb used for calibration

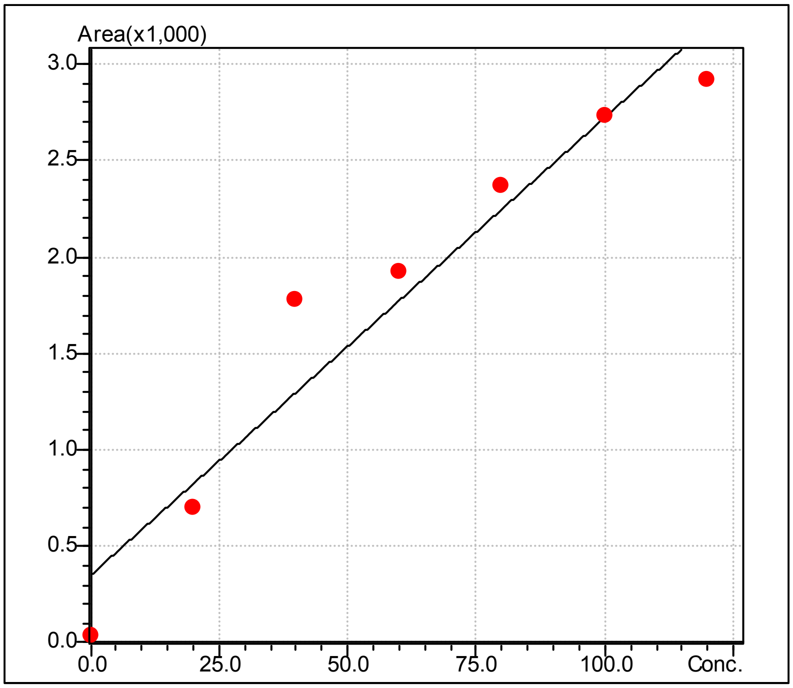


Figure C-5. Standard Curve for Phenanthrene

Y = 23.75179X + 353.6071

R^2 = 0.9329065

R = 0.9658708

External Standard

Curve: Linear

Origin: Force Through(Polyline)

Weighting Method: None

Mean RF : 27.49845

RF SD : 13.72379

RF %RSD : 49.90752

0, 20, 40, 60, 80, 100, 120 ppb used for calibration

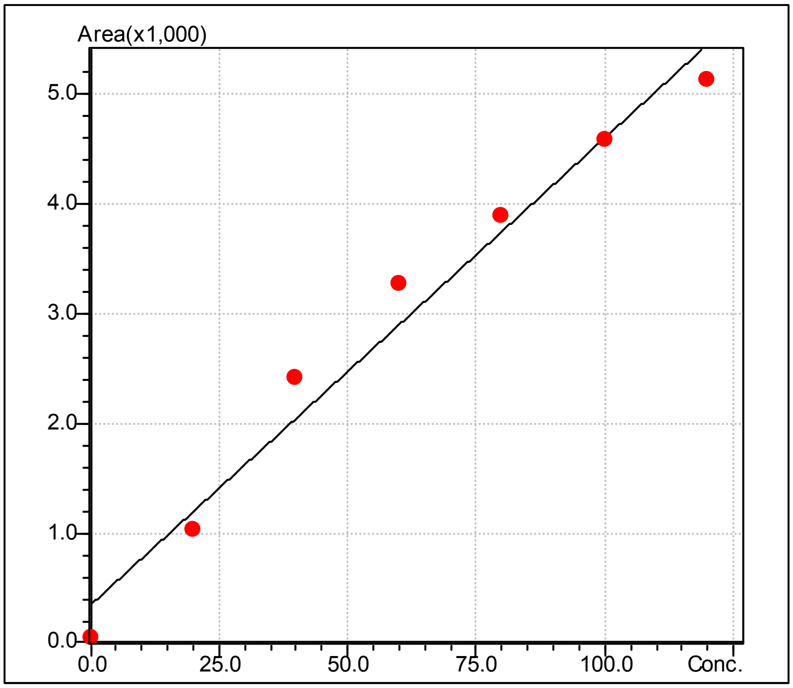


Figure C-6. Standard Curve for Anthracene

Y = 42.61429X + 351.1429
R^2 = 0.9746687
R = 0.9872531
External Standard
Curve: Linear
Origin: Force Through(Polyline)
Weighting Method: None
Mean RF : 43.33095
RF SD : 19.96458
RF %RSD : 46.07465

0, 20, 40, 60, 80, 100, 120 ppb used for calibration

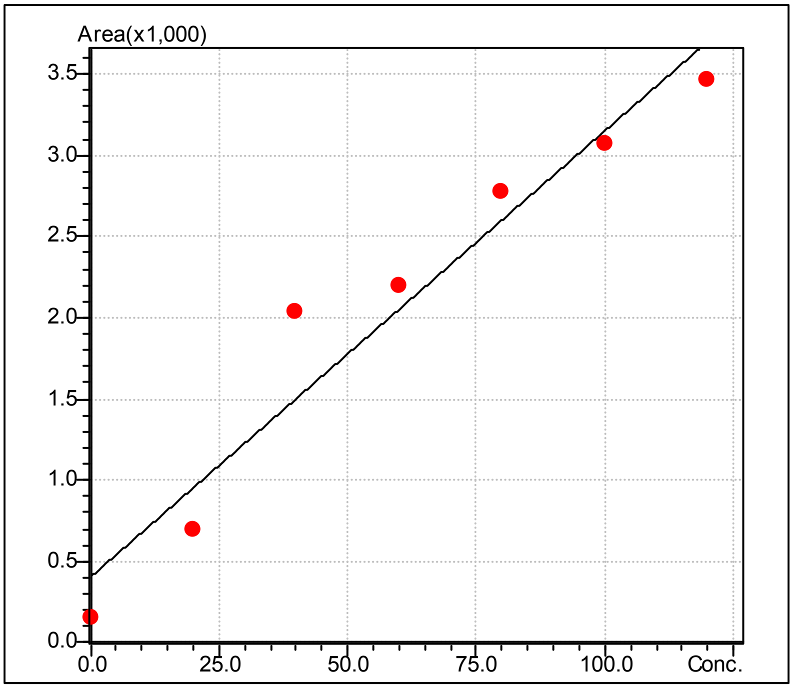


Figure C-7. Standard Curve for Fluoranthene

Y = 27.46786X + 408.9286
R^2 = 0.9403727
R = 0.9697282
External Standard
Curve: Linear
Origin: Force Through(Polyline)
Weighting Method: None
Mean RF : 30.94845
RF SD : 15.42490
RF %RSD : 49.84064

0, 20, 40, 60, 80, 100, 120 ppb used for calibration

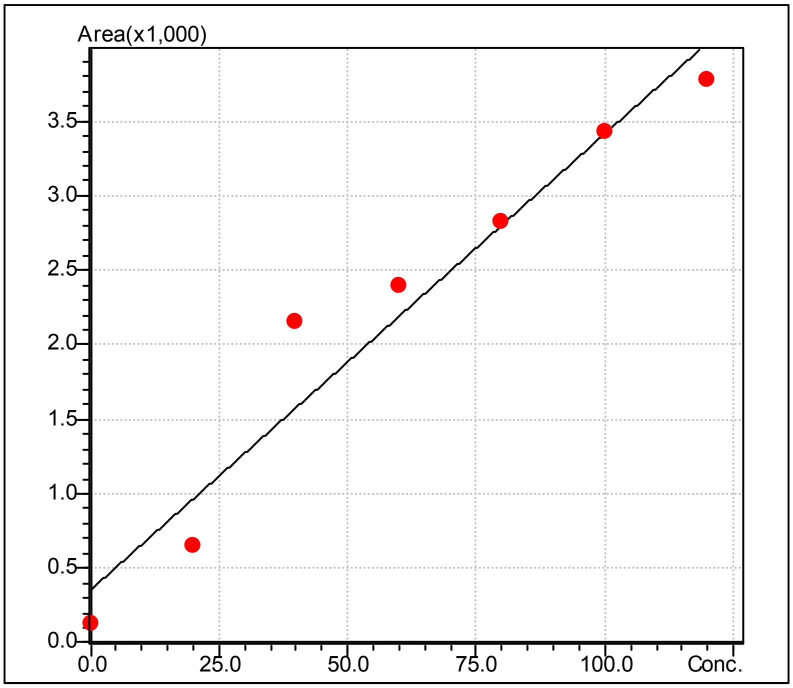


Figure C-8. Standard Curve for Pyrene

Y = 30.62321X + 358.8929
R^2 = 0.9465796
R = 0.9729232
External Standard
Curve: Linear
Origin: Force Through(Polyline)
Weighting Method: None
Mean RF : 32.51202
RF SD : 16.25551
RF %RSD : 49.99846

0, 20, 40, 60, 80, 100, 120 ppb used for calibration

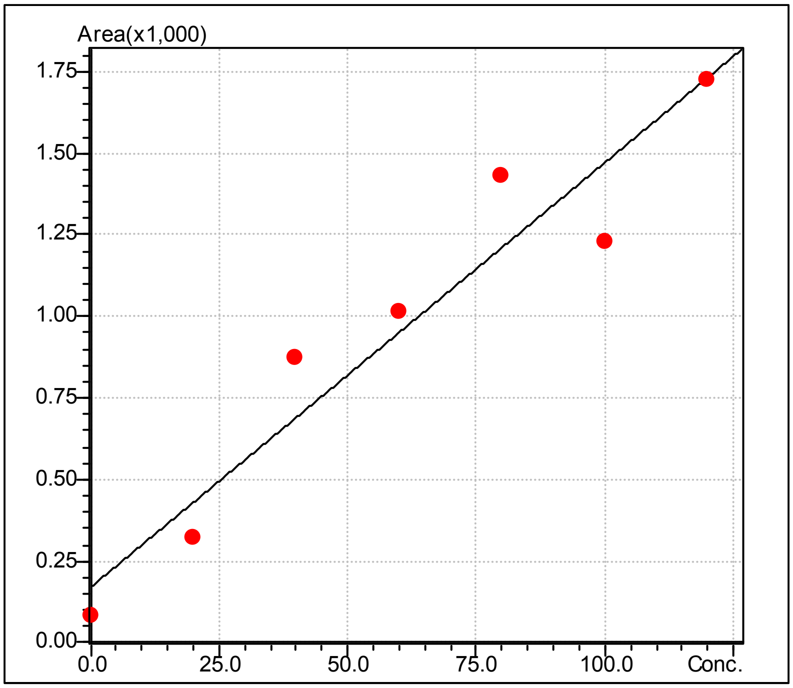


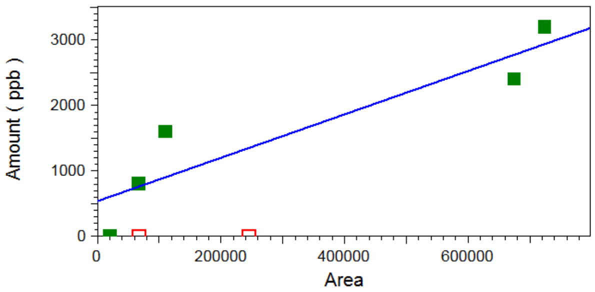
Figure C-9. Standard Curve for Chrysene

Y = 13.02143X + 171.8571
R^2 = 0.9204694
R = 0.959411
External Standard
Curve: Linear
Origin: Force Through(Polyline)
Weighting Method: None
Mean RF : 32.51202
RF SD : 16.25551
RF %RSD : 49.99846

Standard Curves for Pharmaceuticals

```
Ibuprofen (2: 240 nm, 4 nm)
Average RF: 0.00685564 RF StDev: 0.00605063    RF %RSD: 88.2577
Scaling: None          LSQ Weighting: None     Force Through Zero: Off
Replicate Mode: Replace
Fit Type: Linear
y = 0.00331127x + 541.186
Goodness of fit (r^2): 0.834275
```

Peak: Ibuprofen -- ESTD -- 2: 240 nm, 4 nm



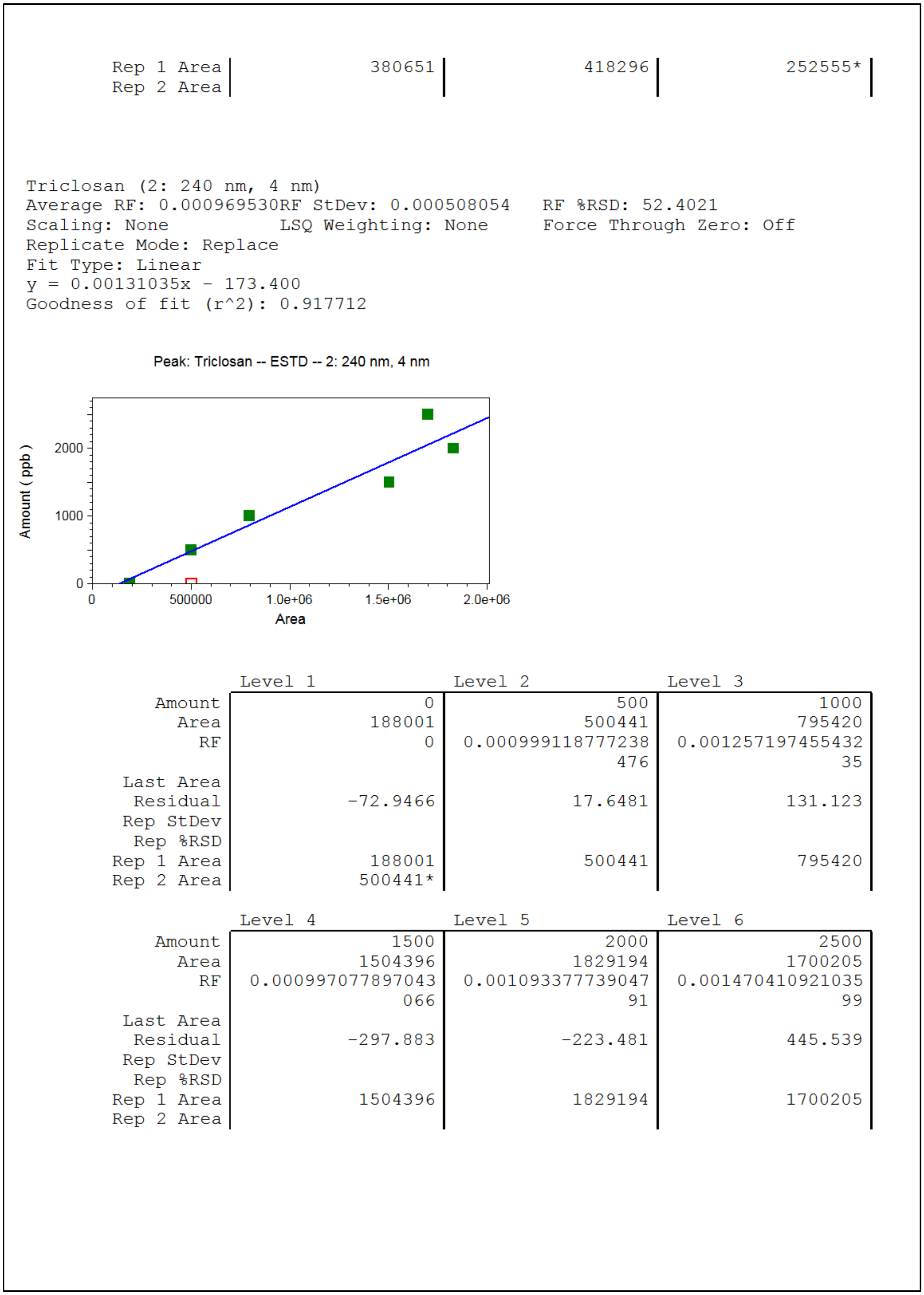
n/a

n/a

	Level 1	Level 2	Level 3
Amount	0	800	1600
Area	20780	67358	110875
RF	0	0.0118768371982541	0.0144306651634724
Last Area			
Residual	-609.994	35.7731	691.676
Rep StDev			
Rep %RSD			
Rep 1 Area	20780	67358	110875
Rep 2 Area	67358*		

	Level 4	Level 5	Level 6
Amount	2400	3200	0
Area	675061	724728	245256*
RF	0.00355523426771803	0.00441544965835458	0
Last Area			
Residual	-376.497	259.042	-1353.3
Rep StDev			

Figure C-10. Standard Curve for Ibuprofen



```
      Rep 1 Area|             380651|             418296|            252555*|
      Rep 2 Area|                   |                   |                   |


Triclosan (2: 240 nm, 4 nm)
Average RF: 0.000969530RF StDev: 0.000508054   RF %RSD: 52.4021
Scaling: None          LSQ Weighting: None     Force Through Zero: Off
Replicate Mode: Replace
Fit Type: Linear
y = 0.00131035x - 173.400
Goodness of fit (r^2): 0.917712
```

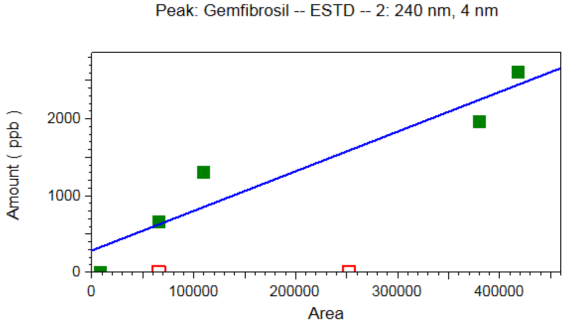
```
                 Level 1            Level 2            Level 3
          Amount|                  0|                500|               1000|
            Area|             188001|             500441|             795420|
              RF|                  0|0.000999118777238  |0.001257197455432  |
                |                   |                476|                 35|
       Last Area|                   |                   |                   |
        Residual|           -72.9466|            17.6481|            131.123|
       Rep StDev|                   |                   |                   |
         Rep %RSD|                   |                   |                   |
      Rep 1 Area|             188001|             500441|             795420|
      Rep 2 Area|            500441*|                   |                   |

                 Level 4            Level 5            Level 6
          Amount|               1500|               2000|               2500|
            Area|            1504396|            1829194|            1700205|
              RF|0.000997077897043  |0.001093377739047  |0.001470410921035  |
                |                066|                 91|                 99|
       Last Area|                   |                   |                   |
        Residual|           -297.883|           -223.481|            445.539|
       Rep StDev|                   |                   |                   |
        Rep %RSD|                   |                   |                   |
      Rep 1 Area|            1504396|            1829194|            1700205|
      Rep 2 Area|                   |                   |                   |
```

Figure C-11. Standard Curve for Triclosan

```
     Rep %RSD|                   |                   |                   |
   Rep 1 Area|             675061|             724728|            245256*|
   Rep 2 Area|                   |                   |                   |
```

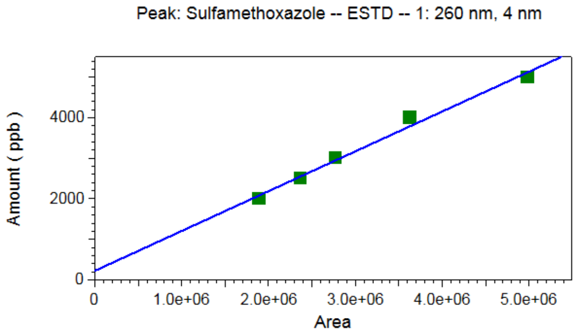
```
Gemfibrosil (2: 240 nm, 4 nm)
Average RF: 0.00660670 RF StDev: 0.00458053    RF %RSD: 69.3315
Scaling: None           LSQ Weighting: None     Force Through Zero: Off
Replicate Mode: Replace
Fit Type: Linear
y = 0.00515612x + 285.983
Goodness of fit (r^2): 0.899636
```



```
              Level 1            Level 2            Level 3
       Amount|                  0|                650|               1300|
         Area|               8601|              65927|             109838|
           RF|                  0| 0.009859389931287| 0.011835612447422|
             |                   |                 64|                  6|
    Last Area|                   |                   |                   |
     Residual|           -330.331|            24.0891|            447.678|
   Rep StDev |                   |                   |                   |
     Rep %RSD|                   |                   |                   |
   Rep 1 Area|               8601|              65927|             109838|
   Rep 2 Area|             65927*|                   |                   |

              Level 4            Level 5            Level 6
       Amount|               1950|               2600|                  0|
         Area|             380651|             418296|            252555*|
           RF| 0.005122802777347| 0.006215694149597|                  0|
             |                 23|                 41|                   |
    Last Area|                   |                   |                   |
     Residual|           -298.667|            157.231|           -1588.19|
   Rep StDev |                   |                   |                   |
     Rep %RSD|                   |                   |                   |
```

Figure C-12. Standard Curve for Gemfibrozil

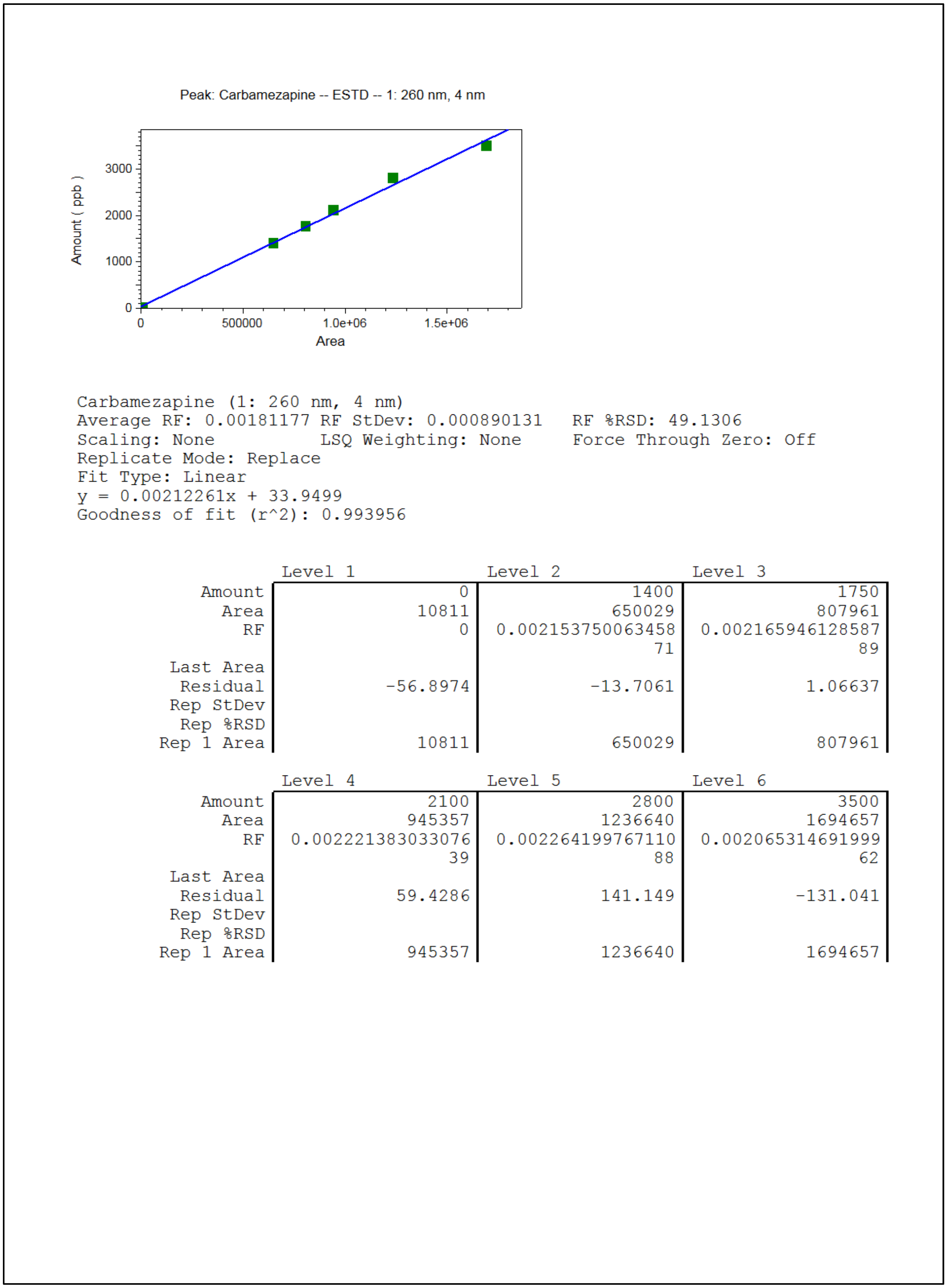


```
Sulfamethoxazole (1: 260 nm, 4 nm)
Average RF: 0.00105963 RF StDev: 3.72906e-005  RF %RSD: 3.51921
Scaling: None           LSQ Weighting: None     Force Through Zero: Off
Replicate Mode: Replace
Fit Type: Linear
y = 0.000982097x + 225.494
Goodness of fit (r^2): 0.987747


                 Level 1             Level 2             Level 3
       Amount|                  0|               2000|               2500|
         Area|                   |            1893140|            2369448|
           RF|                   |0.001056445904687  |0.001055098065034  |
             |                   |                 45|                 56|
    Last Area|                   |                   |                   |
     Residual|                N/A|           -84.7418|           -52.5226|
   Rep StDev |                   |                   |                   |
    Rep %RSD |                   |                   |                   |
  Rep 1 Area |                   |            1893140|            2369448|

                 Level 4             Level 5             Level 6
       Amount|               3000|               4000|               5000|
         Area|            2770526|            3632228|            4987414|
           RF|0.001082826871142  |0.001101252454416  |0.001002523552285  |
             |                 88|                 41|                 81|
    Last Area|                   |                   |                   |
     Residual|            53.5798|            207.305|            -123.62|
   Rep StDev |                   |                   |                   |
    Rep %RSD |                   |                   |                   |
  Rep 1 Area |            2770526|            3632228|            4987414|
```

Figure C-13. Standard Curve for Sulfamethoxazole

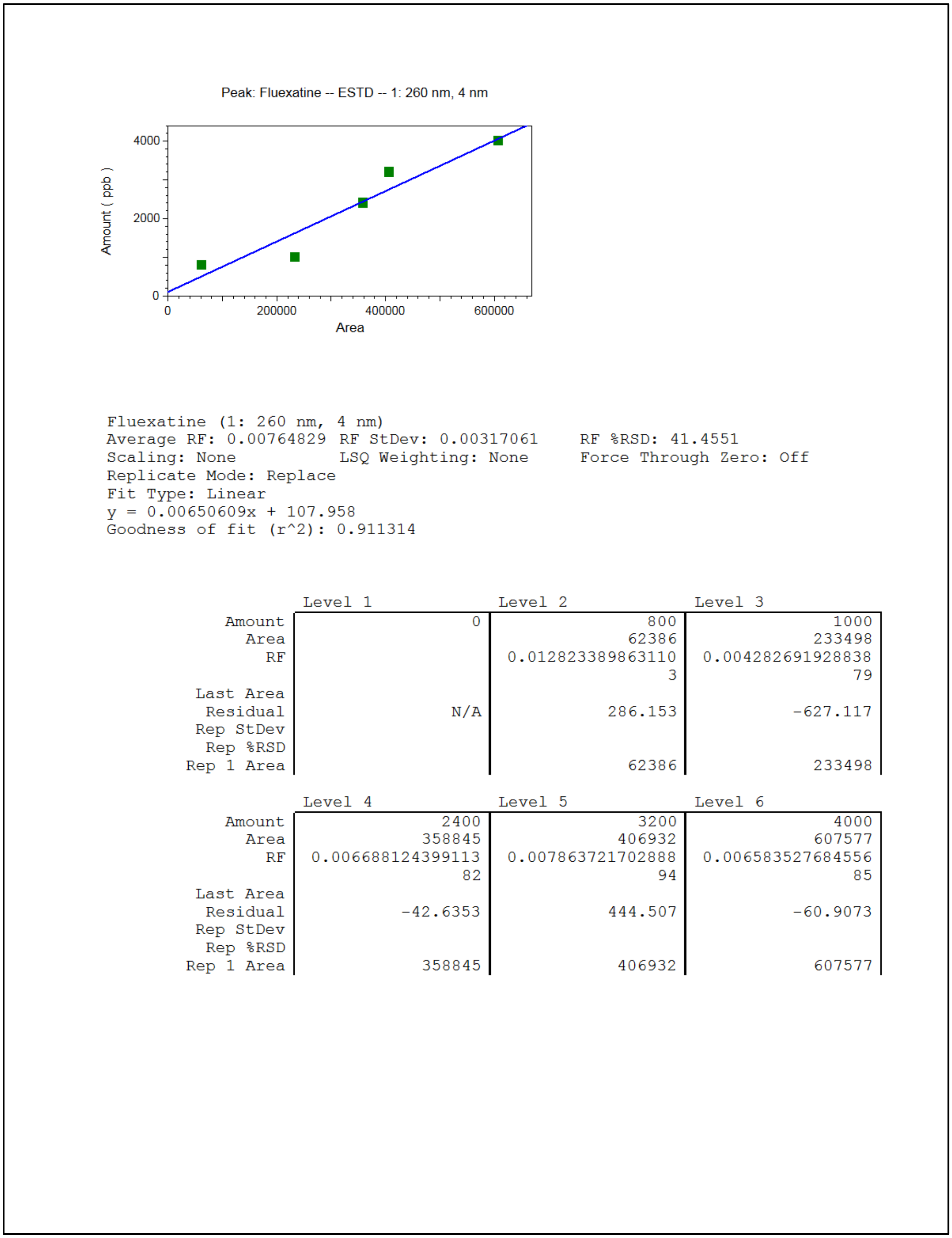


```
Carbamezapine (1: 260 nm, 4 nm)
Average RF: 0.00181177 RF StDev: 0.000890131   RF %RSD: 49.1306
Scaling: None          LSQ Weighting: None     Force Through Zero: Off
Replicate Mode: Replace
Fit Type: Linear
y = 0.00212261x + 33.9499
Goodness of fit (r^2): 0.993956

                 Level 1            Level 2            Level 3
      Amount|                 0|              1400|              1750|
        Area|             10811|            650029|            807961|
          RF|                 0|0.002153750063458|0.002165946128587|
            |                  |                71|                89|
   Last Area|                  |                  |                  |
    Residual|          -56.8974|          -13.7061|           1.06637|
   Rep StDev|                  |                  |                  |
    Rep %RSD|                  |                  |                  |
  Rep 1 Area|             10811|            650029|            807961|

                 Level 4            Level 5            Level 6
      Amount|              2100|              2800|              3500|
        Area|            945357|           1236640|           1694657|
          RF|0.002221383033076|0.002264199767110|0.002065314691999|
            |                39|                88|                62|
   Last Area|                  |                  |                  |
    Residual|           59.4286|           141.149|          -131.041|
   Rep StDev|                  |                  |                  |
    Rep %RSD|                  |                  |                  |
  Rep 1 Area|            945357|           1236640|           1694657|
```

Figure C-14. Standard Curve for Carbamazepine



```
Fluexatine (1: 260 nm, 4 nm)
Average RF: 0.00764829 RF StDev: 0.00317061    RF %RSD: 41.4551
Scaling: None          LSQ Weighting: None     Force Through Zero: Off
Replicate Mode: Replace
Fit Type: Linear
y = 0.00650609x + 107.958
Goodness of fit (r^2): 0.911314
```

```
               Level 1            Level 2            Level 3
      Amount                 0|               800|              1000|
        Area                  |             62386|            233498|
          RF                  |0.01282338986311 0|0.00428269192883 8|
                              |                 3|                79|
   Last Area                  |                  |                  |
    Residual               N/A|           286.153|          -627.117|
    Rep StDev                 |                  |                  |
     Rep %RSD                 |                  |                  |
  Rep 1 Area                  |             62386|            233498|

               Level 4            Level 5            Level 6
      Amount              2400|              3200|              4000|
        Area            358845|            406932|            607577|
          RF 0.006688124399113|0.007863721702888|0.006583527684556|
                            82|                94|                85|
   Last Area                  |                  |                  |
    Residual          -42.6353|           444.507|          -60.9073|
    Rep StDev                 |                  |                  |
     Rep %RSD                 |                  |                  |
  Rep 1 Area            358845|            406932|            607577|
```

Figure C-15. Standard Curve for Fluoxetine

Standard Curves and Recoveries for Pesticides

Surrogate recovery analyses for each sample (acceptable recoveries are 70 to 130%):

IS_1,3-Dimethyl-2- Nitrobenzene (S)
IS_Perylene-d12 (S)
IS_Triphenylphosphate (S)
Pyrene-d10 (S)

Sample flags:

Primary 011610	IS_1,3-Dimethyl-2- Nitrobenzene (S) (244%) 1
Influent 011610	IS_1,3-Dimethyl-2- Nitrobenzene (S) (383%) 3 IS_1,3-Dimethyl-2- Nitrobenzene (S) (249%) (duplicate) 2
Influent 062510	Pyrene-d10 (S) (62.1%) 4
Primary 110210	IS_1,3-Dimethyl-2- Nitrobenzene (S) (215%) 5
Influent 110210	IS_1,3-Dimethyl-2- Nitrobenzene (S) (159%) 6

PARAMETER QUALIFIERS\FLAGS

1) The surrogate IS_1,3-Dimethyl-2-Nitrobenzene for method EPA 525.2 was outside of control limits. The % Recovery was reported as 244 and the control limits were 70 to 130. This result was reported at a dilution of 1.

2) The surrogate IS_1,3-Dimethyl-2-Nitrobenzene for method EPA 525.2 was outside of control limits. The % Recovery was reported as 249 and the control limits were 70 to 130. This result was reported at a dilution of 2.

3) The surrogate IS_1,3-Dimethyl-2-Nitrobenzene for method EPA 525.2 was outside of control limits. The % Recovery was reported as 383 and the control limits were 70 to 130. This result was reported at a dilution of 1.

4) The surrogate Pyrene-d10 for method EPA 525.2 was outside of control limits. The % Recovery was reported as 62.1 and the control limits were 70 to 130. This result was reported at a dilution of 1.

5) The surrogate IS_1,3-Dimethyl-2-Nitrobenzene for method EPA 525.2 was outside of control limits. The % Recovery was

reported as 215 and the control limits were 70 to 130. This result was reported at a dilution of 1.

6) The surrogate IS_1,3-Dimethyl-2-Nitrobenzene for method EPA 525.2 was outside of control limits. The % Recovery was
reported as 159 and the control limits were 70 to 130. This result was reported at a dilution of 1.

Analyses performed by ALS Environmental, Middletown, PA

Detection Limits for Pesticides and PAHs

Analyses performed by ALS Environmental, Middletown, PA

Table C-1. Pesticide and PAH detection limits (from PSH Analysis)

Detection Limits (µg/L)	2,6-Dinitrotoluene 2.5
Acenaphthene 0.50	EPTC 1.0
Acenaphthylene 0.50	Endrin 1.0
Acetochlor 1.0	Di(2-Ethylhexyl)adipate 2.5
Alachlor 1.0	bis(2-Ethylhexyl)phthalate 5.0
Aldrin 1.0	Fluoranthene 0.50
Anthracene 0.50	Fluorene 0.50
Atrazine 1.0	Heptachlor 0.50
gamma-BHC 0.50	Heptachlor Epoxide 0.50
Benzo(a)anthracene 0.50	Hexachlorobenzene 0.50
Benzo(a)pyrene 0.50	Hexachlorocyclopentadiene 1.0
Benzo(b)fluoranthene 0.50	Indeno(1,2,3-cd)pyrene 0.50
Benzo(g,h,i)perylene 0.50	Methoxychlor 1.0
Benzo(k)fluoranthene 0.50	2-Methylnaphthalene 1.0
Butachlor 1.0	Metolachlor 1.0
Butylbenzylphthalate 2.5	Metribuzin 1.0
Chrysene 0.50	Molinate 1.0
4,4'-DDE 1.0	Naphthalene 1.0
Di-n-Butylphthalate 2.5	Phenanthrene 0.50
Dibenzo(a,h)anthracene 0.50	Propachlor 1.0
Dibenzofuran 0.50	Pyrene 0.50
Dieldrin 1.0	Simazine 1.0
Diethylphthalate 5.0	Terbacil 2.5
Dimethylphthalate 2.5	2,4,5-Trichlorobiphenyl 0.50
2,4-Dinitrotoluene 2.5	

Quality Control and Quality Assurance for pH and Conductivity in Metal Release Experiments

FiguresC-17 and C-18 as plots of pH values with time in the containers with initial pH 5 and pH 8, respectively. The graphs show that pH values in the containers were fairly constant throughout the experiments. The pH change with time did not exceed 1 pH unit, with the exception of the containers with concrete samples and initial pH 5. In those conditions, the pH increased from 4.98 to 6.37 due to the increased alkalinity from the immersed concrete sample. Figures C-19 and C-20 show changes in conductivity values with time. The metal releases in the containers with immersed concrete samples were below or just above the detection limits, while the conductivity values in those containers were fairly constant with time. The increase in conductivity values with time in the rest of the containers can be explained by the increase in metal concentrations released from the immersed samples.

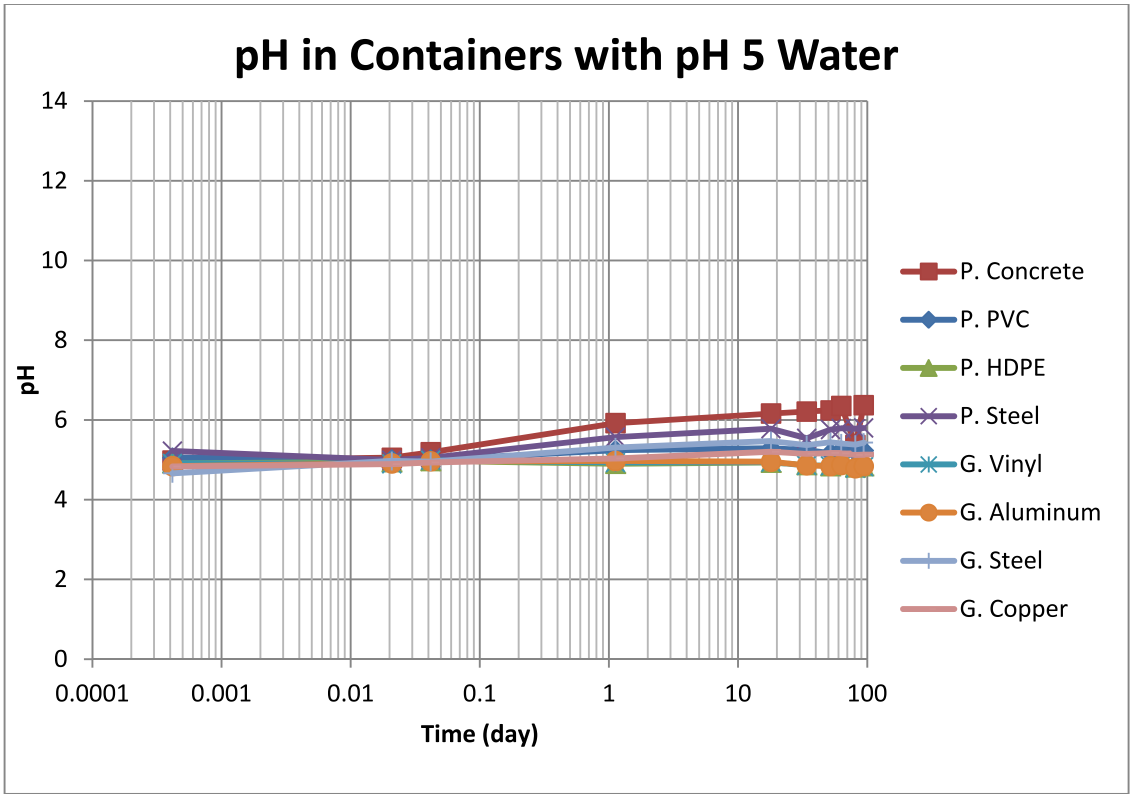


Figure C-17. pH measurements in the containers with pH 5 water.

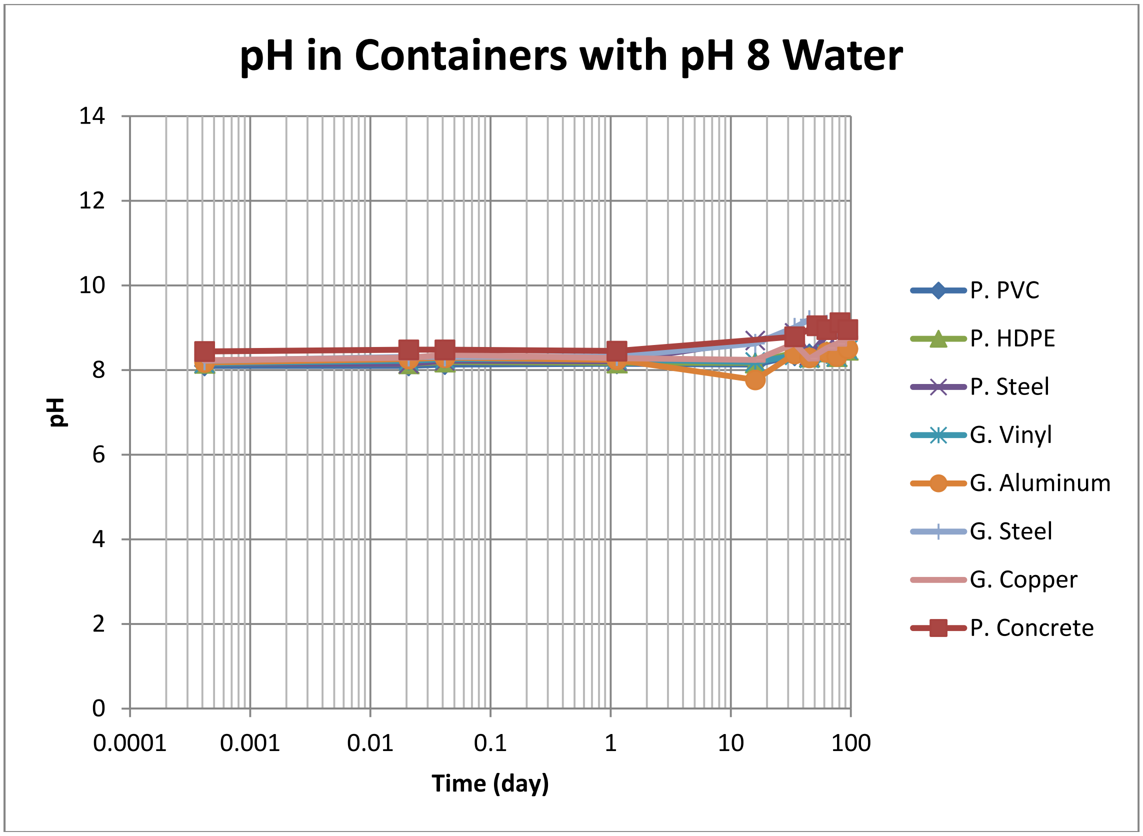


Figure C-18. pH measurements in the containers with pH 8 water.

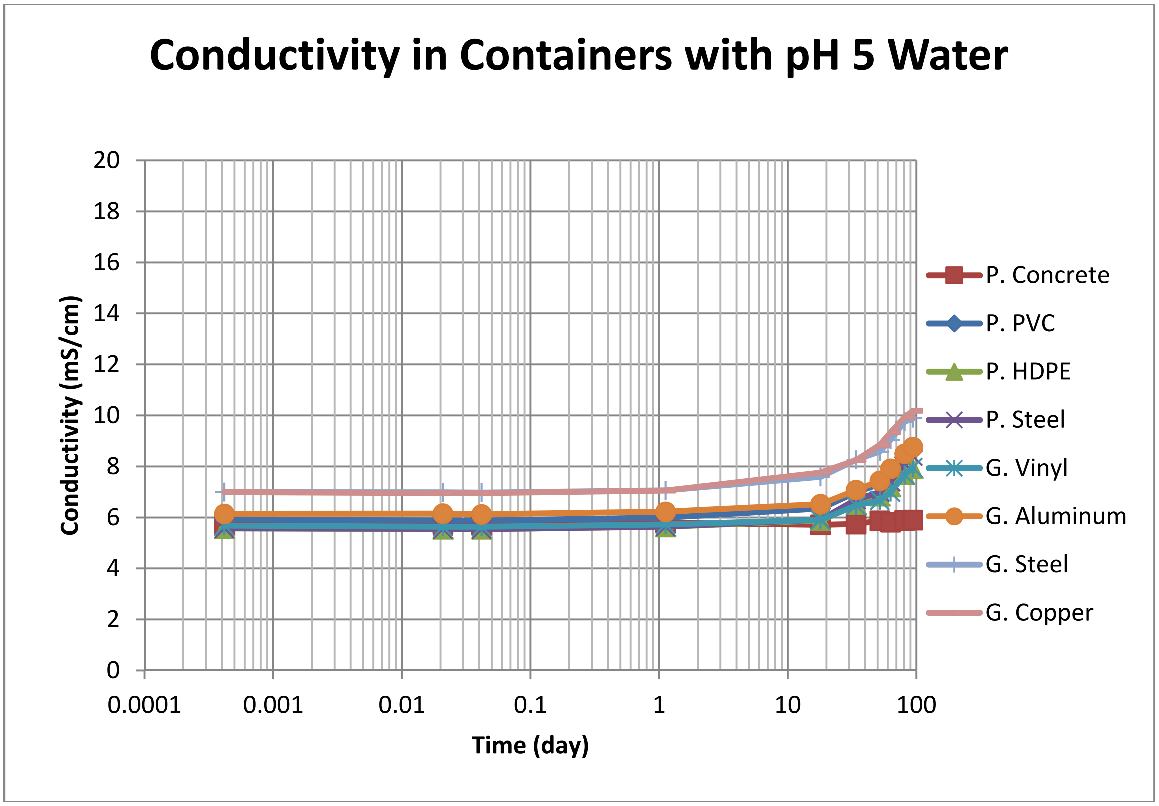


Figure C-19. Conductivity measurements in the containers with pH 5 water.

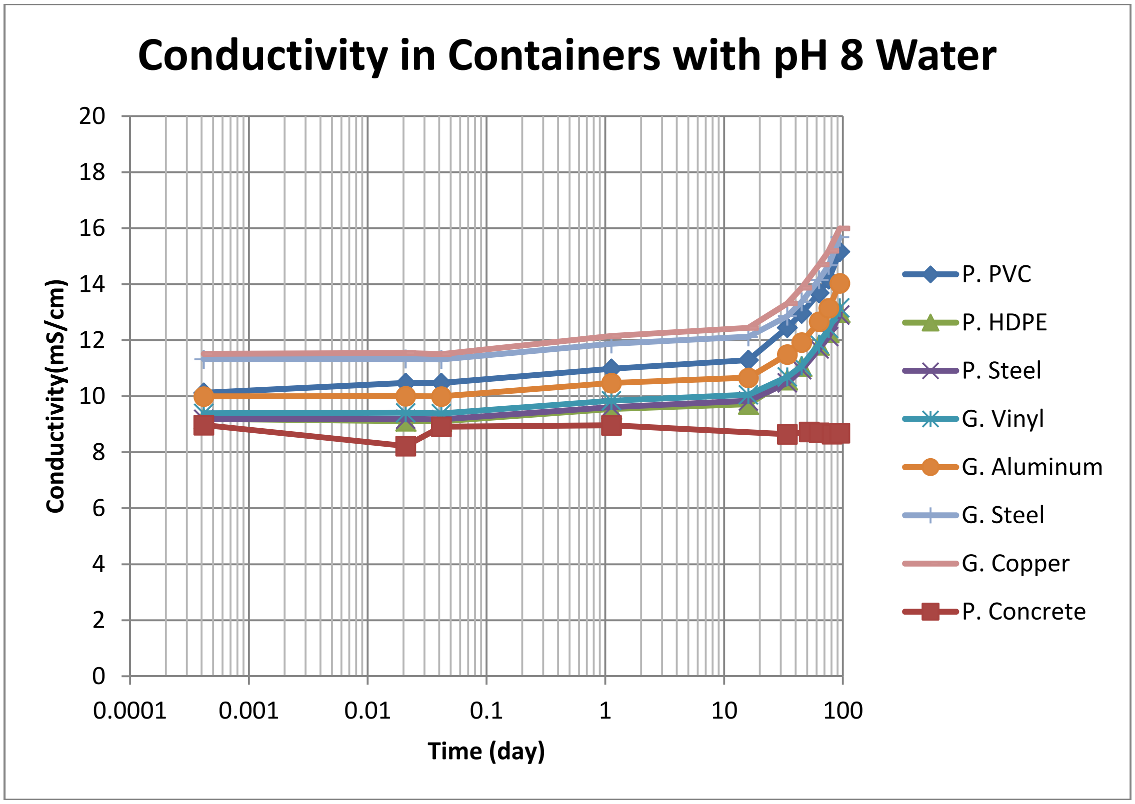


Figure C-20. Conductivity measurements in the containers with pH 8 water.

Metal analyses and associated laboratory quality control procedures were performed by Stillbrook Environmental Lab, in Fairfield, AL using inductively coupled plasma mass spectroscopy (ICP-MS). Stillbrook Environmental Lab also conducted analyses on major constituents using analytical methods.

The lab ware used for sample collection and storage was made of polyethylene and was soaked in 10% nitric acid for at least 24 hours before use and rinsed off with 18mΩ water to avoid heavy metal contamination. High-density polyethylene (HDPE) containers were used for sample storage. Leaching buckets were washed using warm tap water and laboratory phosphate-free detergent, rinsed with tap water, washed with 10% nitric acid, then distilled water, followed by 18mΩ water. Polyethylene bottles were washed using warm tap water and laboratory phosphate-free detergent, rinsed with tap water, then deionized water, soaked in a 10% solution of reagent grade nitric acid for at least 24 hours before use, and rinsed with laboratory grade 18mΩ water. The glassware used for sample collection was also cleaned with phosphate-free detergent, rinsed with tap water, deionized water, and soaked in a 10% nitric acid bath at least overnight before use and rinsed with 18mΩ water. Glassware used for toxicity analysis also was rinsed with sampled water. 18mΩ water was also used for method blanks. If not immediately analyzed, water samples were adjusted to pH <2, as required, and placed in a refrigerator at 4°C until they were analyzed. During this research, the labware preparation and sample storage and preservations requirements that were followed were from Eaton, et al. (2005) and Burton and Pitt (2002).The instruments were calibrated prior to each data collection. Calibration techniques are listed in Table C-2.

Table C-2. Instrument calibration

Instrument	Calibration
pH meter Model IQ 160, conductivity meter model sensION5 by HACH, DR 2010 (for nitrate, nitrogen ammonia, total nitrogen, chemical oxygen demand analysis)	used known standards
ORP meter HI 98120, salinity meter YSI 30	factory calibrated, checked with standard solution
Dissolved oxygen meter YSI Model 57	air calibration
Microtox	$ZnSO_4$ and phenol solutions used as reference toxicants

Toxicity analyses were conducted in duplicate for each water sample. Standards were run together with the samples for nutrient and toxicity analyses to confirm the instrument performance, and methods blanks were used (Appendix C). The observed nutrient values were reasonably close to the standard values. For phenol standards, the toxicity responses were generally constant with bacteria exposure time during each individual experiment. For the majority of the samples, toxicity associated with the ZnSO4standardsincreased with bacteria exposure time. In some cases, there was a change in the sensitivity of the bacteria that can be explained by change in Microtox reagent, as also reported by Morquecho (2005).

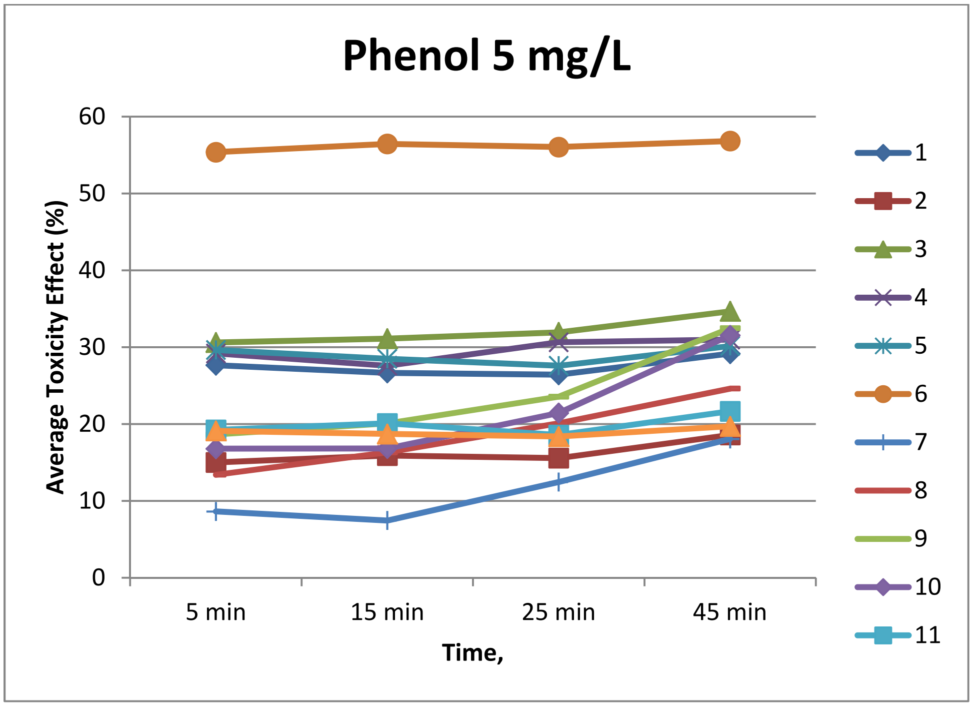


Figure C-21. Average toxicity effect of 5 mg/L of phenol. Controlled pH conditions. (Each point is an average of 2 replicates.)

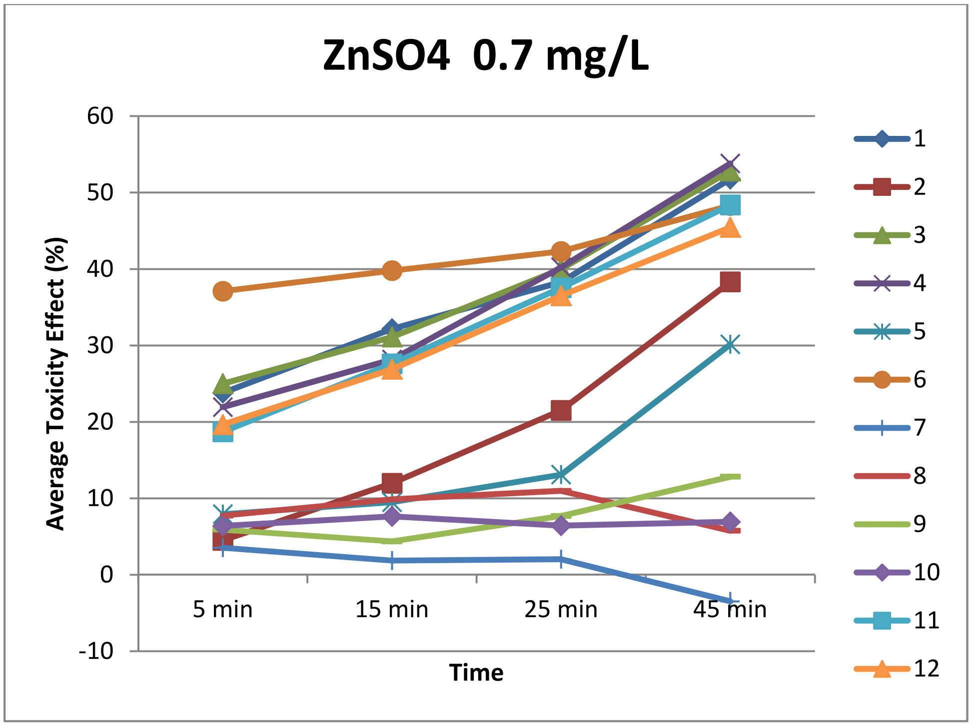


Figure C-22. Average toxicity effect of 0.7 mg/L of $ZnSO_4$. Controlled pH conditions. (Each point is an average of 2 replicates.)

Table C-3. Toxicity effect of phenol on Microtox acute test bacteria with each batch of the water samples at 15 min. Controlled pH tests. Controlled pH tests

Analysis #	Phenol Conc., (mg/L)	Average Toxicity Effect, %
1	5	26.66
2	5	15.91
3	5	31.11
4	5	27.59
5	5	28.48
6	5	56.45
7	5	7.44
8	5	16.31
9	5	20.09
10	5	16.82
11	5	20.08
12	5	18.95
Average		23.82
St. Dev.		12.25
COV		0.514

Table C-4. Toxicity effect of $ZnSO_4$ on Microtox acute test bacteria with each batch of the water samples at 15 min. Controlled pH tests

Analysis #	$ZnSO_4$, (mg/L)	Average Toxicity Effect, %
1	0.7	32.17
2	0.7	11.97
3	0.7	31.11
4	0.7	28.17
5	0.7	9.50
6	0.7	39.79
7	0.7	1.86
8	0.7	9.88
9	0.7	4.37
10	0.7	7.65
11	0.7	27.61
12	0.7	26.89
Average		19.24
St. Dev.		12.90
COV		0.671

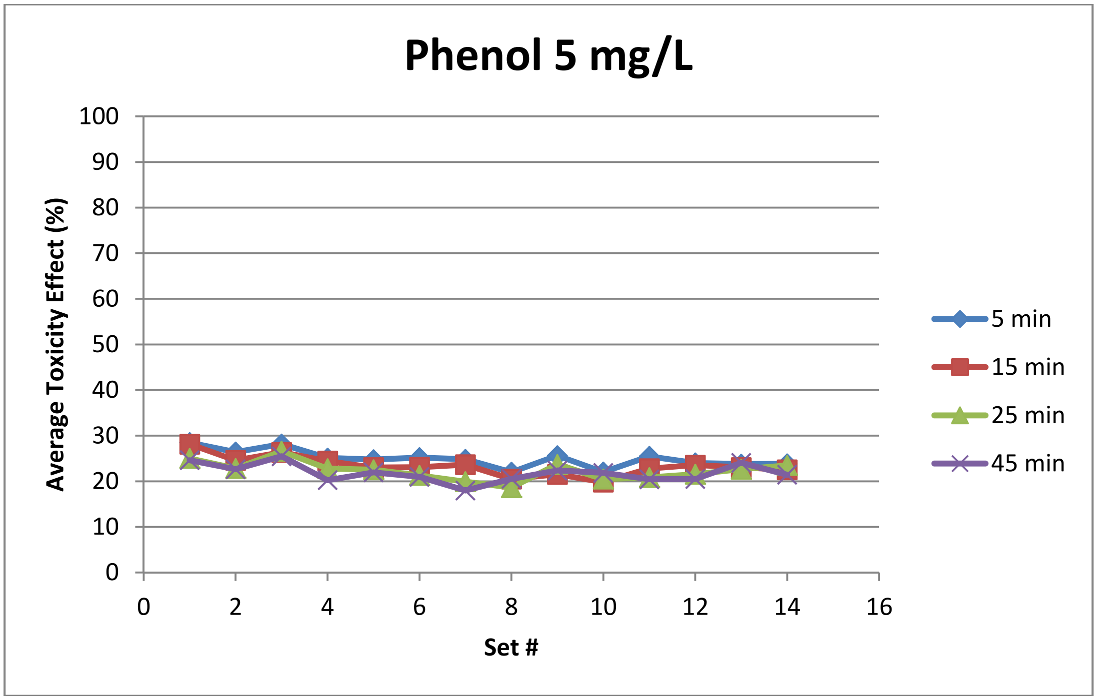


Figure C-23. Average toxicity effect of 5 mg/L of phenol. Natural pH conditions. (Each point is an average of 3 replicates.)

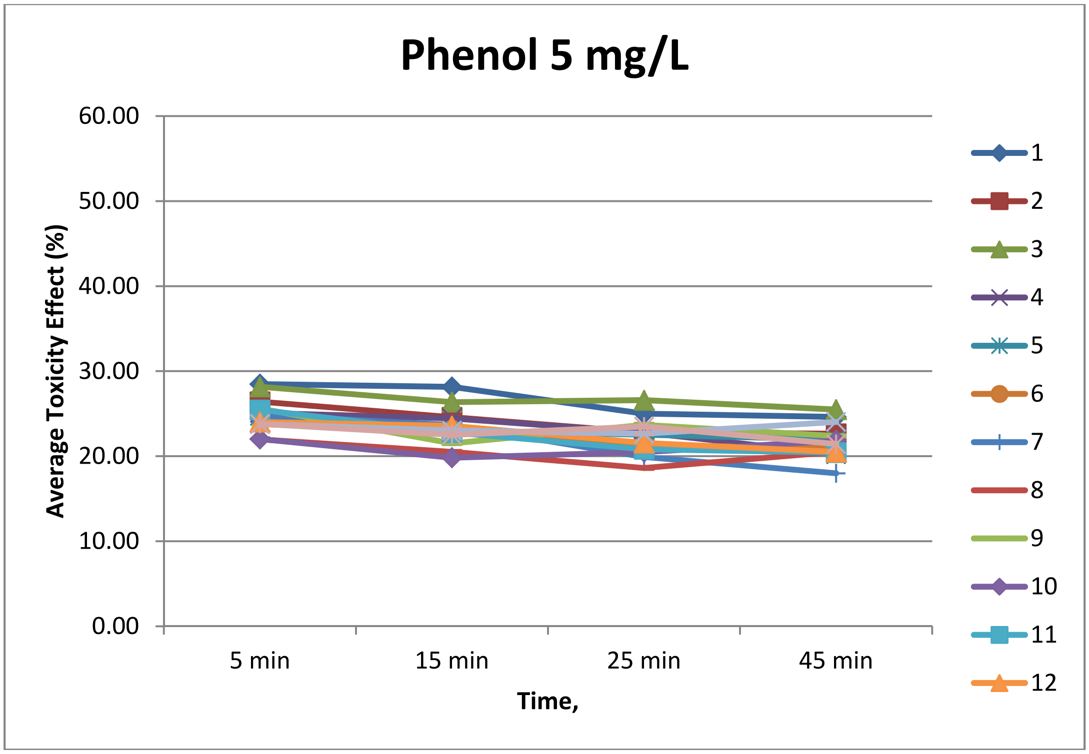


Figure C-24. Average toxicity effect of 5 mg/L of phenol. Natural pH Conditions. (Each point is an average of 3 replicates.)

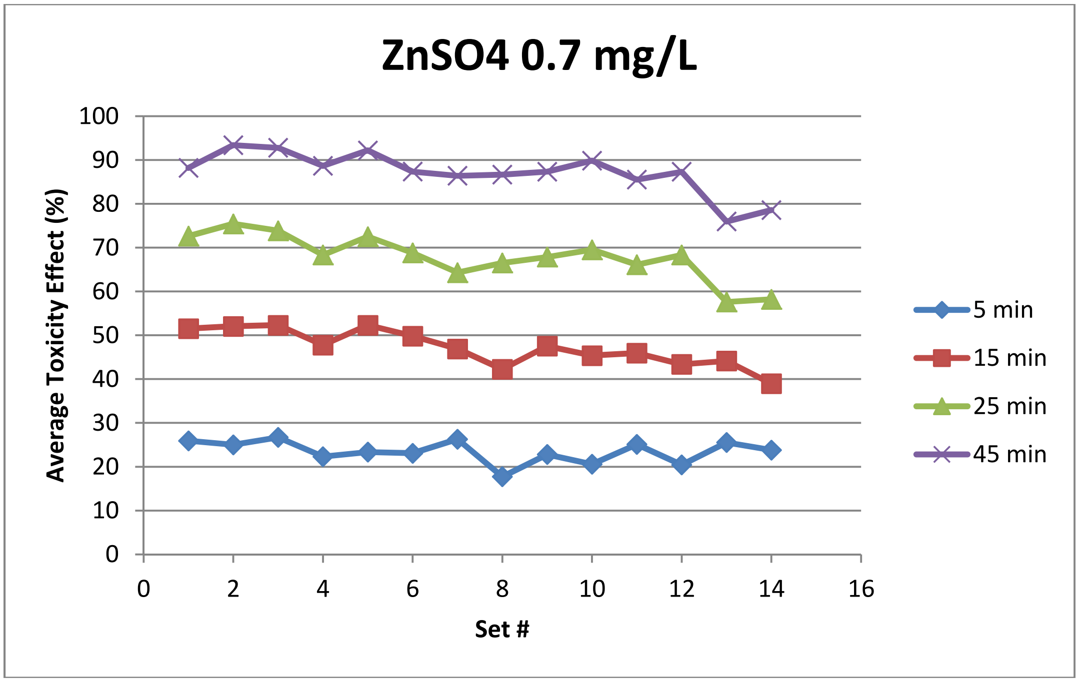


Figure C-25. Average toxicity effect of 0.7 mg/L of $ZnSO_4$. Controlled pH conditions. (Each point is an average of 3 replicates.)

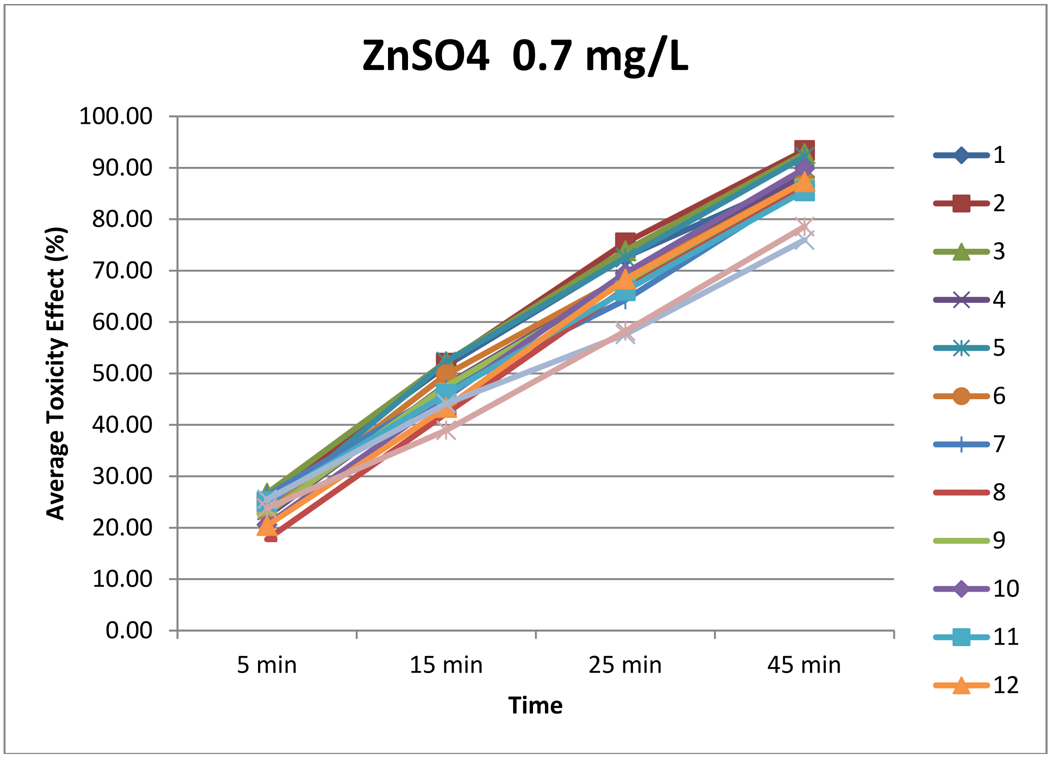


Figure C-26. Average toxicity effect of 0.7 mg/L of $ZnSO_4$. Natural pH conditions. (Each point is an average of 3 replicates.)

Table C-5. Toxicity effect of phenol on Microtox acute test bacteria with each batch of the water samples at 15 min. Natural pH tests

Analysis #	Phenol Conc., (mg/L)	Average Toxicity Effect, %
1	5	28.14
2	5	24.59
3	5	26.36
4	5	24.44
5	5	23.01
6	5	23.08
7	5	23.64
8	5	20.50
9	5	21.51
10	5	19.82
11	5	22.78
12	5	23.55
13		23.02
14		22.51
Average		23.35
St. Dev.		2.15
COV		0.092

Table C-6. Toxicity effect of $ZnSO_4$ on Microtox acute test bacteria with each batch of the water samples at 15 min. Natural pH tests

Analysis #	$ZnSO_4$, (mg/L)	Average Toxicity Effect, %
1	0.7	51.52
2	0.7	52.05
3	0.7	52.30
4	0.7	47.78
5	0.7	52.30
6	0.7	49.82
7	0.7	46.90
8	0.7	42.26
9	0.7	47.55
10	0.7	45.37
11	0.7	45.95
12	0.7	43.39
Average		44.15
St. Dev.		38.96
COV		47.16

pH Trends in Buffered Stormwater Tests

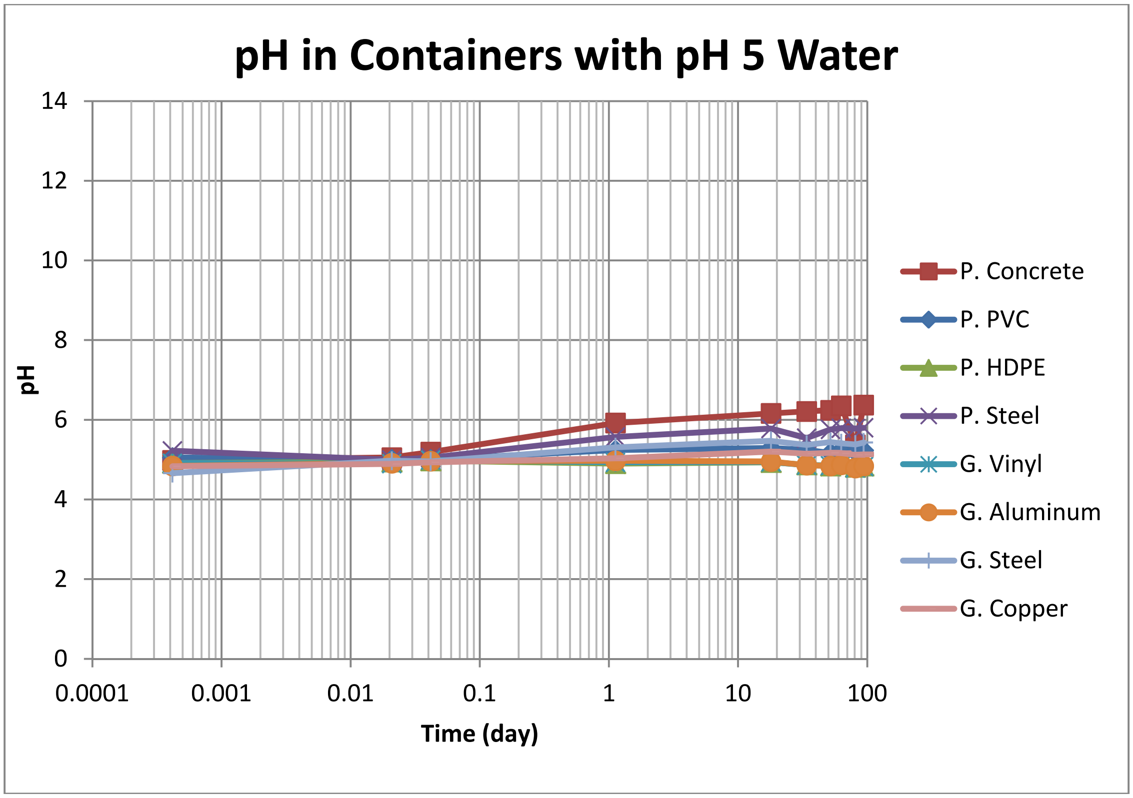


Figure C-27. pH measurements in the containers with pH 5 water.

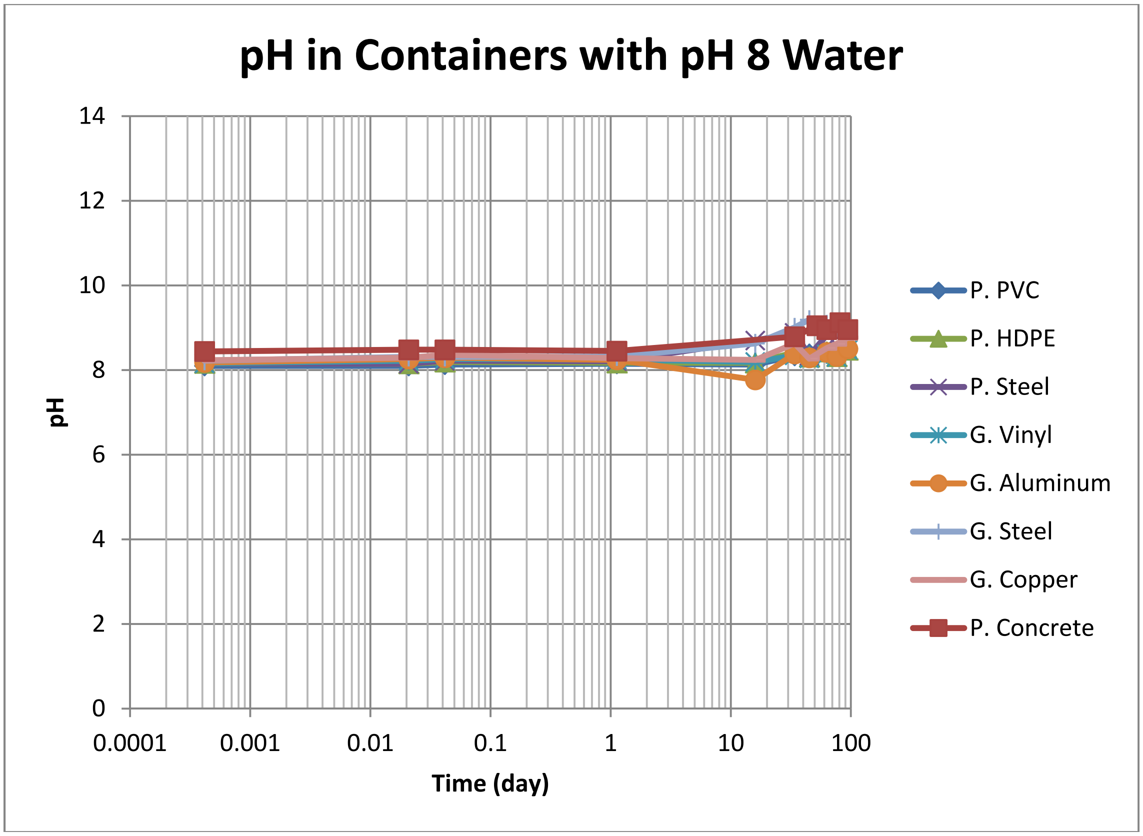


Figure C-28. pH measurements in the containers with pH 8 water.

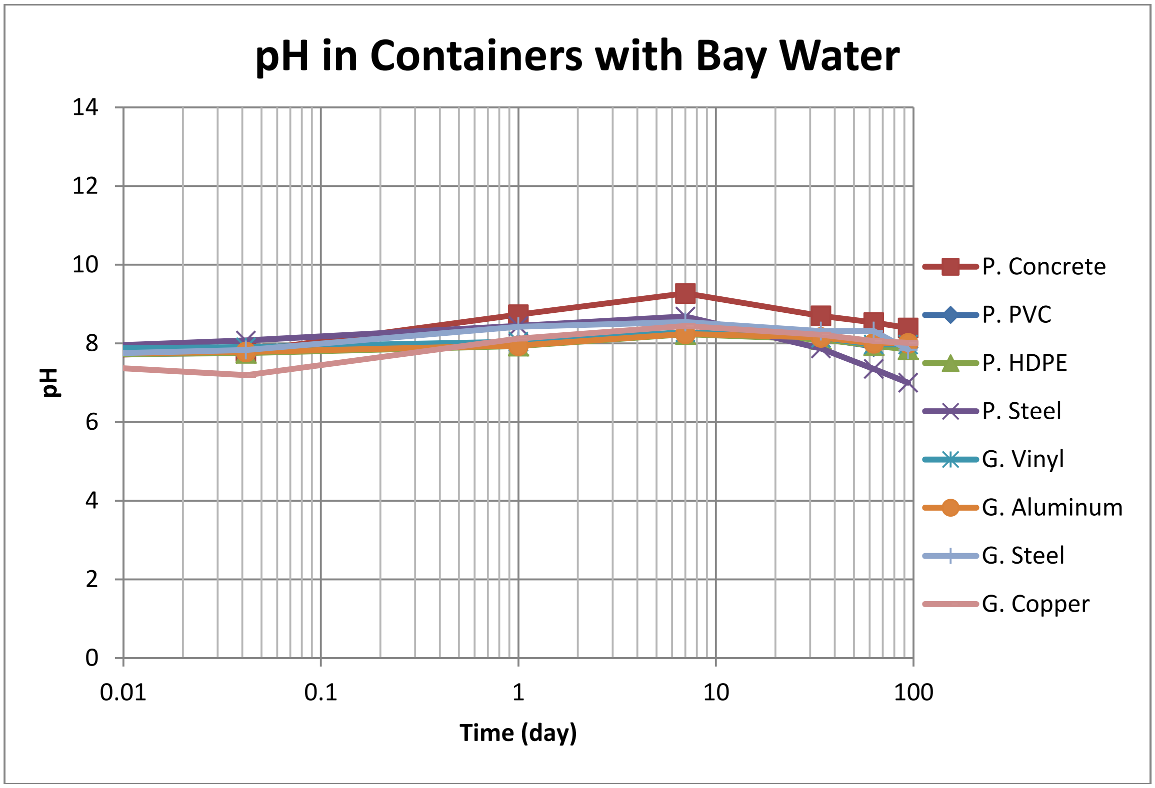


Figure C-29. pH measurements in the containers with bay water.

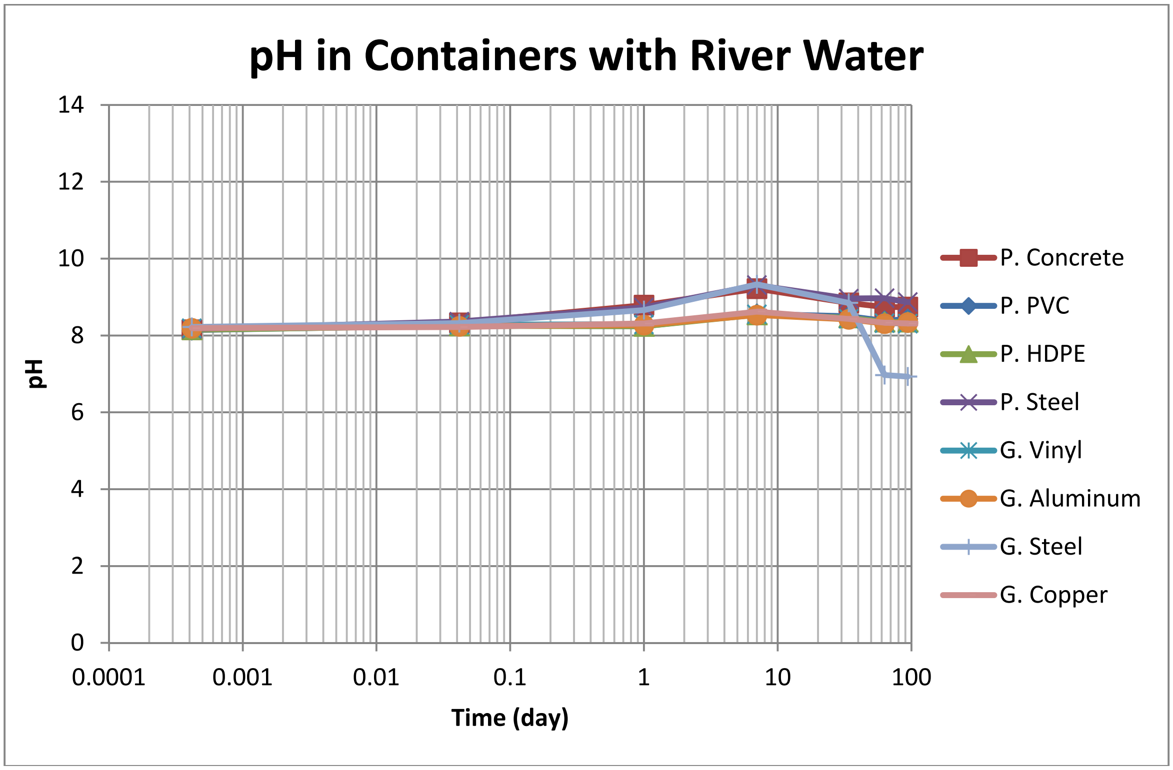


Figure C-30. pH measurements in the containers with river water.

Table C-7. pH in the containers with pH 5 water

	pH for Containers with pH 5							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	4.98	5.05	4.91	5.22	4.91	4.84	4.66	4.83
0.5	5.05	5.00	4.94	4.99	4.90	4.91	4.97	4.89
1	5.19	5.00	4.97	5.05	4.99	4.96	4.95	4.93
27	5.92	5.24	4.90	5.57	4.93	4.97	5.31	5.03
816	6.21	5.24	4.87	5.54	4.86	4.86	5.37	5.15
1512	6.35	5.24	4.89	5.79	4.86	4.87	5.41	5.16
2256	6.37	5.23	4.84	5.8	4.83	4.84	5.43	5.13

Table C-8. pH in the containers with pH 8 water

	pH for Containers with pH 8							
Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	8.44	8.10	8.16	8.16	8.16	8.18	8.22	8.23
0.5	8.48	8.10	8.15	8.15	8.22	8.26	8.31	8.29
1	8.48	8.13	8.19	8.22	8.26	8.29	8.31	8.36
27	8.45	8.15	8.17	8.21	8.25	8.24	8.32	8.28
816	8.79	8.34	8.42	8.88	8.35	8.38	9.01	8.63
1512	8.96	8.42	8.43	8.83	8.37	8.42	9.08	8.52
2256	8.96	8.50	8.47	8.90	8.48	8.50	9.07	8.76

Table C-9. pH in the containers with bay water

	pH for Containers with Bay Water							
Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	7.54	7.64	7.67	7.69	7.81	7.67	7.58	7.75
1	7.79	7.76	7.75	8.07	7.90	7.78	7.83	7.19
27	8.73	7.97	7.93	8.44	8.04	7.94	8.42	8.12
168	9.27	8.26	8.23	8.68	8.28	8.24	8.54	8.44
816	8.70	8.12	8.10	7.87	8.14	8.15	8.31	8.22
1512	8.53	7.92	7.94	7.35	7.97	8.00	8.31	8.06
2256	8.39	7.90	7.84	7.00	7.97	8.00	7.84	8.01

Table C-10. pH in the containers with river water

	pH for Containers with River Water							
Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	8.15	8.14	8.15	8.17	8.19	8.19	8.22	8.19
1	8.33	8.26	8.25	8.36	8.28	8.24	8.32	8.22
27	8.79	8.24	8.24	8.73	8.29	8.27	8.66	8.31
168	9.22	8.56	8.54	9.31	8.55	8.53	9.33	8.62
816	8.85	8.50	8.46	8.96	8.44	8.42	8.85	8.43
1512	8.74	8.38	8.35	8.97	8.32	8.31	6.97	8.33
2256	8.74	8.43	8.35	8.87	8.31	8.34	6.93	8.31

Conductivity Trends in Buffered Stormwater Tests

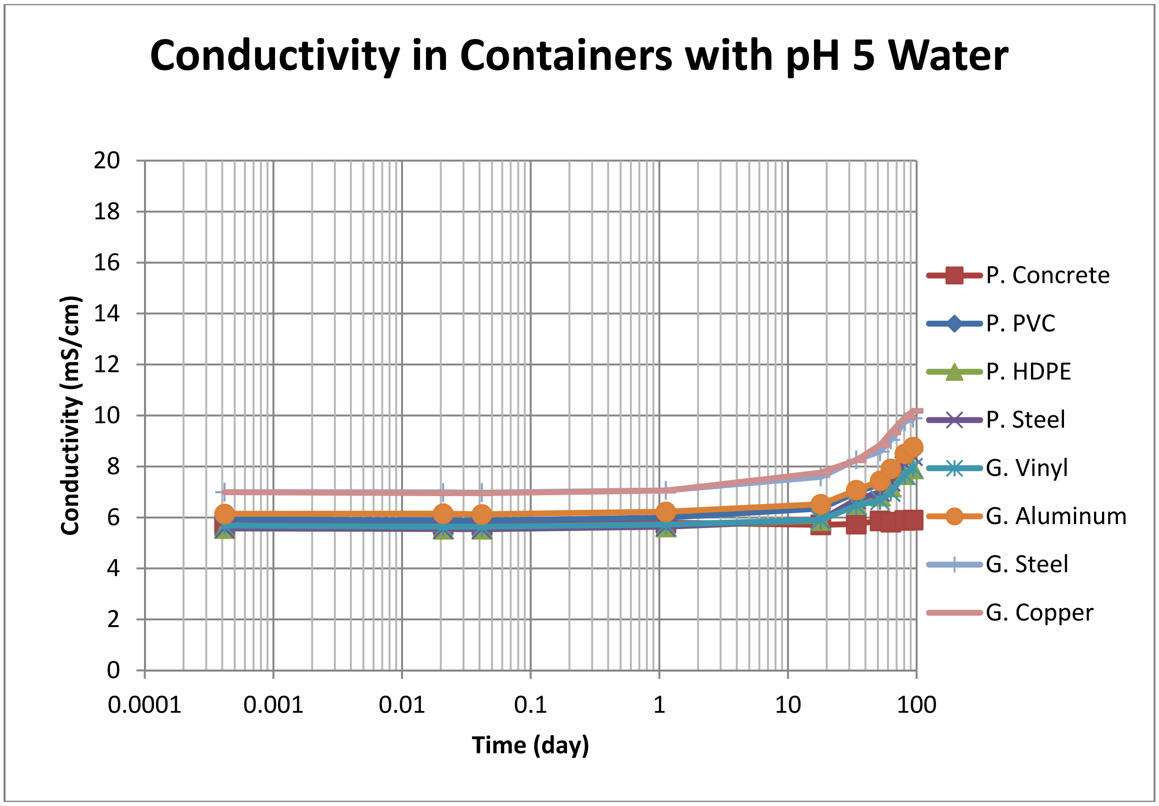


Figure C-31. Conductivity measurements in the containers with pH 5 water.

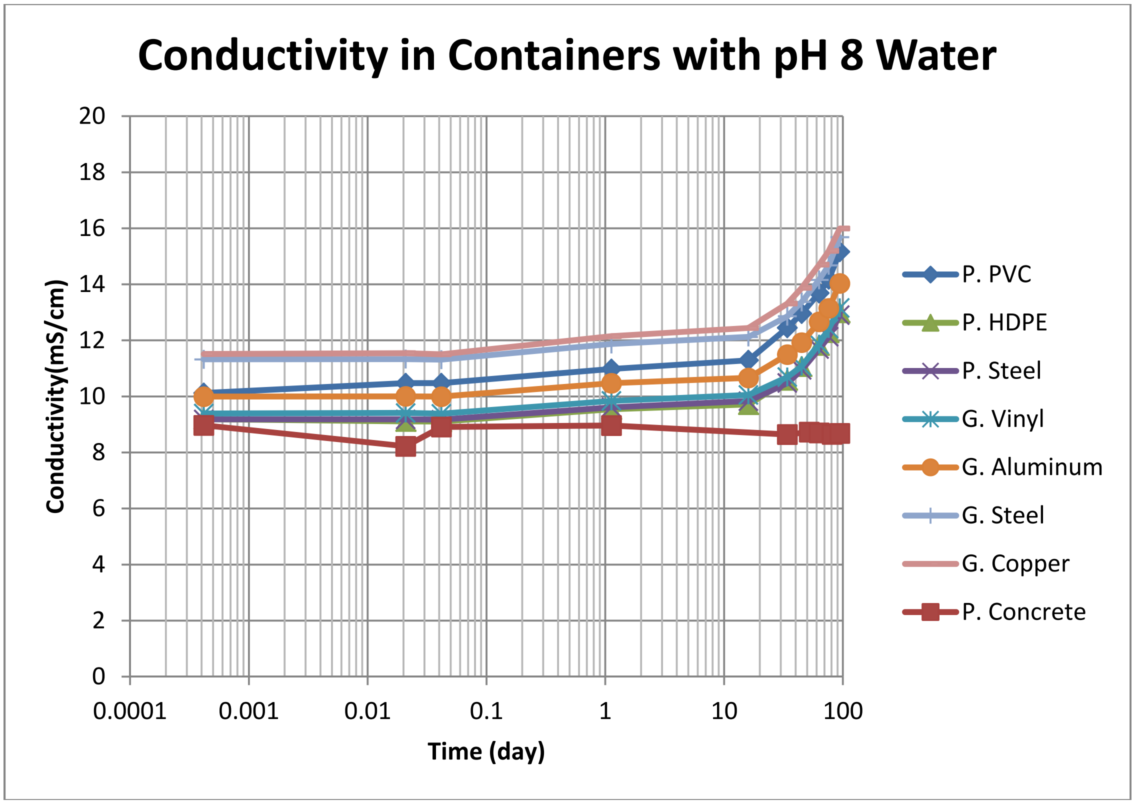


Figure C-32. Conductivity measurements in the containers with pH 8 water.

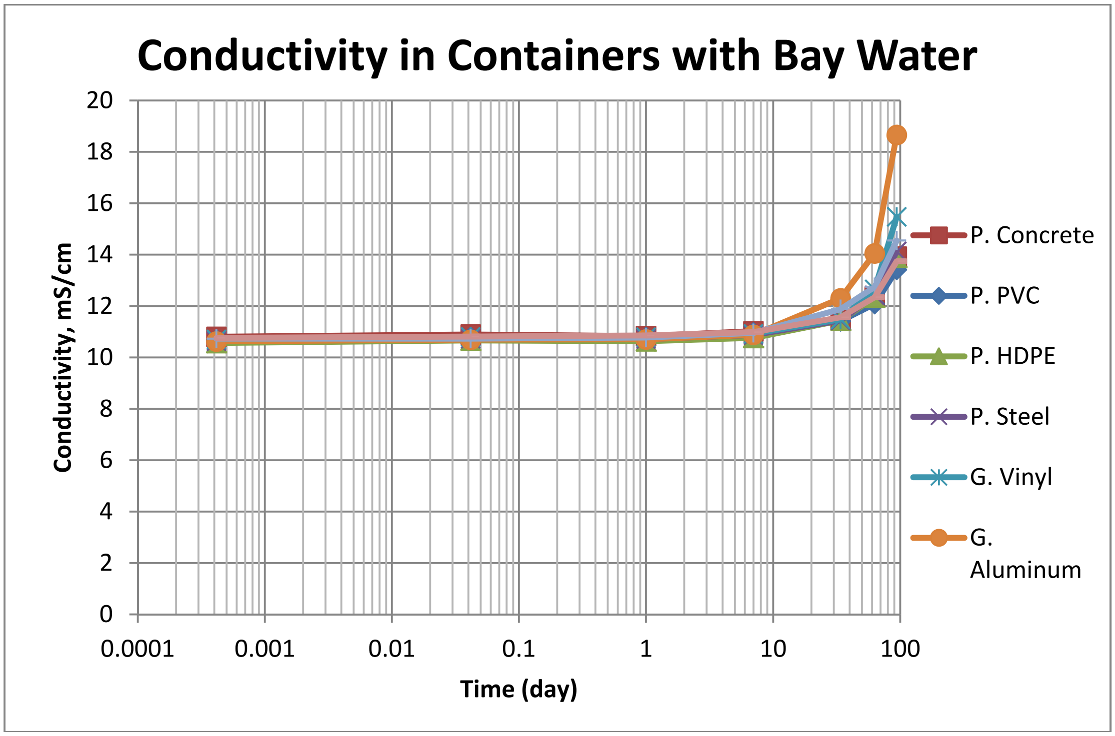


Figure C-33. Conductivity measurements in the containers with bay water.

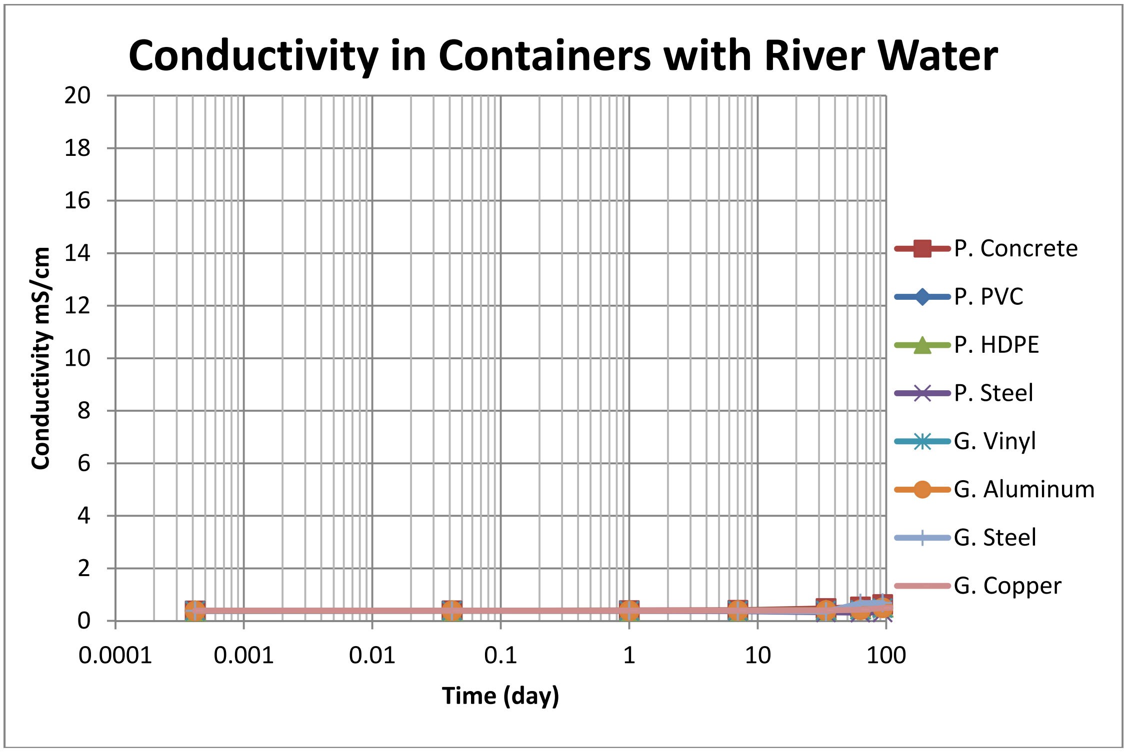


Figure C-34. Conductivity measurements in the containers with river water.

Table C-11. Conductivity in the containers with pH 5 water

	Conductivity for Containers with pH 5, mS/cm							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	5.69	5.92	5.57	5.57	5.68	6.14	6.99	6.99
0.5	5.73	5.87	5.54	5.55	5.63	6.15	6.98	6.95
1	5.71	5.87	5.54	5.54	5.63	6.12	6.97	6.95
27	5.79	5.99	5.63	5.64	5.72	6.22	7.06	7.05
816	5.74	6.99	6.50	6.70	6.47	7.07	8.26	8.24
1512	5.82	7.73	7.20	7.40	6.99	7.91	9.04	9.33
2256	5.90	8.63	7.91	8.40	7.95	8.76	9.89	10.18

Table C-12. Conductivity in the containers with pH 8 water

	Conductivity for Containers with pH 8, mS/cm							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	8.97	10.12	9.19	9.18	9.39	9.99	11.32	11.51
0.5	8.22	10.47	9.11	9.18	9.41	10.00	11.33	11.54
1	8.91	10.47	9.10	9.17	9.38	9.99	11.31	11.50
27	8.96	10.98	9.54	9.61	9.84	10.47	11.87	12.15
816	8.64	12.45	10.58	10.48	10.69	11.49	12.86	13.31
1512	8.70	13.69	11.82	11.69	11.86	12.66	14.16	14.70
2256	8.68	15.16	12.99	12.90	13.16	14.03	15.68	15.99

Table C-13. Conductivity in the containers with bay water

	Conductivity for Containers with Bay Water, mS/cm							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	10.8	10.69	10.56	10.63	10.70	10.62	10.73	10.76
0.5	10.89	10.79	10.66	10.73	10.80	10.69	10.73	10.81
1	10.83	10.78	10.63	10.71	10.79	10.70	10.77	10.85
27	11.02	10.96	10.76	10.87	10.92	10.88	10.95	10.98
816	11.48	11.41	11.44	11.44	11.48	12.30	11.88	11.56
1512	12.34	12.08	12.33	12.42	12.65	14.05	12.74	12.34
2256	13.92	13.41	13.88	14.13	15.47	18.66	14.55	13.74

Table C-14. Conductivity in the containers with river water

	Conductivity for Containers with River Water, mS/cm							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	0.381	0.383	0.383	0.382	0.382	0.383	0.382	0.384
0.5	0.388	0.385	0.386	0.385	0.385	0.386	0.384	0.386
1	0.395	0.387	0.387	0.382	0.386	0.388	0.384	0.386
27	0.405	0.393	0.392	0.370	0.390	0.393	0.378	0.389
816	0.472	0.408	0.409	0.323	0.396	0.401	0.349	0.397
1512	0.533	0.449	0.457	0.313	0.418	0.427	0.673	0.423
2256	0.628	0.582	0.522	0.321	0.485	0.498	0.685	0.492

Nutrient and Toxicity Standard Analyses for Metal Release Experiments

Table C-15. Ammonia nitrogen analysis with the standards

Nitrogen Ammonia Standard, mg/L as N	Observed Value, mg/L as N
20	20
20	19
2	2
24	22
2	3
2	2.15
1.21	1.31
1.21	0.83
1.21	1.45
2.42	2.52
1.21	1.16
2.42	2.44

Table C-16. Total nitrogen analyses with the standards

Nitrogen Ammonia Standard, mg/L as N	Observed Value, mg/L as N
17	17
17	16
2	2
20	18
20	20
2	2
2	3
10	9
10	10
10	10
3	3
1	0

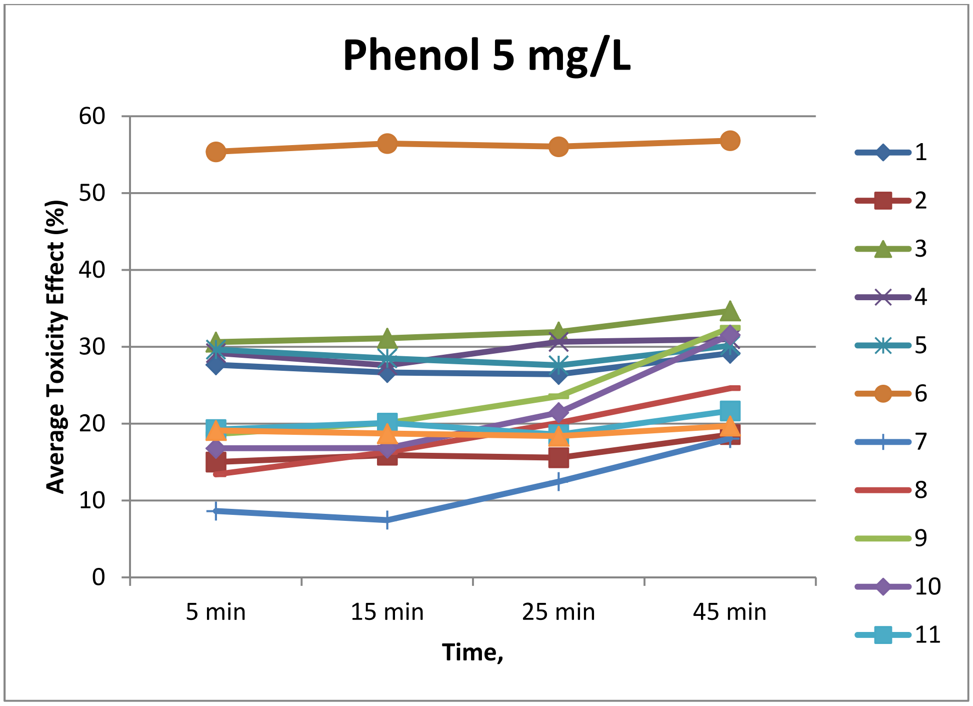


Figure C-35. Average toxicity effect of 5 mg/L of phenol. Controlled pH conditions. (Each point is an average of 2 replicates.)

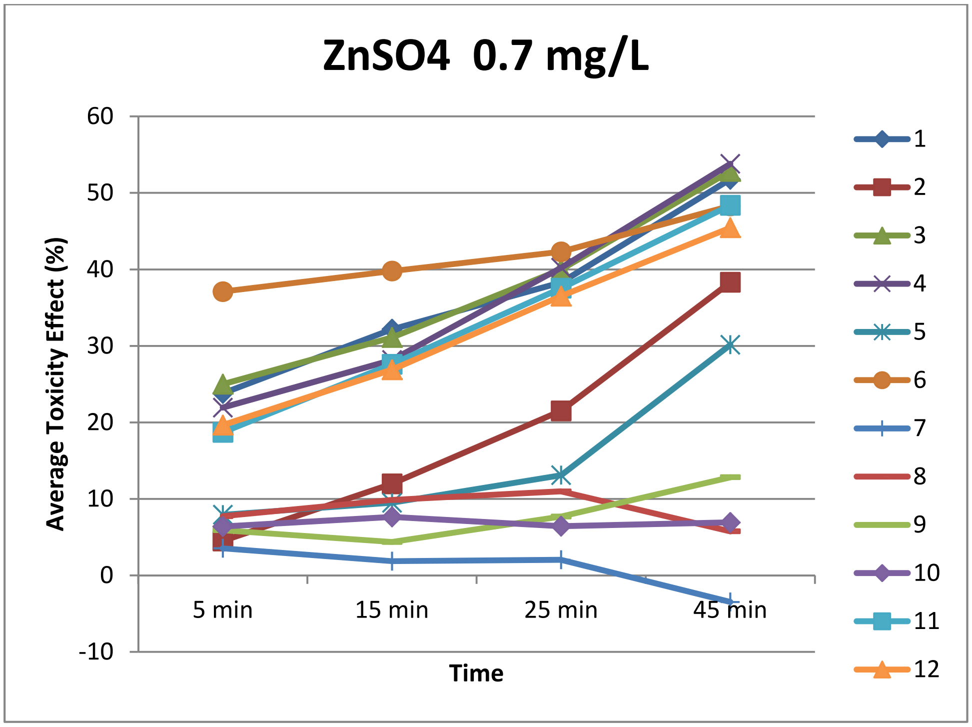


Figure C-36. Average toxicity effect of 0.7 mg/L of $ZnSO_4$. Controlled pH conditions. (Each point is an average of 2 replicates.)

Heavy Metal and Major Ion Standard Analyses for Metal Release Experiments

Table C-17.QA/QC of Stillbrook environmental lab analysis. Containers with pH 5 waters

Batch	Time, hr	Analyte	Assayed	Range	Units	Lab Invoice
1	0	Lead	54.0	45.0-55.0	µg/L	28997
2	0.5	Lead	54.0	45.0-55.0	µg/L	28997
3	1	Lead	54.0	45.0-55.0	µg/L	28998
4	27	Lead	54.0	45.0-55.0	µg/L	28998
5	816	Lead	50.3	45.0-55.0	µg/L	29153
6	1512	Lead	52.2	45.0-55.0	µg/L	29207
7	2256	Lead	49.8	45.0-55.0	µg/L	29280
8	2976	Iron	339.0	314-370	µg/L	29322
9	solid shavings	Lead	49.5	45.0-55.0	µg/L	29452
10	2976*					29323
11	2976*					29324

* not available from commercial lab

Table C-18. QA/QC of Stillbrook environmental lab analysis. Containers with pH 8 waters

Batch	Time, hr	Analyte	Assayed	Range	Units	Lab Invoice
1	0	Lead	54.0	45.0-55.0	µg/L	28997
2	0.5	Lead	54.0	45.0-55.0	µg/L	28997
3	1	Lead	54.0	45.0-55.0	µg/L	28998
4	27	Lead	54.0	45.0-55.0	µg/L	28998
5	816	Lead	52.2	45.0-55.0	µg/L	29153
6	1512	Lead	49.8	45.0-55.0	µg/L	29207
7	2256	Lead	49.6	45.0-55.0	µg/L	29280
8	2544	Iron	339	314-370	µg/L	29322
9	2544*					29323
10	2544*					29324

* not available from commercial lab

Table C-19. QA/QC of Stillbrook environmental lab analysis. Containers with bay waters

Batch	Time, hr	Analyte	Assayed	Range	Units	Lab Invoice
1	0	Lead	50.3	45.0-55.0	µg/L	30605
2	0	Iron	197	180-220	µg/L	30772
3	1	Lead	49.2	45.0-55.0	µg/L	30608
4	27	Lead	49.2	45.0-55.0	µg/L	30606
5	168	Lead	49.2	45.0-55.0	µg/L	30607
6	816	Lead	51.9	45.0-55.0	µg/L	30694
7	1512	Lead	51.4	45.0-55.0	µg/L	30773
8	2256	Lead	52.8	45.0-55.0	µg/L	30935
9	2256	Iron	202	180-220	µg/L	30936
10	0	Calcium	75.4	70.1-81.7	mg/L	30610
11	2256	Calcium	73.3	70.2-81.7	mg/L	30934
12	source water	Manganese	45.8	45.0-55.0	µg/L	31134
13	source water	Chloride	56.5	49.7-60.1	mg/L	30937
14	source water	Sulfate	48.4	37.7-51.4	mg/L	30937

Table C-20. QA/QC of Stillbrook environmental lab analysis. Containers with river waters

Batch	Time, hr	Analyte	Assayed	Range	Units	Lab Invoice
1	0	Lead	50.3	45.0-55.0	µg/L	30605
2	0	Iron	197	180-220	µg/L	30772
3	1	Lead	49.2	45.0-55.0	µg/L	30608
4	27	Lead	49.2	45.0-55.0	µg/L	30606
5	168	Lead	49.2	45.0-55.0	µg/L	30607
6	816	Lead	51.9	45.0-55.0	µg/L	30694
7	1512	Lead	51.4	45.0-55.0	µg/L	30773
8	2256	Lead	52.8	45.0-55.0	µg/L	30935
9	2256	Iron	202	180-220	µg/L	30936
10	0	Calcium	75.4	70.1-81.7	mg/L	30610
11	2256	Calcium	73.3	70.2-81.7	mg/L	30934
12	source water	Manganese	45.8	45.0-55.0	µg/L	31136
13	source water	Chloride	56.5	49.7-60.1	mg/L	30937
14	source water	Sulfate	48.4	37.7-51.4	mg/L	30937

Power Analyses for Metal Release Experiments

Retrospective sensitivity analyses for two full 2^3 factorial experiments were performed to determine what differences could be detected with acceptable power and confidence given the available sample sizes. An assumption was made that the standard deviation of the sample was equal to the standard deviation of the population. Minitab 16 software was used. The analyses were conducted at power 80% and at two alpha levels of 0.05 and 0.1 for copper, zinc, lead, and toxicities (Table C-21). The sample sizes for the full 2^3 factorial experiments were used. Figures C-37 and C-38 are examples of power curves for copper releases under controlled pH conditions at different alpha levels (0.05 and 0.1). The retrospective sensitivity analyses showed that for copper releases under these controlled pH conditions, the full 2^3 factorial analysis with a sample size of 2 can detect difference among mean copper releases of 700 mg/m^2 at an alpha of 0.05; increasing the alpha to 0.1 will allow detecting a difference of 350 mg/m^2. With the sample size of 21, differences of 50 and 43 mg/m^2 for alpha levels of 0.05 and 0.1 respectively could be detected. The increase in standard deviation in copper releases under natural pH conditions compared to the buffered pH tests, increased the difference that could be detected (230 and 200 mg/m^2 for alpha levels of 0.05 and 0.1 respectively). Similar data are shown for zinc releases.

Significant factors and their interactions from the full 2^3 factorial analyses were used to combine the data for metal releases and toxicities into significant groups in order to identify critical combinations of materials, exposure times, and pH (during the first test series) and conductivity (during the second test series) and interaction of these factors. Retrospective sensitivity analyses for two full 2^3 factorial experiments were conducted to determine how small of a difference could be detected with acceptable power and confidence levels given the existing sample sizes for the different sample groupings.

Table C-21. Sensitivity analyses for full 2^3 Factorial experiments. (Power 0.8)

Constituent and Conditions	St. Dev.	Sample Size	Difference (mg/m^2 for metals, % for toxicity)	
			α = 0.05	α = 0.1
Cu Releases (mg/m^2). Buffered pH Waters	61.47	2	709.972	356.084
		3	200.641	141.213
		14	49.800	43.154
		21	39.510	34.541
Cu Releases (mg/m^2). Natural pH Waters	364.2	3	1188.76	836.667
		7	463.47	388.468
		21	234.09	204.653
Zn Releases (mg/m^2). Buffered pH Waters	634.5	4	1350.18	1046.74
		6	910.22	752.37
		12	563.85	486.27
		18	444.61	387.60
Zn Releases (mg/m^2). Natural pH Waters	1498	2	17301.7	8677.62
		6	2148.9	1776.29
		18	1049.7	915.08
Pb Releases (mg/m^2). Buffered pH Waters	4.678	4	9.95455	7.71736
		6	6.71080	5.54704
		12	4.15712	3.58516
		18	3.27798	2.85764
Pb Releases (mg/m^2). Natural pH Waters	0.3243	2	3.74563	1.87861
		6	0.46522	0.38455
		18	0.22724	0.19810
Toxicity (%) at 15 min. Buffered pH Waters	53.57	12	47.6052	41.0553
		18	37.5377	32.7242
		20	35.3799	30.9047
		30	28.3512	24.9065
Toxicity (%) at 45 min. Buffered pH Waters	61.16	12	54.3501	46.8722
		18	42.8562	37.3606
		20	40.3926	35.2834
		30	32.3681	28.4353
Toxicity (%) at 15 min. Natural pH Waters	51.25	6	73.5204	60.7708
		10	51.0451	43.7069
		18	35.9120	31.3069
		30	27.1233	23.8278
Toxicity (%) at 45 min. Natural pH Waters	59.17	6	84.8820	70.1621
		10	58.9334	50.4612
		18	41.4618	36.1450
		30	31.3149	27.5101

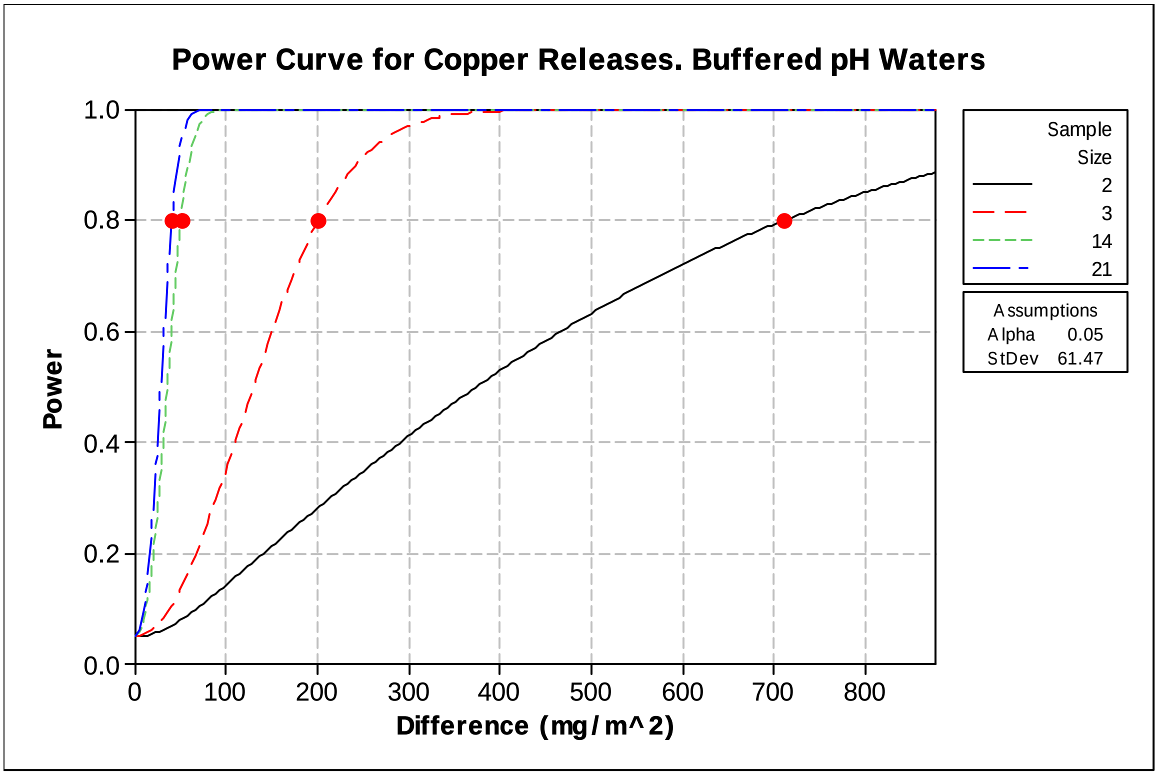


Figure C-37. Power curve for copper releases. Buffered pH waters. (α = 0.05).

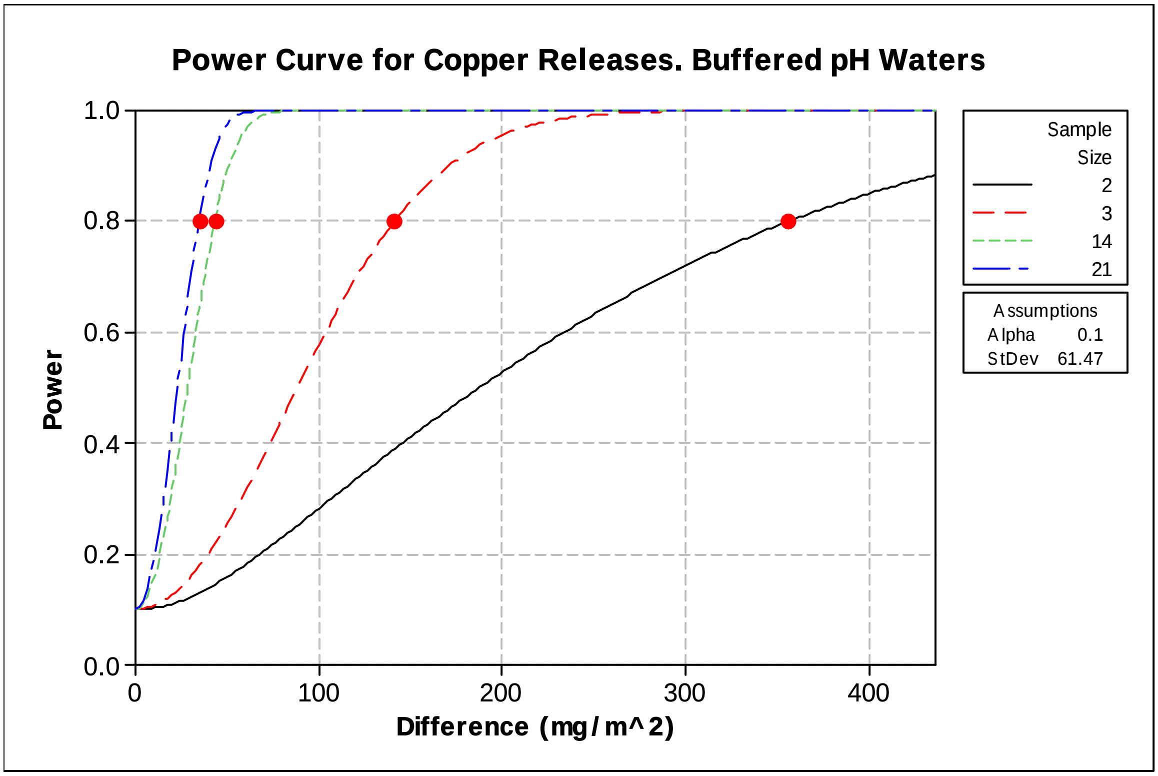


Figure C-38. Power curve for copper releases. Buffered pH waters. (α = 0.1).

Appendix D: Heavy Metal Leaching Test Data

During the natural pH tests, the samples were analyzed at time zero (natural bay or river water without pipe samples), 1 hour, 27 hours, 1week, 1 month, 2 months, and 3 months for the total metal concentrations of lead, copper, and zinc. During the controlled pH tests with stormwater, the 1 week samples were not obtained. The samples were also analyzed for the total aluminum and iron concentrations at time zero (no sample) and for the total aluminum, iron, and the filterable iron concentrations after 3 months. The following tables show the measured concentrations in the test containers for these time steps, along with the calculated unit area losses.

Lead Leaching Test Data

The concentration values that were above the detection limits are highlighted in green.

Table D-1. Total lead (mg/L), containers at pH 5

Time	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0 (No sample)	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
30 min	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
1 hr	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
1 day	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
1 month	< 0.005	< 0.005	< 0.005	0.183	< 0.005	< 0.005	0.02	< 0.005
2 months	< 0.005	< 0.005	< 0.005	0.268	< 0.005	< 0.005	0.028	< 0.005
3 months	< 0.005	< 0.005	< 0.005	0.247	< 0.005	< 0.005	0.037	< 0.005

Table D-2. Total lead (mg/L), containers at pH 8

Time	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0 (No sample)	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
30 min	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
1 hr	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
1 day	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.008	< 0.005
1 month	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.097	< 0.005
2 months	< 0.005	< 0.005	< 0.005	0.710	< 0.005	< 0.005	0.107	< 0.005
3 months	< 0.005	< 0.005	< 0.005	0.628	< 0.005	< 0.005	0.100	< 0.005

Table D-3 Total lead (mg/L), containers with bay water

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
30 min	< 0.005	< 0.005	< 0.005	0.009	< 0.005	< 0.005	< 0.005	< 0.005
1 hr	< 0.005	< 0.005	< 0.005	0.012	< 0.005	< 0.005	0.005	< 0.005
1 week	< 0.005	< 0.005	< 0.005	0.008	< 0.005	< 0.005	< 0.005	< 0.005
1 month	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.005	< 0.005
2 months	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.007	< 0.005
3 months	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005

Table D-4. Total lead (mg/L), containers with river water

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
30 min	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
1 hr	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
1 week	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.006	< 0.005
1 month	< 0.005	< 0.005	< 0.005	0.001	< 0.005	< 0.005	0.011	< 0.005
2 months	< 0.005	< 0.005	< 0.005	0.019	< 0.005	< 0.005	0.017	< 0.005
3 months	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.058	< 0.005

Table D-5. Total lead (mg/m^2), containers at pH 5

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	<0.8	<0.1	<0. 1	<0. 2	<0.5	<0.5	<0.2	<0.4
30 min	<0.8	<0.1	<0. 1	<0. 2	<0.5	<0.5	<0.2	<0.4
1 hr	<0.8	<0.1	<0. 1	<0. 2	<0.5	<0.5	<0.2	<0.4
1 day	<0.8	<0.1	<0. 1	<0. 2	<0.5	<0.5	<0.2	<0.4
1 month	<0.8	<0.1	<0. 1	7.96	<0.5	<0.5	0.97	<0.4
2 months	<0.8	<0.1	<0. 1	11.2	<0.5	<0.5	1.31	<0.4
3 months	<0.8	<0.1	<0. 1	9.98	<0.5	<0.5	1.67	<0.4

Table D-6. Total lead (mg/m^2), containers at pH 8

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	<0.8	<0.2	<0.1	<0.2	<0.5	<0.5	<0.3	<0.4
30 min	<0.8	<0.2	<0.1	<0.2	<0.5	<0.5	<0.3	<0.4
1 hr	<0.8	<0.2	<0.1	<0.2	<0.5	<0.5	<0.3	<0.4
1 day	<0.8	<0.2	<0.1	<0.2	<0.5	<0.5	4.72	<0.4
1 month	<0.8	<0.2	<0.1	<0.2	<0.5	<0.5	5.02	<0.4
2 months	<0.8	<0.2	<0.1	29.8	<0.5	<0.5	4.52	<0.4
3 months	<0.8	<0.2	<0.1	25.4	<0.5	<0.5	4.72	<0.4

Table D-7. Total lead (mg/m^2), containers with bay water

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	<0.7	<0.25	<0.1	<0.2	<0.5	<0.5	<0.25	<0.35
30 min	<0.7	<0.25	<0.1	0.38	<0.5	<0.5	<0.25	<0.35
1 hr	<0.7	<0.25	<0.1	0.50	<0.5	<0.5	0.23	<0.35
1 week	<0.7	<0.25	<0.1	0.33	<0.5	<0.5	<0.25	<0.35
1 month	<0.7	<0.25	<0.1	<0.2	<0.5	<0.5	0.23	<0.35
2 months	<0.7	<0.25	<0.1	<0.2	<0.5	<0.5	0.31	<0.35
3 months	<0.7	<0.25	<0.1	<0.2	<0.5	<0.5	<0.25	<0.35

Table D-8. Total lead (mg/m^2), containers with river water

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	<0.7	<0.25	<0.1	<0.5	<0.5	<0.5	<0.25	<0.35
30 min	<0.7	<0.25	<0.1	<0.5	<0.5	<0.5	<0.25	<0.35
1 hr	<0.7	<0.25	<0.1	<0.5	<0.5	<0.5	<0.25	<0.35
1 week	<0.7	<0.25	<0.1	<0.5	<0.5	<0.5	0.28	<0.35
1 month	<0.7	<0.25	<0.1	0.10	<0.5	<0.5	0.50	<0.35
2 months	<0.7	<0.25	<0.1	0.10	<0.5	<0.5	0.76	<0.35
3 months	<0.7	<0.25	<0.1	<0.5	<0.5	<0.5	2.54	<0.35

Table D-9. Filterable fraction of lead after three months of exposure

Water	Material	Total, mg/L	Filtered, mg/L	% Filterable
pH 5	Concrete Pipe	< 0.005	< 0.005	n/a
	PVC Pipe	< 0.005	< 0.005	n/a
	HDPE Pipe	< 0.005	< 0.005	n/a
	Steel Pipe	0.247	< 0.005	<2.0
	Vinyl Gutter	< 0.005	< 0.005	n/a
	Aluminum Gutter	< 0.005	< 0.005	n/a
	Steel Gutter	0.037	< 0.005	<13.5
	Copper Gutter	< 0.005	< 0.005	n/a
pH 8	Concrete Pipe	< 0.005	< 0.005	n/a
	PVC Pipe	< 0.005	< 0.005	n/a
	HDPE Pipe	< 0.005	< 0.005	n/a
	Steel Pipe	0.628	0.479	76
	Vinyl Gutter	< 0.005	< 0.005	n/a
	Aluminum Gutter	< 0.005	< 0.005	n/a
	Steel Gutter	0.100	0.096	96
	Copper Gutter	< 0.005	< 0.005	n/a

Copper Leaching Test Data

Table D-10. Total copper (mg/L), containers with pH 5

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	< 0.02	0.09	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
30 min	< 0.02	0.10	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.58
1 hr	< 0.02	0.09	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	1.05
1 day	< 0.02	0.08	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	6.82
1 month	< 0.02	0.22	0.02	0.11	0.02	0.03	< 0.02	4.08
2 months	< 0.02	0.19	0.03	< 0.02	0.03	0.03	< 0.02	4.39
3 months	< 0.02	0.23	0.03	< 0.02	0.03	0.03	< 0.02	5.10

Table D-11. Total copper (mg/L), containers with pH 8

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	< 0.02	0.09	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
30 min	< 0.02	0.09	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.03
1 hr	< 0.02	0.08	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.05
1 day	< 0.02	0.08	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.29
1 month	< 0.02	0.15	< 0.02	< 0.02	< 0.02	0.03	0.02	1.84
2 months	< 0.02	0.19	0.06	0.03	0.02	0.03	0.03	2.05
3 months	< 0.02	0.21	0.03	0.03	0.02	0.03	0.03	2.13

Table D-12. Total copper (mg/L), containers with bay water

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
30 min	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.26
1 hr	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	2.11
1 week	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	6.11
1 month	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	5.64
2 months	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	30.3
3 months	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	35.9

Table D-13. Total copper (mg/L), containers with river water

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
30 min	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.07
1 hr	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.60
1 week	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	1.22
1 month	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	2.09
2 months	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	4.10
3 months	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	5.47

Table D-14. Total copper (mg/m^2), containers with pH 5

Exposure Time	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0 (No sample)	<3.5	0.00	<0.5	<1.0	<2.0	<2.0	<1.0	<1.5
30 min	<3.5	0.51	<0.5	<1.0	<2.0	<2.0	<1.0	44
1 hr	<3.5	0.00	<0.5	<1.0	<2.0	<2.0	<1.0	77
1 day	<3.5	-0.48	<0.5	<1.0	<2.0	<2.0	<1.0	483
1 month	<3.5	5.99	0.43	4.79	1.87	2.70	<1.0	280
2 months	<3.5	4.45	0.62	<1.0	2.70	2.60	<1.0	290
3 months	<3.5	5.99	0.60	<1.0	2.60	2.50	<1.0	324

Table D-15. Total copper (mg/m^2), containers with pH 8

Exposure Time	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0 (No sample)	<3.5	0.00	<0.5	<1.0	<2.0	<2.0	<1.0	<1.5
30 min	<3.5	0.00	<0.5	<1.0	<2.0	<2.0	<1.0	2.27
1 hr	<3.5	-0.49	<0.5	<1.0	<2.0	<2.0	<1.0	3.66
1 day	<3.5	-0.48	<0.5	<1.0	<2.0	<2.0	<1.0	21
1 month	<3.5	2.77	<0.5	<1.0	<2.0	2.70	0.97	126
2 months	<3.5	4.45	1.24	1.3	1.80	2.60	1.41	135
3 months	<3.5	5.14	0.60	1.2	1.74	2.50	1.36	135

Table D-16. Total copper (mg/m^2), containers with bay water

Exposure Time	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0 (No sample)	<3.0	<1.0	<0.4	<1.0	<2.0	<2.0	<1.0	<1.5
30 min	<3.0	<1.0	<0.4	<1.0	<2.0	<2.0	<1.0	17
1 hr	<3.0	<1.0	<0.4	<1.0	<2.0	<2.0	<1.0	139
1 week	<3.0	<1.0	<0.4	<1.0	<2.0	<2.0	<1.0	395
1 month	<3.0	<1.0	<0.4	<1.0	<2.0	<2.0	<1.0	359
2 months	<3.0	<1.0	<0.4	<1.0	<2.0	<2.0	<1.0	1895
3 months	<3.0	<1.0	<0.4	<1.0	<2.0	<2.0	<1.0	2207

Table D-17. Total copper (mg/m^2), containers with river water

Exposure Time	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0 (No sample)	<3.0	<1.0	<0.4	<1.0	<2.0	<2.0	<1.0	<1.5
30 min	<3.0	<1.0	<0.4	<1.0	<2.0	<2.0	<1.0	4.7
1 hr	<3.0	<1.0	<0.4	<1.0	<2.0	<2.0	<1.0	39
1 week	<3.0	<1.0	<0.4	<1.0	<2.0	<2.0	<1.0	79
1 month	<3.0	<1.0	<0.4	<1.0	<2.0	<2.0	<1.0	133
2 months	<3.0	<1.0	<0.4	<1.0	<2.0	<2.0	<1.0	256
3 months	<3.0	<1.0	<0.4	<1.0	<2.0	<2.0	<1.0	336

Table D-18. Filterable fraction of copper after three months of exposure

Water	Material	Total, mg/L	Filtered, mg/L	% Filterable
pH 5	Concrete Pipe	< 0.02	< 0.02	n/a
	PVC Pipe	0.23	0.22	96
	HDPE Pipe	0.03	0.03	100
	Steel Pipe	< 0.02	< 0.02	n/a
	Vinyl Gutter	0.03	0.03	100
	Aluminum Gutter	0.03	0.04	133
	Steel Gutter	< 0.02	< 0.02	n/a
	Copper Gutter	5.10	5.10	100
pH 8	Concrete Pipe	< 0.02	< 0.02	n/a
	PVC Pipe	0.21	0.15	71
	HDPE Pipe	0.03	0.03	100
	Steel Pipe	0.03	0.02	67
	Vinyl Gutter	0.02	0.02	100
	Aluminum Gutter	0.03	0.03	100
	Steel Gutter	0.03	0.03	100
	Copper Gutter	2.13	0.36	17

Zinc Leaching Test Data

Table D-19. Total zinc (mg/L), containers at pH 5

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	< 0.02	<0.25	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
30 min	< 0.02	<0.25	< 0.02	1.8	< 0.02	< 0.02	1.33	0.03
1 hr	< 0.02	<0.25	0.02	3.9	< 0.02	< 0.02	2.14	0.03
1 day	< 0.02	<0.25	0.02	10.2	< 0.02	< 0.02	14.2	0.04
1 month	< 0.02	0.36	0.03	8.5	< 0.02	< 0.02	8.5	< 0.02
2 months	< 0.02	0.42	0.05	12.7	0.03	0.03	10.2	0.03
3 months	< 0.02	0.44	0.06	11.7	< 0.02	0.02	14.1	0.13

Table D-20. Total zinc (mg/L), containers at pH 8

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	< 0.02	<0.2	< 0.03	0.02	< 0.02	< 0.02	<0.02	<0.02
30 min	0.02	<0.2	< 0.03	0.07	0.03	0.03	0.10	<0.02
1 hr	< 0.02	<0.2	< 0.03	0.10	0.02	0.02	0.14	<0.02
1 day	< 0.02	<0.2	< 0.03	1.01	< 0.02	0.02	2.1	<0.02
1 month	< 0.02	0.28	< 0.03	16.3	0.03	0.04	27.8	0.03
2 months	0.03	0.34	0.04	24.8	0.04	0.04	89.9	0.03
3 months	0.03	0.68	0.05	84.3	0.04	0.21	9.7	<0.02

Table D-21. Total zinc (mg/L), containers with bay water

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
30 min	< 0.02	< 0.02	< 0.02	1.40	< 0.02	< 0.02	0.48	< 0.02
1 hr	< 0.02	< 0.02	< 0.02	8.40	< 0.02	< 0.02	4.84	0.05
1 week	< 0.02	< 0.02	< 0.02	8.28	< 0.02	< 0.02	4.43	0.03
1 month	< 0.02	< 0.02	< 0.02	18.9	< 0.02	< 0.02	3.95	0.03
2 months	< 0.02	< 0.02	< 0.02	69.5	0.04	0.70	16.6	0.05
3 months	< 0.02	< 0.02	< 0.02	78.6	< 0.02	< 0.02	36.7	< 0.02

Table D-22. Total zinc (mg/L), containers with river water

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	< 0.02	< 0.02	0.02	< 0.02	< 0.02	0.02	0.02	0.02
30 min	< 0.02	< 0.02	< 0.02	0.96	< 0.02	< 0.02	0.27	< 0.02
1 hr	< 0.02	< 0.02	< 0.02	6.06	< 0.02	< 0.02	1.2	0.02
1 week	< 0.02	< 0.02	< 0.02	4.93	< 0.02	< 0.02	5.73	0.02
1 month	< 0.02	< 0.02	0.03	19.9	< 0.02	< 0.02	20.1	0.03
2 months	< 0.02	0.02	0.03	84.1	0.02	0.02	156	0.06
3 months	< 0.02	0.03	0.03	67.8	< 0.02	0.03	190	0.50

Table D-23. Total zinc (mg/m^2), containers at pH 5

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	<3.5	<2.0	<0.5	<1.0	<2.0	<2.0	<1.0	<1.5
30 min	<3.5	<2.0	<0.5	87	<2.0	<2.0	72	2.27
1 hr	<3.5	<2.0	0.46	183	<2.0	<2.0	112	2.20
1 day	<3.5	<2.0	0.44	460	<2.0	<2.0	716	2.83
1 month	<3.5	5.07	0.64	368	<2.0	<2.0	412	1.37
2 months	<3.5	7.56	1.03	533	2.7	2.6	479	1.98
3 months	<3.5	8.13	1.19	473	<2.0	1.7	637	8.26

Table D-24. Total zinc (mg/m^2), containers at pH 8

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	<3.5	<1.0	<1.0	0.01	<2.0	<2.0	<0.02	<0.5
30 min	3.41	<1.0	<1.0	2.41	3.11	2.99	4.31	<0.5
1 hr	<3.5	<1.0	<1.0	3.73	2.00	1.93	6.26	<0.5
1 day	<3.5	<1.0	<1.0	45	<2.0	1.86	104	<0.5
1 month	<3.5	5.07	<1.0	708	2.80	3.60	1352	0.68
2 months	4.99	7.56	0.21	1040	3.61	3.47	4219	0.66
3 months	4.96	21.83	0.40	3405	3.47	17.5	437	0.00

Table D-25. Total zinc (mg/m^2), containers with bay water

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	<2.5	<1.0	<0.4	<0.8	<2.0	<2.0	<1.0	<1.5
30 min	<2.5	<1.0	<0.4	59.5	<2.0	<2.0	22.8	<1.5
1 hr	<2.5	<1.0	<0.4	351	<2.0	<2.0	227	3.29
1 week	<2.5	<1.0	<0.4	341	<2.0	<2.0	204	1.94
1 month	<2.5	<1.0	<0.4	765	<2.0	<2.0	179	1.91
2 months	<2.5	<1.0	<0.4	2764	3.42	57.55	739	3.13
3 months	<2.5	<1.0	<0.4	3073	<2.0	<2.0	1605	<1.5

Table D-26. Total zinc (mg/m^2), containers with river water

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	<2.5	<1.0	0.20	<1.0	<2.0	0.6	<1.0	<1.0
30 min	<2.5	<1.0	<0.2	40.8	<2.0	<0.5	11. 9	<1.0
1 hr	<2.5	<1.0	<0.2	253	<2.0	<0.5	55.2	<1.0
1 week	<2.5	<1.0	<0.2	203	<2.0	<0.5	262	<1.0
1 month	<2.5	<1.0	0.20	805	<2.0	<0.5	907	<1.0
2 months	<2.5	0.84	0.20	3345	1.71	0.6	6943	2.50
3 months	<2.5	1.24	0.19	2650	<2.0	0.81	8311	29.5

Table D-27. Filterable fraction of zinc after three months of exposure

Water	Material	Total, mg/L	Filtered, mg/L	% Filterable
pH 5	Concrete Pipe	< 0.02	< 0.02	n/a
	PVC Pipe	0.44	0.39	89
	HDPE Pipe	0.06	0.05	83
	Steel Pipe	11.7	2.77	24
	Vinyl Gutter	< 0.02	< 0.02	n/a
	Aluminum Gutter	0.02	0.04	200
	Steel Gutter	14.1	7.23	51
	Copper Gutter	0.13	< 0.02	< 15.4
pH 8	Concrete Pipe	0.03	< 0.02	< 66.7
	PVC Pipe	0.68	0.12	18
	HDPE Pipe	0.05	0.05	100
	Steel Pipe	84.3	0.29	0.34
	Vinyl Gutter	0.04	0.04	100
	Aluminum Gutter	0.21	0.05	24
	Steel Gutter	9.69	0.16	1.7
	Copper Gutter	0.02	0.02	100

Aluminum Leaching Test Data

Table D-28. Total aluminum (mg/L), in containers at pH 5

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
3 months	< 0.1	0.1	< 0.1	< 0.1	< 0.1	0.3	< 0.1	< 0.1

Table D-29. Total aluminum (mg/L), in containers at pH 8

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
3 months	< 0.1	0.1	0.2	< 0.1	0.2	0.4	0.2	< 0.1

Table D-30. Total aluminum (mg/L), in containers with bay water

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
3 months	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.30	< 0.1	< 0.1

Table D-31. Total aluminum (mg/L), in containers with river water

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
3 months	0.10	0.20	0.30	< 0.1	< 0.1	1.00	0.10	< 0.1

Table D-32. Filterable fraction of aluminum after three months of exposure

Water	Material	Total, mg/L	Filtered, mg/L	% Filterable
pH 5	Concrete Pipe	< 0.1	< 0.1	n/a
	PVC Pipe	0.10	0.10	100
	HDPE Pipe	< 0.1	< 0.1	n/a
	Steel Pipe	< 0.1	< 0.1	n/a
	Vinyl Gutter	< 0.1	< 0.1	n/a
	Aluminum Gutter	0.30	0.30	100
	Steel Gutter	< 0.1	< 0.1	n/a
	Copper Gutter	< 0.1	< 0.1	n/a
pH 8	Concrete Pipe	< 0.1	< 0.1	n/a
	PVC Pipe	0.10	< 0.1	< 100
	HDPE Pipe	0.20	0.20	100
	Steel Pipe	< 0.1	< 0.1	n/a
	Vinyl Gutter	0.20	0.10	50
	Aluminum Gutter	0.40	0.40	100
	Steel Gutter	0.20	0.10	50
	Copper Gutter	< 0.1	< 0.1	n/a

Iron Leaching Test Data

Table D-33. Total iron (mg/L), in containers at pH 5

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
3 months	0.10	0.12	0.15	21.90	0.12	0.12	5.89	0.15

Table D-34. Total iron (mg/L) in containers with pH 8

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
3 months	< 0.02	0.13	0.13	1.18	0.15	0.13	0.34	0.15

Table D-35. Total iron (mg/L), in containers with bay water

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	0.06	0.63	0.63	0.65	0.75	0.78	0.78	0.74
3 months	2.59	0.93	1.10	1.95	1.08	1.25	2.30	2.10

Table D-36. Total iron (mg/L), in containers with river water

Exposure Time	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0 (No sample)	0.21	0.24	0.21	0.19	0.17	0.22	0.19	0.20
3 months	1.14	0.62	0.43	1.42	0.45	0.46	1.44	1.78

Table D-37. Filterable fraction of iron after three months of exposure

		After Three Months of Exposure		
Water	**Material**	**Total, mg/L**	**Filtered, mg/L**	**% Filterable**
Bay	Concrete Pipe	2.59	0.76	29
	PVC Pipe	0.93	0.84	90
	HDPE Pipe	1.10	0.92	84
	Steel Pipe	1.95	0.96	49
	Vinyl Gutter	1.08	0.99	92
	Aluminum Gutter	1.25	1.10	88
	Steel Gutter	2.30	0.95	41
	Copper Gutter	2.10	0.90	43
River	Concrete Pipe	1.14	0.21	18
	PVC Pipe	0.62	0.45	73
	HDPE Pipe	0.43	0.33	77
	Steel Pipe	1.42	0.08	6
	Vinyl Gutter	0.45	0.31	69
	Aluminum Gutter	0.46	0.32	70
	Steel Gutter	1.44	0.27	19
	Copper Gutter	1.78	0.29	16

Pipe and Gutter Material Composition Data

Shavings of the pipe and gutter materials were analyzed to determine the basic heavy metal contents of the samples, as shown in Table D-38. The copper gutter was almost 100% copper, the aluminum gutter samples was almost 100% aluminum, and the galvanized steel pipe and gutter samples were almost 100% iron. The galvanized steel samples also had the greatest zinc contents (about 2 to 3%). The concrete pipe sample also had about 15% iron. As expected, the plastic (PVC, HDPE, and vinyl) samples had relatively low metal contents. The greatest lead content was found in the steel pipe, at about 50 mg/kg.

Table D-38. Pipe and gutter material composition (mg/kg).

	Material Composition, mg/kg				
Material	**Lead, Pb**	**Copper, Cu**	**Zinc, Zn**	**Aluminum, Al**	**Iron, Fe**
Concrete Pipe	14.9	72	45	6,500	150,000
PVC Pipe	< 0.5	< 2	< 2	34	89
HDPE Pipe	< 0.5	3	< 2	690	51
Steel Pipe	46.5	275	28,000	452	971,000
Vinyl Gutter	< 0.5	< 2	< 2	93	48
Aluminum Gutter	13.4	1,210	943	943,000	3,100
Steel Gutter	12.2	520	18,100	685	980,000
Copper Gutter	7.0	998,000	7	1,020	102
Detection Limit, mg/kg	0.5	2	2	10	2

Observed Time Series Releases of Heavy Metals from Pipe and Gutter Materials

This appendix section describes metal releases from different pipe and gutter materials subjected to different water conditions for different periods of exposure. For the first series of tests, the data for 0.5 h, 1 h and 27 h were defined as short exposure periods, and for 1 month, 2 months and 3 months as long term exposure periods, based on results of statistical grouping analyses described later. For the second series of the experiments, the data for 1 h, 27 h and 1 week were defined as short exposure periods, and for 1 month, 2 months and 3 months as long term exposure periods. Statistical analyses were performed to determine the effect of time, pH, and salinity on the releases of the metals for each type of material. Model fitting was performed on the time series plots to predict the release rates of the metals as a function of exposure time and surface area. Chemical speciation modeling was performed to determine the forms of heavy metals in solution in order to identify their toxicity effects and treatability. Part of this section contains information presented by Ogburn, et al. (2013).

These tests showed that pipe and gutter materials can release substantial amounts of metals and can be a significant source of toxicity. The highest lead and zinc concentrations were observed for galvanized steel samples under buffered and natural pH conditions during both short and long exposure. The greatest copper release was, unsurprisingly, observed from copper materials. Cadmium and chromium were not detected in any of the containers with controlled pH values.

Zinc Releases during Controlled pH Tests

During short term exposures, zinc was released from the galvanized steel pipe and gutter at both low and high pH conditions, as well as from the copper and HDPE gutter samples at pH 5, and from vinyl and aluminum gutters at pH 8. For other materials, zinc releases were noted after 1 or 2 months of exposure. After the first day of exposure, the galvanized steel pipes and gutters had very high levels of zinc concentrations (1 mg/L to >14 mg/L; 45-720 mg/m^2), with greater and faster releases observed under the lower pH conditions. These concentrations exceeded the aquatic life freshwater criteria of 120 μg/L established by the US Environmental Protection Agency (US EPA) by 8 to 116 times. Zinc releases were the highest from galvanized steel materials. During long term exposures (after 1 month), zinc concentrations in the samples with galvanized metals under pH 8 conditions were >90 mg/L (4200 mg/m^2), compared with 14 mg/L (640 mg/m^2) values under the pH 5 conditions. Higher zinc losses at pH 8 compared to pH 5 can be attributed to zinc being an amphoteric species which dissolves well in acidic environments (with the formation of zinc salts). It also dissolves well in basic environments (with the formation of divalent zincate-anion (i.e. $CaZnO_2$) or complex tetrahedral zincate ion (i.e. $Na_2[Zn(OH)_4]$)) (Klinskiy and Skopinzev 2001). Typically, zinc releases were greater in galvanized steel gutter samples compared to samples with galvanized pipes. The second highest sources of zinc were the copper gutters; greater releases occurred under pH 5 conditions (>0.13 mg/L, 8 mg/m^2). Zinc was also released from plastic materials, but the resultant concentrations were much lower. The smallest sources of zinc were concrete (<30 μg/L; 5 mg/m^2) and plastic materials (for PVC pipes ≤680 μg/L (22 mg/m^2), for HDPE pipes ≤60 μg/L (1 mg/m^2), and for vinyl gutters ≤40 μg/L (3.47 mg/m^2)).

Zinc concentrations resulting from different gutter and pipe materials during the tests with buffered waters are shown in Figures D-1 and D-2. Figures D-3 and D-4 show the corresponding zinc releases in mg/m^{2}normalized for pipe or gutter surface area. These graphs show that zinc releases from galvanized steel pipes and gutters were very similar; other zinc sources included plastic, aluminium, and copper materials, but they released much smaller amounts of zinc.

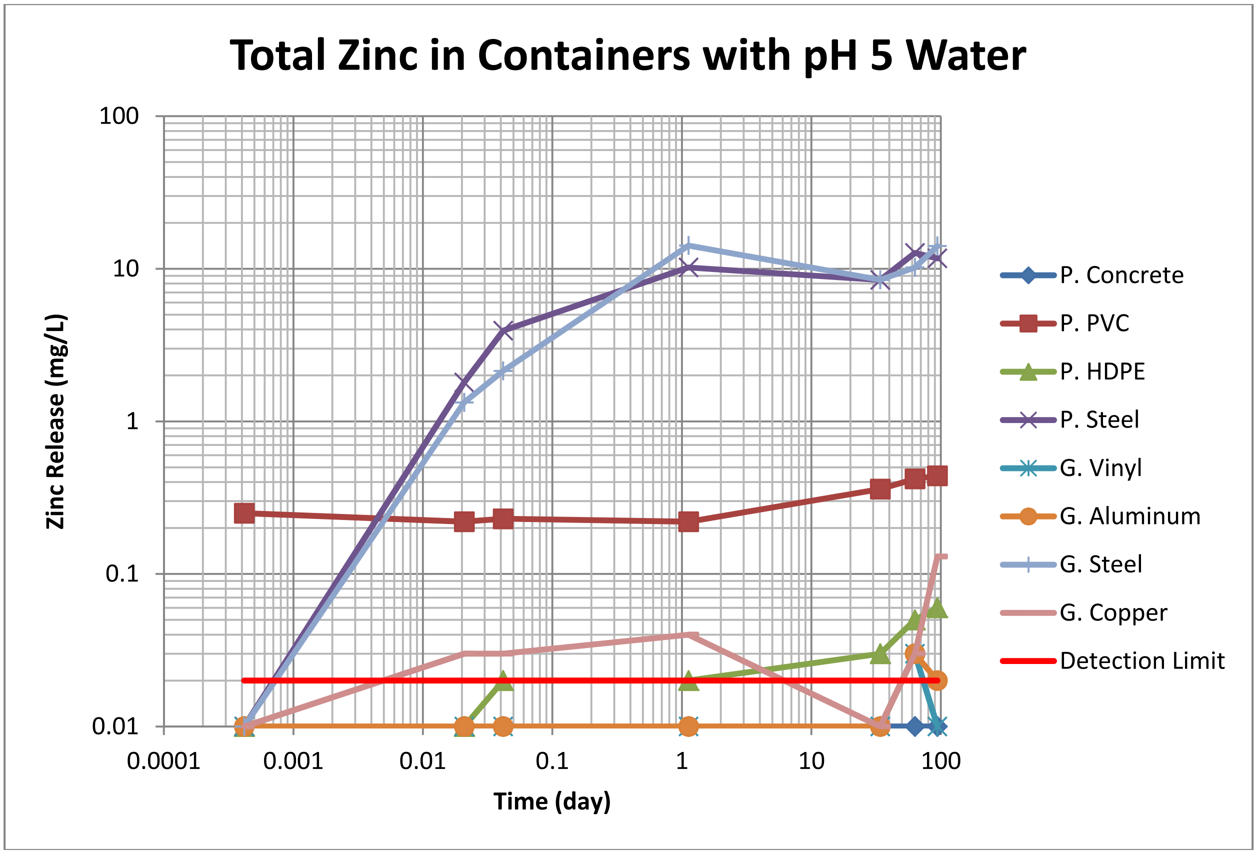


Figure D-1. Total zinc concentrations in containers with pH 5 water.

Footnote: P. = Pipe, G. = Gutter

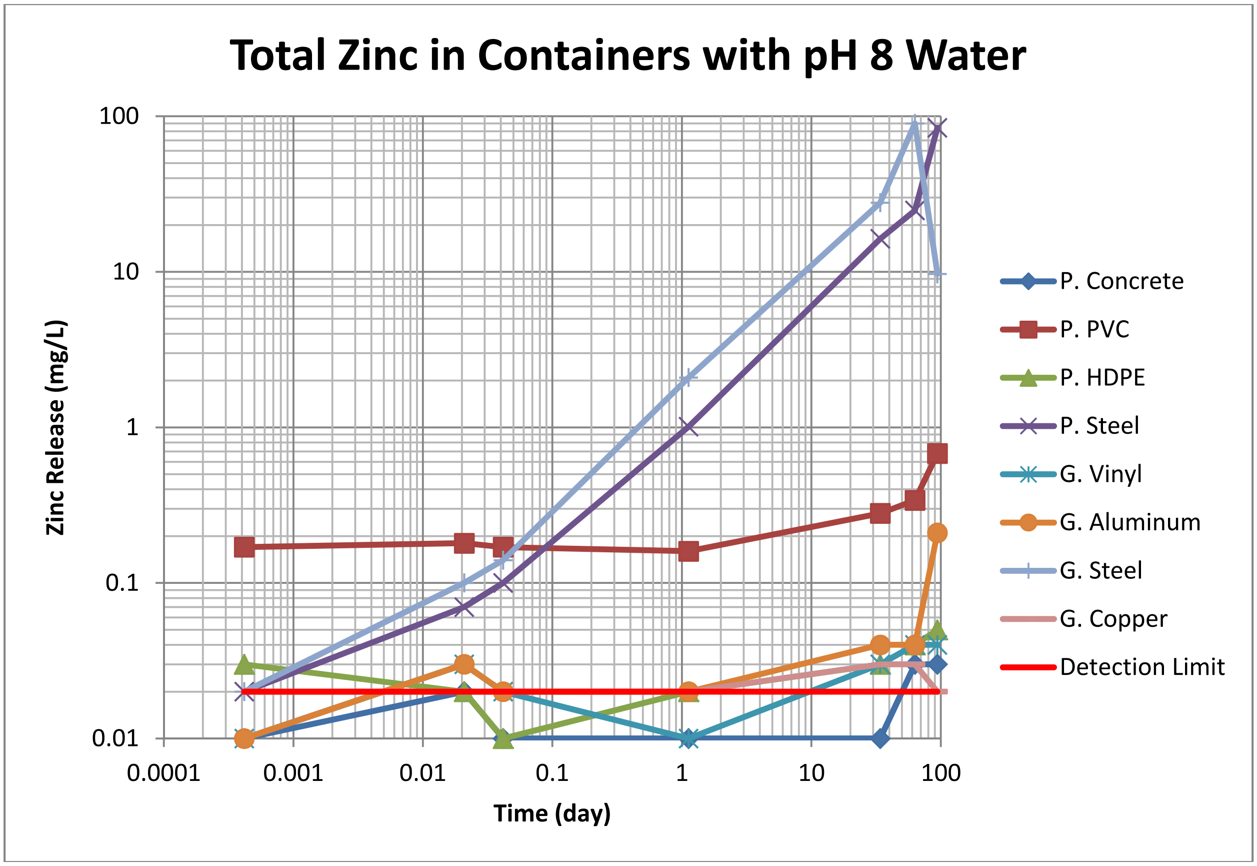


Figure D-2. Total zinc concentrations in containers with pH 8 water.

Footnote: P. = Pipe, G. = Gutter

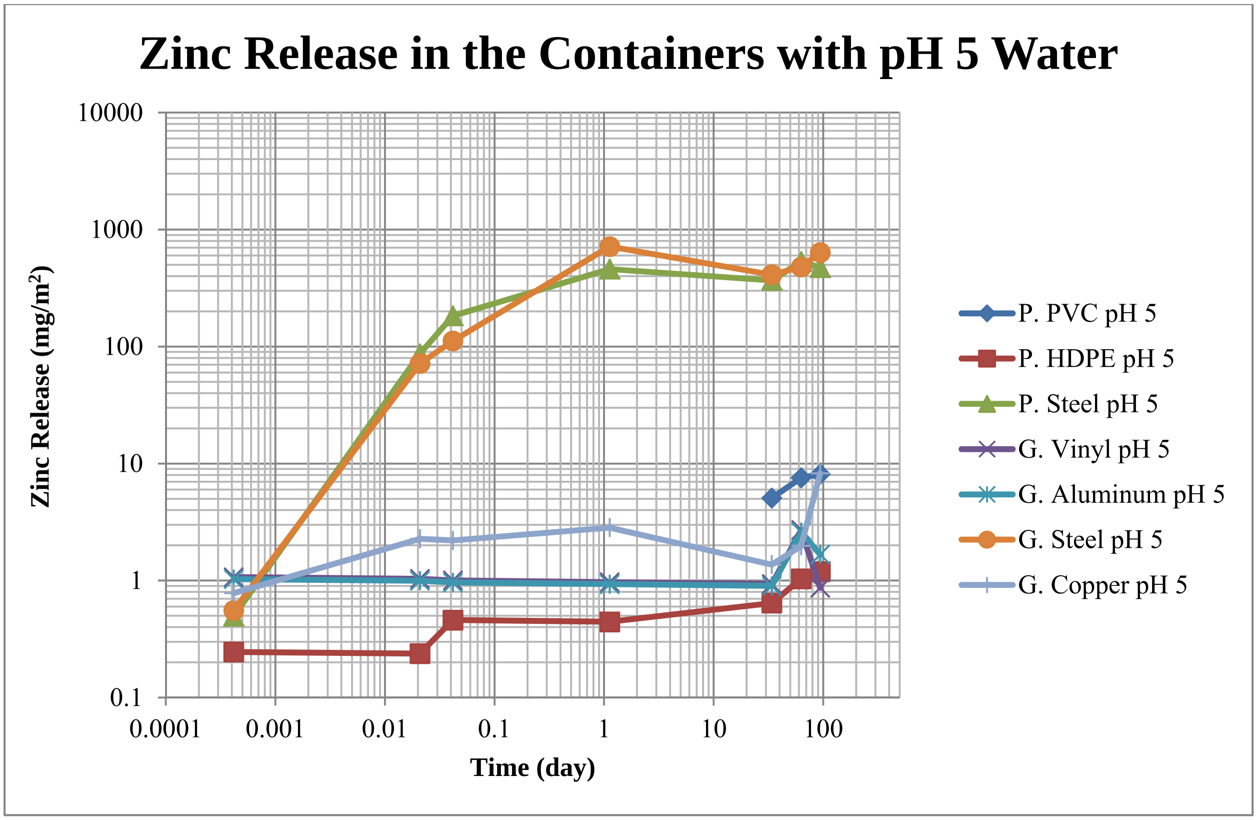


Figure D-3. Total zinc losses in containers with pH 5 water.

Footnote: P. = Pipe, G. = Gutter

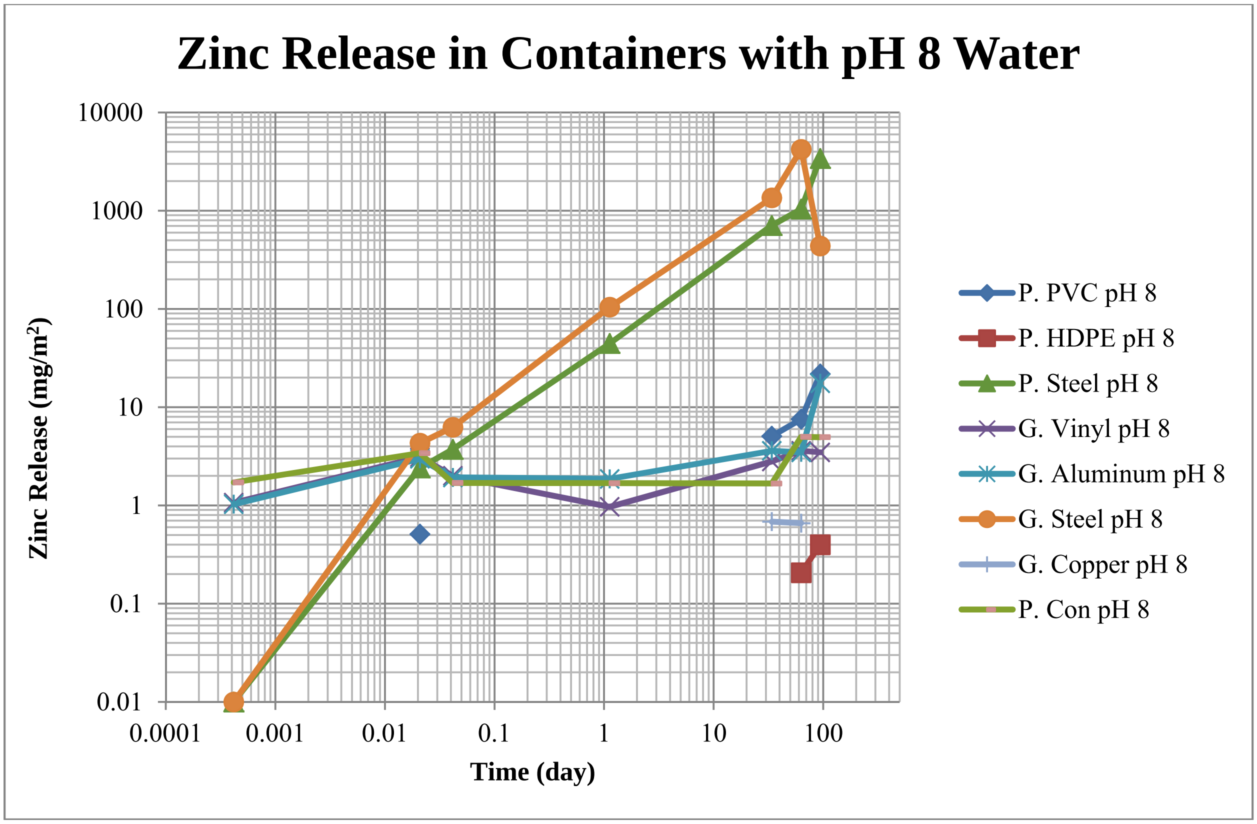


Figure D-4. Total zinc losses in containers with pH 8 water.
Footnote: P. = Pipe, G. = Gutter

Zinc Releases during Natural pH Tests

Short term exposures (≤1 week) resulted in zinc releases from the galvanized steel pipe and gutter materials immersed in both bay and river water and from copper gutter materials immersed in bay water. Zinc losses from the other materials were noted after 1 or 2 months of exposure. As for controlled pH conditions, galvanized steel materials in the containers under natural pH conditions were the greatest sources of zinc releases. The samples with galvanized steel gutters and pipes had very high levels of zinc concentrations (5 mg/L to >8 mg/L; 230 mg/m^2 to 350 mg/m^2) after the first day of exposure, with greater releases observed for samples immersed into bay water. These concentrations exceeded the aquatic freshwater toxicity criteria of 120 µg/L established by the US EPA by more than 40 times. However, after one day of exposure, these concentrations were lower than the zinc concentrations in containers at controlled pH 5 conditions (>14 mg/L; 720 mg/m^2) and greater than zinc releases in containers at controlled pH 8 tests (>2 mg/L; 100 mg/m^2).

For galvanized pipes, zinc concentrations in bay water samples were generally higher than samples in river water samples. After long term exposures (approaching 3 months), galvanized steel pipe samples immersed into bay waters resulted in zinc concentrations >70 mg/L (3070 mg/m^2). However, galvanized gutter materials indicated a different trend and after 1 week exposure, zinc releases from galvanized gutters immersed in containers with river water exceeded those in bay water. After long term exposures, zinc losses from galvanized gutters in river water reached 190 mg/L (8,310 mg/m^2) compared to 40 mg/L (1,610 mg/m^2) in bay water. The higher zinc releases from the galvanized gutter specimen immersed in river water compared to the bay water can be explained by the lower pH and higher fluoride concentration in the river water sample. The different trends in the zinc releases from pipes and gutters are explained by different material compositions.

The second highest sources of zinc releases were the copper materials, with higher concentrations observed in containers with river water samples (0.48 mg/L; 30 mg/m^2) compared to bay samples. Plastic and aluminum materials had much lower zinc releases. Zinc was not detected in concrete pipe samples with either bay or river waters.

Due to the high chloride content of the bay water, the zinc releases from galvanized steel pipe tended to be greater in bay water samples compared to river water samples. Figures D-5 and D-6 show zinc concentrations released from various gutter and pipe materials during the un-buffered experiments. Figures D-7 and D-8 show the corresponding zinc releases in mg per m^2 pipe/gutter surface area. Similar to the controlled pH tests, during natural pH tests, the zinc releases from galvanized steel pipes and gutters tracked each other very closely; copper, aluminium, and plastics showed much smaller zinc releases.

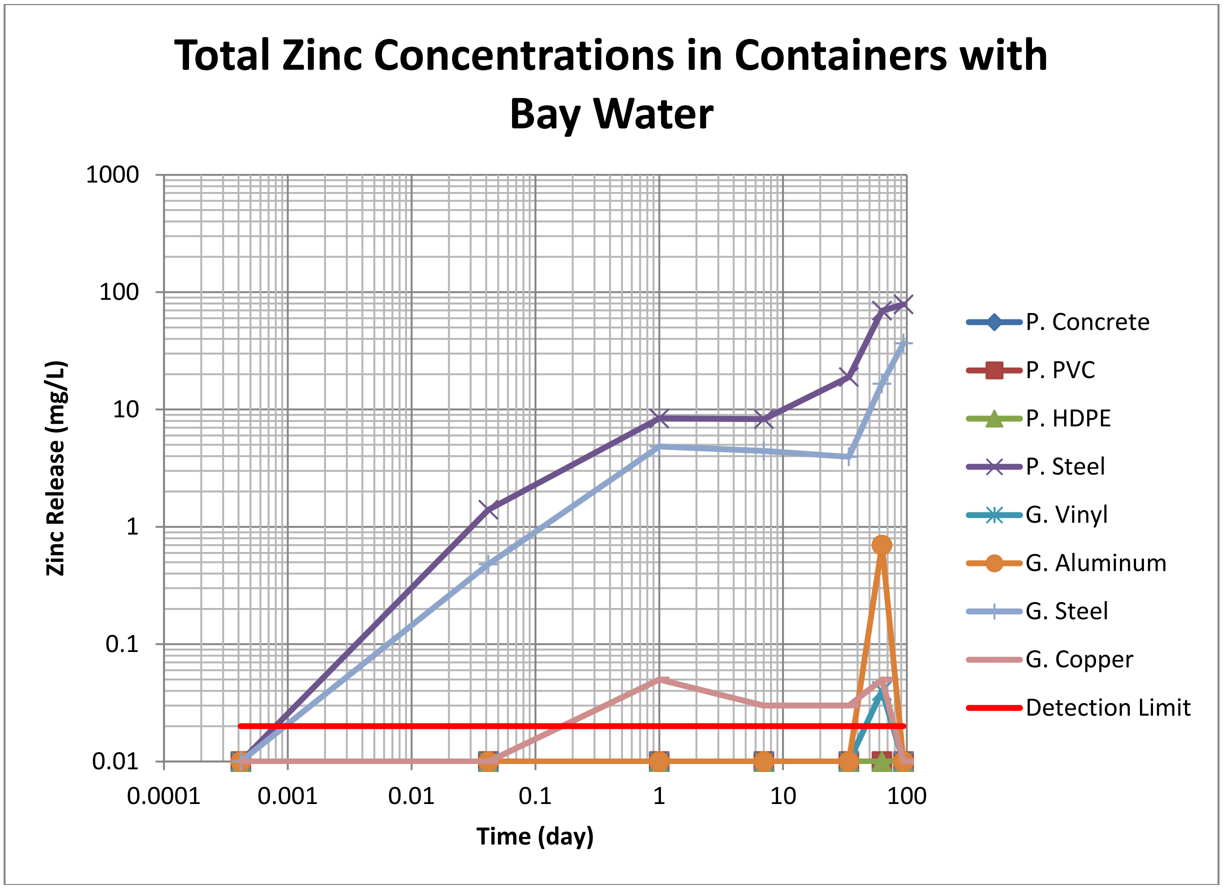


Figure D-5. Total zinc concentrations in containers with bay water.

Footnote: P. = Pipe, G. = Gutter

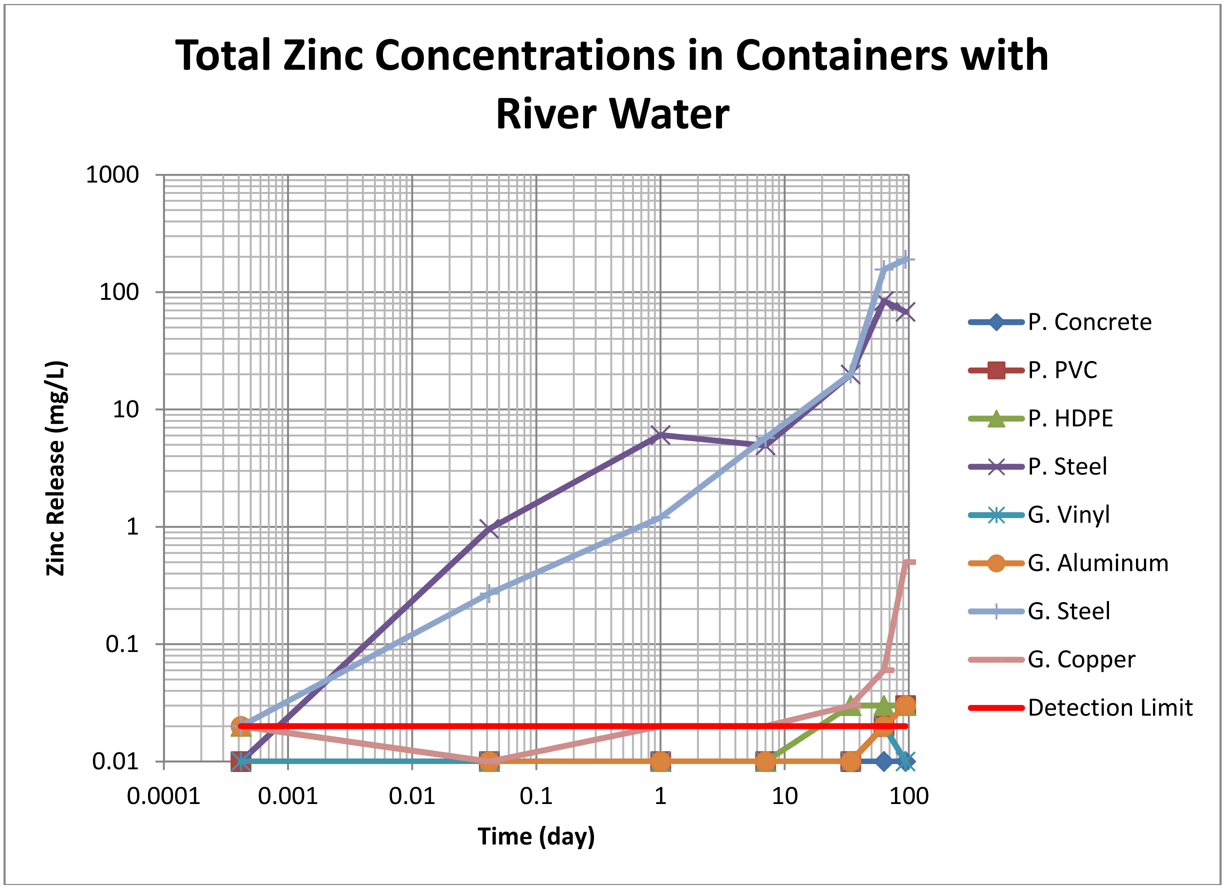


Figure D-6. Total zinc concentrations in containers with river water.

Footnote: P. = Pipe, G. = Gutter

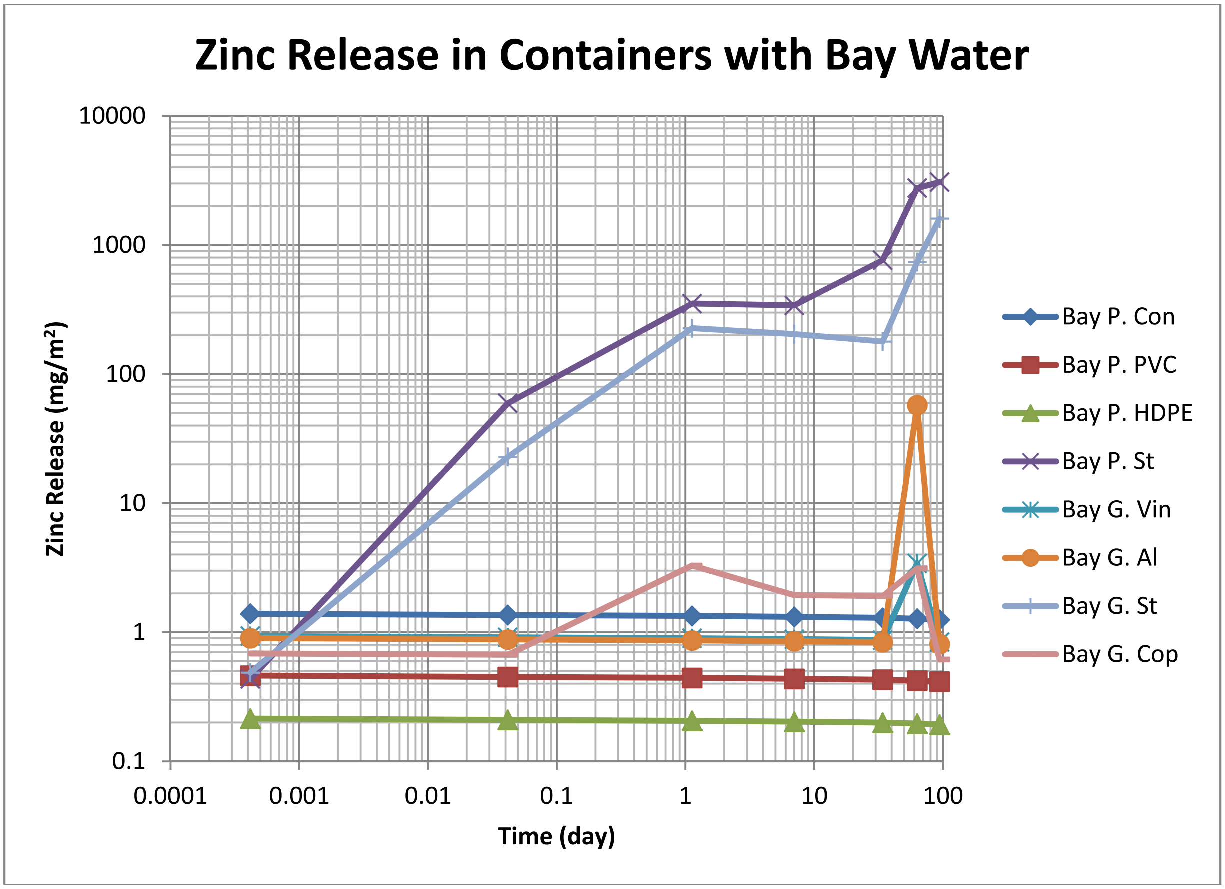


Figure D-7. Total zinc losses in containers with bay water.

Footnote: P. = Pipe, G. = Gutter

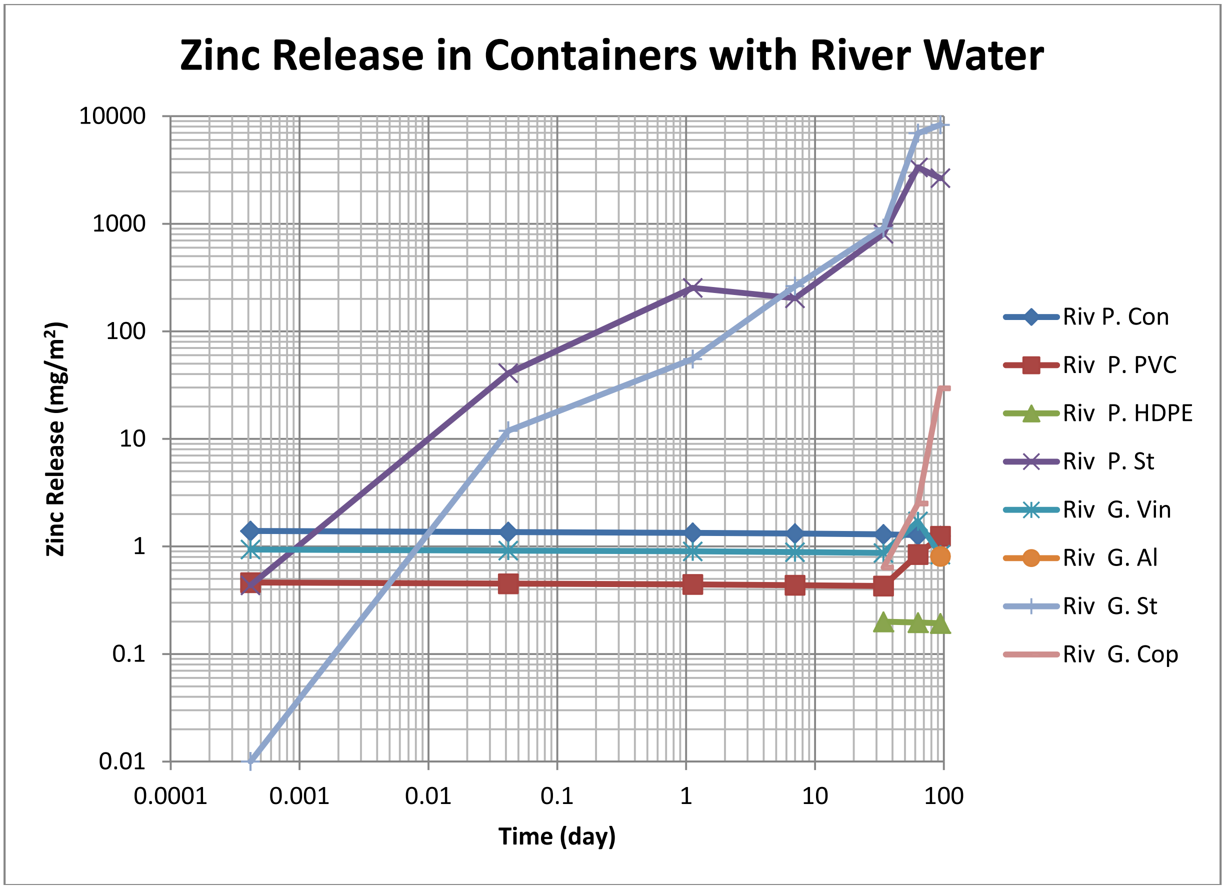


Figure D-8. Total zinc losses in containers with river water.
Footnote: P. = Pipe, G. = Gutter

Copper Releases during Controlled pH Tests
Copper materials were the greatest source of copper under controlled pH conditions, as expected. During short term exposure times, copper was released only in the copper gutter samples under both low and high pH values. Copper releases from most of the other materials were detected after 1 or 2 months of exposure.

After the first day of exposure, copper concentrations in copper test containers were about 7 mg/L (480 mg/m^2) under pH 5 conditions (exceeding the mean acute toxicity value for certain freshwater animals; US EPA, 2007b) and <1 mg/L (21 mg/m^2) under pH 8 conditions. Greater and faster releases occurred at lower pH conditions. Copper concentrations >5 mg/L (320 mg/m^2) were detected in the copper gutter sample container under pH 5 conditions after long term exposure, compared to 2 mg/L (135 mg/m^2) values under the pH 8 conditions. The greatest copper releases (>6 mg/L, 480 mg/m^2) were detected from copper sample containers after 27 h exposure before they started to level off. Some of the plastic, aluminum and galvanized steel materials also released copper, but the concentrations were much lower. After the copper materials, PVC pipe samples had the highest copper releases of about 5 mg/m^2 after long exposure periods. Copper releases were detected from galvanized steel gutter and pipe samples under pH 8 conditions. However, under pH 5 conditions, the copper release was detected only at 1 month exposure for steel pipes. HDPE and galvanized steel materials had the lowest copper releases of ≤60 µg/L (1.24 mg/m^2) and ≤30 µg/L (1.36 mg/m^2) respectively. Copper releases were not detected in the concrete pipes samples at both pH 5 and pH 8 values.

Copper concentrations resulting from different materials during the buffered tests are shown in Figures D-9 and D-10. The corresponding copper releases in mg per m^2 pipe surface area during the buffered tests are shown in Figures D-11 and D-12. The general shapes of the metal releases expressed in mg/L are similar to the releases expressed in mg/m^2.

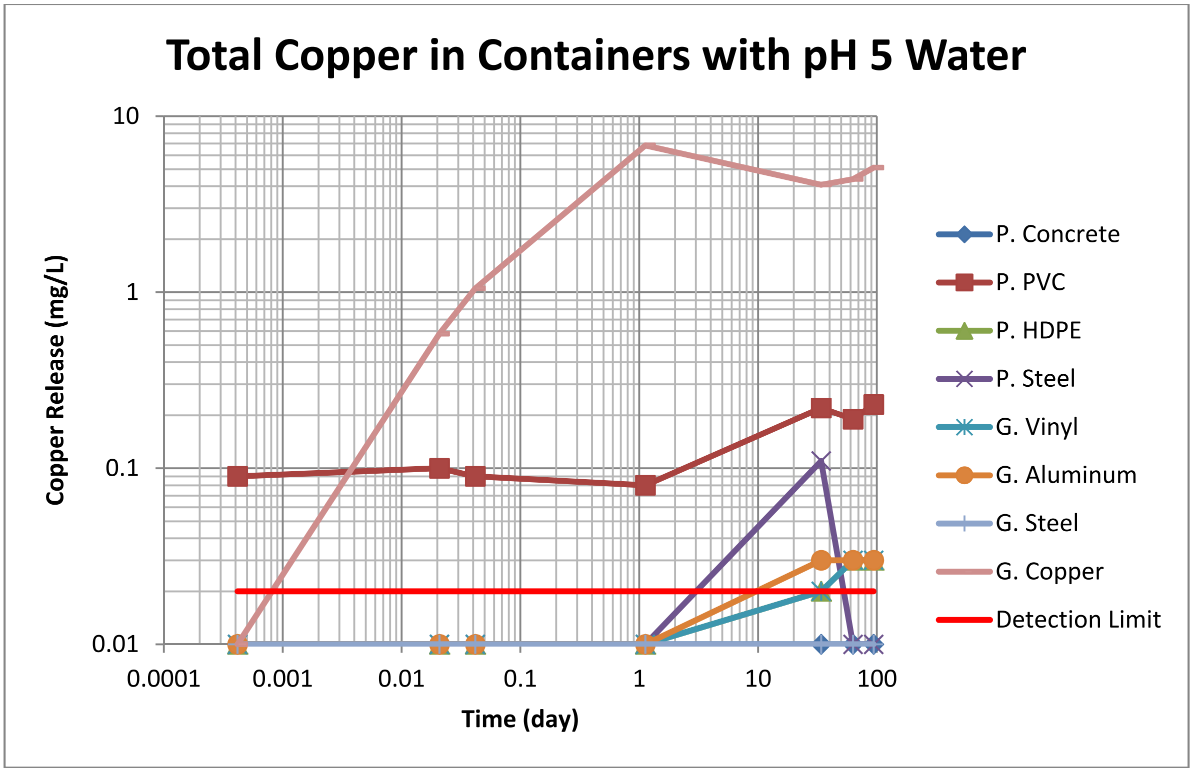


Figure D-9.Total copper concentrations in containers with pH 5 water.
Footnote: P. = Pipe, G. = Gutter

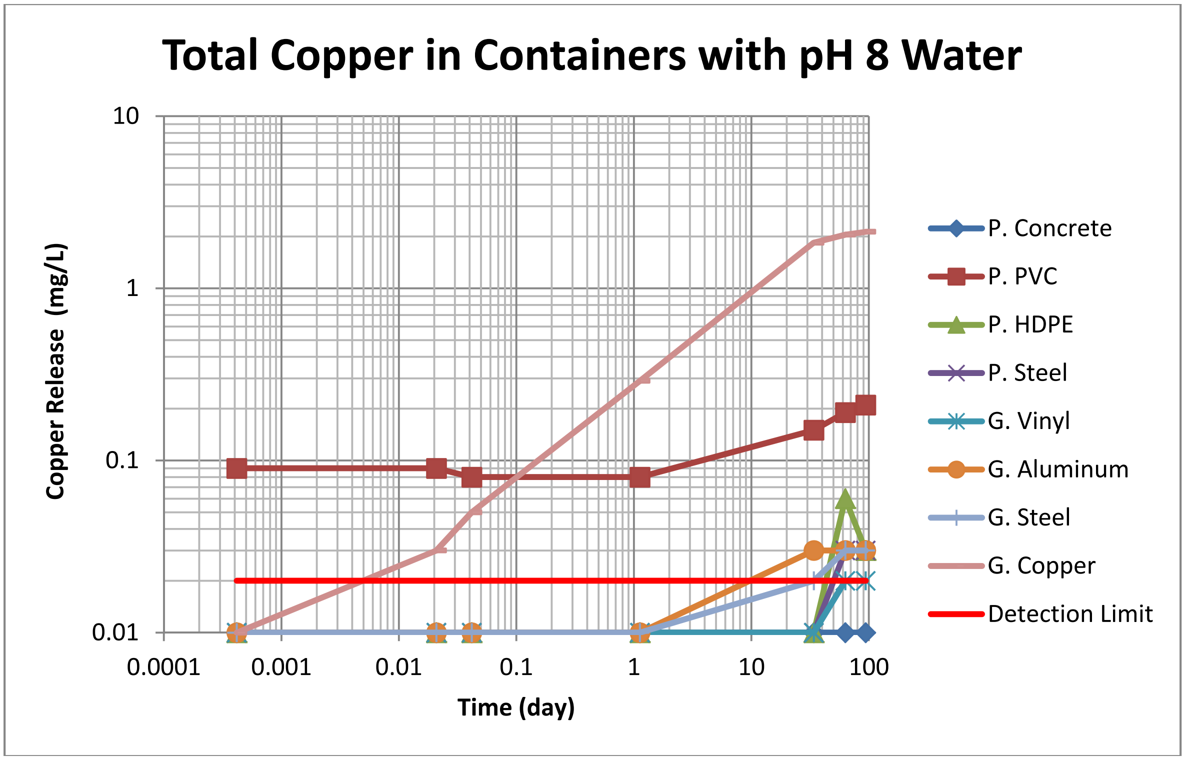


Figure D-10.Total copper concentrations in containers with pH 8 water.
Footnote: P. = Pipe, G. = Gutter

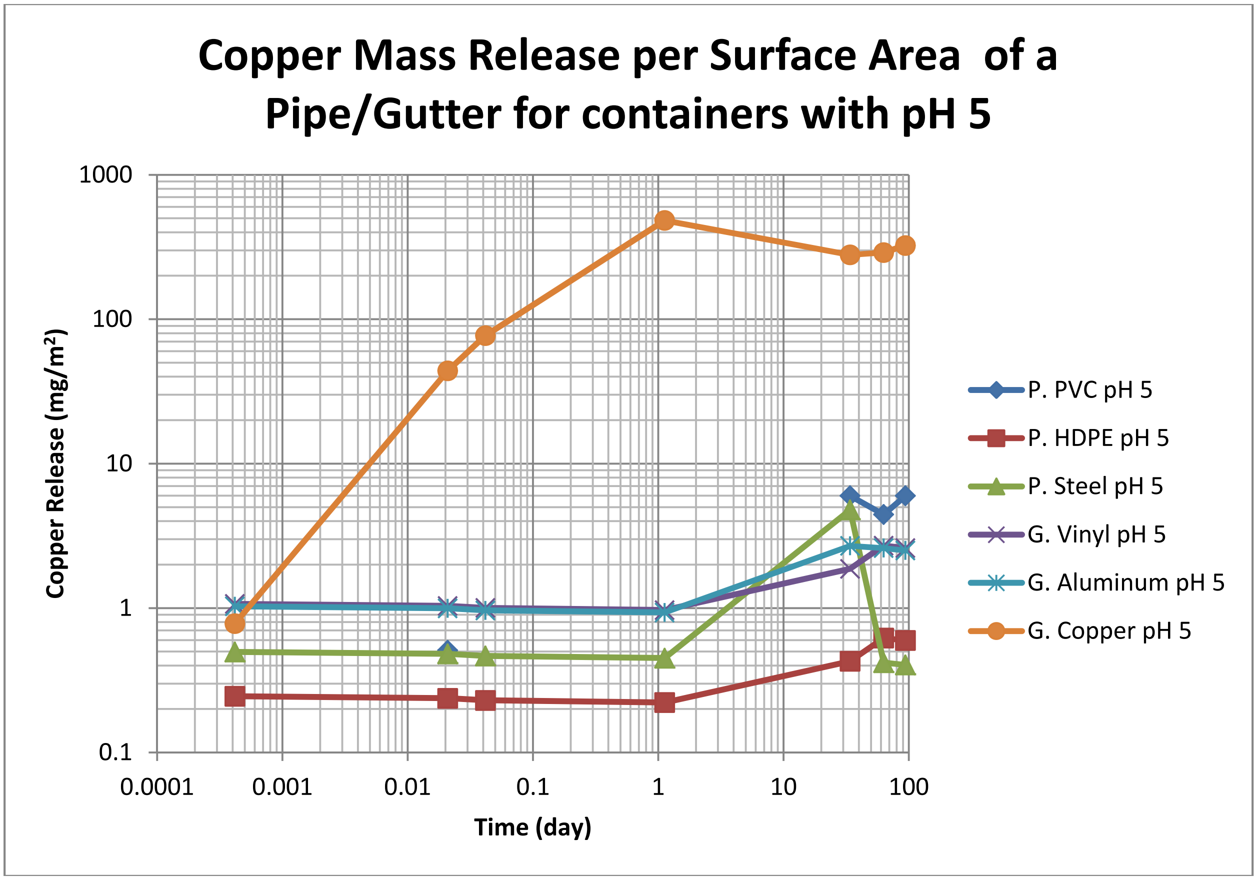


Figure D-11.Total copper losses in containers with pH 5 water.

Footnote: P. = Pipe, G. = Gutter

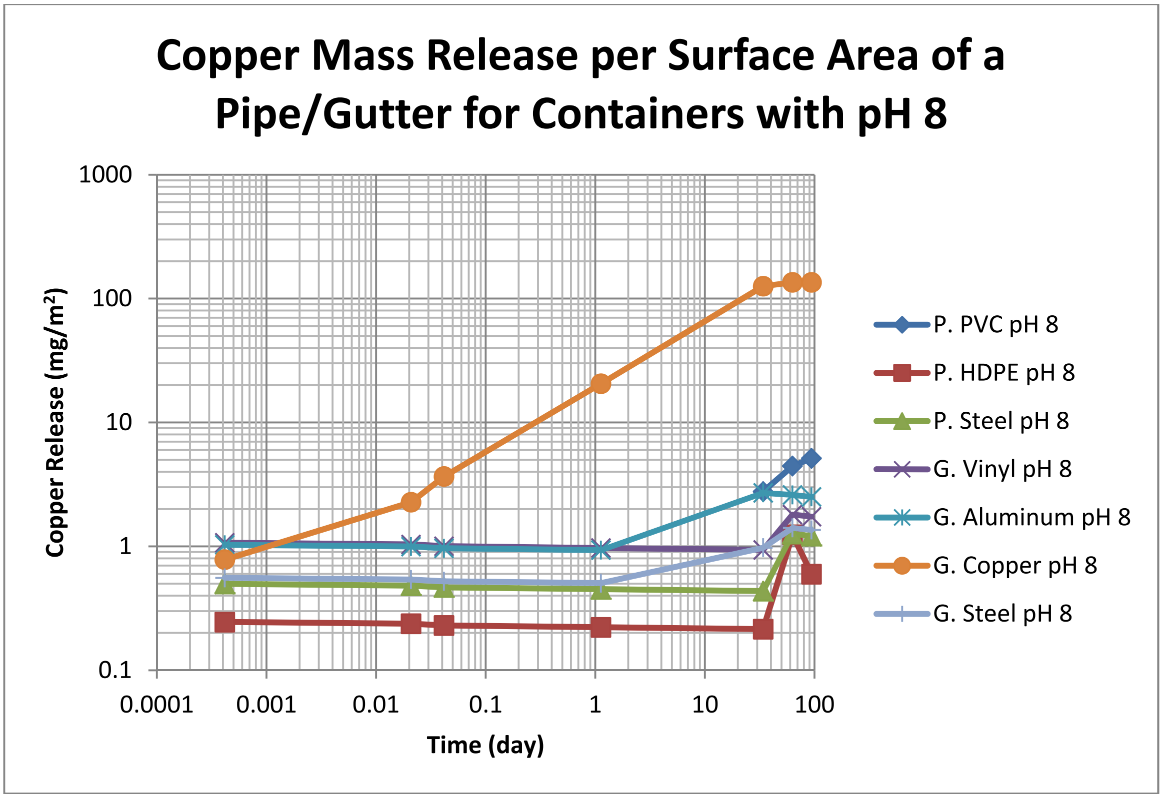


Figure D-12.Total copper losses in containers with pH 8 water.
Footnote: P. = Pipe, G. = Gutter. (Ogburn and Pitt 2011)

Copper Releases during Natural pH Tests
Copper releases were detected only from copper materials during both short and long exposure periods under natural pH conditions in the river and saline bay sample test containers.

For both bay and river waters, copper releases were observed after 1 h exposure. Copper materials immersed into bay water had slightly greater copper releases compared to containers with river water samples. After the first day of exposure, copper releases in bay water samples exceeded 2 mg/L (140 mg/m^2).

After long term exposures (3 months), the greatest copper releases were noted from copper gutter sections immersed in bay water and reached 36 mg/L (2,200 mg/m^2), compared to 5.5 mg/L (340 mg/m^2) from copper gutter sections immersed in river water, 5.1 mg/L (320 mg/m^2) from copper gutter sections under pH 5 conditions, and 2.1 mg/L (135 mg/m^2) from copper sections under pH 8 conditions. Copper releases were greater under pH 5 conditions compared to pH 8 conditions and could be explained by the more acidic environment. Higher copper releases in bay water compared to river water are attributed to the more aggressive environment due to the high chloride content (3,350 mg/L).

Figures D-13 and D-14 show copper concentrations in containers with various materials during the un-buffered tests. Copper releases in mg per m^2 pipe surface area during the un-buffered tests are shown in Figures D-15 and D-16.

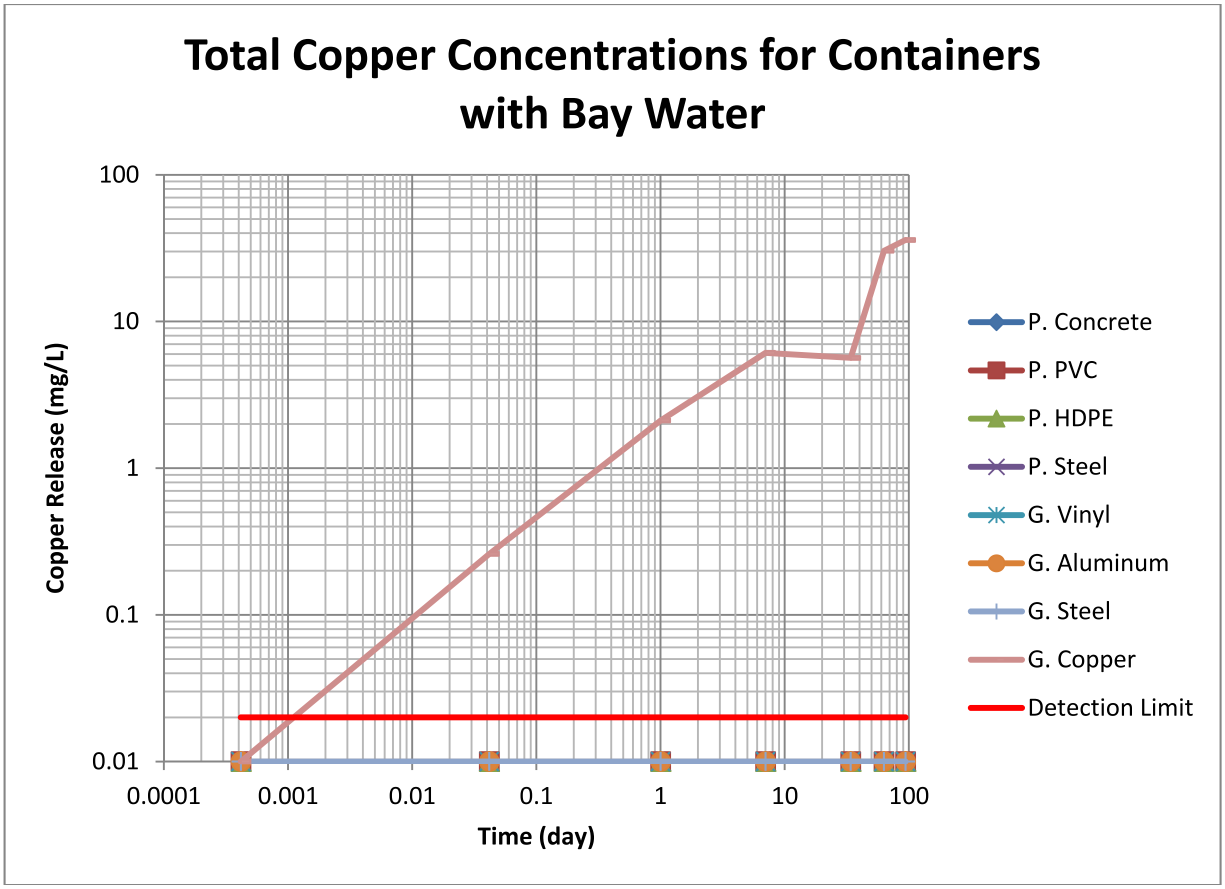


Figure D-13.Total copper concentrations in containers with bay water.
Footnote: P. = Pipe, G. = Gutter

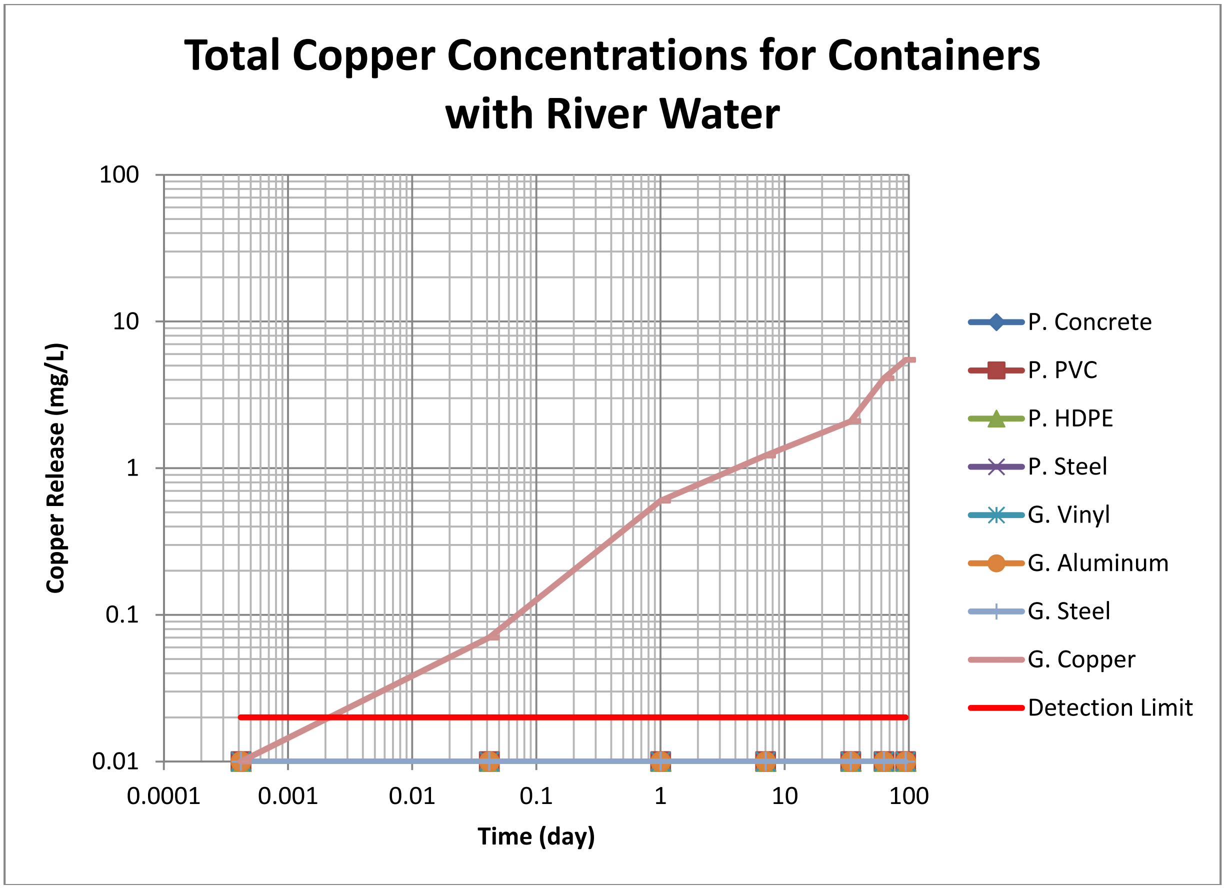


Figure D-14.Total copper concentrations in containers with river water.

Footnote: P. = Pipe, G. = Gutter

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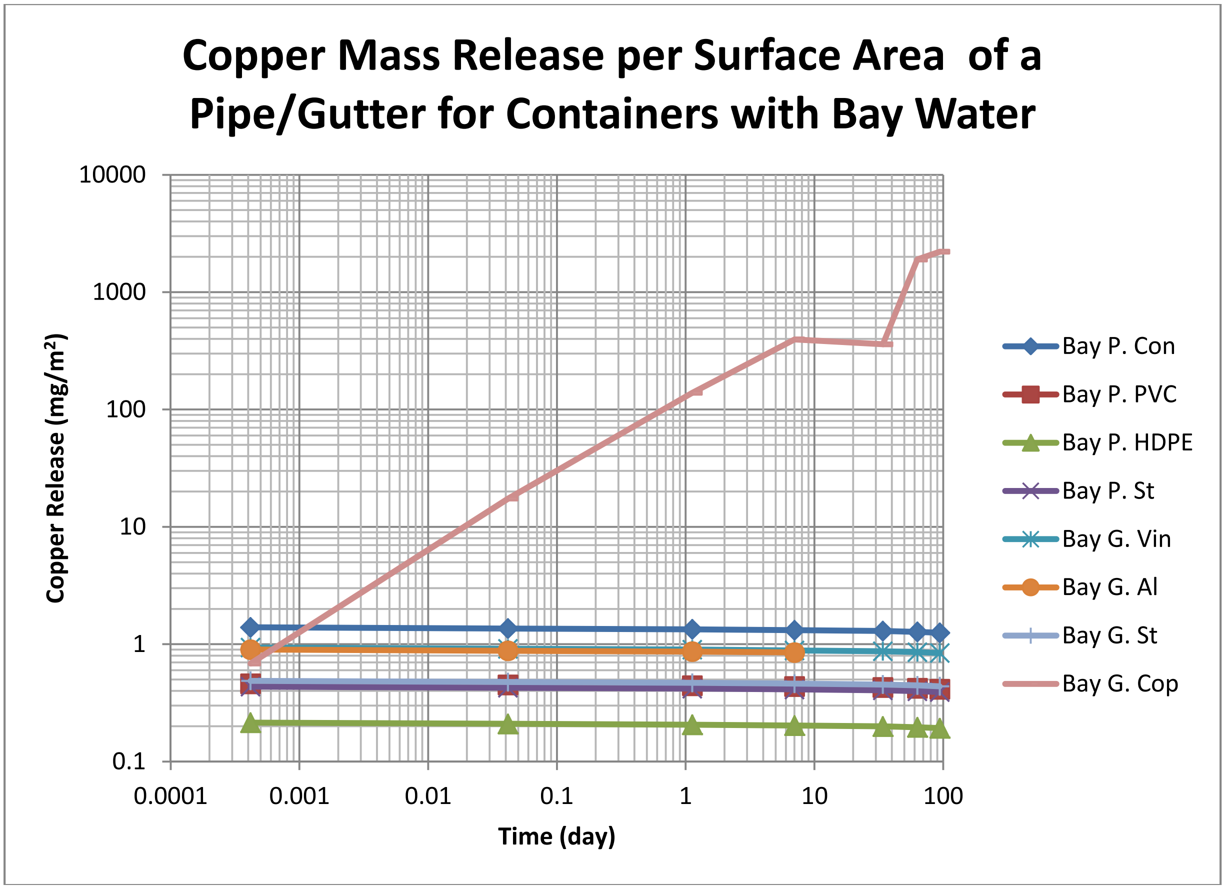


Figure D-15.Total copper losses in containers with bay water.

Footnote: P. = Pipe, G. = Gutter

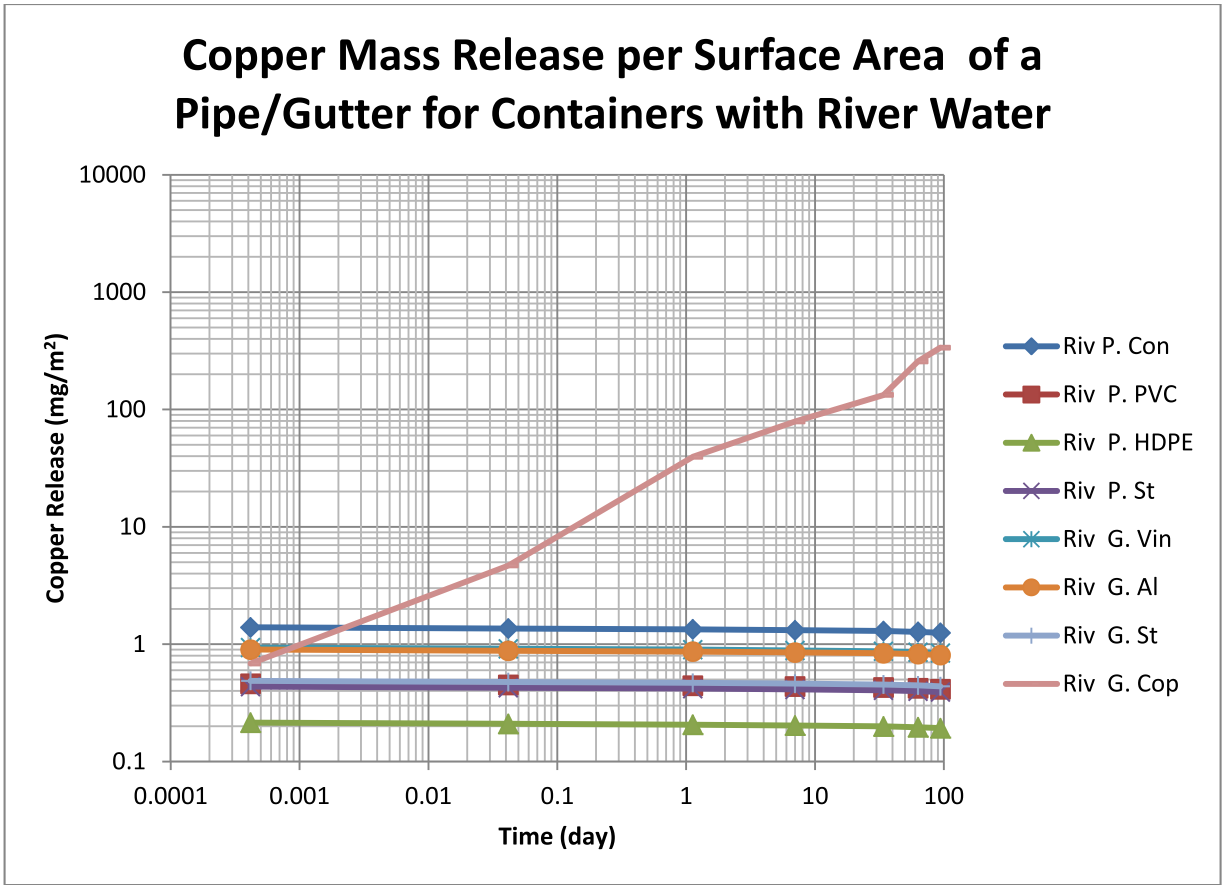


Figure D-16. Total copper losses in containers with river water.
Footnote: P. = Pipe, G. = Gutter

Lead Releases during Controlled pH Tests
Only galvanized materials were a source of lead releases during both short (0.5 h to 27 h) and long (1 month to 3 months) exposure periods for the samples tested.

During short exposure times, lead was not detected in any of the containers having galvanized steel, with the exception of the galvanized steel gutter sample under the pH 8 conditions. This sample had a lead concentration of 8 µg/L (0.4 mg/m^2) at 27 h exposure and didn't exceed the aquatic toxicity criteria of 65 µg/L established by the US EPA. For the steel pipe and gutter specimens exposed at pH 5, lead was detected after 1 month exposure, while the steel pipe sample exposed to pH 8 conditions released lead after 2 months. Under both pH 5 and pH 8 conditions, the release of lead was greater for steel pipe samples than for steel gutter samples probably due to different material compositions. For a given material, the releases of lead were greater at high pH conditions compared to low pH conditions and can be explained by lead amphoteric properties; lead can dissolve well in acidic environments with the formation of salts in which lead is a divalent cation; lead can also dissolve well in alkaline solutions and form complexes (i.e. $Na_2[Pb(OH)_4]$) (Klinskiy and Skopinzev 2001).

The greatest lead releases were observed for the galvanized steel pipe sample at pH 8 which reached lead concentrations of 600 µg/L to 700 µg/L (25 mg/m^2 to30 mg/m^2), followed by the galvanized steel pipe sample at pH 5 with concentrations of 250 µg/L (9.98 mg/m^2) after 3 months exposure. Samples with aluminum, copper, and plastic materials did not contain any detectable lead concentrations. Figures D-17 and D-18 show lead concentrations released from different materials under controlled pH conditions. Corresponding lead releases in mg per m^2 pipe/gutter surface area are shown in Figures D-19 and D-20.

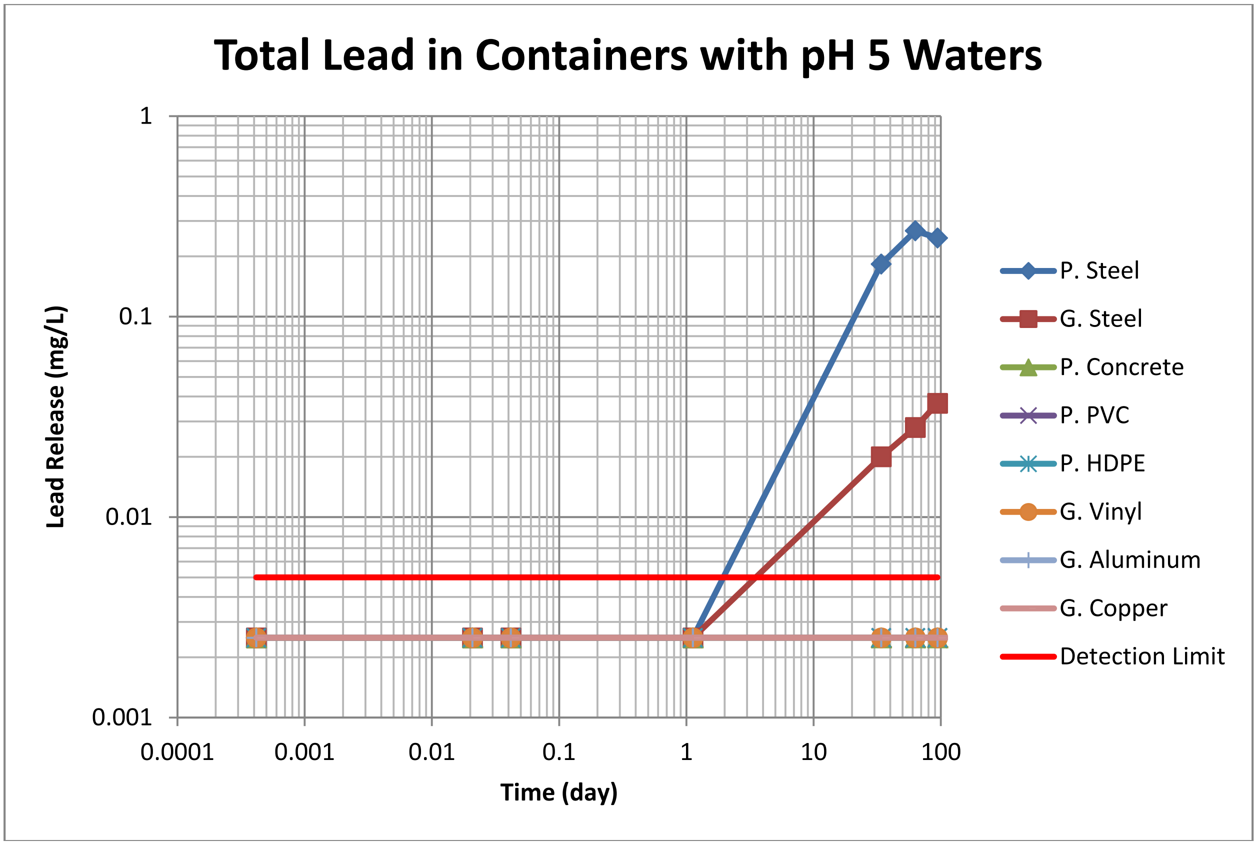


Figure D-17.Total lead concentrations in containers with pH 5 water.
Footnote: P. = Pipe, G. = Gutter

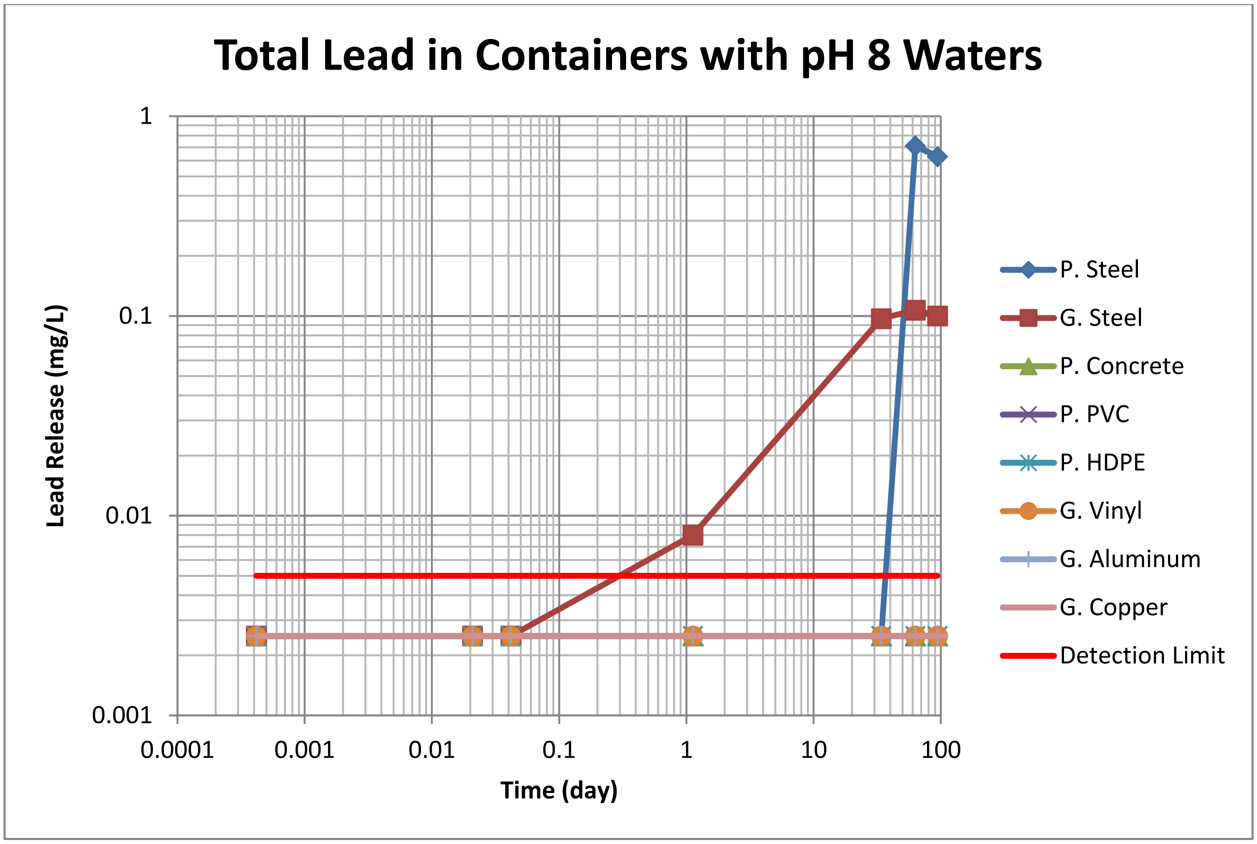


Figure D-18.Total lead concentrations in containers with pH 8 water.

Footnote: P. = Pipe, G. = Gutter

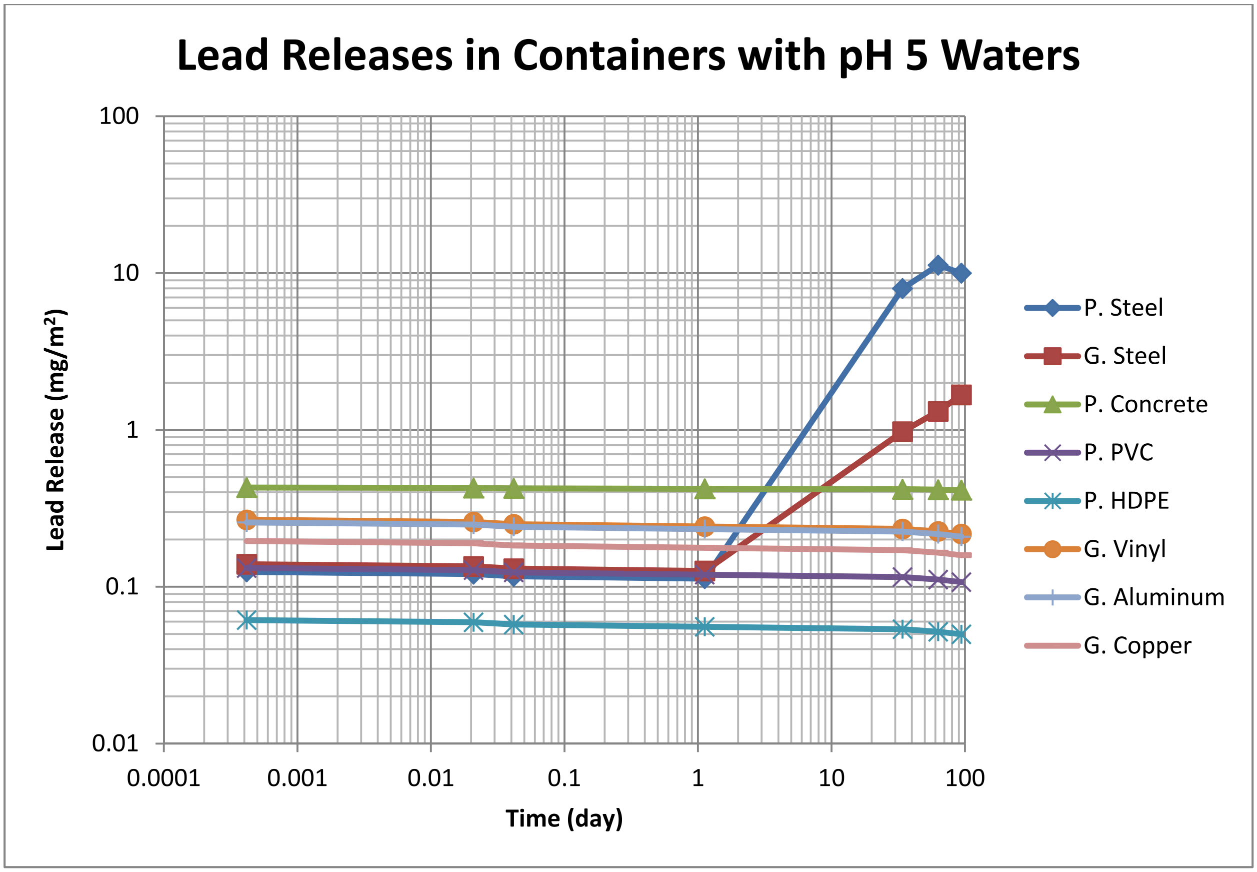


Figure D-19.Total lead losses in containers with pH 5 water.

Footnote: P. = Pipe, G. = Gutter

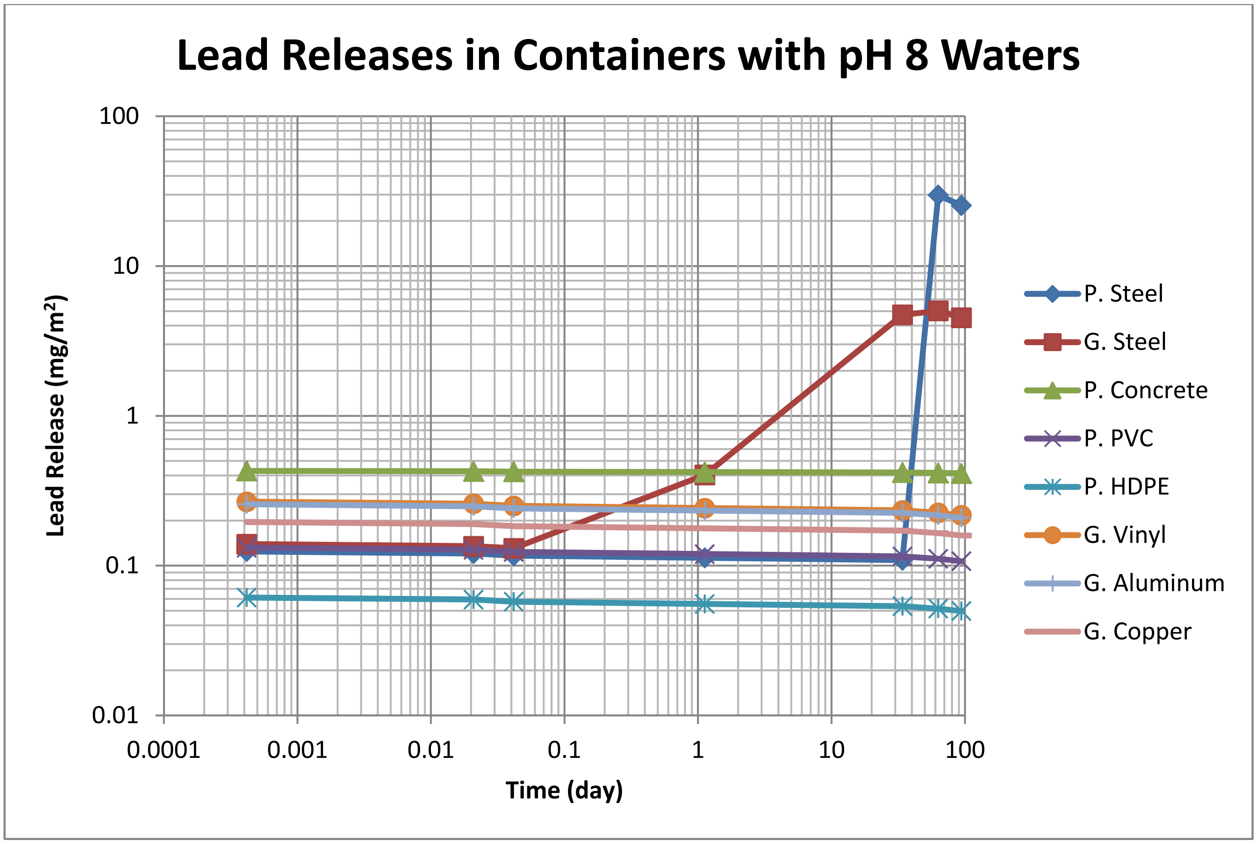


Figure D-20.Total lead losses in containers with pH 8 water.
Footnote: P. = Pipe, G. = Gutter

Lead Releases during Natural pH Tests
As during the controlled pH conditions, lead releases were detected only for galvanized steel materials during both short and long exposures for the bay and river waters under natural pHs. During short exposure periods (1h to 1 week), there were elevated lead concentrations noted from the galvanized steel materials immersed in bay and river waters. For example, a lead concentration of 0.012 mg/L (0.5 mg/m^2) was detected for the galvanized steel pipe section immersed into the bay water after 27 h exposure.

During long exposure periods (1 to 3 months), periodic lead concentrations were detected only for galvanized steel materials immersed in containers having either bay or river waters. The greatest lead release of 0.058 mg/L (2.54 mg/m^2) was observed after 3 months exposure of the steel gutter sample with river water. For galvanized steel materials, lead releases were greater in samples under controlled pH conditions compared to samples under natural pH conditions. Figures D-21 and D-22 show lead concentrations released from different pipe and gutter materials under un-controlled pH conditions. Figures D-23 and D-24 show the corresponding lead releases in mg per m^2 pipe/gutter surface area during these tests.

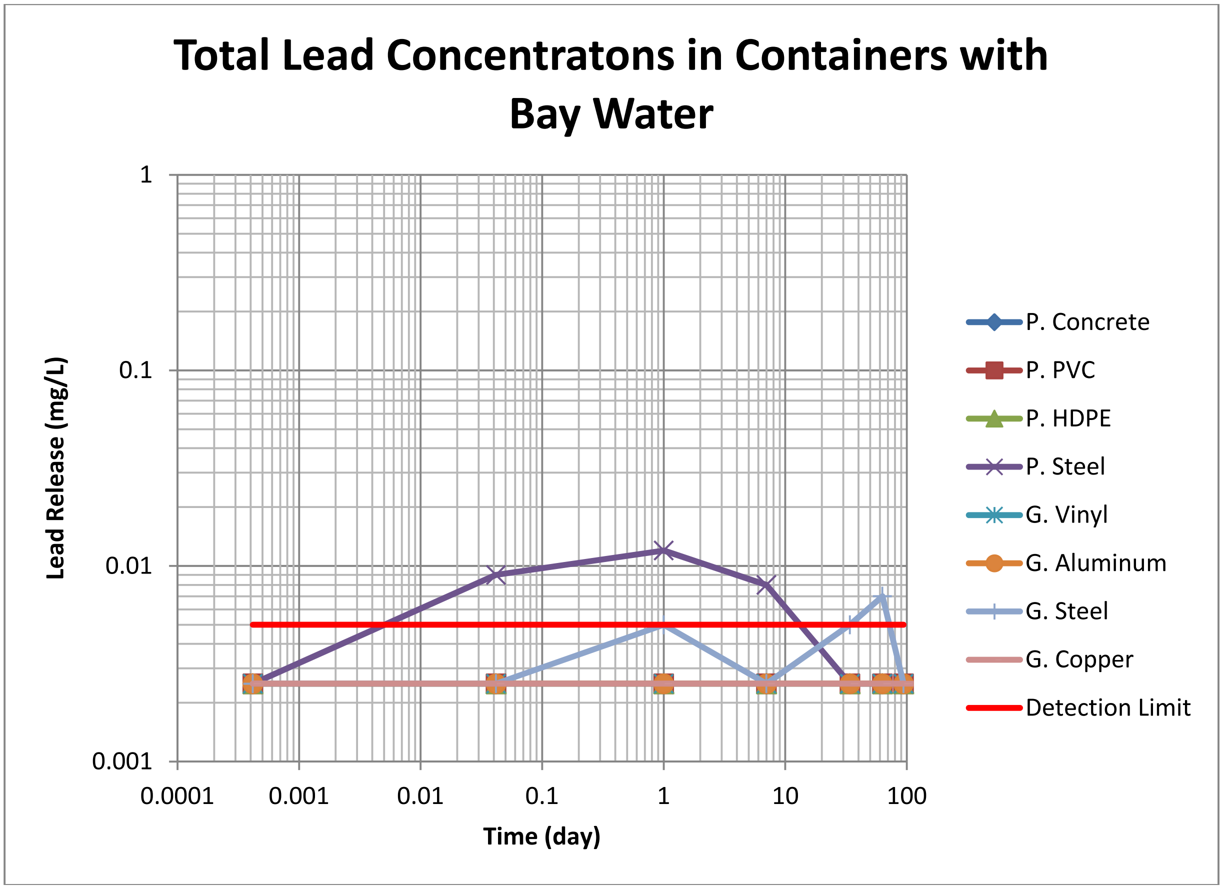


Figure D-21.Total lead concentrations in containers with bay water.

Footnote: P. = Pipe, G. = Gutter

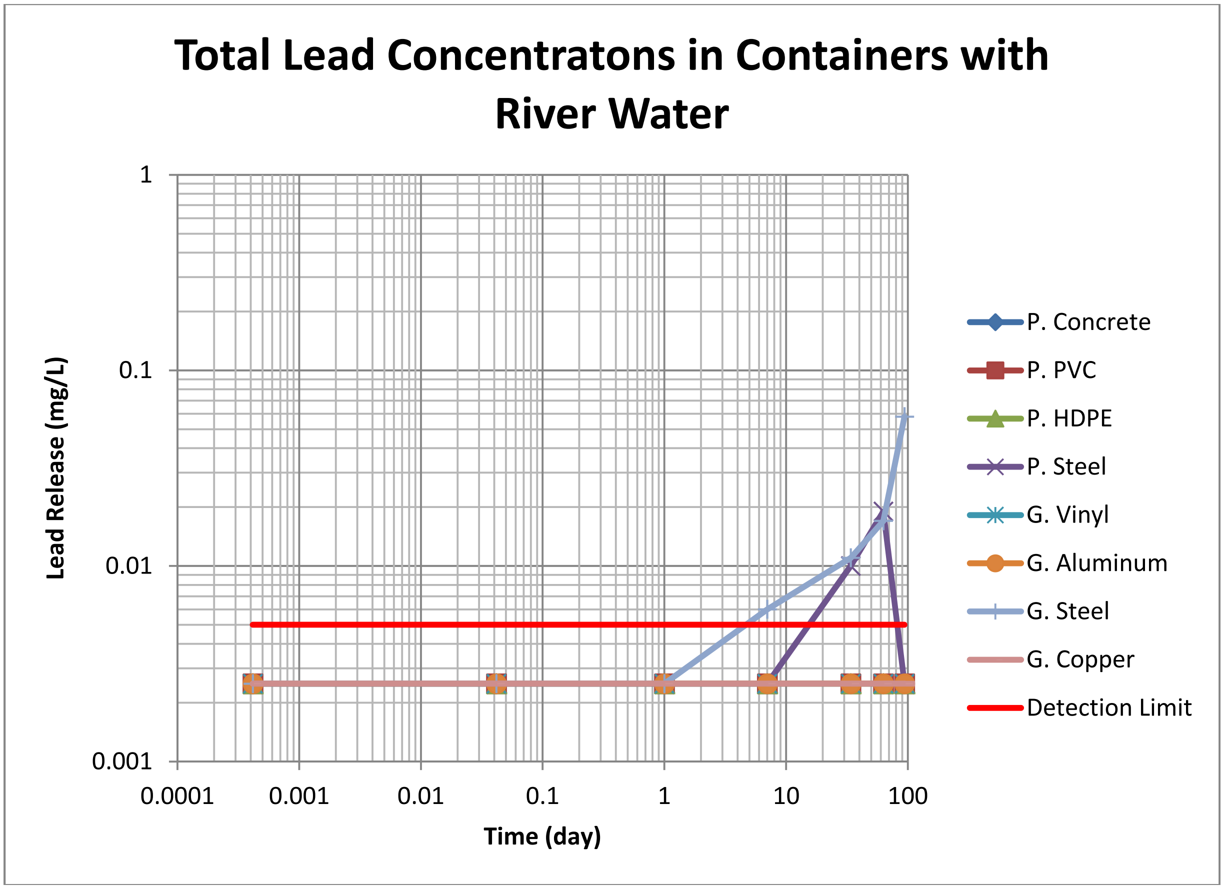


Figure D-22.Total lead concentrations in containers with river water.

Footnote: P. = Pipe, G. = Gutter

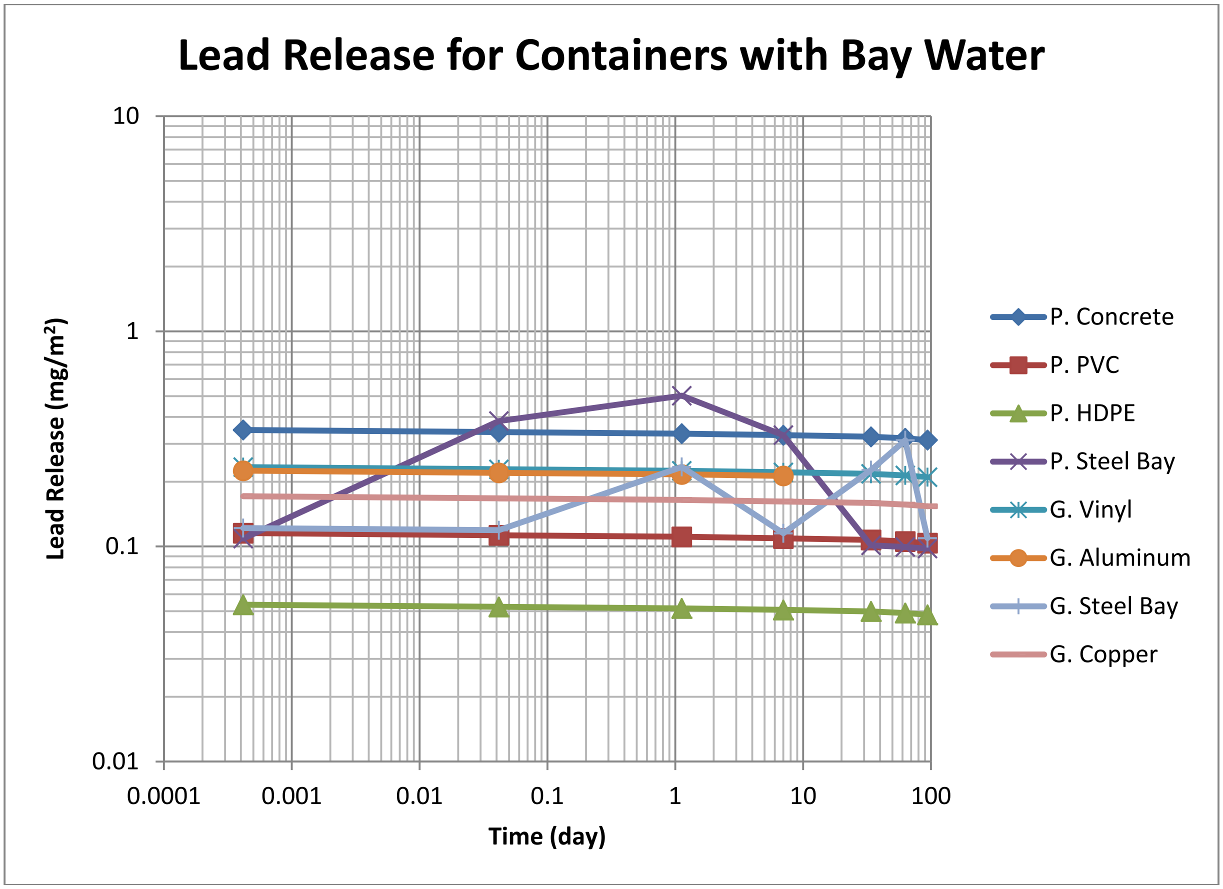


Figure D-23.Total lead losses in containers with bay water.

Footnote: P. = Pipe, G. = Gutter

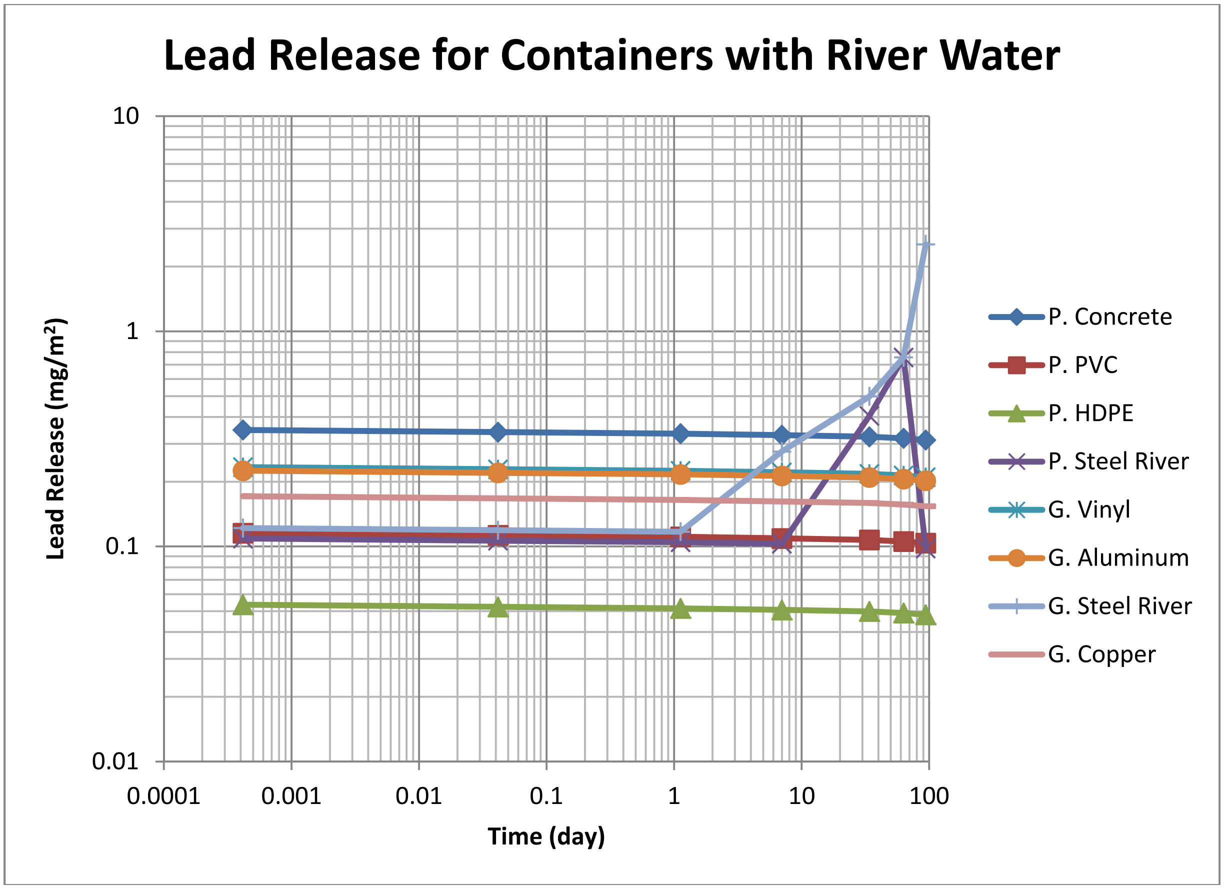


Figure D-24.Total lead losses in containers with river water.
Footnote: P. = Pipe, G. = Gutter

Table D-39 lists zinc, lead and copper releases from the most significant sources under various water conditions after three months exposure.

Table D-39.Final zinc, lead, and copper releases (mg/m^2 after 3 months of exposure).

Metal	Material	pH 5	pH 8	Bay	River
Zn	P. Galv. Steel	470	3,400	3,100	2,600
Zn	G. Galv. Steel	640	4,200*	1,600	8,300
Pb	P. Galv. Steel	10	25	ND	ND
Pb	G. Galv. Steel	1.7	4.5	ND	2.5
Cu	G. Copper	320	140	2,200	340

* After 2 months exposure

Aluminum and Iron Releases during Controlled and Natural pH Tests

Iron releases from galvanized steel materials exceeded those from other materials and were greater under pH 5 conditions than under pH 8 conditions. At pH 5 the releases ranged between 6 mg/L and 22 mg/L (260 mg/m2 and 850 mg/m2) and around 1 mg/L (<45 mg/m2) at pH 8. Iron releases from the galvanized steel specimens submerged into bay and river water were between 1 and 2 mg/L (<66.49 mg/m2) and were similar to iron releases at pH 8 values. Iron concentrations leached from concrete pipes in bay water (>2 mg/L; 68.3 mg/m2) were greater than those in river water (<1 mg/L; 25 mg/m2). The highest concentrations of aluminum were detected in the containers having aluminum materials and were ≤1 mg/L (<80 mg/m2) for all conditions and did not exceed the aquatic freshwater toxicity criteria for aluminum of 750 µg/L established by the US EPA. For pH 5 tests, aluminum was detected in the samples with aluminum and PVC materials. Under pH 8 conditions materials that released aluminum included aluminum, PVC, HDPE, vinyl, and steel gutter.

The Effect of Pipe and Storage Tank Materials, Exposure Time, pH, and Salinity on Heavy Metal Releases

Statistical analyses were conducted to determine the behavior of pollutant leaching from the gutter and piping materials depending on exposure time and pH (during the first test series) and on exposure time and salinity (during the second series of tests). The heavy metal releases per unit area were compared for the various gutter and pipe materials.

Kruskal–Wallis tests were performed on the metals data (zinc, copper and lead) for each of the test series after 1, 2, and 3 months exposure to determine if there was a statistically significant difference between these data points. The tests showed that the data for these exposure periods can be combined as replicates of long term exposure times. Also, Kruskal–Wallis tests were conducted on the metal data after 0.5, 1, and 27 h exposures during the first test series, and on the metal data after 1 and 27 h, and 1 week exposures during the second series of the experiments. These tests also showed that these data can be combined as replicates of short term exposure times at the 0.05 significance level.

Next, 2^2 factorial analyses were performed to evaluate the effects of exposure times (short vs. long) and pH (low vs. high) and the interactions of those factors on the metal releases in mg/m^2 surface area for each pipe and gutter material during the first series of tests. During the second test series, 2^2 factorial analyses were conducted to estimate the effect of exposure time and salinity (high vs. low), and the interaction of those factors.

By using the P-values (0.05) and the factorial effect/pooled standard error ratios of the factorial analysis, a determination was made as to whether or not the data could be combined into groups for each pipe and gutter material based on the effect (or absence of effect) of the factors and their interactions. Table D-40 shows significant groupings for each sample type for the different exposure conditions for zinc, lead, and copper releases according to the separate 2^2 factorial analyses.

Table D-40. Significant groups for lead, copper and zinc releases.

Material	Constituent	Varying pH Conditions	Varying Conductivity Conditions
Concrete (pipe sample)	Pb	ND	ND
	Cu	ND	ND
	Zn	all combined into one group	ND
PVC (pipe sample)	Pb	ND	ND
	Cu	short* vs. long** exp periods	ND
	Zn	short vs. long exp periods	all combined into one group
HDPE (pipe sample)	Pb	ND	ND
	Cu	short vs. long exp periods	ND
	Zn	pH 5 vs. pH 8; and short vs. long exp. periods	Short bay vs. short river vs. long bay vs. long river
Galvanized steel (pipe sample)	Pb	short vs. long exp periods	Short bay vs. short river vs. long bay vs. long river
	Cu	all combined into one group	ND
	Zn	all combined into one group	short vs. long exp periods
Vinyl (gutter sample)	Pb	ND	ND
	Cu	Short at pH 5 vs. short at pH 8 vs. long at pH 5 vs. long at pH 8	ND
	Zn	pH 5 vs. pH 8	all combined into one group
Aluminum (gutter sample)	Pb	ND	ND
	Cu	short vs. long exp periods	ND
	Zn	all combined into one group	all combined into one group
Galvanized steel (gutter sample)	Pb	short at pH 5 vs. short at pH 8 vs. long at pH 5 vs. long pH 8	all combined into one group
	Cu	Short at pH 5 vs. short at pH 8 vs. long at pH 5 vs. long at pH 8	ND
	Zn	all combined into one group	short vs. long exp periods
Copper (gutter sample)	Pb	ND	ND
	Cu	pH 5 vs. pH 8	short vs. long exp periods
	Zn	pH 5 vs. pH 8	all combined into one group

* Short exposure period (0 h to 27 h) for the varying pH tests, and short exposure period (0 week to 1 week) for varying conductivity tests.

** Long exposure period (27 h to 3 months) for the varying pH tests, and long exposure period (1 week to 3 months) for varying conductivity tests.

ND: the concentrations in the test solutions were mostly non-detected, therefore statistical analyses were not possible for these conditions.

Mann–Whitney tests were performed next to determine whether there were any statistically significant differences between the groups at a chosen significance level. These tests were performed as a pairwise comparison. The Mann–Whitney test was used because some of the data did not meet the assumptions of normality and equal variance (log transformations of the data also did not result in normally distributed values). As an example, the Mann-Whitney Test P-values for zinc releases from different pipe and gutter materials under controlled pH conditions indicated that there was a difference (at 0.05 significance level) between the majority of the groups. The exception included the difference between HDPE groups and copper pH8 group. Also, there was no difference between steel pipe and steel gutter groups.

For zinc releases from different materials under natural pH conditions, pairwise comparison of the groups indicated that there were differences between the majority of the groups; the exceptions included the differences between HDPE groups and aluminum and steel gutter (short exposure time) groups. There was no difference between steel gutter (short exposure) and steel pipe (short exposure) groups; also, there was no difference between steel gutter (long exposure) and steel pipe (long exposure) groups. However, there was a difference between the groups of steel gutter (short exposure) and steel gutter (long exposure), as well as between the groups of steel pipe during short exposure and the same material during the long exposure times.

For copper releases during buffered tests, there was a statistically significant difference between the majority of copper groups and groups with the other materials. There was no difference between copper releases from copper materials at pH 5 and pH 8 conditions. For copper releases under natural pH conditions, there was a statistically significant difference between the copper groups the groups with other materials. There was a difference between copper material (short exposure time) group and copper material (long exposure time) group.

For lead releases during controlled pH conditions, there were no statistically significant differences between short and long exposure releases for steel pipe; no differences between short and long exposure releases for steel gutter at pH 5 conditions; and no differences between short and long exposure releases for steel gutter at pH 8 conditions. Also, there were no differences between lead releases from steel gutter during short term exposure at pH 5 and at pH 8 conditions; and there were no differences between lead releases from steel gutter during long exposure time at pH 5 and pH 8 conditions. However there was a statistically significant difference (at the 0.05 significance level) between the majority of the steel gutter groups and the groups of the other materials.

For lead releases during the natural pH tests, there were no statistically significant differences for steel pipe during short exposure time in bay and river waters; no differences between steel pipes during long exposure in bay and river waters. Also, there were no differences between lead releases from steel pipe submerged in bay water during short and long exposure times; no difference between lead releases from steel pipe immersed into river water during short and long exposure times. However, there was a statistically significant difference between releases from steel pipe immersed into bay water during short exposure and the groups of materials other than steel. Also, there was a statistically significant difference between steel gutter group and the groups of materials other than-steel.

Factorial Test Setups

Tables D-41 andD-42 show different levels of the factors and contrast coefficients used for 2^2 factorial analyses.

Table D-41. Table of Contrast Coefficients (Controlled pH Conditions)

Mean	pH	Time	pH x Time
+	5 (-)	Short (-)	+
+	8 (+)	Short (-)	-
+	5 (-)	Long (+)	-
+	8 (+)	Long (+)	+

Table D-42. Table of Contrast Coefficients (Natural pH Conditions)

Mean	Conductivity	Time	Cond. x Time
+	High (-)	Short (-)	+
+	Low (+)	Short (-)	-
+	High (-)	Long (+)	-
+	Low (+)	Long (+)	+

Tables D-43 and D-44 show an example of the ANOVA results for the factorial analyses for copper releases from PVC pipe under controlled pH conditions. Time was a significant factor in this example (indicated by the p-value of 0). pH and the interaction of pH and time were not significant at 0.05 alpha level. Constant term and time coefficients were significant at the 0.05 alpha level. Residual analyses (Figure D-25) show that the residuals are approximately normally distributed with constant variance and have zero mean. ANOVA analyses indicated that only the effect of time was significant, therefore the final model was constructed that used only time as variable (Tables D-45 and D-46, and Figure D-26).

Table D-43. Example for Copper Releases from PVC Pipe Material for Controlled pH Conditions - Analysis of Variance.

Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
pH	1	2.157	2.157	2.157	3.31	0.106
Time	1	73.593	73.593	73.593	112.89	0.000
pH*Time	1	0.790	0.790	0.790	1.21	0.303
Error	8	5.215	5.215	0.652		
Total	11	81.755				

Table D-44. Example for Copper Releases from PVC Pipe Material for Controlled pH Conditions - Coefficients.

Term	Coef.	SE Coef.	T	P
Constant	2.3200	0.2331	9.95	0.000
pH	0.4239	0.2331	1.82	0.106
Time	-2.4764	0.2331	-10.63	0.000
pH*Time	-0.2566	0.2331	-1.10	0.303

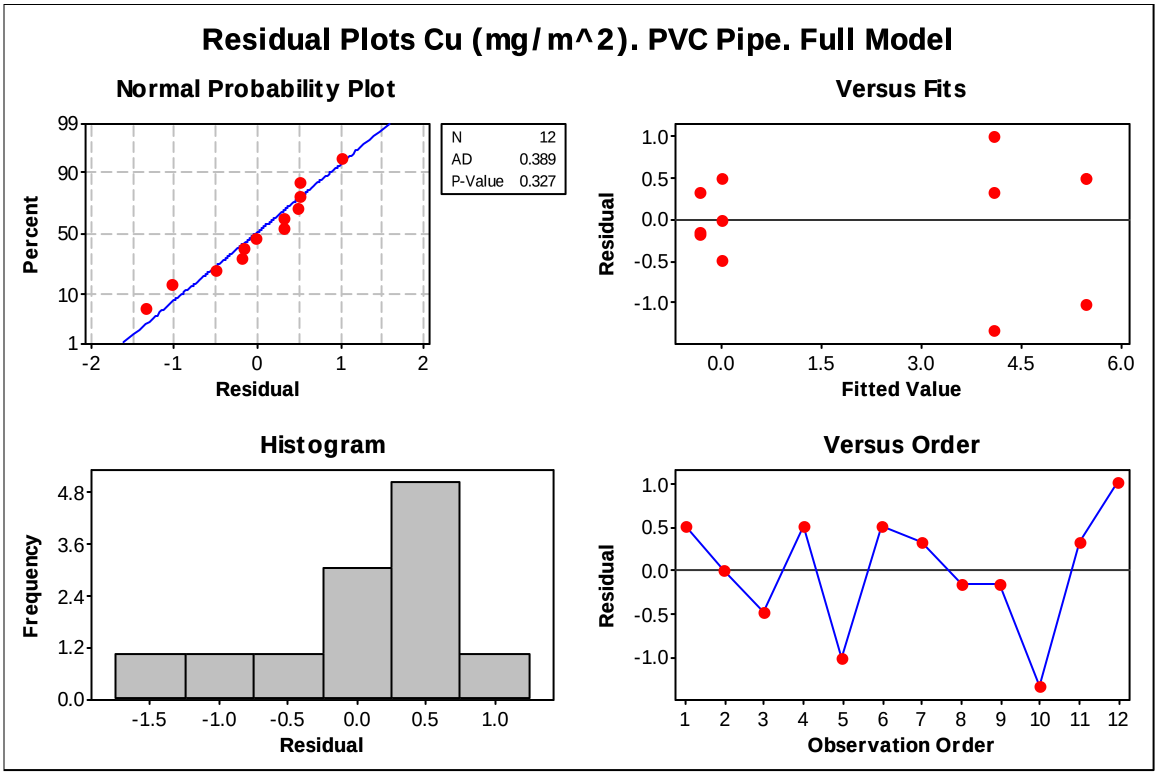


Figure D-25. Residual plots for Cu releases from PVC pipe under controlled pH conditions. Full Model.

Table D-45. Example - Analysis of Variance for Final Model.

Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
Time	1	73.593	73.593	73.593	90.17	0.000
Error	10	8.162	8.162	0.816		
Total	11	81.755				

Table D-46. Example – Coefficients for Final Model.

Term	Coef.	SE Coef.	T	P
Constant	2.3200	0.2608	8.90	0.000
Time	-2.4764	0.2608	-9.50	0.000

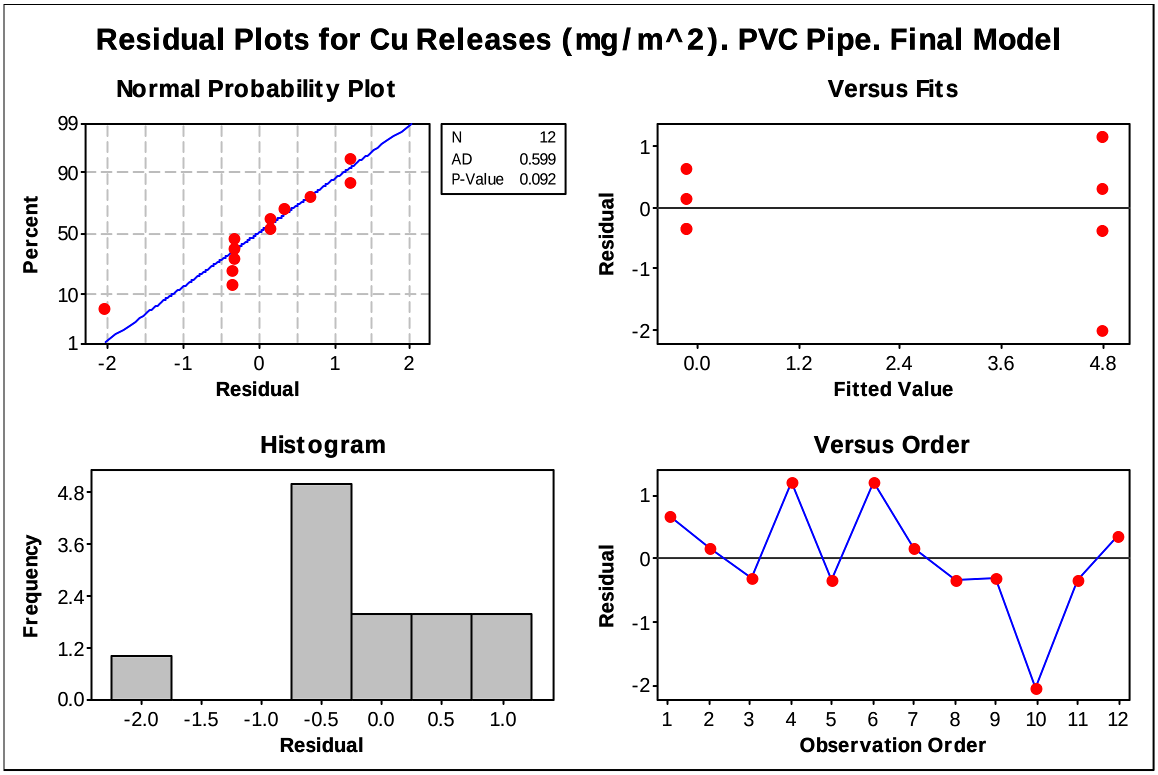


Figure D-26. Residual plots for Cu releases from PVC pipe under controlled pH conditions. Final Model.

Scatter plots of observed vs. modeled values were constructed to evaluate the overall performance of the models. Figure D-27 is an example of copper releases from PVC pipe under controlled pH conditions. It shows that the model predicts values for copper that are close to the observed values.

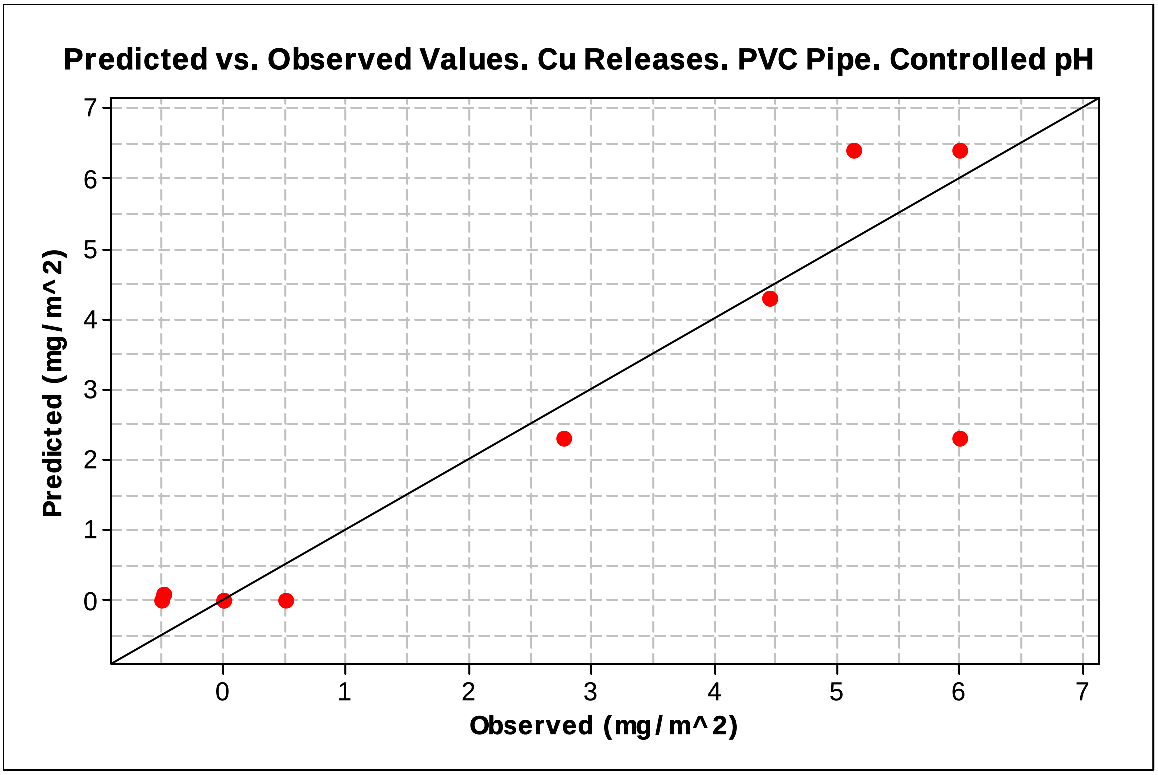


Figure D-27. Observed vs. fitted values for copper releases. PVC pipe. Controlled pH conditions.

Because Zn releases from galvanized pipe and gutter materials tracked each other very closely with respect to time under different water conditions, non-parametric Signed Rank test was performed to compare Zn releases from galvanized steel pipes and gutters. Non-parametric test was used because not all the data was normally distributed. Table D-47 shows p-values for Signed Rank test created using Sigma Plot statistical software. The test indicated that there was no statistical difference (at 0.05 alpha level) between pipe and gutter samples for pH 5, pH 8, and river waters, therefore, the data for pipe and gutter samples for each of those waters could be combined. Kruskal-Wallis test indicated that Zn releases after 0.5, 1, and 27 hours of exposure can be combined into “short” time group, and after 1, 2, and 3 months of exposure can be combined into “long” time group. Factorial analysis was performed for Zn releases from galvanized steel pipes and gutters (the data for pipes and gutters was combined) under controlled pH conditions. The factors were time (short vs. long) and pH (5 vs. 8). Factorial analysis for Zn releases from galvanized steel materials with combined data for pipes and gutters under natural pH conditions was not performed because Signed Rank test indicated that the data for Zn releases from pipe and gutter immersed into bay water are significantly different at 0.05 alpha level.

Table D-47. Signed Rank test for galvanized steel comparing pipe vs. gutter samples

Water	p-value
Controlled pH 5	0.688
Controlled pH 8	0.313
Bay	0.036
River	0.313

Tables D-48 through D-64 show significant conditions from the factorial analyses.

Table D-48. Significant groups based on 2^2 Factorial analyses. Concrete pipe. Controlled pH tests

Constituent	Concrete Pipe. Controlled pH Conditions		p-value
Pb, mg/m^2	ND at pH 5 and 8		
Cu, mg/m^2	ND at pH 5 and 8		
Zn, mg/m^2	pH 5: Avg.= 1.68 (COV = 0.01)	pH 8: Avg.=3.07 (COV = 0.53)	0.062

Footnote: ND = non-detects

Table D-49. Significant groups based on 2^2 Factorial analyses. Concrete pipe. Natural pH tests

Constituent	Concrete Pipe. Natural pH Conditions
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	ND in bay and river waters

Footnote: ND = non-detects

Table D-50. Significant groups based on 2^2 Factorial analyses. PVC pipe. Controlled pH tests

Constituent	PVC Pipe. Controlled pH Conditions		p-value
Pb, mg/m^2	ND at pH 5 and 8		
Cu, mg/m^2	S.: Avg.= -0.16* (COV= -2.58; St. Dev. = 0.40)	L.: Avg.= 4.8 (COV = 0.25)	0.000
Zn, mg/m^2	S.: Avg.= -0.65 (COV = -1.24; St. Dev. = 0.81)	L.: Avg.= 9.2 (COV = 0.69)	0.004

Footnote: S. = short exposure time; L. = long exposure time; ND = non-detects.

* the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table D-51. Significant groups based on 2^2 Factorial analyses. PVC pipe. Natural pH tests

Constituent	PVC Pipe. Natural pH Conditions
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	Avg.= 0.17-0.9; Median = 0-0.02; Min = 0.41; Max =1.24; # of Pts above DL: 2

Footnote: ND = non-detects

Table D-52. Significant groups based on 2^2 Factorial analyses. HDPE pipe. Controlled pH tests

Constituent	HDPE Pipe. Controlled pH Conditions				p-value
Pb, mg/m^2	ND at pH 5 and 8				
Cu, mg/m^2	S.: Avg.= 0.23 (COV = 0.03)		L.: Avg.= 0.62 (COV = 0.56)		0.02
Zn, mg/m^2	pH5: Avg.= 1 (COV = 0.56)	pH8: -0.05* (COV = -6.1; St. Dev. = 0.32)	S.: 0.04 (COV = 10.6)	L.: 0.54 (COV = 0.8)	0.000 (for pH) 0.001 (for Time)

Footnote: S. = short exposure time; L. = long exposure time; ND = non-detects.

* the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table D-53. Significant groups based on 2^2 Factorial analyses. HDPE pipe. Natural pH tests

Constituent	HDPE Pipe. Natural pH Conditions				p-value
Pb, mg/m^2	ND in bay and river waters				
Cu, mg/m^2	ND in bay and river waters				
Zn, mg/m^2	S.B-: Avg.= 0.21 (COV = 0.02)	S.R.: Avg.= -0.21* (COV = -0.02; St.Dev. = 0.0034)	L.B-: Avg.= 0.2 (COV = 0.02)	L.R.: Avg.= 0.2 (COV = 0.02)	0.000 (for Cond.) 0.000 (for Time) 0.000 (for Cond.*Time)

Footnote: S. = short exposure time; L. = long exposure time; B- = bay water; R. = river water; ND = non-detects.

* the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table D-54. Significant groups based on 2^2 Factorial analyses. Steel pipe. Controlled pH tests

Constituent	Galvanized Steel Pipe. Controlled pH Conditions		p-value
Pb, mg/m^2	S.: Avg. =0.12 (COV = 0.03)	L. Avg.=14.1 (COV = 0.8)	0.012
Cu, mg/m^2	Avg.= 0.60 - 1.28; Median = 0- 0.02; Min= 0; Max= 4.785; # of Pts above DL: 3		

Footnote: S. = short exposure time; L. = long exposure time.

Table D-55. Significant groups based on 2^2 Factorial analyses. Steel pipe. Natural pH tests

Constituent	Galvanized Steel Pipe. Natural pH Conditions				p-value
Pb, mg/m^2	S.B-: Avg.= 0.4 (COV = 0.22)	S.R.: Avg.= 0.1 (COV = 0.02)	L.B-: Avg.= 0.1 (COV = 0.02)	L.R.: Avg.= 0.42 (COV = 0.79)	0.922 (for Cond.) 0.962 (for Time) 0.014 (for Cond.*Time)
Cu, mg/m^2	ND in bay and river waters				
Zn, mg/m^2	S.: Avg.= 208 (COV = 0.65)		L.: Avg.= 2230 (COV = 0.51)		p = 0.002

Footnote: S. = short exposure time; L. = long exposure time; B- = bay; R. = river; ND = non-detects.

Table D-56. Significant groups based on 2^2 Factorial analyses. Vinyl gutter. Controlled pH tests

Constituent	Vinyl Gutter. Controlled pH Conditions				p-value
Pb, mg/m^2	ND at pH 5 and 8				
Cu, mg/m^2	S. pH 5: Avg.= 1.0 (COV = 0.03)	S. pH 8: Avg.= 1.0 (COV = 0.03)	L. pH 5: Avg.= 2.4 (COV = 0.19)	L. pH 8: Avg.= 1.5 (COV = 0.32)	0.047 (for pH) 0.001 (for Time) 0.047 (for pH*Time)
Zn, mg/m^2	pH5: Avg.=1 (COV = 0.57)		pH8: Avg.= 2.7 (COV = 0.38)		p =0.019

Footnote: S. = short exposure time; L. = long exposure time; ND = non-detects.

Table D-57. Significant groups based on 2^2 Factorial analyses. Vinyl gutter. Natural pH tests

Constituent	Vinyl Gutter. Natural pH Conditions
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	Avg.= 0.43 – 1.9; Median = 0-0.02; Min= 0; Max= 3.419; # of Pts above DL: 2

Footnote: ND = non-detects.

Table D-58. Significant groups based on 2^2 Factorial analyses. Aluminum gutter. Controlled pH tests

Constituent	Aluminum Gutter. Controlled pH Conditions		p-value
Pb, mg/m^2	ND at pH 5 and 8		
Cu, mg/m^2	S.: Avg.= 0.96 (COV = 0.03)	L.: Avg.= 2.6 (COV = 0.03)	0.000
Zn, mg/m^2	Avg.= 2.97 – 3.60; Median = -0.88 – 0.02; Min= 0; Max = 17.53; # of Pts above DL: 8		

Footnote: S. = short exposure time; L. = long exposure time; ND = non-detects.

Table D-59. Significant groups based on 2^2 Factorial analyses. Aluminum gutter. Natural pH tests

Constituent	**Aluminum Gutter. Natural pH Conditions**
Pb, mg/m^2	ND in bay and river waters
Cu, mg/m^2	ND in bay and river waters
Zn, mg/m^2	Avg.= 4.29 – 5.57; Median = 0 - 0.02; Min= -0.88*; Max= 57.55; # of Pts above DL: 3

Footnote: ND = non-detects.

* the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table D-60. Significant groups based on 2^2 Factorial analyses. Steel gutter. Controlled pH tests

Constituent	**Galvanized Steel Gutter. Controlled pH Conditions**				**p-value**
Pb, mg/m^2	S. pH5: Avg.= 0.13 (COV = 0.03)	S. pH8: Avg.= 0.22 (COV = 0.7)	L. pH5: Avg.= 1.3 (COV = 0.26)	L. pH8: Avg.= 4.8 (COV = 0.05)	0.000 (for pH) 0.000 (for Time) 0.000 (for pH*Time)
Cu, mg/m^2	S. pH5: Avg.= 0.52 (COV = 0.03)	S. pH8: Avg.= 0.52 (COV = 0.03)	L. pH5: Avg.= 0.47 (COV = 0.04)	L. pH8: Avg.= 1.3 (COV = 0.19)	0.000 (for pH) 0.001 (for Time) 0.000 (for pH*Time)

Footnote: S. = short exposure time; L. = long exposure time.

Table D-61. Significant groups based on 2^2 Factorial analyses. Steel gutter. Natural pH tests

Constituent	**Galvanized Steel Gutter. Natural pH Conditions**				**p-value**
Pb, mg/m^2	Avg. = 0.41 – 0.49; Median = 0.23 - 0.24; Min= 0; Max= 2.54; # of Pts above DL: 7				
Cu, mg/m^2	ND in bay and river waters				
Zn, mg/m^2	S. B-: Avg.= 151; COV = 0.74	S.R.: Avg.= 91; COV = 1.62	L. B-: Avg.= 841; COV = 0.85	L.R.: Avg.= 5387; COV = 0.73	0.089 (for Cond.) 0.032 (for Time) 0.082 (for Cond.*Time)

Footnote: S. = short exposure time; L. = long exposure time; B- = bay water; R. = river water; ND = non-detects.

Table D-62. Significant groups based on 2^2 Factorial analyses. Copper gutter. Controlled pH tests

Constituent	Copper Gutter. Controlled pH Conditions		p-value
Pb, mg/m^2	ND at pH 5 and 8		
Cu, mg/m^2	pH5: Avg.= 250 (COV = 0.66)	pH 8: Avg.= 70.5 (COV = 0.96)	0.033
Zn, mg/m^2	pH5: Avg.= 3.2 (COV = 0.81)	pH 8: Avg.= 0.22 (COV = 1.55)	0.019

Footnote: ND = non-detects.

Table D-63. Significant groups based on 2^2 Factorial analyses. Copper gutter. Natural pH tests

Constituent	Copper Gutter. Natural pH Conditions				p-value
Pb, mg/m^2	ND in bay and river waters				
Cu, mg/m^2	S.B: Avg.= 184 (COV = 1.04)	S.R: Avg.= 841 (COV = 0.91)	L.B-: Avg.= 1487 (COV = 0.67)	L.R.: Avg.= 242 (COV = 0.42)	0.045 (for Cond.) 0.033 (for Time) 0.096 (for Cond.*Time)
Zn, mg/m^2	Avg.= 3.46 - 3.79; Median = 1.27-1.62; Min= -0.67*; Max= 29.51; # of Pts above DL: 9				

Footnote: S. = short exposure time; L. = long exposure time; B- = bay water; R. = river water; ND = non-detects.
* the mg/m^2 releases are compared to initial time zero conditions without the material in the test water. If the observed concentrations decreased with time (such as from precipitation on the material), the observed release rate was negative. Obviously, zero should be used in predictions instead of negative values.

Table D-64. Significant groups based on 2^2 Factorial analyses. Steel materials. Controlled pH.

Constituent	Galvanized Steel Materials (Pipe and Gutter). Controlled pH Conditions				p-value
Zn, mg/m^2	S. pH 5: Avg.= 270 (COV = 0.96)	S. pH 8: Avg.= 28 (COV = 1.48)	L. pH 5: Avg.= 480 (COV = 0.20)	L. pH 8: Avg.= 1860 (COV = 0.84)	0.096 (for pH) 0.005 (for Time) 0.021 (for pH*Time)

Appendix E: Major Ion Concentrations during Metal Leaching Tests

During the buffered tests, the samples were analyzed for alkalinity, total hardness as $CaCO_3$ and calcium hardness as $CaCO_3$, chloride and sulfate after three months of exposure in each bucket. These concentrations were assumed to be constant during the test series. During the natural pH experiments, alkalinity, total hardness as $CaCO_3$ and calcium hardness as $CaCO_3$ were measured at time zero and after three months of exposure; chloride and sulfate concentrations were measured in the source water. The detection limits for the constituents are shown in Table E-1.

Table E-1. Water constituents in containers with pH 5 water

	Containers with pH 5							
Constituent, mg/L	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
Total Alkalinity	644	190	70	570	72	84	350	210
Total Hardness as $CaCO_3$	37.5	64.1	1.87	2.41	1.13	0.99	1.42	0.45
Calcium Hardness as $CaCO_3$	1.35	60.9	1.37	1.05	0.8	0.5	1.05	< 0.02
Calculated Calcium Ca^{2+}	0.54	24.39	0.55	0.42	0.32	0.20	0.42	4.0E-03
Calculated Magnesium Mg^{2+}	10.42	0.92	0.14	0.39	0.10	0.14	0.11	0.13
Chloride, Cl^-	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Sulfate, SO_4^{2-}	8.50	14.30	1.59	5.11	1.35	1.90	2.02	2.65
Calculated sodium Na^+	29	29	29	29	29	29	29	29
Calculated potassium K^+	2582	2582	2582	2582	2582	2582	2582	2582
Calculated HPO_4^{2-}	61	61	61	61	61	61	61	61
Calculated $H_2PO_4^-$	6404	6404	6404	6404	6404	6404	6404	6404
H^+	4.30E-04	5.94E-03	1.46E-02	1.60E-03	1.49E-02	1.46E-02	3.75E-03	7.47E-03
OH^-	3.99E-04	2.89E-05	1.18E-05	1.07E-04	1.15E-05	1.18E-05	4.58E-05	2.29E-05

Table E-2. Water constituents in containers with pH 8 water

	Containers with pH 8							
Constituent, mg/L	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
Total Alkalinity	3690	6900	5800	5900	5800	6300	7400	7300
Total Hardness as $CaCO_3$	1.64	7.00	1.23	0.87	0.83	0.25	0.97	0.48
Calcium Hardness as $CaCO_3$	0.65	4.69	0.77	0.37	0.50	< 0.02	0.47	0.15
Calculated Calcium Ca^{2+}	0.26	1.88	0.31	0.15	0.20	4.00E-03	0.19	0.06
Calculated Magnesium Mg^{2+}	0.29	0.67	0.13	0.14	0.10	0.07	0.14	0.10
Chloride, Cl^-	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Sulfate, SO_4^{2-}	4.32	16.3	0.53	2.28	0.50	0.76	0.69	2.38
Calculated sodium Na^+	2970	2970	2970	2970	2970	2970	2970	2970
Calculated potassium K^+	81	81	81	81	81	81	81	81
Calculated HPO_4^{2-}	6200	6200	6200	6200	6200	6200	6200	6200
Calculated $H_2PO_4^-$	200	200	200	200	200	200	200	200
H^+	1.11E-06	3.19E-06	3.42E-06	1.27E-06	3.34E-06	3.19E-06	8.58E-07	1.75E-06
OH^-	1.55E-01	5.38E-02	5.02E-02	1.35E-01	5.14E-02	5.38E-02	2.00E-01	9.79E-02

Table E-3. Water constituents in containers with bay water (time zero)

	Containers with Bay Water. Time Zero							
Constituent, mg/L	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
Total Alkalinity	70	60	60	60	60	70	60	60
Total Hardness as $CaCO_3$	1160	1090	1110	1010	1100	1110	1010	1010
Calcium Hardness as $CaCO_3$	221	213	209	215	209	226	215	226
Calculated Calcium Ca^{2+}	89	85	84	86	84	91	86	91
Calculated Magnesium Mg^{2+}	271	253	260	229	257	255	229	226

Table E-4. Water constituents in containers with river water (time zero)

	Containers with River Water. Time Zero							
Constituent, mg/L	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
Total Alkalinity	60	90	85	90	90	85	90	85
Total Hardness as $CaCO_3$	136	145	133	133	123	122	130	191
Calcium Hardness as $CaCO_3$	57	68	62	57	51	51	57	102
Calculated Calcium Ca^{2+}	23	27	25	23	21	21	23	41
Calculated Magnesium Mg^{2+}	23	22	20	22	21	20	21	26

Table E-5. Water constituents in containers with bay water after three months of exposure

	Containers with Bay Water. After Three Months of Exposure							
Constituent, mg/L	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
Total Alkalinity	184	80	80	12	92	108	16	100
Total Hardness as $CaCO_3$	1240	1560	1640	1360	1610	1860	1430	1270
Calcium Hardness as $CaCO_3$	332	365	382	347	400	459	432	337
Calculated Calcium Ca^{2+}	133	146	153	139	160	184	173	135
Calculated Magnesium Mg^{2+}	262	344	363	292	349	404	288	269
Fluoride F^-	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Nitrate NO_3^-	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Total Phosphorus	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Bromide Br^-	12.8	12.8	12.8	12.8	12.8	12.8	12.8	12.8
Manganese Mn	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Boron as BO_3^{3-}	4.05	4.05	4.05	4.05	4.05	4.05	4.05	4.05
Silicon Si	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Sodium Na^+	1760	1760	1760	1760	1760	1760	1760	1760
Potassium K^+	67.3	67.3	67.3	67.3	67.3	67.3	67.3	67.3
Chloride Cl^-	3350	3350	3350	3350	3350	3350	3350	3350
Sulfate SO_4^{2-}	674	674	674	674	674	674	674	674
H^+	4.11E-06	1.27E-05	1.46E-05	1.01E-04	1.08E-05	1.01E-05	1.46E-05	1.33E-05
OH^-	4.17E-02	1.35E-02	1.18E-02	1.70E-03	1.59E-02	1.70E-02	1.18E-02	1.74E-02

Table E-6. Water constituents in containers with river water after three months of exposure

	Containers with River Water. After Three Months of Exposure							
Constituent, mg/L	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
Total Alkalinity	156	140	124	56	116	116	16	116
Total Hardness as $CaCO_3$	107	195	177	70	171	181	171	175
Calcium Hardness as $CaCO_3$	48	104	92	16	92	100	100	100
Calculated Calcium Ca^{2+}	19	42	37	6.3	37	40	40	40
Calculated Magnesium Mg^{2+}	17	26	25	16	23	23	21	22
Fluoride F^-	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28
Nitrate NO_3^-	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68
Total Phosphorus	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Bromide Br^-	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23
Manganese Mn	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Boron as BO_3^{3-}	0.54	0.54	0.54	0.54	0.54	0.54	0.54	0.54
Silicon Si	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Sodium Na^+	66.4	66.4	66.4	66.4	66.4	66.4	66.4	66.4
Potassium K^+	5.82	5.82	5.82	5.82	5.82	5.82	5.82	5.82
Chloride Cl^-	89.0	89.0	89.0	89.0	89.0	89.0	89.0	89.0
Sulfate SO_4^{2-}	106	106	106	106	106	106	106	106
H^+	1.83E-06	3.75E-06	4.50E-06	1.36E-06	4.94E-06	4.61E-06	1.18E-04	4.94E-06
OH^-	9.35E-02	4.58E-02	3.81E-02	1.26E-01	3.47E-02	3.72E-02	1.45E-03	3.47E-02

Table E-7. Oxidation Reduction Potential for Buffered tests after three months of exposure

	Oxidation Reduction Potential (ORP), Volts. Buffered Tests. After Three Months of Exposure.							
Condition	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
pH 5	0.16	0.22	0.21	0.17	0.21	0.20	0.19	0.25
pH 8	0.13	0.13	0.13	0.11	0.13	0.14	0.12	0.17

Table E-8. Oxidation Reduction Potential (Bay water)

	Oxidation Reduction Potential (ORP), Volts. Bay Water							
Time, hr	**P. Concrete**	**P. PVC**	**P. HDPE**	**P. Steel**	**G. Vinyl**	**G. Aluminum**	**G. Steel**	**G. Copper**
0.01	-0.13	-0.13	-0.13	-0.13	-0.13	-0.13	-0.13	-0.13
1	-0.12	-0.13	-0.12	-0.12	-0.12	-0.12	-0.12	-0.11
27	-0.15	-0.14	-0.15	-0.15	-0.15	-0.15	-0.15	-0.14
168	-0.21	-0.21	-0.21	-0.20	-0.20	-0.20	-0.20	-0.19
816	-0.19	-0.19	-0.19	-0.18	-0.19	-0.19	-0.19	-0.16
1512	-0.16	-0.16	-0.16	-0.17	-0.17	-0.18	-0.18	-0.12
2256	-0.18	-0.18	-0.18	-0.18	-0.18	-0.18	-0.18	-0.14

Table E-9. Oxidation Reduction Potential (River water)

	Oxidation Reduction Potential (ORP), Volts. River Water							
Time, hr	P. Concrete	P. PVC	P. HDPE	P. Steel	G. Vinyl	G. Aluminum	G. Steel	G. Copper
0.01	-0.15	-0.15	-0.14	-0.14	-0.15	-0.14	-0.15	-0.15
1	-0.13	-0.13	-0.12	-0.12	-0.12	-0.11	-0.11	-0.14
27	-0.14	-0.14	-0.14	-0.14	-0.14	-0.14	-0.14	-0.11
168	-0.19	-0.19	-0.19	-0.21	-0.20	-0.20	-0.21	-0.17
816	-0.12	-0.12	-0.19	-0.15	-0.13	-0.13	-0.15	-0.73
1512	-0.95	-0.92	-0.11	-0.12	-0.11	-0.11	-0.96	-0.63
2256	-0.12	-0.12	-0.12	-0.13	-0.12	-0.12	-0.10	-0.06

Appendix F. Corrosion Processes and Chemical Modeling of Heavy Metals

Corrosion Processes Affecting Contaminant Releases from Materials used in Stormwater Management

Contact with water can damage materials in several ways. The corrosion of metals is one of the most common types of material damage. Other causes include the dissolving of calcareous materials and the degradation of concrete (Degremont 1979).

The products of reaction are formed under ambient conditions by a gaseous oxidizing atmosphere which results in the physical adsorption of oxygen, leading to the formation of one or more monolayers of oxide. Electron tunneling through the stable oxide film to the adsorbed oxygen also occurs, which sets up a potential. This is followed by a film rearrangement which results in the formation of oxide grains boundaries. At first, the oxide films that are formed at ambient temperatures are continuous and amorphous but may undergo local crystallization with the incorporation of the oxide "islands", which is facilitated by water, heat, high electric fields, and mechanical stress. In dry air, films consisting essentially of an anhydrous oxide are formed and may reach a thickness of 3 nm. However, in the presence of water, which can range from condensed films deposited from humid atmospheres to bulk aqueous phases, increases in electron tunneling conductivity will result in further thickening as partial hydration increases. Other constituents, such as H_2S, SO_2, CO_2, Cl^-, present in contaminated atmospheres, may become incorporated (Shreir 1976).

When metal is submerged in an electrolyte solution, the metal itself retains a negative charge but positively charged metal ions have a tendency to dissolve. An electrode with a potential which is expressed by Nernst's equation is formed (Garrels and Christ 1990; Degremont 1979). The potential for this half-cell reaction is:

$E = E^o + RT/(nF)*\ln[\text{oxidized state}]/[\text{reduced state}]$
Where,
E^o = standard potential measured against a standard hydrogen electrode.
n = the valence of the metal ions in question
T = absolute temperature
R = the molar constant of perfect gases = 8.31 J/(mol K)
F = the Faraday number

Corrosion by oxygen is the result of an electrochemical process and can be demonstrated by submerging an iron sample into an electrolyte solution. The dissociation of water will be observed (Degremont 1979):

$H_2O \leftrightarrow OH^- + H^+$
Slow diffusion of O_2 occurs into the water.

This oxygenic corrosion is an electrochemical process. It creates positive and negative electric poles, called the cathode and the anode, respectively, with an electric current flowing between them. Oxidation occurs at the anode (metal dissolves), while the cathode is protected against corrosion.

Reaction of oxidation of iron:
$Fe \rightarrow Fe^{2+} + 2e^-$
Anode reactions:
$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$
$Fe(OH)_2 + 2H_2O + O_2 \rightarrow Fe(OH)_3$
Cathode reactions:
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
$2H^+ + \frac{1}{2} O_2 + 2e^- \rightarrow H_2O$

The oxygen in aerated water facilitates the complementary electrode process needed to balance the electron transfers ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$). Because of its ability to absorb electrons, this electrode is acting as a cathode.In this case, the equilibrium potential is governed by the concentration of OH^- ions (and therefore pH value), and by partial oxygen pressure.

$E' = E^o – RT/F*\ln(OH^-) + RT/(4F) \ln pO_2$

Where,
E^o = the standard potential
p = partial oxygen pressure

The electrode potential is directly proportional to the level of dissolved oxygen. This leads to the evident paradox that if part of the metal does not come in contact with the oxygen, it becomes anodic and hence is more likely to corrode compared to the rest of the surface which is protected by the oxygen. This accounts for the damage caused by various deposits which prevent oxygen from reaching the underlying surfaces and creates an anodic area. The release of the OH^- ions at the cathode increase the pH of the water, at least in the immediate vicinity of the metal surface. Also, in the presence of oxygen, Fe^{2+} ions oxidize to Fe^{3+} ions. Ferric oxide ($Fe(OH)_3$) is only marginally soluble. Rather than being carried away by the water and leaving a clean surface, the corrosion products collect around the anode and form “pustules” which create an additional barrier to the diffusion of the oxygen and strengthen the anodic character of the covered surface. This is the reason that corrosion by oxygen perforates the metal.

Areas in the metal containing no dissolved oxygen, such as screw threads, cavities, and cracks, form anodic regions. Areas containing dissolved oxygen form cathodic regions. A difference in potential may also appear between zones where there is variation in the concentration of dissolved oxygen in the liquid film.

Therefore the concept of a large number of elementary microcells formed by the difference in oxygen concentration can be extended to all irregularities in metal parts resulting from their nature, construction, degree of fouling, or from temperature differences.

The development of corrosion by differential oxygen concentration in the interfacial layer is dictated primarily by the solubility of oxygen and, specifically, by its rate of diffusion, because slower rates boost corrosion. The solubility of oxygen is a function of temperature and partial pressure, decreasing as temperatures rise, but never dropping to zero (Degremont 1979).

In nature, water is not pure. It contains numerous dissolved chemical elements, with calcium bicarbonate being the most abundant. Chemical reactions such as the dissolution of calcium carbonate (aggressive water) or scale formation can result with any shift in equilibrium between $CaCO_3$ salt and carbon dioxide. Calcium bicarbonate is unstable in aqueous solutions and has a tendency to lose carbonic acid and precipitate $CaCO_3$:

$Ca(HCO_3)_2 \leftrightarrow CaCO_3 + H_2O + CO_2$

A quantity of free CO_2, known as the equilibrium CO_2, is necessary to reverse the precipitation and maintain the calcium bicarbonate in solution. In natural water containing more free CO_2 than is required to keep the calcium bicarbonate in solution, the excess of CO_2 is aggressive to limestone. The water will form scale when the free CO_2 is less than the equilibrium CO_2 (Degremont 1979).

Dissociation of carbonic acid occurs according to the following equations:

$H_2CO_3\ (H_2O + CO) \leftrightarrow H^+ + HCO_3^-$
$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$

Dissociation constants for the equations above:

$K_1 = [H^+]\,[HCO_3^-]/[CO_2]$
$K_2 = [H^+]\,[CO_3^{2-}]/[HCO_3^-]$

From dissociation equations of carbonic acid, it can be seen that the proportions of free carbon dioxide, bicarbonate and carbonate in the water depend on the pH of water solving the equations; at pH values of 3.7 to 4, all carbonic acid is represented by carbon dioxide. As the pH increases, the proportion of CO_2 decreases and at the same time the proportion of HCO_3^- increases. At pH values = 8.3 to 8.4, practically all carbonic acid is represented by bicarbonate ions (> 98%), and proportions of ($CO_2 + CO_3^{2-}$) account for less than 2 %. At pH values above 8.3 to 8.4, free carbon dioxide in the water is absent, the proportion of carbonate ions increases, however the proportion of bicarbonate ions decreases. At pH values of approximately 12, all carbonic acid is represented only by carbonate ions (Klyachko 1971).

Langelier (Snoeyink and Jenkins 1980) suggested the use of the Saturation Index (or the Langelier Index) to determine whether or not a water is in equilibrium with $CaCO_{3(s)}$. The Langelier Index is the difference between the actual pH of water and the pH the water would have if it were in equilibrium with $CaCO_{3(s)}$.

L.I. = pH_a-pH_s
Where,
pH_a = actual pH of water
pH_s = pH of water if it were in equilibrium with $CaCO_{3(s)}$ at the existing solution concentrations of HCO^{3-} and Ca^{2+}.

If the L.I. is a positive value, the water is oversaturated with $CaCO_{3(s)}$ and will tend to precipitate $CaCO_{3(s)}$, and the water is scale-forming. If the L.I. is a negative value, the water is undersaturated with $CaCO_{3(s)}$ and will tend to dissolve $CaCO_{3(s)}$, and the water is corrosive. If L.I of the water is zero, it is in equilibrium with $CaCO_{3(s)}$.

$pH_s = pK_{a,2} – pK_{so} + p[Ca^{2+}] + p[HCO_3^-] – \log \gamma_{Ca2+} - \log \gamma_{HCO3-}$
Where,
$pK_{a,2}$ =- log (equilibrium constant of the reaction $HCO_3^- = CO_3^{2-} + H^+$)
pK_{so} =- log (equilibrium constant of the reaction $CaCO_{3(s)} = Ca^{2+} + CO_3^{2-}$)
γ_{Ca2+} = the activity coefficient of ion Ca^{2+}
γ_{HCO3}^- = the activity coefficient of ion HCO_3^-
$pK_{a,2}$ = 10.43 at 15 °C; 10.38 at 20 °C; 10.33 at 25 °C
pK_{so} = 8.22 at 15 °C; 8.28 at 20 °C; 8.34 at 25 °C

The LSI is indicative of the solubility of calcium carbonate in the water. If the LSI is positive, calcium carbonate may be deposited, if the LSI is negative, the calcium carbonate may be dissolved. Negative LSI is commonly interpreted as an indicator of corrosive water (Snoeyink and Jenkins 1980).

Calcium bicarbonate water containing enough oxygen and which is in carbonic equilibrium generates a natural protective film on the cathodic regions when cold. This layer, known as the Tillmans' film, is composed of a mixed precipitate of $CaCO_3$ and iron oxides. The process occurs in a pH range from about 7 to 8.5 (Degremont 1979).The formation of natural or manufactured protective films can reduce corrosion. Artificial protective films can be produced by the application of inhibitors or an electric voltage. The natural inhibiting process is linked to the presence of OH^- ions and consequently it can occur at neutral or alkaline pH values (Degremont 1979).
In the cathodic regions, the H^- ions are absorbed and alkalinity increases. The excess OH^- ions combine with the Fe^{2+} ions which are released to form ferrous hydroxide $Fe(OH)_2$ which precipitates as a reasonably uniform film on the cathodic or anodic zones. This hydroxide is unstable and depending on the temperature and chemical

composition of the water, undergoes transformations which determine the protective nature of the film formed (Degremont 1979).

If substantial amounts of oxygen are diffused on the cathodic areas, there is direct and swift oxidation of the non-protective ferrous hydroxide (II) into ferric hydroxide (III). In the presence of enough calcium bicarbonate there is simultaneous local precipitation of $CaCO_3$ which syncrystallises with the various iron oxides and a natural protective film is formed. Oxygen can aid passivation by the formation of oxides. Chemical inhibitors, such as polyphosphates, are used when there is oxygen corrosion. Polyphosphates, which have a liner structure, decompose progressively by hydrolysis, and create orthophosphate ions (PO_4^{3-}) that precipitate in the form of tricalcium phosphate ($Ca_3(PO_4)_2$), which is only slightly soluble and results in the formation of calcium phosphocarbonate (Degremont 1979).

Oxygen and CO_2content are two of the primary parameters influencing corrosion. Other factors affecting corrosion include the presence of dissolved salts chiefly chlorides, temperature variations, suspended solids, and the presence of microorganisms. The influence of chlorides is significant. During the initial stage of corrosion, the concentration of Cl^- ions carried by the current increases and simultaneously, H^+ ions appear because of remote precipitation of OH^- ions in the form of ferrous hydroxide. A heavy local concentration of H^+ and Cl^- ions is produced preventing local precipitation of the hydroxides. A rise in the chloride ion content of water increases the probability of the creation of huge numbers of micro-anodes and leads to an increase in general corrosion and pitting. This is the reason for the appearance of pitting corrosion due to the HCl formation. Sulfates impact corrosion by aiding the cycle of sulfate-reducing bacteria and in the spread of biological corrosion. OH^- ions, chromates, and silicates, on the other hand, have a tendency to form a protective film and to minimize corrosion (Degremont 1979). Corrosion rates were found to correlate with the content of the sulfates and chlorides in the water (Gabriel and Moran 1998). This relationship was determined to be unreliable when the sum of sulfate (SO_4) and chloride (Cl) ions was less than 100 ppm (mg/L). Chlorides and other dissolved salts increase the electrical conductivity and therefore promote the flow of corrosion currents.

Often, biological corrosion is a secondary form of corrosion. It usually manifests itself by the formation of concretions in the shape of tightly packed nodules. These nodules commonly create significant obstructions and underlying pitting which often develops into perforations. These concretions which frequently contain calcium carbonate consist of large quantities of fibrous ferro-bacteria, enclosed in partially dehydrated ferric oxide (Degremont 1979).

Existing deposits already in an old fouled system or deposits originating from the distribution of badly-filtered water can cause corrosion due either to non-aerated areas that can create anodic areas under the deposit or to the formation of regions where various strains of bacteria develop and reducing depassivating reactions occur (Degremont 1979).

Corrosion resulting from flow velocity is an important parameter involving physical, mechanical, and electrochemical phenomena (Gabriel and Moran 1998; Degremont 1979). Three types of damage can be produced as follows: 1) by cavitation caused by the existence of variation in local levels of hydrostatic pressure, above and below the vapor tension of the water, which can result in vapor bubbles being released and then annihilated by implosion at very high pressures, resulting in an uneven hollowing out of the solid metal, 2) by erosion-abrasion produced by the kinetic energy of particulate matter in the water, which results in continuous damage to the protective layer by regular, uniform abrasion of the solid metal, 3) by erosion-corrosion caused by interference with the development of the continuous film as oxygen is diffused at a rate determined by the water flow rate (Degremont 1979).

Concrete Corrosion

Concrete is made from various types of fine and coarse aggregate that are bonded together with a lime-based cement matrix and often contains steel reinforcement (Gabriel and Moran 1998). In theory, because of the positive electrical charge of the iron in the concrete, the reinforcement cannot corrode until degradation of the encasing concrete occurs. The iron in the concrete which has a pH of about 11.6 has a potential of approximately + 100 mV in reference to the hydrogen electrode. Any action to prevent or retard degradation must therefore be focused first on the concrete (Degremont 1979).

The causes of concrete degradation can be mechanical or chemical. The mechanical causes include excessive permeability or the existence of cavities and cracks which can occur during manufacture of the concrete. This can be minimized by increasing its plasticity by maintaining an optimal water/cement ratio, or adding a plasticizer. Another mechanical cause of concrete degradation is erosion resulting from excessive water velocities (especially if carrying sediment) through concrete pipes. The chemical causes of concrete corrosion are determined by the composition of the cement and the corrosiveness of the water. Silica (SiO_2), lime ($Ca(OH)_2$), and alumina (Al_2O_3) are the main ingredients of cement, with iron, magnesia (MgO) and alkalis being secondary constituents. Cement usually forms a very basic (high pH) medium that includes substantial quantities of soluble salts (Degremont 1979). Chemical degradation can result from the aggressiveness of CO_2, attack by strong acids (mainly produced by sulfate containing wastewaters), the action of ammonia, a content of high sulfates and chlorides, attack by strong alkalis, or bacterial corrosion with the formation of H_2S and low pH (Gabriel and Moran 1998, Degremont 1979).

Concrete is attacked by carbon dioxide (CO_2) when CO_2 concentrations exceed equilibrium CO_2 concentration $CaCO_3 + H_2O + CO_2 \leftrightarrow Ca(HCO_3)_2$. However, a high residue of lime (CaO) alkalinity in the pores of the concrete allows the precipitation of deposits of $CaCO_3$ and other salts, which delays the degradation of the concrete in the short term. When the calcium bicarbonate alkalinity of the water exceeds 61 to 73 mg/L and its pH is greater than 6.5, corresponding to conditions near $CaCO_3/CO_2$ equilibrium, the destruction can be tolerated (Degremont 1979).

Concrete is susceptible to acid attack because of its alkaline nature. Increasing corrosivity occurs in the presence of acids such as phosphoric, sulfuric, nitric, hydrochloric, etc. Organic acids are also destructive. Acids dissolve cement compounds and calcareous aggregate and form water-soluble calcium compounds that will be leached away (Gabriel and Moran 1998). Concrete is often prone to cracking and the correct coating must be used to protect it completely (Degremont 1979).

Concrete can also be attacked by strong alkalis. Water with a strong alkali content (pH >12) is harmful to all kinds of cements because certain alumina-based components are likely to be solubidized (Degremont 1979).

Ammonia in wastewater increases the degradation of concrete by facilitating nitrifying reactions which occur only in an aerobic medium and lead to the acid formation (Degremont 1979). The action of sulfates is complex and is based on the transformation of calcium sulfate ($CaSO_4$) into expanding Candlot salt (Gabriel and Moran 1998; Degremont 1979), also known as ettringite:

$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4{}^* \; 2H_2O + NaOH$
$2CaOAl_2O_3,\ 12H_2O + 3CaSO_4,\ 2H_2O + 13H_2O \rightarrow 3\ CaO,\ Al_2O_3,\ 3\ CaSO_4,\ 31\ H_2O$

Ettringite is often formed during the sulfate attack and can result in cracking and scaling of concrete. Also, sulfate attack is often manifested, not by expansion or cracking, but by loss of cohesion and strength (Quyang, et al. 1988). Deteriorated invert surface becomes fragile and an abrasive bed load will more easily erode invert concrete surface at lower velocities of effluent flow (Gabriel and Moran 1998). If calcium and magnesium chlorides are present, they can react with calcium aluminate hydrates to form chloroaluminates which may result in low to medium expansion of concrete (Gabriel and Moran 1998). Seawater has a high chloride and sulfate content.

Cyclic freezing and thawing of moisture that remains in or has been absorbed by concrete will cause spalling of the surface (due to the water expansion when it freezes causing expansion and degradation of concrete). The deterioration of concrete will leave the surface open to further acid and/or sulfate attack. Too high a water/cement ratio in the concrete will cause a greater porosity of hardened concrete, faster diffusion of chloride ions to the steel/concrete interface, easier ingress of oxygen, and lower electrical resistivity, all of which will result in the reduction in the initiation time for corrosion. The larger volume required by the steel corrosion end products will lead to debonding of the steel and spalling of the concrete (Gabriel and Moran 1998).

Aluminum Corrosion

Aluminum is corrosive in strong acid solutions that have a pH of less than 4 and in strong caustic solutions. A protective scale forms in aerated areas (Gabriel and Moran

1998). Aluminum is passivated by oxidation in moist air and by the formation of a protective film alumina $2Al + 3H_2O – 3e^- = Al_2O_3 + 6H^+$ (Degremont 1979).

Under soft water conditions, the resistance to pitting corrosion is high. Pitting corrosion is more likely to take place in waters containing ions of copper, bicarbonate, chloride, sulfate, and oxygen. Such heavy metal ions as copper and iron increase the possibility of electrochemical corrosion by forming stray electrical currents and galvanic couples. It was noted that a combination of low resistivity with low pH values tend to increase the average metal loss. When low resistivity was paired with high pH, substantial corrosion was observed (Gabriel and Moran 1998).

Copper Corrosion

In copper plumbing systems, corrosion can lead to a number of problems including colored (blue) water, and pinhole leaks in the pipe or fittings. Copper can form ions in water by losing one or two electrons (e^-) (oxidation), and oxygen often accepts the electrons (reduction). Copper reacts with oxygen in water (Oliphant 2010):

$Cu(s) \leftrightarrow Cu^+ + e^-$
$Cu(s) \leftrightarrow Cu^{2+} + 2e^-$
$2Cu(s) + ½ O_2(aq) \leftrightarrow Cu_2O(s)$
$Cu(s) + ½ O_2(aq) \leftrightarrow CuO(s)$

Cu^{2+} ions predominate when air is present (aerobic conditions). Cu^{2+} ions can exist in the solution or form soluble or solid complexes with various anions (negatively charged ions) such as hydroxide (OH^-), chloride (Cl^-), carbonate (CO_3^{2-}), and sulfate (SO_3^{2-}). These anions along with oxygen are a part of the major corrosion products which are found on copper roofs and in copper pipes. If organic compounds are present, copper ions can combine with them and form complexes. Soluble complexes can significantly increase the copper concentration in water and thereby the corrosion rate.

Copper forms an adherent layer of green patina comprised roughly of bronchantite, $CuSO_4*3Cu(OH)_2$. Patina is protective and isolates the metal from the atmosphere (Shreir 1976). Surface patina is formed when copper is spontaneously oxidized at atmospheric conditions. Patinas have different aesthetic appearances, thicknesses, and corrosion products and evolve in different ways depending on factors such as age, environmental and pollution conditions, and building geometries (Wallinder et. al 2009). In Stockholm, the patinas are primary brownish (with the main patina constituent Cu_2O) and/or greenish (an inner layer consists of Cu_2O and an outer layer of $Cu_4SO_4(OH)_6$) (Wallinder et. al 2009; Wallinder and Leygraf 2001). Patina formation is generally governed by electrochemical processes. The rate of oxidation gradually decreases with time as an adherent and protective patina typically evolves. In the environment of repeated dry and wet cycles, patina interacts with pollutants, and can partly dissolve and either re-precipitate on the surface as corrosion products, or be released and transported from the surface during of atmospheric precipitation. This released amount of copper from the patina is referred to as metal release, or metal runoff.

Under some water conditions, the Cu $^{2+}$ ions stay dissolved in solution rather than being precipitated. These kinds of waters are said to be cuprosolvent (copper dissolving). An example of cuprosolvent waters is the water that contains high concentration of carbon dioxide (CO_2), which lowers the water pH often to the values below 6.5 which increases the solubility of copper (Oliphant 2010) . The same effect results in very soft, low pH upland waters. The same waters cause plumbosolvency, the condition when elevated lead concentrations are present in drinking water). High copper ion Cu $^{2+}$ concentrations are often associated with long stagnation of drinking water in the water systems. Copper (II) hydroxide, $Cu(OH)_2$ is the initial corrosion product that forms in all waters. Typically, the soluble copper (II) species precipitate in a relatively short period of time and form much less soluble copper oxides and copper carbonates depending on water composition (Oliphant 2010).

When copper comes in contact with most drinking water, it develops a protective layer of copper oxides and copper carbonates on the inside of the pipe. This protective layer limits the amount of copper that can be dissolved into the water to values well below the 2 mg/L limit stipulated in the Drinking Water Directive (European Council, Council Directive 98/83/EC) that specifies the drinking water quality to be supplied at the consumer's tap; Oliphant 2010). Small amounts of corrosion at the pipe's surface forms a protective layer that stifles further corrosion. The amount of the corrosion that will occur and its type depends on the environment to which it is subjected. For cold waters: (1) In waters that have low oxygen content (anaerobic conditions; stagnant water) the copper itself is stable and will not corrode readily. (2) If the waters have pH<6 and with oxygen present (aerobic conditions; in a moving water), the copper will dissolve to form Cu^{2+} ions (the most stable form under these condition). (3) In waters with pH ranging between 6 and 8 with reasonably high oxygen level (> 2 mg O_2/L), initially insoluble layer of copper (I) oxide Cu_2O (cuprite) will be formed which has the magenta red to brown color and is the most stable species under described conditions. The cuprite will form a semi-protective scale against further corrosion. (4) In the waters with pH>8 with a high oxygen content, copper (II) oxide CuO (tenorite) layer will be formed. The corrosion product will have jet black to brown color and will form a protective scale against further corrosion. In hot waters the protective black tenorite is almost always formed. Of the corrosion product species mentioned above, only the Cu^{2+} ion is significantly soluble. The layers that form on the copper's surface are only semi-protective and corrosion will continue, though at much lower rates compared with that of the initial bare metal. The semi-protective scales that at first form in cases (3) and (4) frequently develop further into insoluble layers of basic copper carbonate $Cu_2(OH)_2CO_3$ (the mineral malachite) which has turquoise/green color. The water must contain carbonate and have pH high enough to produce this deposit. This copper mineral will limit the amount of copper dissolved in the water and will be beneficial in the long run. Long periods of static water conditions must be avoided for the layer to be protective (Oliphant 2010).

If the protective film that is formed on copper is broken, the pipe becomes vulnerable to various forms of pitting corrosion. The layer may be non-protective if during its formation there was a long period of stagnation or if certain water types are present. New copper pipes release considerably more copper than old ones. The copper release typically decreases with time as the protective corrosion layer develops (Oliphant 2010).

Steel Corrosion

When exposed to the atmosphere, steel reacts and forms the reaction product rust, of approximate composition $Fe_2O_3 * H_2O$, which is loosely adherent to the surface and does not form a protective barrier that isolates the metal from the environment. Hence the reaction proceeds at a roughly linear rate until the metal is completely consumed.

Lead Corrosion

Lead oxide PbO and hydroxide $Pb(OH)_2$ are comparatively soluble and all waters containing oxygen are highly corrosive for lead (Degremont 1979).

Galvanized Steel Corrosion

Hot-dip galvanized steel when exposed to atmospheric conditions forms a passive surface layer (zinc patina) that protects galvanized steel from further corrosion. When zinc surface is exposed to the atmosphere, zinc reacts with oxygen in the air forming zinc oxide ZnO. Zinc oxide ZnO then reacts with the moisture in the air (humidity, rain events) and forms zinc hydroxide ($Zn(OH)_2$). Zinc hydroxide ($Zn(OH)_2$) reacts with carbon dioxide (CO_2) in the air and forms dense, insoluble, zinc carbonate ($2\ ZnCO_3 \cdot Zn(OH)_2$) that retards corrosion of the underlying zinc (American Galvanizers Association; http://www.galvanizeit.org/aga/animation/4741?keepThis=true&TB_iframe=true&height=480&width=640).

Coatings produced by electrodepositing of zinc or by hot dip galvanizing have variable thicknesses and are strongly bonded to the steel. The external surface of the zinc is oxidized and zinc hydroxide, oxide, or hydroxycarbonate are formed. This film impedes the corrosion of the zinc by inhibiting the diffusion of oxygen. When the water is corrosive, the film is destroyed and the zinc will undergo accelerated corrosion and rust will form. The corrosion rate increases quickly with temperature and reaches a peak at 60°C. At this temperature, all the zinc hydroxide is transformed into a more porous oxide which is not as adhesive, causing an accelerated corrosion of the bare iron surface. The zinc oxide film is conductive when Cu^{2+} ions are present in the water and may cause the iron to corrode rapidly (Degremont 1979).

Veleva, et al. (2010) noted that zinc has the ability to galvanically protect steel because zinc has more negative potential than that of steel. Under neutral pH conditions, zinc is relatively resistant to corrosion, however, when chloride ions are present (marine coastal environment), zinc is prone to increased localized corrosion. Also zinc is very sensitive to atmospheric acidity, e.g. the presence of SO_2. Zinc corrosion is affected by acidic rainfall with atmospheric aerosols. Sulfuric and nitric acids are the most abundant atmospheric acids and in the environment of high humidity, or even when condensed water is available, their formation proceeds more swiftly, due to the atmospheric oxidation of the aggressive sulfur and nitrogen oxides. The corrosion layer that has formed on the zinc surface can be either removed physically by winds and sand erosion or by dissolution of soluble corrosion products during precipitation or water condensation on the metal surface. Dissolved by rain and dew, zinc corrosion products are released from the corroded surface into the environment. Factors that influence release of zinc corrosion products include the intensity, amount, flow rate, frequency, and pH of precipitation, as well as concentration and solubility of atmospheric aggressive gases during the precipitation, the relative humidity and air temperature. During the dry period, zinc salts $ZnSO_4$ or $Zn(NO_3)_2$ are often formed, which have high solubility constants, and they are easily dissolved during the first flush, whereby less soluble zinc salts are formed, including zinc hydrosulfates and zinc hydrocarbonates, which solubility properties influence the subsequent dissolution rate during the steady state runoff (Veleva, et al. 2010).

Plastic Corrosion

Plastic pipes are very resistant to pH and to chemically and electrochemically induced types of corrosion. Pipes made of these materials are therefore highly resistant to corrosive agents, including sulfates, chlorides and other aggressive salts (Gabriel and Moran 1998). Plastic materials are nonconductors and consequently are also not subject to galvanic corrosion.

Modeling Metal Speciation under Varying Environmental Conditions

Eh-pH (Pourbaix) Diagrams

pH and redox potential (Eh) influence the form of the metal (US EPA 2007a). The Pourbaix diagrams show the different zones of corrosion, passivation, and immunity according to the redox potential and pH of the system (Degremont 1979). A given field is marked with the ion that is predominant within it, and a boundary is placed where the ion becomes equal to an adjacent prevailing ion (Garrels and Christ 1990). The solubility of most metal-containing minerals is greatest under acid conditions, decreasing with increasing pH. The location of measured values of oxidation potential (Eh) and pH in aquatic systems can be seen on Figure F-1 (US EPA 2007a). The dashed lines depict the limits of measurements in natural environments. The main factors that control Eh are atmospheric oxygen and organic matter. High Eh (oxidizing or aerobic) conditions are found in the atmosphere, in most surface waters, and shallow soils in contact with atmospheric oxygen. The lowest Eh (reducing or anaerobic) conditions are observed in water-logged soils and sediments that contain organic matter and in groundwaters that contain a few mg/L or more of dissolved organic carbon (DOC). Intermediate Eh conditions are maintained in waters and sediments that are only partially oxidized due to their relative isolation from the atmosphere. Measured Eh values may not coincide with Eh values computed from the concentrations of redox-sensitive species.

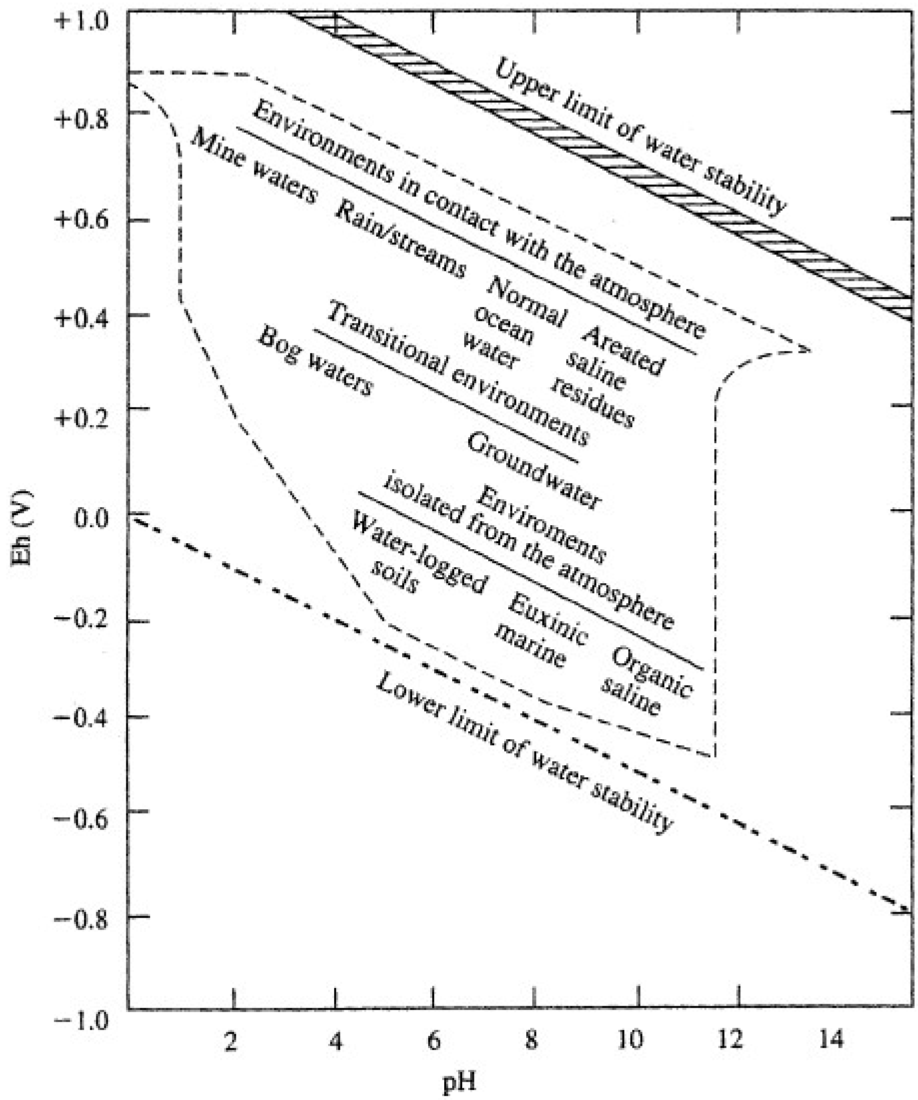


Figure F-1. Estimated locations of some natural environments of Eh-pH diagram. Source: US EPA (2007a).

Eh-pH diagrams of metals in aqueous solutions are a valuable means of predicting the corrosion problems and regions of stable conditions. Eh-pH diagrams delineate the predominant area of each chemical or ionic species in aqueous solutions (Garrels and Christ 1990, Degremont 1979; Chen and Aral 1982). When a metal is submerged into an aqueous solution that contains various chemicals (such as oxygen, boric acid, sulfur compounds, chlorides, fluorides, etc.) corrosion problems frequently occur. Eh-pH diagrams of metals in aqueous solutions illustrate the equilibrium phases of metal, its oxides, its ions, or metal compounds associated with the solution’s components are a valuable means of predicting corrosion problems. The use of such diagrams helps to avoid separate investigations of every combination of metal, solution, pH, and temperature in order to ensure that certain corrosion problems would not take place (Chen and Aral 1982).

Silverman (1982) noted that Pourbaix diagrams can help to predict corrosion because pH is a measure of acidity and potential is a measure of oxidizing power and both are important determinants of corrosion in electrolytes. These diagrams depict the thermodynamically stable states at varied pH and potential and provide insight whether or not corrosion is possible and can predict the pH and potential conditions at which corrosion will not occur. The diagrams also allow the prediction of the effect that the changes in pH and potential are likely to have (Siverman 1982).

The construction of the Pourbaix diagrams requires that all possible species in the system that are important to corrosion are considered. If possible, actual activities in the solution should be used. For example, a Pourbaix diagram for iron (Figure F-2) shows that during favorable oxidizing and alkaline conditions, natural passivation (formation of natural protective film) is detected. Also, passivation occurs at pH values above10.5. At Eh values below – 0.58 volt, the immunity field is noted. Immunizing the steel is the method of cathodic protection employed to protect buried pipes or equipment used in sea water. It is generally recognized that cathodic protection is effective for applied potential values between – 0.85 and -1 volt (Degremont 1979).

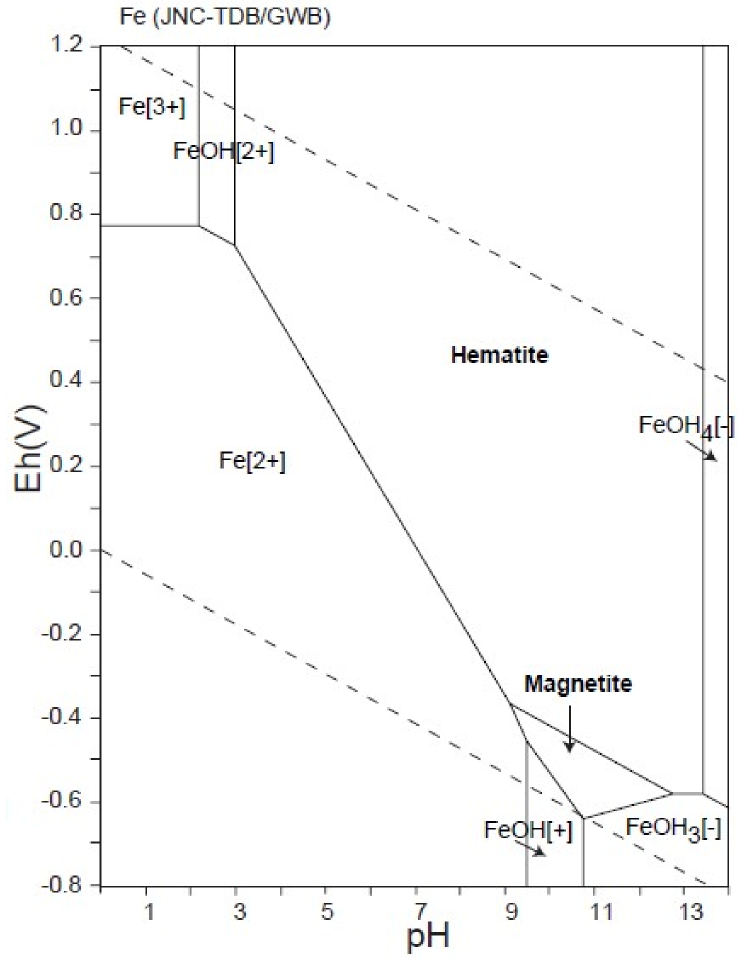


Figure F-2.Eh-pH diagram of the system Fe-O-H.

Σ Fe = 10^{-10} mole/kg, 298.15 K, 10^5 Pa. Source: National Institute of Advanced Industrial Science and Technology (2005).

The solubility of Fe^{2+} drops significantly when pH increases, resulting in the formation of an insulating film of ferrous hydroxide and other oxides. This leads to an appreciable increase in the cathodic regions and the reduction of the anodic areas to very small surfaces. As the areas of the anodic regions decrease, the density of the corrosion current increases. As the pH approaches 10, the chance of perforating or pitting corrosion in the presence of oxygen decreases and, in most natural water, corrosion stops at pH 10.5 (Degremont 1979). Figures F-3 a, b and F-4 a, b show Eh-pH diagrams for zinc, copper, lead, and aluminum respectively.

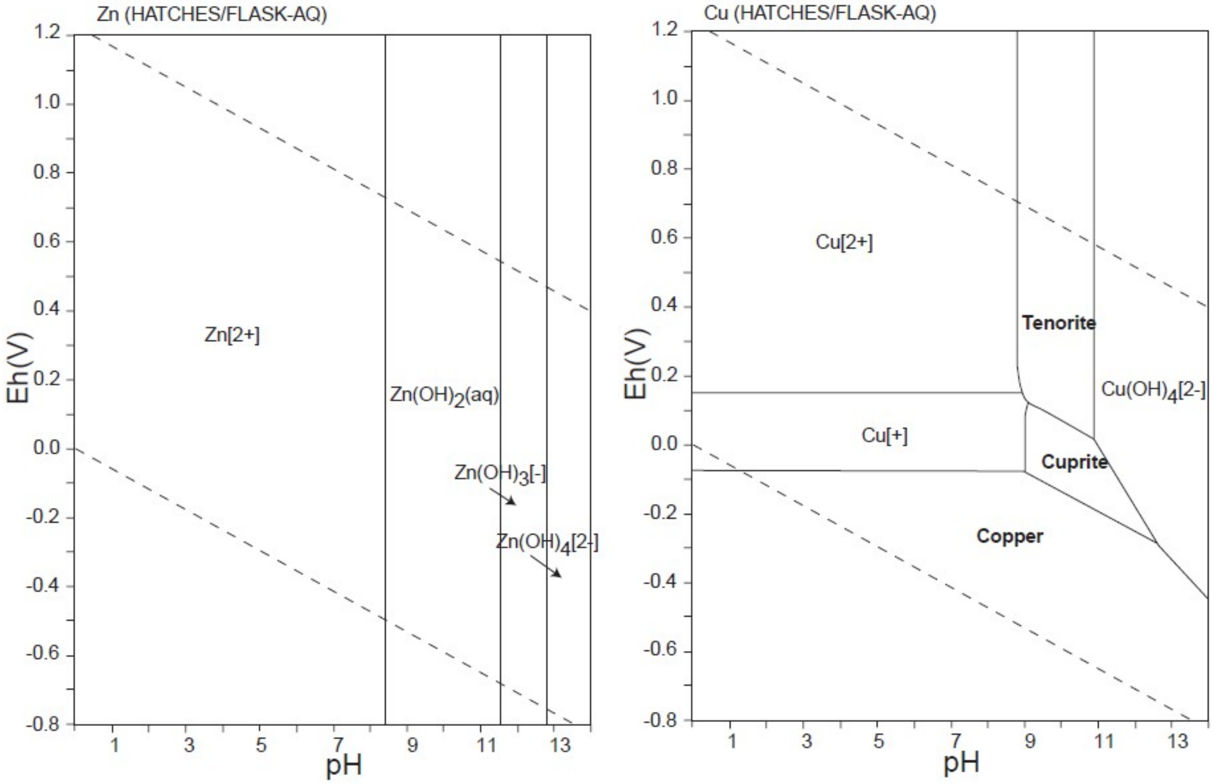


Figure F-3, a, B- Eh-pH diagrams of the systems Zn-O-H (left) and Cu-O-H (right).

Σ Zn = 10^{-10} mole/kg, Σ Cu = 10^{-10}mole/kg, 298.15 K, 10^5 Pa Source: National Institute of Advanced Industrial Science and Technology (2005).

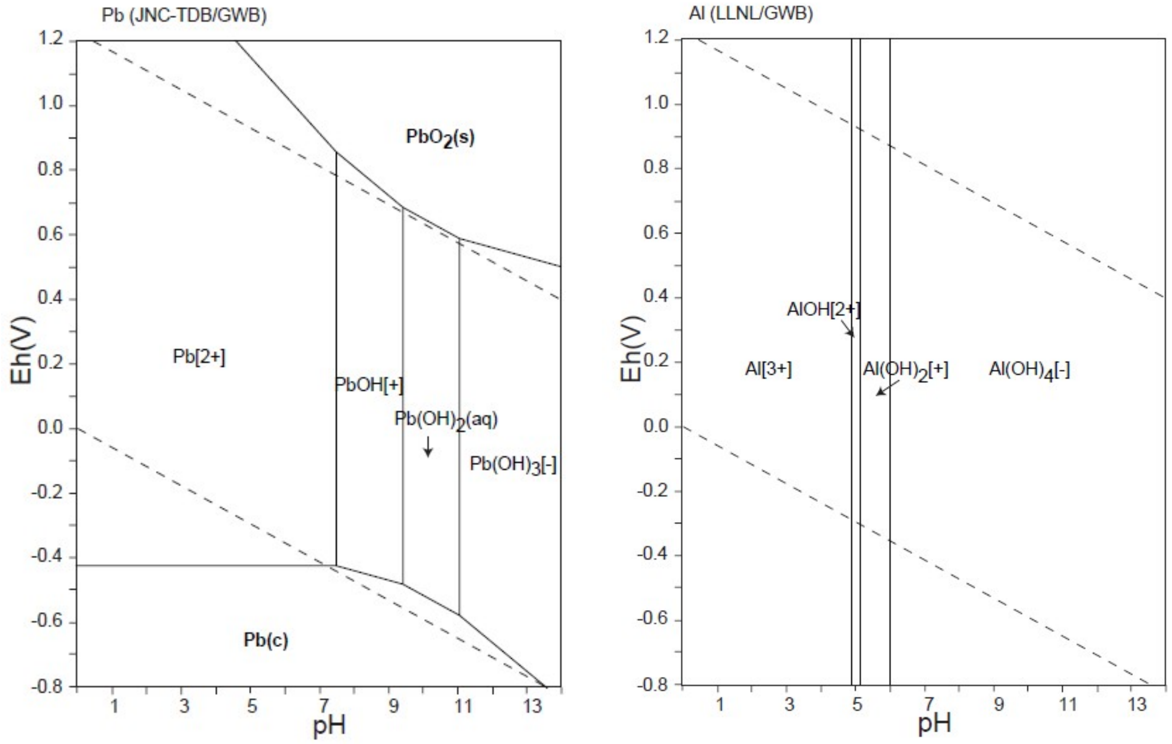


Figure F-4, a, B- Eh-pH diagrams of the systems Pb-O-H (left) and Al-O-H (right).

Σ Pb = 10^{-10} mole/kg, Σ Al = 10^{-10}mole/kg, 298.15 K, 10^5 Pa Source: National Institute of Advanced Industrial Science and Technology (2005).

pC-pH Diagrams

Phase (pC – pH) diagrams are useful in determining equilibrium concentrations of various species present in the solution and their total concentrations. The diagrams can be utilized to identify regions in which certain metal-containing species are predominant (Snoeyink and Jenkins 1980). These diagrams can also be used to show the predominant species and their concentrations in a given pH range (Snoeyink and Jenkins 1980). For example, Figure F-5 shows a phase diagram of hydrolysis products of Fe (II). Fe^{2+} is the predominant species at pH values between 1 and 8.7. At pH values greater than 8.7, $Fe(OH)_2$(c) precipitates. A $Fe(OH)_3^-$complex forms at pH values greater than 11.4; and a $Fe(OH)_4^-$complex forms at pH values greater than 12.2.

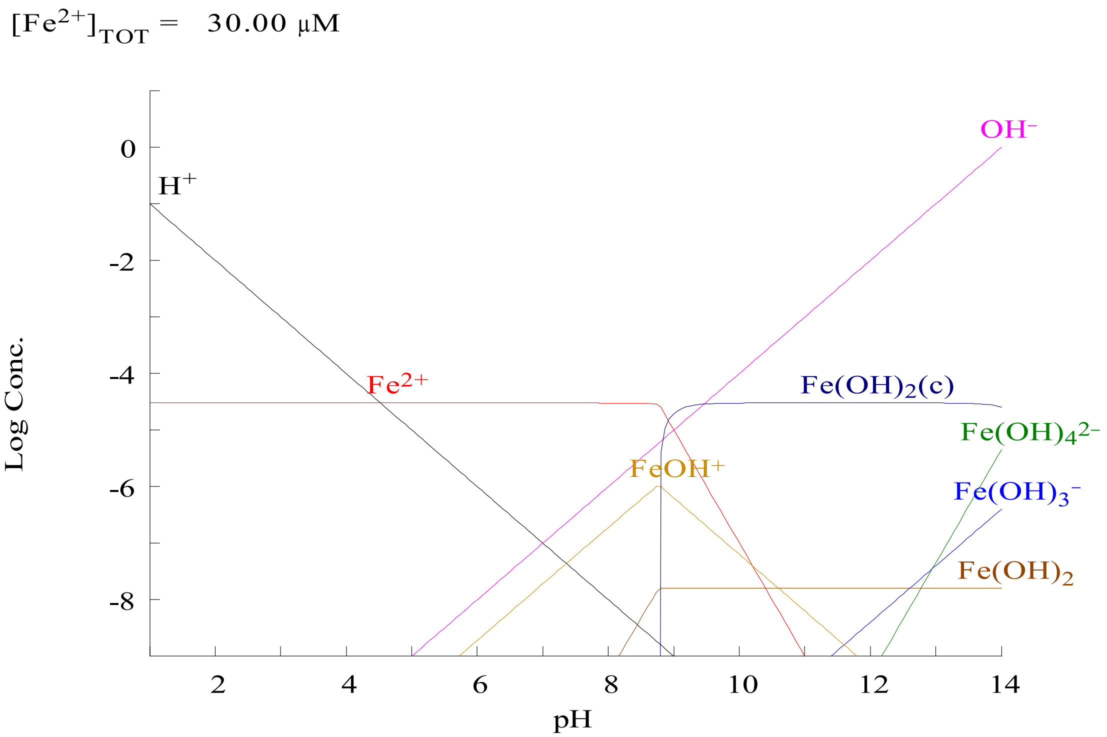


Figure F-5. Phase diagram of hydrolysis products of Fe (II).

Partitioning, Fate, and Transport of Heavy Metals in the Environment

Water can transport metals that are associated with particles or are in dissolved forms. The major route for particulate-metal transport is overland flow. Dissolved metals are mainly transported in overland flows, however some underground transport can occur. Many dissolved metals that are carried below the land surface readily sorb to soil particles (NC State University, NCSU Water Quality Group).

Studies have been conducted on associations of heavy metals with particulates in stormwater and it was found that heavy metals are predominantly associated with particulate matter, with the exception of zinc, which is mainly associated with the filterable fraction (Morquecho 2005; US EPA 2007a; Pitt, et al. 1995; Horvath 2011; Schriewer, et al. 2007; Athanasiadis, et al. 2004; Gromaire-Mertz, et al. 1999). However, research conducted on zinc in stormwater runoff from industrial storage areas in Birmingham, AL, revealed that zinc was mostly associated with particulates that were transported by runoff coming from areas affected by heavy truck traffic and not galvanized metals (Pitt, et al. 1999). Also, Tobiason (2004) found that zinc leaching from Galvalume roofing into roof runoff was strongly sorbed to sediments in open drainage channels and stormwater ponds prior to the ultimate discharge to receiving waters. Fan, et al. (2001) also found that zinc in urban stormwater runoff was in particulate form, or sorbed onto particulates. Gumbs and Dierberg (1985) found that heavy metals (zinc, lead, chromium, and cadmium) are bound with particulate matter. Zobrist, et al. (2000) found that Pb and Fe in tile and polyester roof runoff samples were mainly associated with particulate fraction, however Cu, Zn, Cd, Mn and Cr were chiefly associated with in the dissolved fraction. Faller and Reiss (2005) studied roof runoff from roofing materials that included copper and zinc with different surface treatment, tinned copper, galvanized steel, aluminum, stainless steel, tinned stainless steel, titanium, and lead in Dubendorf, Switzerland. Copper, zinc and lead released measurable amounts of metallic ions, however a fraction bounded with particulate matter was small.

Pollutants that are mainly associated with filterable fractions have a greater ability to contaminate groundwater and are more difficult to control with traditional stormwater control practices that usually use sedimentation and filtration techniques (Pitt, et al. 1999).

Factors that affect the behavior of metals in natural waters include the suspended sediment and substrate sediment composition, and the water chemistry. Many heavy metals readily sorb to organic and inorganic particulates which accumulate as bedded sediments. During rain events, these sediments may become resuspended and more biologically active by pollutant desorption, transformation, or particle uptake by organism ingestion (Burton and Pitt 2002). Sediment made of fine sand and silt will usually have higher levels of adsorbed metal than quartz, feldspar, and detrital carbonate-rich sediment (NC State University, NCSU Water Quality Group).

Fates of metals in the environment and effects of metals on “ecological receptors” strongly depend on the environmental chemistry of metals (US EPA 2007a). Metals do not degrade. The transformation of species from one form to another depends on the environmental chemistry of the medium. Factors that control metal sorption to sediments include chemical identity, complexation chemistry, solubility, precipitation chemistry, redox behavior, and vapor pressure (US EPA 2007a).

The mobility and bioavailability of metals greatly depends on the metal speciation, therefore the knowledge of metal speciation is very important to an understanding of metal behavior in the environment (Benjamin 2002).

Glenn, et al. (2001) studied how traffic activities and winter maintenance practices influence the behavior of particulates in the runoff at highway test sites in Cincinnati, OH. The authors noted that urban snow has a much greater capacity to accumulate traffic-related pollutants when compared to stormwater, which was attributed to longer residence times before melting, and the snow’s porous matrix. Factors such as residence time, solids loadings, alkalinity, hardness and pH affect the heavy metal partitioning in the snow (Glenn, et al. 2001). Glenn, et al. (2001) observed that Cu, Pb, Zn, Al, Fe, and Cd were mainly associated with particulate forms. Partition coefficients for most heavy metals in snowmelt water ranged from 103 to 106 L/kg.

DeCarloet al. (2004) investigated the composition of water and suspended sediment in streams of urbanized watersheds in Hawaii. It was determined that the transport of the most trace metals was influenced by suspended particles. Deletic and Orr (2005) studied sediment from a road in Aberdeen, Scotland. The authors analyzed particulate fractions of copper, zinc, lead, and cadmium. It was determined that the greatest heavy metal concentrations were associated the smallest particle size fraction examined of being less than 63 µm. Magnuson, et al. (2001) obtained similar results and concluded that the fate and transport of metal contaminants through a watershed were dependent on the characteristics of the solid particles to which they are bound. It was noted that the particles most frequently associated with metal pollutants have nominal diameters of < 50 µm.

The zinc contaminants in the roof runoff originate from dissolution of the roofing and gutter material rather than from atmospheric deposition (Horvath 2011). Schriewer, et al. (2008) also found that the major portion of zinc in roof runoff from zinc material exposure has been mostly bioavailable in the speciation form Zn^{2+}. After roof runoff comes in contact with other surfaces, changes in runoff properties occurs (Heijerick, et al. 2002). These changes are difficult to predict and treatment for zinc roof runoff is advised in order to avoid potential detrimental effects on the ecosystem.

Sarin, et al. (2004) examined iron release from the corroded pipes under flow and stagnant water conditions. Iron released from corroded iron pipes mainly in the ferrous form (Fe^{2+}). Table F-1.summarizes metal associations from different source areas.

Table F-1. Metal distributions in stormwater runoff from various source areas.

Metal	Source Area	Partitioning	Reference
Zinc	Zinc-based roofing materials	94.3-99.9% dissolved	Heijerick, et al. (2002)
Zinc	Zinc-galvanized metal roofs	66 to 92% dissolved	Tobiason and Logan (2000)
Zinc	Unpainted Galvalume metal roof	86% dissolved	Tobiason (2004)
Zinc	Sawmills	85±15% Dissolved	Bailey, et al. (1999)
Zinc	15 (different zinc panels or zinc coatings, which included new and naturally aged sheets) commercial zinc-based construction materials	greater than 95% dissolved	Wallinder, et al. (2001) Wallinder, et al. (2000) He, et al. (2001)
Copper	Copper sheets as fittings around roof windows and the chimney base	1.4 ratio dissolved to particulate	Förster (1999)
Lead	Painted structures in an urban area	70% or greater particulate	Davis and Burns (1999)
Lead	Zinc roof	0.15 ratio dissolved to particulate	Förster (1999)
Cadmium	Tar felt roof	24 ratio dissolved to particulate	Förster (1999)
Cadmium	Zinc roof	10 ratio dissolved to particulate	Förster (1999)

Speciation and Complexes

The behavior and toxicity of metals are determined by the metal speciation. Metal chemical forms may consist of free metal ions, metal complexes dissolved in a solution

and sorbed on solid surfaces, and metal species that have been coprecipitated in metal solids. Besides toxicity, the speciation of a metal also influences its sorption, acid/base equilibrium, complexation, electron-transfer reactions, solubility and precipitation equilibria, and diffusivity (US EPA 2007a; Benjamin 2002.)
In most natural waters lead and copper are most often found as complexes and not as free ions (US EPA 2007a). Some elements occur in more than one oxidation state, which governs the chemical and biological behavior of the element including toxicity and mobility (Langmuir 1997).

The fate of heavy metals entering an estuary is influenced by salinity changes, physical mixing and dilution, and chemical processes such as sorption, complexation, cation exchange and redox reactions (Turner, et al. 1993). Often, heavy metals in estuarine systems occur in greater concentrations in the sediments than the water column (Morse, et al. 1993).

Complexes can form between metals (acids) and ligands (bases), both in solution and at the surfaces of minerals and organisms. The nature of the metal complexes formed in solution and at the surface of the organism affects the toxic reaction of organisms to metals (US EPA 2007a).

The idea of hard and soft acids and bases (HSAB) helps to describe the strength of metal complexing and metal toxicity. According to this concept, metal cations are Lewis acids and ligands are Lewis bases. The metal cation and ligand in a complex act as electron acceptor and donor, respectively. The electron cloud of soft species is deformable or polarizable, the electrons are mobile and can easily move. These soft species prefer to participate in covalent bonding. The electron cloud of hard species is comparatively rigid and non-deformable, has low polarizability. Hard species prefer to participate in ionic bonds in complex formation (Langmuir, 1997). Strong, mainly ionic bonds are formed between hard acids and hard bases. If the complex is formed by soft acids and soft bases, mainly covalent bonds are formed which are very strong. In a complex formed by hard-soft or soft-hard acids and bases, bonds are weak. Such complexes tend to be rare (US EPA 2007a). Such ions as Ag^+, Cd^{2+}, Cu^+, Hg^{2+}, and Hg^+ are soft acids; on the other hand, Al^{3+}, Co^{3+}, Cr^{3+}, Fe^{3+}, Mn^{2+}, Sr^{2+} are hard acids. Borderline (between hard and soft) acids include Co^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}. Such ions as I^-, HS^-, S^{2-}, CN^-, SCN^-, Se^{2-}, $S_2O_3^{2-}$, R^-(where R is an organic molecule) C_2H_4, C_6H_6, RNC, CO, R_3P, $(RO)_3P$, R_2S, RS^- are soft bases; F^-, H_2O, OH^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-, $C_2O_4^{2-}$, CrO_4^{2-}, MoO_4^{2-}, $H_nPO_4^{n-3}$, SeO_4^{2-}, NH_3, RNH_2, N_2H_4, ROH, RO^- are hard bases. Borderline (between hard and soft) bases include Cl^-, Br^-, NO_2^-, SO_3^{2-}, $H_nAsO_3^{n-3}$, $C_6H_5NH_2$, C_5H_5N.

Hard metals (acids) are the least toxic and the majority are macronutrients. Hard metals prefer to bind with hard bases which contain oxygen. When hard metals bind with soft nitrogen and sulfur species, weaker bonds are formed. The strength of bonds between hard metals and hard ligands is usually dependent on pH. Soft metals (acids) prefer to bind with soft S and N ligands, and form weaker bonds with hard bases (hydroxide, sulfate). Soft and borderline metals, and hard Mn^{2+}, binding with soft ligands such as sulfide, have bonds' strength generally in the following decreasing order: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Co^{2+} – Fe^{2+} > Ni^{2+} > Zn^{2+} >Mn^{2+}$. Soft and borderline metals have the greatest tendency to bind to soft ligands or to organic substrates (which are usually soft), followed by the hard metals, usually in the order $Pb^{2+} > Cu^{2+} >Cd^{2+} > Zn^{2+} > Ca^{2+} > Mg^{2+} >> Na^{+}$ (US EPA 2007a).

The inclination of metals to form solid phases, such as sulfides in sediments, is also affected by their HSAB characteristics. For example, soft acid metal cations, such as Hg^{2+} or Ag^{+} form very insoluble complexes with sulfides in anoxic sediments. On the other hand, hard or borderline hard metal cations such as Mn^{2+} or Fe^{2+} form marginally more soluble, although still highly insoluble, metal sulfides.

Solubility Product

Solubility product (Ksp) indicates water solubility of a solid (Clark and Pitt 2012). The definition of solubility product is given by Degremont (1979) using the notion of the ionic equilibrium state of a sparingly soluble or insoluble substance:

$AC \leftarrow\rightarrow A^{-}+C^{+}$
$[A^{-}][C^{+}] = Ksp$

Where,
$[A^{-}]$ and $[C^{+}]$ are the activities of products of the reaction
Ksp is the solubility product.

The magnitude of solubility product is constant for a given temperature and ionic strength of the solution. The less soluble the substance is, the smaller the value of the solubility product. The solutions, in which the product of activities is less than solubility product is undersaturated with respect to the solid, and in such solutions, the solid will dissolve as the system equilibrates. However, if the product of activities is greater than solubility product, the solution is said to be oversaturated with respect to the solid, and in such solutions the solid will tend to precipitate (Benjamin 2002). The activity product of the compounds is compared to the solubility products to determine whether the solution is oversaturated or undersaturated with respect to a compound. The use of the equilibrium constants in estimating phase separation may not be accurate if the system is dynamic (Clark and Pitt 2012).

To determine the activity product of the compounds in the solution, the dissolved concentrations of constituents in the compound were multiplied by their activity coefficients.

Ionic strength is calculated using the formula (from Snoeyink and Jenkins 1980; Klyachko 1971):

$\mu = 0.5\ \Sigma\ (C_iZ_i^2)$
Where,
Ci = concentration of ionic species i, mol/L
Zi = charge of species i

Activity coefficients in aqueous solutions are calculated using the Maclinnes assumption, which allows for the effect of the decrease in concentration of solvent in concentrated solutions (Truesdell and Jones 1974):

$\log\gamma_i = -\ A\ Z_i^2\ \mu^{1/2}\ /\ (1 + B\ \alpha_i\ \mu^{1/2}) + b_i\ \mu$

A = a constant that relates to the solvent
B = a constant that relates to the solvent
A = 0.509 at 25 ^{o}C (Snoeyink and Jenkins, 1980)
B = $0.328*10^8$ at 25 ^{o}C (Snoeyink and Jenkins, 1980)
α_i = the quantity dependent upon the "effective diameter" of the ion in solution (Garrels and Christ 1990). For Ca^{2+}, α_i = 6.00E-08; for HCO_3^-, α_i = 4.00E-08 (Garrels and Christ, 1990).
b_i = an adjustable parameter, which allows for the effect of the decrease in concentration of solvent in concentrated solution (Truesdell and Jones 1974). For Ca^{2+}, b_i = 0.165; for HCO_3^-, b_i = 0 (Truesdell and Jones, 1974).

Metals of zero valence and some inorganic metal compounds are not readily soluble (US EPA 2007a). Many ligands that form solids with metals produce soluble complexes, thus metal solubility is dependent on the solubility of the ligands (Benjamin 2002).

Heavy metals can form insoluble complexes with such ions as hydroxides, carbonates, and phosphates (Stumm and Morgan, 1996). The solubility product can be used to calculate the maximum concentrations of these ions in the water at a given pH value (Clark and Pitt 2012).

Solubility is associated with surface charge (Clark and Pitt 2012).Water is a polar molecule and therefore contaminant ions, colloids, and complexes with surface charges have a tendency to dissolve in water. To remove these pollutants, other chemical properties can be used. Water solubilities of inorganic ions very widely and are influenced by the presence of other ions in the water. Such ions as hydroxides and chlorides can form complexes and increase the water solubility of metals above the value estimated using the K_{SP} (Snoeyink and Jenkins, 1980).

The formation of soluble complexes with ions can complicate the calculation of precipitation of these ions (Clark and Pitt 2012). For instance, besides precipitating, zinc can form various soluble complexes with hydroxide ions, with the valence of complexes ranging from +1 to -2 (Snoeyink and Jenkins, 1980). Complexation can provide an explanation to the discrepancy between ionic concentrations estimated using K_{SP} and the measured concentrations in the solution (Clark and Pitt 2012).

Appendix G. Emerging Contaminant Observations at Source Areas

Pharmaceuticals and Personal Care Products in Stormwater Sheetflows

Site (concentrations are μg/L)	Sample Date	Time	Land Use	Surface	Trimethoprim	Sulfamethoxazole	Carbamezapine	Fluexatine
28Jun11 Galleria Grass	6/28/2011	1430	Commercial	Landscaped	BDL	9.0	1.2	BDL
23Mar12 Galleria Landsc	3/22/2012	900	Commercial	Landscaped	BDL	14.0	4.0	BDL
22Jun11 Galleria Paved	6/22/2011	1610	Commercial	Paved	BDL	16.0	5.0	12.0
23Mar12 Galleria Paved	3/22/2012	900	Commercial	Paved	BDL	BDL	7.0	BDL
22Jun11 Galleria Roof	6/22/2011	1610	Commercial	Roof	BDL	6.0	9.5	4.0
23Mar12 Galleria Roof	3/22/2012	900	Commercial	Roof	BDL	14.0	6.0	BDL
5Sep11 Bama Belle Grass	9/5/2011	1115	Institutional	Landscaped	BDL	19.0	2.0	BDL
26Jan12 Bama Belle Landsc	1/26/2012	945	Institutional	Landscaped	9.0	BDL	1.0	TR
17Aug12BamaBelleLandsc	8/17/2012	700	Institutional	Landscaped	6.1	26.5	1.5	BDL
28Jun Bama Belle Paved	6/28/2011	1430	Institutional	Paved	BDL	21.5	3.2	7.5
26Jan12 Bama Belle Paved	1/26/2012	1005	Institutional	Paved	10.0	BDL	2.0	BDL
28Jun11 Bama Belle Roof	6/28/2011	1430	Institutional	Roof	BDL	BDL	4.0	BDL
26Jan12 Bama Belle Roof	1/26/2012	1005	Institutional	Roof	BDL	BDL	2.0	BDL
28Jun11 Bama Belle FilterInfluent	6/28/2011	1430	Institutional	yOutfall	BDL	BDL	3.5	2.0
26Jan12 Bama BelleFilterInfluent	1/26/2012	1010	Institutional	yOutfall	BDL	BDL	4.0	BDL
17Aug12BamaBelleFilterInfluent	8/17/2012	700	Institutional	yOutfall	BDL	7.0	5.5	11.0
5Sep11 Acad Dr. Landsc	9/5/2011	1010	Residential	Landscaped	BDL	17.0	BDL	BDL
14Oct12Acad Cr. Landsc	10/14/2012	1125	Residential	Landscaped	6.0	6.8	1.0	5.1
28Jun11 Acad Dr. Paved	6/28/2011	1430	Residential	Paved	BDL	BDL	4.0	8.0
20Sep11 Acad Dr. Paved	9/20/2011	715	Residential	Paved	5.5	5.5	3.3	2.3
28Jun11 Acad Dr. Roof	6/28/2011	1430	Residential	Roof	BDL	BDL	3.0	7.0
20Sep11 Acad Dr. Roof	9/20/2011	715	Residential	Roof	BDL	9.0	2.0	BDL
				count	5	13	21	9
				% detected	23	59	95	41
				max	10.0	26.5	9.5	12.0

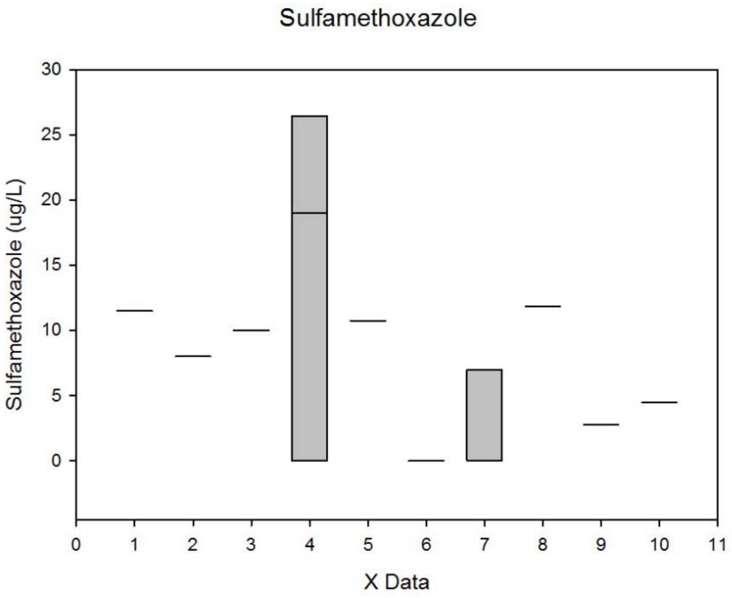
Site (concentrations are µg/L)	Sample Date	Time	Land Use	Surface	Ibuprofen	Gemfibrozil	Triclosan
23Mar12 Galleria Roof	3/22/2012	900	Commercial	Roof	BDL	35	BDL
23Mar12 Galleria Roof	3/22/2012	900	Commercial	Roof	BDL	35	BDL
23Mar12 Galleria Paved	3/22/2012	900	Commercial	Paved	BDL	28	BDL
23Mar12 Galleria Landsc	3/22/2012	900	Commercial	Landscaped	BDL	35	BDL
23MarGalleria	3/22/2012	900	Commercial		BDL	34	BDL
26JanBamaBelle	1/26/2012		Institutional		13	34	BDL
17AugBamaBelle	8/17/2012	700	Institutional		BDL	32	BDL
17AugBamaBelle	8/17/2012	700	Institutional		62	320	BDL
17AugBamaBelle	8/17/2012	700	Institutional		BDL	25	BDL
17AugBamaBelle	8/17/2012	700	Institutional		BDL	33	BDL
17AugBamaBelle	8/17/2012	700	Institutional		BDL	327	BDL
17AugBamaBelle	8/17/2012	700	Institutional		BDL	23	BDL
17AugBamaBelle	8/17/2012	700	Institutional		BDL	30	BDL
			count		2	13	0
			% detected		15	100	0
			max		62	327	0

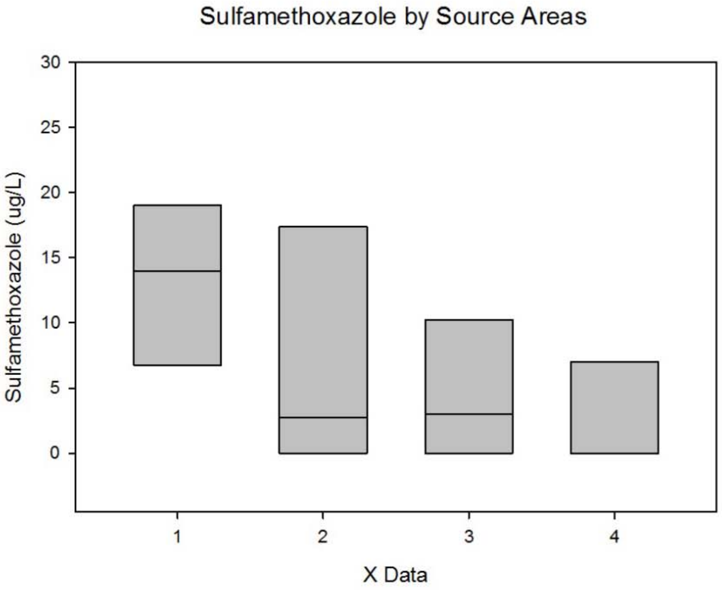
Trimethoprim

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Trimethoprim source area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
lands	8	1	0	0	6.133
paved	7	1	0	0	6.625
roof	7	1	0	0	0
institOF	4	1	0	0	0
H = 4.342 with 3 degrees of freedom. (P = 0.227)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.227)					

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Trimethoprim source area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	7	1	0	0	0
institutional	11	1	0	0	6.85
residential	7	1	0	0	5.625
H = 2.299 with 2 degrees of freedom. (P = 0.317)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.317)					

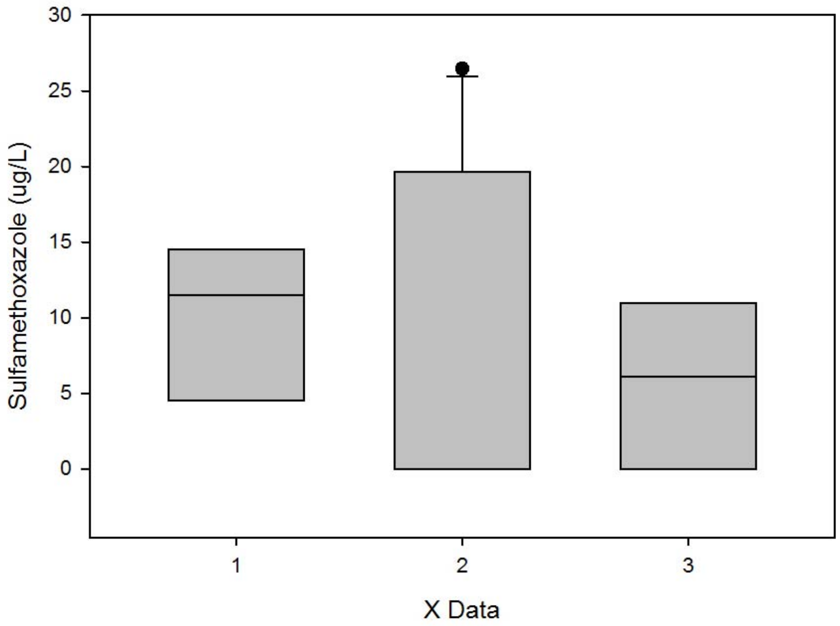
Sulfamethoxazole


Sulfamethoxazole
Sulfamethoxazole (ug/L)
30
25
20
15
10
5
0
0
1
2
3
4
5
6
7
8
9
10
11
X Data


Sulfamethoxazole by Source Areas
Sulfamethoxazole (ug/L)
30
25
20
15
10
5
0
1
2
3
4
X Data

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Sulfamethoxazole source area.JNB					
Normality Test (Shapiro-Wilk)	Passed	(P = 0.391)			
Equal Variance Test:	Passed	(P = 0.590)			
Group	N	Missing	Median	25%	75%
lands	8	1	14	6.75	19
paved	7	1	2.75	0	17.375
roof	7	1	3	0	10.25
institOF	4	1	0	0	7
H = 4.796 with 3 degrees of freedom. (P = 0.187)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.187)					

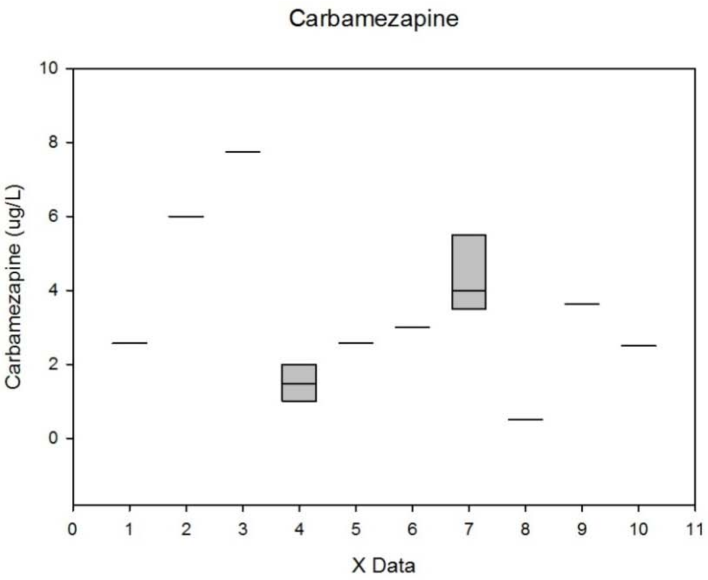
Sulfamethoxazole by Land Use

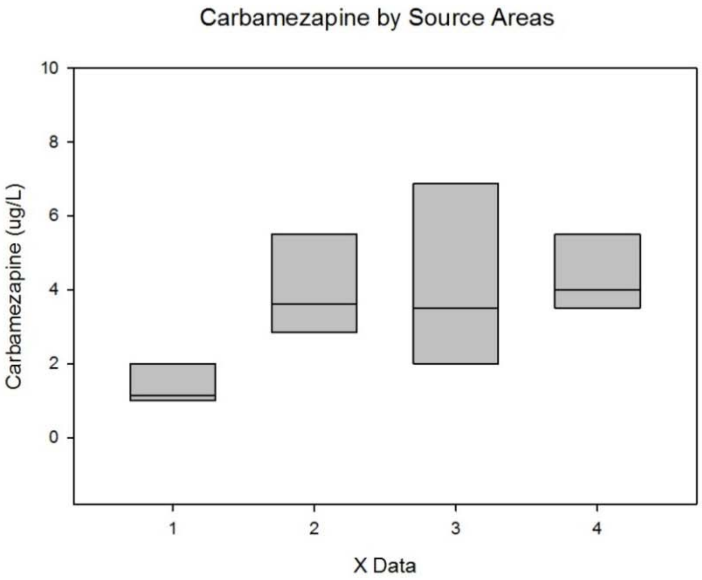


Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Sulfamethoxazole source area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	7	1	11.5	4.5	14.5

institutional	11	1	0	0	19.625
residential	7	1	6.125	0	11
H = 0.922 with 2 degrees of freedom. (P = 0.631)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.631)					

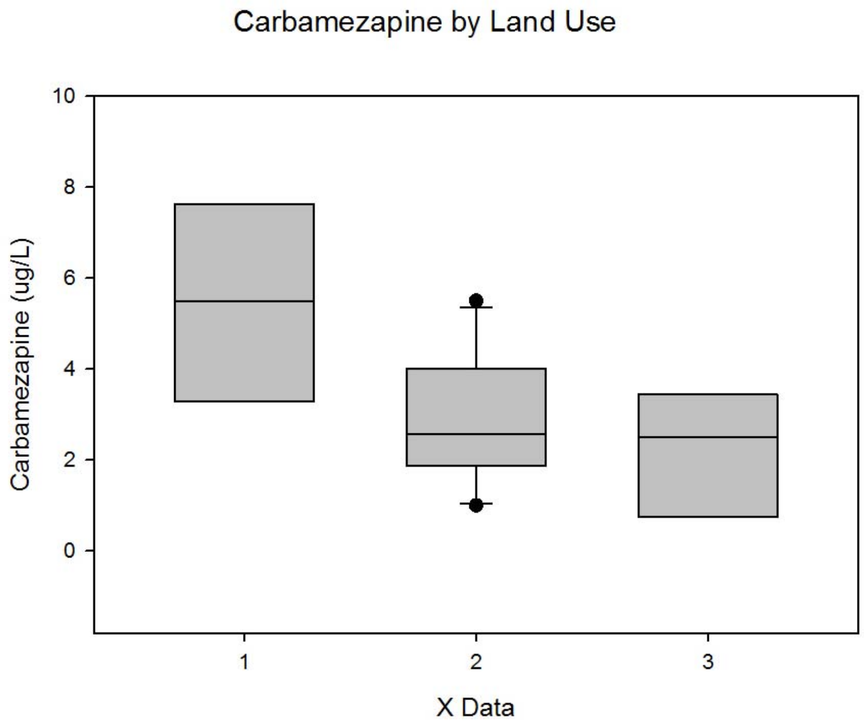
Carbamazepine


Carbamezapine
Carbamezapine (ug/L)
10
8
6
4
2
0
0
1
2
3
4
5
6
7
8
9
10
11
X Data


Carbamezapine by Source Areas
Carbamezapine (ug/L)
10
8
6
4
2
0
1
2
3
4
X Data

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Carbamezapine source area.JNB					
Normality Test (Shapiro-Wilk)	Passed	(P = 0.056)			
Equal Variance Test:	Passed	(P = 0.548)			
Group	N	Missing	Median	25%	75%
lands	8	1	1.15	1	2
paved	7	1	3.625	2.862	5.5
roof	7	1	3.5	2	6.875
institOF	4	1	4	3.5	5.5
H = 9.298 with 3 degrees of freedom. (P = 0.026)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.026)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					

All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
institOF vs lands	10.405	2.322	No		
institOF vs roof	2.083	0.454	Do Not Test		
institOF vs paved	1.667	0.363	Do Not Test		
paved vs lands	8.738	2.419	Do Not Test		
paved vs roof	0.417	0.111	Do Not Test		
roof vs lands	8.321	2.303	Do Not Test		


Carbamezapine by Land Use
Carbamezapine (ug/L)
10
8
6
4
2
0
1
2
3
X Data

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Carbamezapine source area.JNB					
Normality Test (Shapiro-Wilk)	Passed	(P = 0.952)			
Equal Variance Test:	Passed	(P = 0.266)			
Group	N	Missing	Median	25%	75%
commercial	7	1	5.5	3.288	7.625
institutional	11	1	2.575	1.868	4
residential	7	1	2.5	0.75	3.438
H = 5.940 with 2 degrees of freedom. (P = 0.051)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.051)					

Fluoxetine

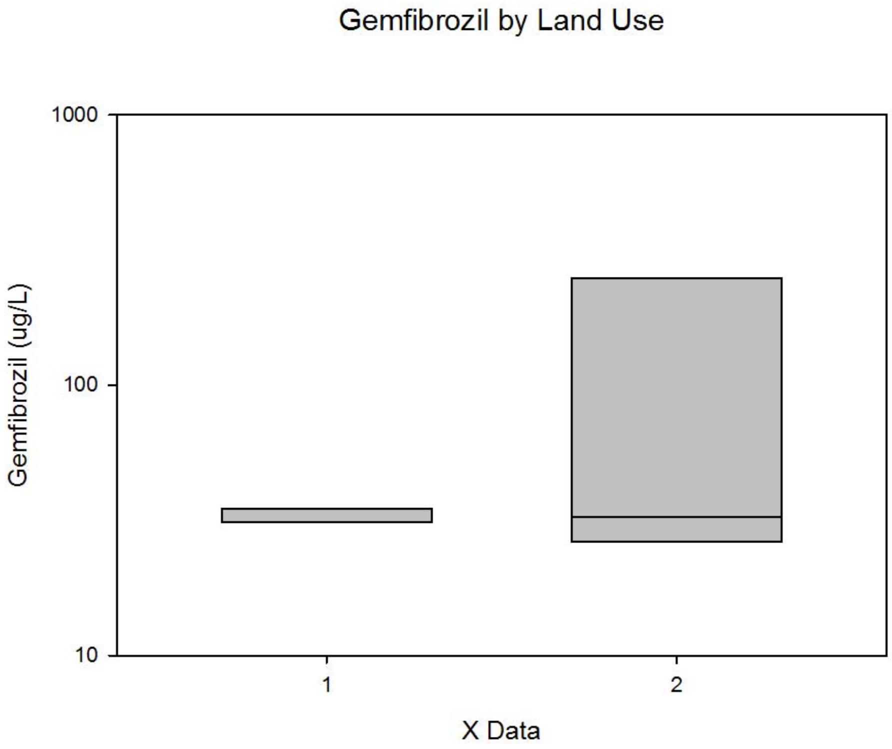
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Fluexatine source area.JNB					
Normality Test (Shapiro-Wilk)	Passed	(P = 0.057)			
Equal Variance Test:	Passed	(P = 0.361)			
Group	N	Missing	Median	25%	75%
lands	8	1	0	0	0.1
paved	7	1	4.875	0	9
roof	7	1	0	0	4.75
institOF	4	1	2	0	11
H = 4.038 with 3 degrees of freedom. (P = 0.257)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.257)					

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Fluexatine source area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	7	1	0	0	6
institutional	11	1	0	0	3.375
residential	7	1	3.663	0	7.25
H = 1.271 with 2 degrees of freedom. (P = 0.530)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.530)					

Ibuprofen

Mann-Whitney Rank Sum Test					
Data source: Data 1 in other pharms source.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
ibuprofen commer	5	0	0	0	0
ibuprofen instit	8	0	0	0	9.75
Mann-Whitney U Statistic= 15.000					
T = 30.000 n(small)= 5 n(big)= 8 P(est.)= 0.295 P(exact)= 0.524					
The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.524)					

Gemfibrozil



Mann-Whitney Rank Sum Test					
Data source: Data 1 in other pharms source.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
gemfibrozil commer	5	0	35	31	35
gemfibrozil instit	8	0	32.5	26.25	248.5
Mann-Whitney U Statistic= 14.500					
T = 40.500 n(small)= 5 n(big)= 8 P(est.)= 0.461 P(exact)= 0.435					
The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.435)					

Polycyclic Aromatic Hydrocarbons (PAHs) in Stormwater Sheetflows

Site (concentrations µg/L)	Sample Date	Land Use	Surface	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene
28Jun11 Galleria Grass	6/28/2011	Commercial	Landscaped	0.2	BDL	BDL	BDL
23Mar12 Galleria Landsc	3/22/2012	Commercial	Landscaped	1.3	BDL	TR	TR
22Jun11 Galleria Paved	6/22/2011	Commercial	Paved	0.5	BDL	BDL	BDL
23Mar12 Galleria Paved	3/22/2012	Commercial	Paved	0.2	TR	TR	TR
22Jun11 Galleria Roof	6/22/2011	Commercial	Roof	BDL	BDL	BDL	BDL
5Sep11 Bama Belle Grass	9/5/2011	Institutional	Landscaped	3.1	BDL	TR	BDL
26Jan12 Bama Belle Landsc	1/26/2012	Institutional	Landscaped	2.0	TR	TR	TR
17Aug12BamaBelleLandsc	8/17/2012	Institutional	Landscaped	BDL	BDL	BDL	BDL
Bama052811OpenSpa120111	12/1/2011	Institutional	Landscaped	4.2	BDL	TR	TR
x10Bama052811OpenSpa120111	12/1/2011	Institutional	Landscaped	3.9	BDL	BDL	BDL
Bama062811OpenSpa1201	6/28/2011	Institutional	Landscaped	TR	BDL	TR	TR
x10Bama062811OpenSpa1201	6/28/2011	Institutional	Landscaped	BDL	TR	BDL	BDL
040712BamaBelle042712	4/27/2012	Institutional	Landscaped	0.6	BDL	TR	TR
040712BamaBelle?2mL031512x10	3/15/2012	Institutional	Landscaped	BDL	BDL	BDL	BDL
28Jun Bama Belle Paved	6/28/2011	Institutional	Paved	3.7	BDL	TR	BDL
26Jan12 Bama Belle Paved	1/26/2012	Institutional	Paved	0.3	TR	TR	0.3
28Jun11 Bama Belle Roof	6/28/2011	Institutional	Roof	TR	BDL	BDL	BDL
26Jan12 Bama Belle Roof	1/26/2012	Institutional	Roof	0.7	BDL	TR	TR
17Aug12BamaBelleRoof	8/17/2012	Institutional	Roof	BDL	BDL	BDL	BDL
28Jun11 Bama Belle FilterInfluent	6/28/2011	Institutional	yOutfall	8.7	BDL	BDL	BDL
5Sep11 Acad Dr. Landsc	9/5/2011	Residential	Landscaped	2.9	BDL	BDL	BDL
5Sep11 Acad Dr. Landsc	9/5/2011	Residential	Landscaped	0.3	TR	TR	TR
20Sep11 Acad Dr. Grass	9/20/2011	Residential	Landscaped	4.5	BDL	BDL	BDL
14Oct12Acad Cr. Landsc	10/14/2012	Residential	Landscaped	BDL	BDL	BDL	BDL
28Jun11 Acad Dr. Paved	6/28/2011	Residential	Paved	BDL	BDL	BDL	BDL
20Sep11 Acad Dr. Paved	9/20/2011	Residential	Paved	4.4	BDL	BDL	BDL
28Jun11 Acad Dr. Roof	6/28/2011	Residential	Roof	1.2	BDL	BDL	BDL
20Sep11 Acad Dr. Roof	9/20/2011	Residential	Roof	TR	BDL	TR	BDL
			count	18	0	0	1

			% above TR	64	0	0	4
			average	2.4	n/a	n/a	0.3
			max	8.7	n/a	n/a	0.3

Site (concentrations µg/L)	Sample Date	Land Use	Surface	Phenanthrene	Anthracene	Fluoranthene	Pyrene
28Jun11 Galleria Grass	6/28/2011	Commercial	Landscaped	BDL	BDL	BDL	BDL
23Mar12 Galleria Landsc	3/22/2012	Commercial	Landscaped	0.3	TR	TR	BDL
22Jun11 Galleria Paved	6/22/2011	Commercial	Paved	BDL	BDL	BDL	BDL
23Mar12 Galleria Paved	3/22/2012	Commercial	Paved	1.1	TR	2.7	1.9
22Jun11 Galleria Roof	6/22/2011	Commercial	Roof	BDL	BDL	BDL	BDL
5Sep11 Bama Belle Grass	9/5/2011	Institutional	Landscaped	TR	BDL	BDL	BDL
26Jan12 Bama Belle Landsc	1/26/2012	Institutional	Landscaped	0.4	TR	TR	TR
17Aug12BamaBelleLandsc	8/17/2012	Institutional	Landscaped	BDL	BDL	BDL	BDL
Bama052811OpenSpa120111	12/1/2011	Institutional	Landscaped	TR	TR	TR	BDL
x10Bama052811OpenSpa120111	12/1/2011	Institutional	Landscaped	BDL	BDL	BDL	BDL
Bama062811OpenSpa1201	6/28/2011	Institutional	Landscaped	0.3	TR	TR	BDL
x10Bama062811OpenSpa1201	6/28/2011	Institutional	Landscaped	BDL	BDL	BDL	BDL
040712BamaBelle042712	4/27/2012	Institutional	Landscaped	0.4	TR	TR	BDL
040712BamaBelle?2mL031512x10	3/15/2012	Institutional	Landscaped	BDL	BDL	BDL	BDL
28Jun Bama Belle Paved	6/28/2011	Institutional	Paved	TR	BDL	TR	BDL
26Jan12 Bama Belle Paved	1/26/2012	Institutional	Paved	1.1	TR	2.7	2.3
28Jun11 Bama Belle Roof	6/28/2011	Institutional	Roof	TR	BDL	TR	BDL
26Jan12 Bama Belle Roof	1/26/2012	Institutional	Roof	0.3	BDL	TR	BDL
17Aug12BamaBelleRoof	8/17/2012	Institutional	Roof	BDL	BDL	BDL	BDL
28Jun11 Bama Belle FilterInfluent	6/28/2011	Institutional	yOutfall	BDL	BDL	BDL	BDL
5Sep11 Acad Dr. Landsc	9/5/2011	Residential	Landscaped	TR	BDL	BDL	BDL
5Sep11 Acad Dr. Landsc	9/5/2011	Residential	Landscaped	TR	TR	TR	BDL
20Sep11 Acad Dr. Grass	9/20/2011	Residential	Landscaped	TR	BDL	BDL	BDL
14Oct12Acad Cr. Landsc	10/14/2012	Residential	Landscaped	BDL	BDL	BDL	BDL
28Jun11 Acad Dr. Paved	6/28/2011	Residential	Paved	0.3	TR	BDL	BDL
20Sep11 Acad Dr. Paved	9/20/2011	Residential	Paved	TR	BDL	BDL	BDL
28Jun11 Acad Dr. Roof	6/28/2011	Residential	Roof	TR	TR	TR	BDL

20Sep11 Acad Dr. Roof	9/20/2011	Residential	Roof	TR	BDL	BDL	BDL
			count	8	0	2	2
			% above TR	29	0	7	7
			average	0.5	n/a	2.7	2.1
			max	1.1	n/a	2.7	2.3

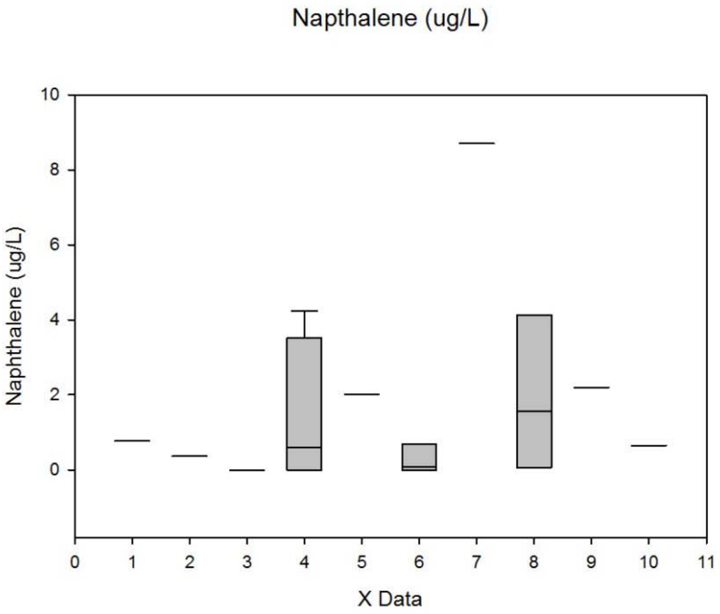
Site (concentrations μg/L)	Sample Date	Land Use	Surface	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoroanthene
28Jun11 Galleria Grass	6/28/2011	Commercial	Landscaped	BDL	BDL	BDL	BDL
23Mar12 Galleria Landsc	3/22/2012	Commercial	Landscaped	BDL	BDL	BDL	BDL
22Jun11 Galleria Paved	6/22/2011	Commercial	Paved	BDL	BDL	BDL	BDL
23Mar12 Galleria Paved	3/22/2012	Commercial	Paved	2.9	1.7	7.1	2.5
22Jun11 Galleria Roof	6/22/2011	Commercial	Roof	BDL	BDL	BDL	BDL
5Sep11 Bama Belle Grass	9/5/2011	Institutional	Landscaped	BDL	BDL	BDL	BDL
26Jan12 Bama Belle Landsc	1/26/2012	Institutional	Landscaped	BDL	BDL	BDL	BDL
17Aug12BamaBelleLandsc	8/17/2012	Institutional	Landscaped	BDL	BDL	BDL	BDL
Bama052811OpenSpa120111	12/1/2011	Institutional	Landscaped	BDL	BDL	BDL	BDL
x10Bama052811OpenSpa120111	12/1/2011	Institutional	Landscaped	BDL	BDL	BDL	0.8
Bama062811OpenSpa1201	6/28/2011	Institutional	Landscaped	BDL	BDL	BDL	BDL
x10Bama062811OpenSpa1201	6/28/2011	Institutional	Landscaped	BDL	BDL	BDL	BDL
040712BamaBelle042712	4/27/2012	Institutional	Landscaped	BDL	BDL	BDL	BDL
040712BamaBelle?2mL031512x10	3/15/2012	Institutional	Landscaped	BDL	BDL	BDL	BDL
28Jun Bama Belle Paved	6/28/2011	Institutional	Paved	BDL	BDL	BDL	BDL
26Jan12 Bama Belle Paved	1/26/2012	Institutional	Paved	3.0	2.0	7.2	2.5
28Jun11 Bama Belle Roof	6/28/2011	Institutional	Roof	BDL	BDL	BDL	BDL
26Jan12 Bama Belle Roof	1/26/2012	Institutional	Roof	BDL	BDL	BDL	BDL
17Aug12BamaBelleRoof	8/17/2012	Institutional	Roof	BDL	BDL	BDL	BDL
28Jun11 Bama Belle FilterInfluent	6/28/2011	Institutional	yOutfall	BDL	BDL	BDL	BDL
5Sep11 Acad Dr. Landsc	9/5/2011	Residential	Landscaped	BDL	BDL	BDL	BDL
5Sep11 Acad Dr. Landsc	9/5/2011	Residential	Landscaped	BDL	BDL	BDL	BDL
20Sep11 Acad Dr. Grass	9/20/2011	Residential	Landscaped	BDL	BDL	BDL	BDL

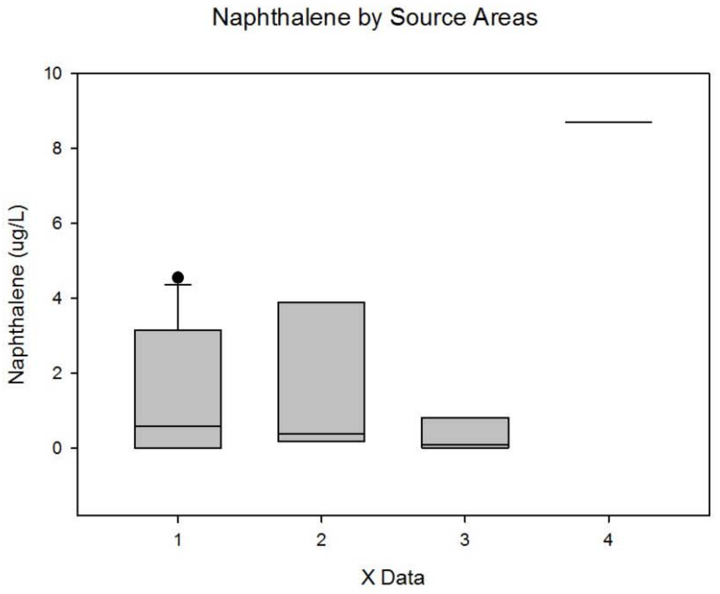
14Oct12Acad Cr. Landsc	10/14/2012	Residential	Landscaped	BDL	BDL	BDL	BDL
28Jun11 Acad Dr. Paved	6/28/2011	Residential	Paved	BDL	BDL	BDL	BDL
20Sep11 Acad Dr. Paved	9/20/2011	Residential	Paved	BDL	BDL	BDL	BDL
28Jun11 Acad Dr. Roof	6/28/2011	Residential	Roof	BDL	BDL	BDL	BDL
20Sep11 Acad Dr. Roof	9/20/2011	Residential	Roof	BDL	BDL	BDL	BDL
			count	2	2	2	3
			% above TR	7	7	7	11
			average	2.9	1.9	7.1	2.0
			max	3.0	2.0	7.2	2.5

Site (concentrations µg/L)	Sample Date	Land Use	Surface	Benzo(a)pyrene	Indeno(1,2,3-cd)anthracene	Benzo(a,h) anthracene	Benzo(ghi)perylene
28Jun11 Galleria Grass	6/28/2011	Commercial	Landscaped	BDL	TR	BDL	BDL
23Mar12 Galleria Landsc	3/22/2012	Commercial	Landscaped	BDL	TR	BDL	BDL
22Jun11 Galleria Paved	6/22/2011	Commercial	Paved	BDL	BDL	0.4	BDL
23Mar12 Galleria Paved	3/22/2012	Commercial	Paved	1.3	BDL	BDL	1.5
22Jun11 Galleria Roof	6/22/2011	Commercial	Roof	BDL	BDL	BDL	BDL
5Sep11 Bama Belle Grass	9/5/2011	Institutional	Landscaped	BDL	BDL	BDL	BDL
26Jan12 Bama Belle Landsc	1/26/2012	Institutional	Landscaped	BDL	0.2	BDL	BDL
17Aug12BamaBelleLandsc	8/17/2012	Institutional	Landscaped	BDL	1.0	BDL	0.4
Bama052811OpenSpa120111	12/1/2011	Institutional	Landscaped	BDL	TR	BDL	BDL
x10Bama052811OpenSpa120111	12/1/2011	Institutional	Landscaped	BDL	BDL	BDL	BDL
Bama062811OpenSpa1201	6/28/2011	Institutional	Landscaped	BDL	BDL	BDL	BDL
x10Bama062811OpenSpa1201	6/28/2011	Institutional	Landscaped	BDL	BDL	BDL	BDL
040712BamaBelle042712	4/27/2012	Institutional	Landscaped	BDL	TR	BDL	BDL
040712BamaBelle?2mL031512x10	3/15/2012	Institutional	Landscaped	BDL	BDL	BDL	BDL
28Jun Bama Belle Paved	6/28/2011	Institutional	Paved	BDL	0.3	BDL	BDL
26Jan12 Bama Belle Paved	1/26/2012	Institutional	Paved	1.3	BDL	BDL	1.6
28Jun11 Bama Belle Roof	6/28/2011	Institutional	Roof	BDL	TR	BDL	BDL
26Jan12 Bama Belle Roof	1/26/2012	Institutional	Roof	BDL	BDL	BDL	BDL
17Aug12BamaBelleRoof	8/17/2012	Institutional	Roof	BDL	BDL	BDL	0.2

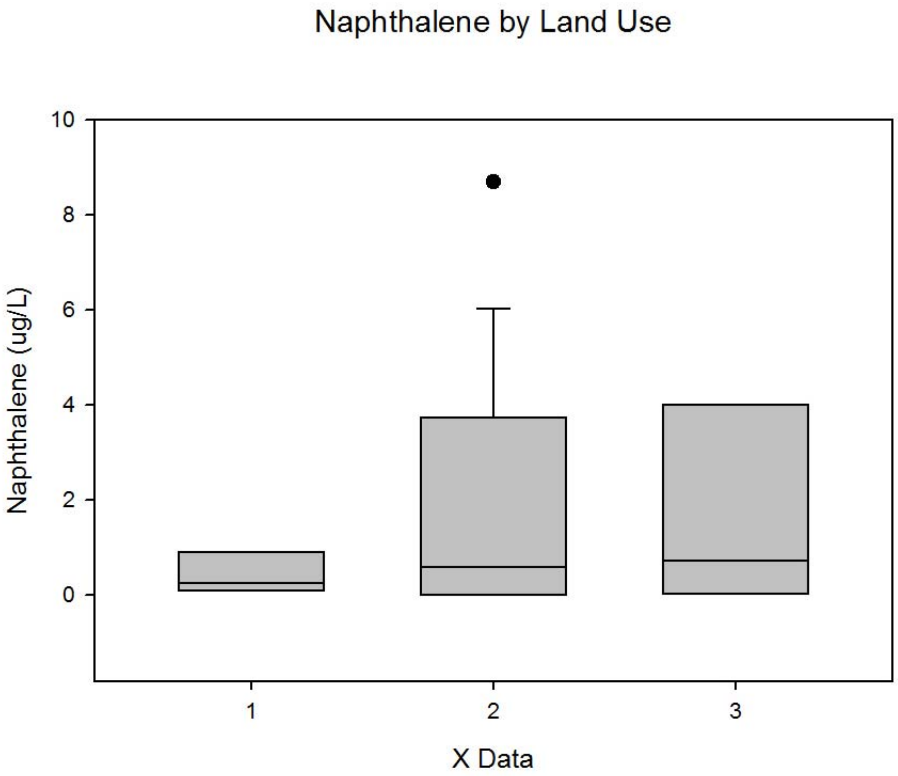
28Jun11 Bama Belle FilterInfluent	6/28/2011	Institutional	yOutfall	BDL	BDL	BDL	BDL
5Sep11 Acad Dr. Landsc	9/5/2011	Residential	Landscaped	BDL	TR	BDL	BDL
5Sep11 Acad Dr. Landsc	9/5/2011	Residential	Landscaped	TR	TR	BDL	BDL
20Sep11 Acad Dr. Grass	9/20/2011	Residential	Landscaped	BDL	TR	BDL	BDL
14Oct12Acad Cr. Landsc	10/14/2012	Residential	Landscaped	BDL	BDL	BDL	BDL
28Jun11 Acad Dr. Paved	6/28/2011	Residential	Paved	BDL	0.3	BDL	BDL
20Sep11 Acad Dr. Paved	9/20/2011	Residential	Paved	BDL	0.3	BDL	BDL
28Jun11 Acad Dr. Roof	6/28/2011	Residential	Roof	BDL	BDL	BDL	BDL
20Sep11 Acad Dr. Roof	9/20/2011	Residential	Roof	BDL	0.3	BDL	BDL
			count	2	6	1	4
			% above TR	7	21	4	14
			average	1.3	0.4	0.4	0.9
			max	1.3	1.0	0.4	1.6

Napthalene


Napthalene (ug/L)
Naphthalene (ug/L)
10
8
6
4
2
0
0
1
2
3
4
5
6
7
8
9
10
11
X Data


Naphthalene by Source Areas
Naphthalene (ug/L)
10
8
6
4
2
0
1
2
3
4
X Data

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Naphthalene source areas.JNB					
Group	N	Missing	Median	25%	75%
lands	16	1	0.591	0	3.146
paved	7	1	0.389	0.186	3.901
roof	7	1	0.092	0	0.822
institOF	2	1	8.699	8.699	8.699
H = 4.441 with 3 degrees of freedom. (P = 0.218)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.218)					

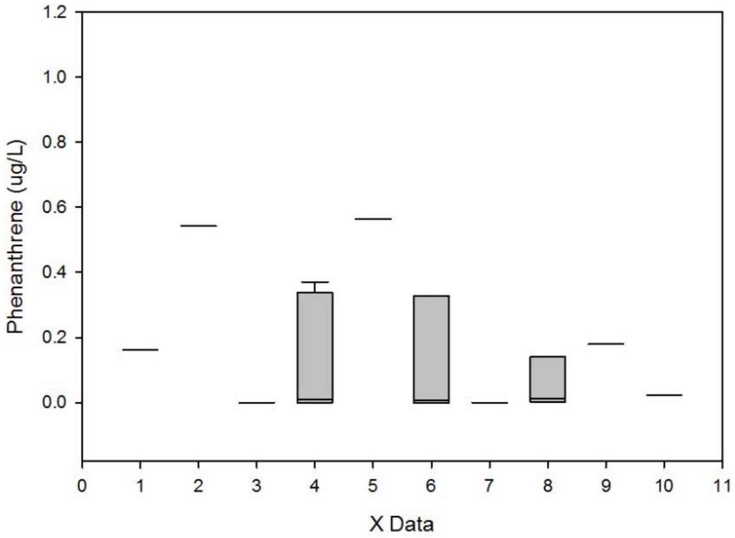


Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Naphthalene source areas.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%

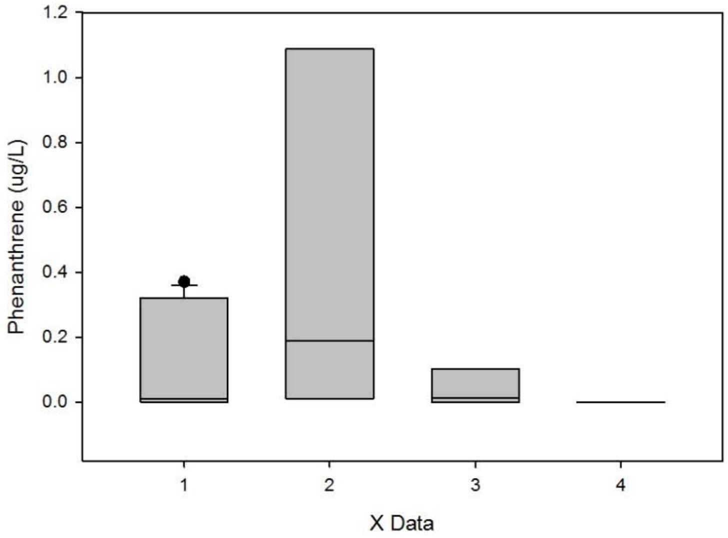
commercial	6	1	0.249	0.102	0.91
institutional	16	1	0.591	0	3.74
residential	9	1	0.726	0.0247	4.008
H = 0.509 with 2 degrees of freedom. (P = 0.775)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.775)					

Phenanthrene

Phenanthrene

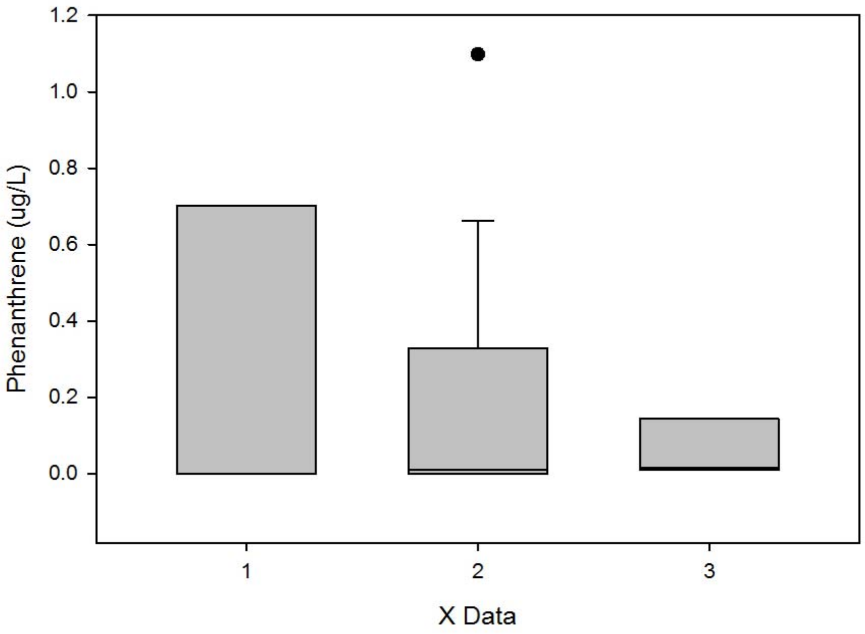


Phenanthrene by Source Areas



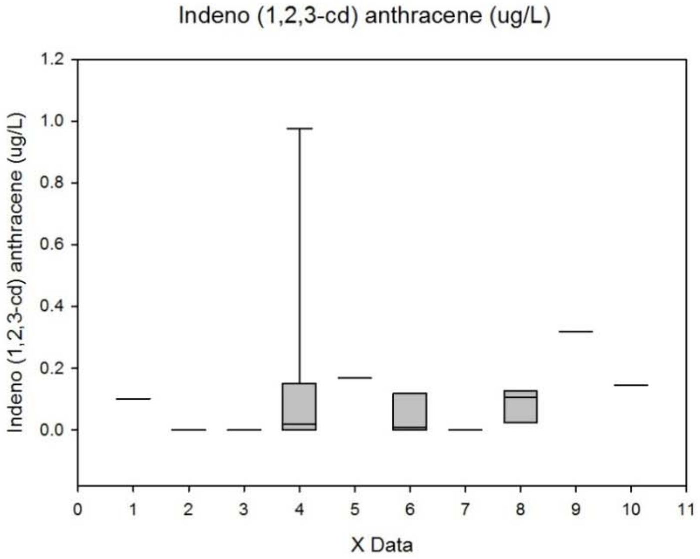
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Phenanthrene source area.JNB					
Group	N	Missing	Median	25%	75%
lands	15	0	0.00971	0	0.321
paved	6	0	0.189	0.0103	1.088
roof	6	0	0.0132	0	0.103
institOF	1	0	0	0	0
H = 3.844 with 3 degrees of freedom. (P = 0.279)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.279)					

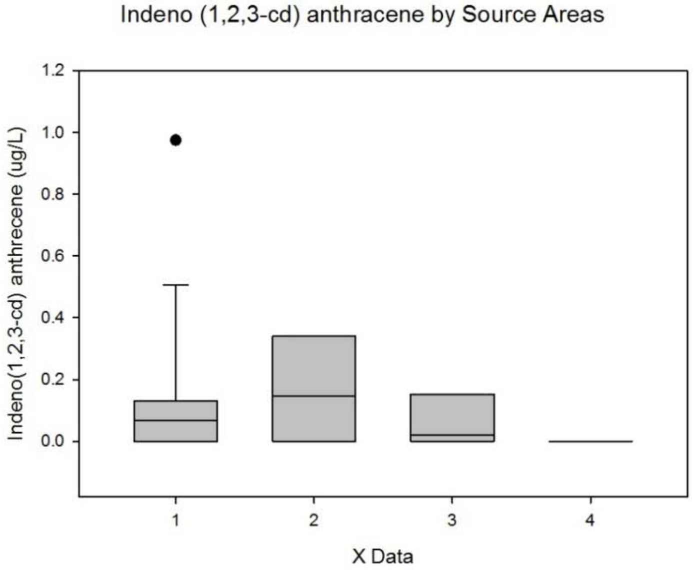
Phenanthrene by Land Uses



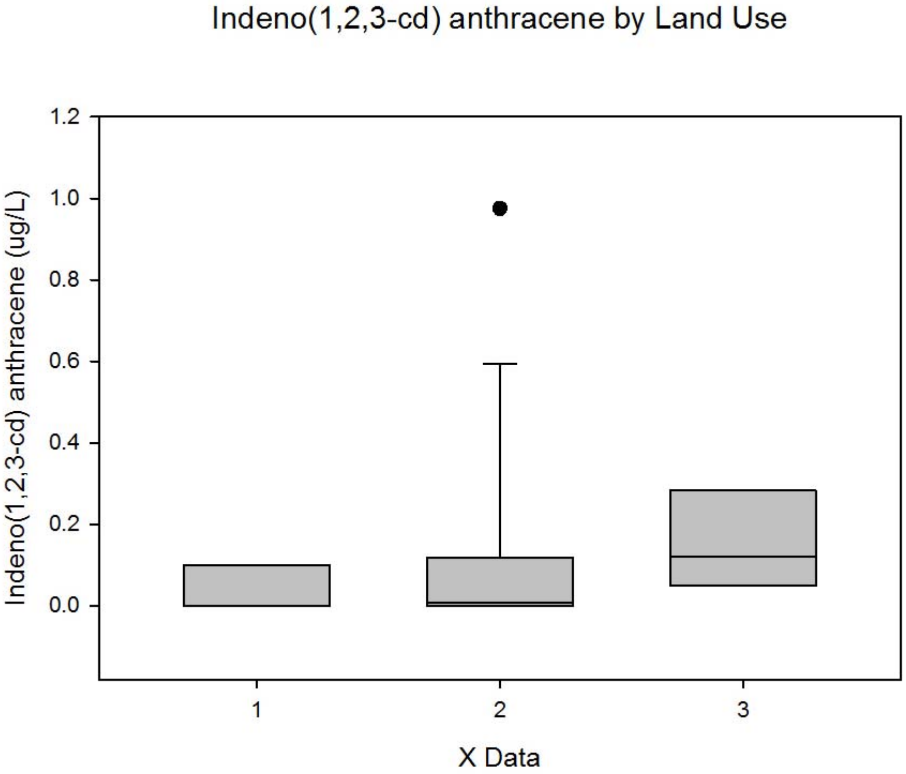
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Phenanthrene source area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	5	0	0	0	0.703
institutional	15	0	0.00971	0	0.328
residential	8	0	0.0167	0.00922	0.144
H = 0.307 with 2 degrees of freedom. (P = 0.858)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.858)					

Indeno(1,2,3-cd)anthracene


Indeno (1,2,3-cd) anthracene (ug/L)


Indeno (1,2,3-cd) anthracene by Source Areas

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Indendoanthracene source areas.JNB					
Group	N	Missing	Median	25%	75%
lands	15	0	0.0668	0	0.131
paved	6	0	0.145	0	0.34
roof	6	0	0.0204	0	0.153
institOF	1	0	0	0	0
H = 1.550 with 3 degrees of freedom. (P = 0.671)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.671)					


Indeno(1,2,3-cd) anthracene by Land Use
Indeno(1,2,3-cd) anthracene (ug/L)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1
2
3
X Data

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Indendoanthracene source areas.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	5	0	0	0	0.101
institutional	15	0	0.0086	0	0.117
residential	8	0	0.121	0.0487	0.283
H = 4.011 with 2 degrees of freedom. (P = 0.135)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.135)					

Heavy Metals in Stormwater Sheetflows

Site	Sample Date	Time	Land Use	Surface	TSS (mg/L)	Total Aluminum (mg/L)	Filtered Aluminum (mg/L)	mg part AL/kg SS
28Jun11 Galleria Grass	6/28/2011	1430	Commercial	Landscaped	46.8	0.25	0.077	3,697
23Mar12 Galleria Landsc	3/22/2012	900	Commercial	Landscaped	46	0.079	0.02	1,283
22Jun11 Galleria Paved	6/22/2011	1610	Commercial	Paved	81	1.25	0.06	14,691
23Mar12 Galleria Paved	3/22/2012	900	Commercial	Paved	295.5	4.38	0.028	14,728
22Jun11 Galleria Roof	6/22/2011	1610	Commercial	Roof	8.4	0.098	0.09	952
23Mar12 Galleria Roof	3/22/2012	900	Commercial	Roof	31.5	0.014	0.008	190
5Sep11 Bama Belle Grass	9/5/2011	1115	Institutional	Landscaped	203.5	1.76	0.053	8,388
26Jan12 Bama Belle Landsc	1/26/2012	945	Institutional	Landscaped	505	4.08	0.098	7,885
17Aug12BamaBelleLandsc	8/17/2012	700	Institutional	Landscaped	568.2	3.03	0.049	5,246
28Jun Bama Belle Paved	6/28/2011	1430	Institutional	Paved	19.5	0.214	0.132	4,205
26Jan12 Bama Belle Paved	1/26/2012	1005	Institutional	Paved	18	0.095	0.036	3,278
17Aug12BamaBellePaved	8/17/2012	700	Institutional	Paved	2.5	0.111	0.057	21,600
28Jun11 Bama Belle Roof	6/28/2011	1430	Institutional	Roof	2.5	0.015	0.015	0
26Jan12 Bama Belle Roof	1/26/2012	1005	Institutional	Roof	2.5	0.007	0.005	800
17Aug12BamaBelleRoof	8/17/2012	700	Institutional	Roof	2.5	0.02	0.006	5,600
28Jun11 Bama Belle FilterInfluent	6/28/2011	1430	Institutional	yOutfall	n/a	0.227	0.059	n/a
26Jan12 Bama BelleFilterInfluent	1/26/2012	1010	Institutional	yOutfall	10.1	0.193	0.138	5,446
17Aug12BamaBelleRoofFilterInfluent	8/17/2012	700	Institutional	yOutfall	2.5	0.148	0.059	35,600
16Nov10 FoxRunLandsc	11/16/2010	unrecorded	Residential	Landscaped	n/a	2.14	1.18	n/a
5Sep11 Acad Dr. Landsc	9/5/2011	1010	Residential	Landscaped	423	2.34	0.11	5,272
20Sep11 Acad Dr. Grass	9/20/2011	940	Residential	Landscaped	414.5	2.04	0.0058	4,908
16Nov10 FoxRunStreet	11/16/2010	unrecorded	Residential	Paved	n/a	0.355	0.191	n/a
28Jun11 Acad Dr. Paved	6/28/2011	1430	Residential	Paved	17	0.123	0.04	4,882
20Sep11 Acad Dr. Paved	9/20/2011	715	Residential	Paved	2.4	0.057	0.009	20,000
30Sep12 Acad Dr. Paved	9/30/2012	1315	Residential	Paved	2.5	0.211	0.175	14,400
16Nov10AcadDrRoof	11/16/2010	unrecorded	Residential	Roof	n/a	0.015	0.005	n/a
28Jun11 Acad Dr. Roof	6/28/2011	1430	Residential	Roof	5.5	0.011		2,000
20Sep11 Acad Dr. Roof	9/20/2011	715	Residential	Roof	2.5	0.074	0.074	0

30Sep12 Acad Dr. Roof	9/30/2012	1335	Residential	Roof	2.5	0.039	0.016	9,200
			count detected		25	29	28	25
			percentage detected		86	100	97	86
			maximum		568.2	4.38	1.18	35,600

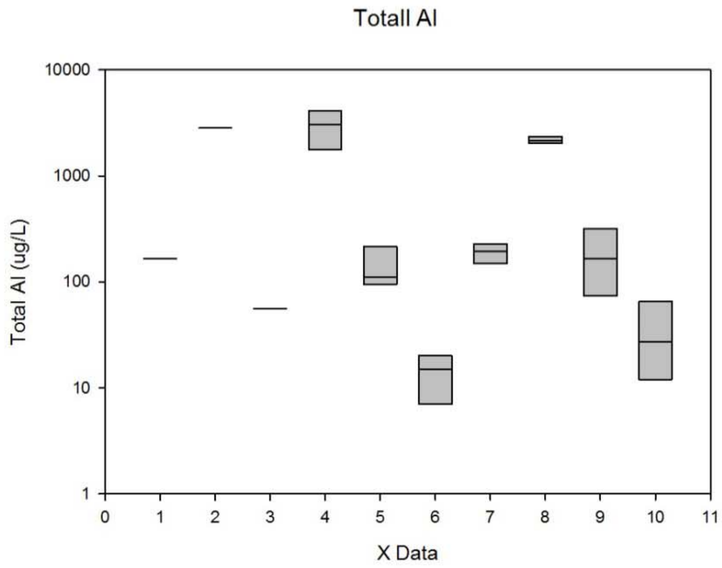
Site	Sample Date	Time	Land Use	Surface	Total Copper (mg/L)	Total Zinc (mg/L)	Filtered Zinc (mg/L)	mg part Zn/kg SS
28Jun11 Galleria Grass	6/28/2011	1430	Commercial	Landscaped	0.012	0.092	0.088	85
23Mar12 Galleria Landsc	3/22/2012	900	Commercial	Landscaped	0.007	0.016	0.016	0
22Jun11 Galleria Paved	6/22/2011	1610	Commercial	Paved	0.014	0.2	0.014	2,296
23Mar12 Galleria Paved	3/22/2012	900	Commercial	Paved	0.027	0.35	0.041	1,046
22Jun11 Galleria Roof	6/22/2011	1610	Commercial	Roof	0.054	0.188	0.185	357
23Mar12 Galleria Roof	3/22/2012	900	Commercial	Roof	BDL	0.041	0.041	0
5Sep11 Bama Belle Grass	9/5/2011	1115	Institutional	Landscaped	0.029	0.045	0.018	133
26Jan12 Bama Belle Landsc	1/26/2012	945	Institutional	Landscaped	0.014	0.06	0.006	107
17Aug12BamaBelleLandsc	8/17/2012	700	Institutional	Landscaped	0.018	0.077	0.014	111
28Jun Bama Belle Paved	6/28/2011	1430	Institutional	Paved	BDL	0.009	BDL	333
26Jan12 Bama Belle Paved	1/26/2012	1005	Institutional	Paved	0.005	0.007	0.007	0
17Aug12BamaBellePaved	8/17/2012	700	Institutional	Paved	0.005	0.007	BDL	1,800
28Jun11 Bama Belle Roof	6/28/2011	1430	Institutional	Roof	BDL	0.031	0.031	0
26Jan12 Bama Belle Roof	1/26/2012	1005	Institutional	Roof	BDL	0.008	0.008	0
17Aug12BamaBelleRoof	8/17/2012	700	Institutional	Roof	BDL	0.027	0.007	8,000
28Jun11 Bama Belle FilterInfluent	6/28/2011	1430	Institutional	yOutfall	0.005	0.035	0.024	n/a
26Jan12 Bama BelleFilterInfluent	1/26/2012	1010	Institutional	yOutfall	0.012	0.012	0.012	0
17Aug12BamaBelleRoofFilterInfluent	8/17/2012	700	Institutional	yOutfall	BDL	0.009	BDL	2,600
16Nov10 FoxRunLandsc	11/16/2010	unrecorded	Residential	Landscaped	0.011	0.019	0.016	n/a
5Sep11 Acad Dr. Landsc	9/5/2011	1010	Residential	Landscaped	0.009	0.022	0.009	31
20Sep11 Acad Dr. Grass	9/20/2011	940	Residential	Landscaped	BDL	0.018	BDL	37
16Nov10 FoxRunStreet	11/16/2010	unrecorded	Residential	Paved	0.009	0.01	0.01	n/a
28Jun11 Acad Dr. Paved	6/28/2011	1430	Residential	Paved	BDL	0.019	0.017	118
20Sep11 Acad Dr. Paved	9/20/2011	715	Residential	Paved	0.007	0.009	0.009	0
30Sep12 Acad Dr. Paved	9/30/2012	1315	Residential	Paved	0.039	BDL	BDL	n/a
16Nov10AcadDrRoof	11/16/2010	unrecorded	Residential	Roof	0.006	BDL	BDL	n/a

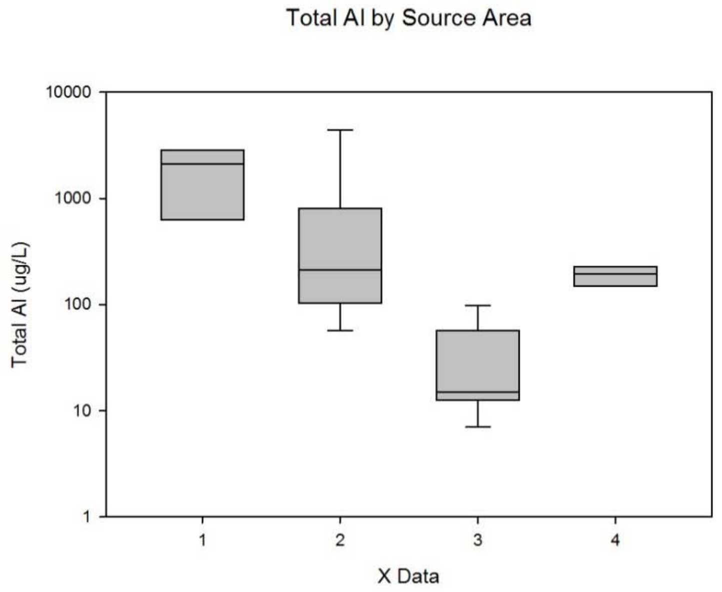
28Jun11 Acad Dr. Roof	6/28/2011	1430	Residential	Roof		0.019		3,455
20Sep11 Acad Dr. Roof	9/20/2011	715	Residential	Roof	BDL	0.007	0.006	400
30Sep12 Acad Dr. Roof	9/30/2012	1335	Residential	Roof	0.019	0.034	0.005	11,600
			count detected		19	27	22	24
			percentage detected		66	93	76	83
			maximum		0.054	0.35	0.185	11,600

Site	Sample Date	Time	Land Use	Surface	Total Iron (mg/L)	Filtered Iron (mg/L)	mg part Fe/kg SS
28Jun11 Galleria Grass	6/28/2011	1430	Commercial	Landscaped	0.24	0.09	3,205
23Mar12 Galleria Landsc	3/22/2012	900	Commercial	Landscaped	0.08	0.03	1,087
22Jun11 Galleria Paved	6/22/2011	1610	Commercial	Paved	1.46	0.4	13,086
23Mar12 Galleria Paved	3/22/2012	900	Commercial	Paved	5.32	0.27	17,090
22Jun11 Galleria Roof	6/22/2011	1610	Commercial	Roof	0.1	0.1	0
23Mar12 Galleria Roof	3/22/2012	900	Commercial	Roof	0.02	0.02	0
5Sep11 Bama Belle Grass	9/5/2011	1115	Institutional	Landscaped	2.21	0.36	9,091
26Jan12 Bama Belle Landsc	1/26/2012	945	Institutional	Landscaped	4.03	0.26	7,465
17Aug12BamaBelleLandsc	8/17/2012	700	Institutional	Landscaped	3.66	0.4	5,737
28Jun Bama Belle Paved	6/28/2011	1430	Institutional	Paved	0.17	0.17	0
26Jan12 Bama Belle Paved	1/26/2012	1005	Institutional	Paved	0.09	0.09	0
17Aug12BamaBellePaved	8/17/2012	700	Institutional	Paved	0.12	0.07	20,000
28Jun11 Bama Belle Roof	6/28/2011	1430	Institutional	Roof	0.04	0.04	0
26Jan12 Bama Belle Roof	1/26/2012	1005	Institutional	Roof	BDL	BDL	n/a
17Aug12BamaBelleRoof	8/17/2012	700	Institutional	Roof	0.02	BDL	6,000
28Jun11 Bama Belle FilterInfluent	6/28/2011	1430	Institutional	yOutfall	0.23	0.15	n/a
26Jan12 Bama BelleFilterInfluent	1/26/2012	1010	Institutional	yOutfall	0.19	0.19	0
17Aug12BamaBelleRoofFilterInfluent	8/17/2012	700	Institutional	yOutfall	0.11	0.07	16,000
16Nov10 FoxRunLandsc	11/16/2010	unrecorded	Residential	Landscaped	1.14	0.67	n/a
5Sep11 Acad Dr. Landsc	9/5/2011	1010	Residential	Landscaped	1.1	0.07	2,435
20Sep11 Acad Dr. Grass	9/20/2011	940	Residential	Landscaped	0.88	0.05	2,002
16Nov10 FoxRunStreet	11/16/2010	unrecorded	Residential	Paved	0.26	0.26	n/a

28Jun11 Acad Dr. Paved	6/28/2011	1430	Residential	Paved	0.09	0.09	0
20Sep11 Acad Dr. Paved	9/20/2011	715	Residential	Paved	0.04	0.04	0
30Sep12 Acad Dr. Paved	9/30/2012	1315	Residential	Paved	0.09	0.09	0
16Nov10AcadDrRoof	11/16/2010	unrecorded	Residential	Roof	BDL	BDL	n/a
28Jun11 Acad Dr. Roof	6/28/2011	1430	Residential	Roof	BDL	n/a	n/a
20Sep11 Acad Dr. Roof	9/20/2011	715	Residential	Roof	0.04	0.04	0
30Sep12 Acad Dr. Roof	9/30/2012	1335	Residential	Roof	0.05	0.05	0
			count detected		26	25	23
			percentage detected		90	86	79
			maximum		5.32	0.67	20,000

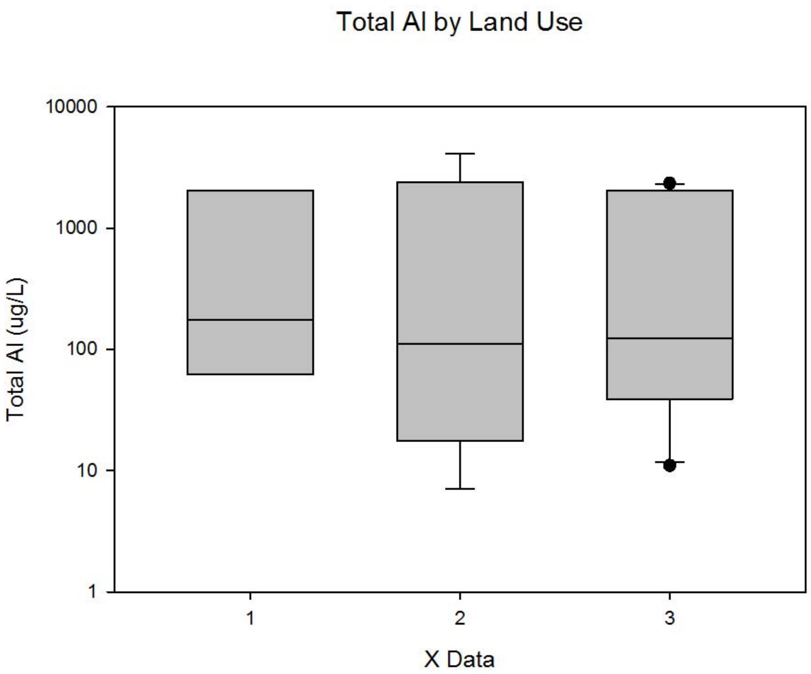
Aluminum


Totall Al


Total Al by Source Area

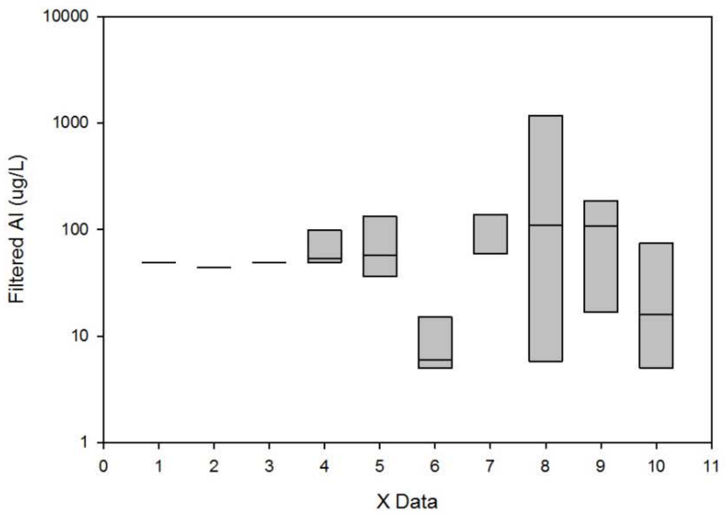
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Total AL.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
lands	8	0	2090	627.5	2857.5
paved	9	0	211	103	802.5
roof	9	0	15	12.5	56.5
institOF	3	0	193	148	227
H = 18.794 with 3 degrees of freedom. (P = <0.001)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					
All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
lands vs roof	17.431	4.213	Yes		
lands vs institOF	6.208	1.077	No		
lands vs paved	5.875	1.42	Do Not Test		
paved vs roof	11.556	2.879	Yes		
paved vs institOF	0.333	0.0587	Do Not Test		

instit OF vs roof	11.222	1.977	No		
Note: The multiple comparisons on ranks do not include an adjustment for ties.					

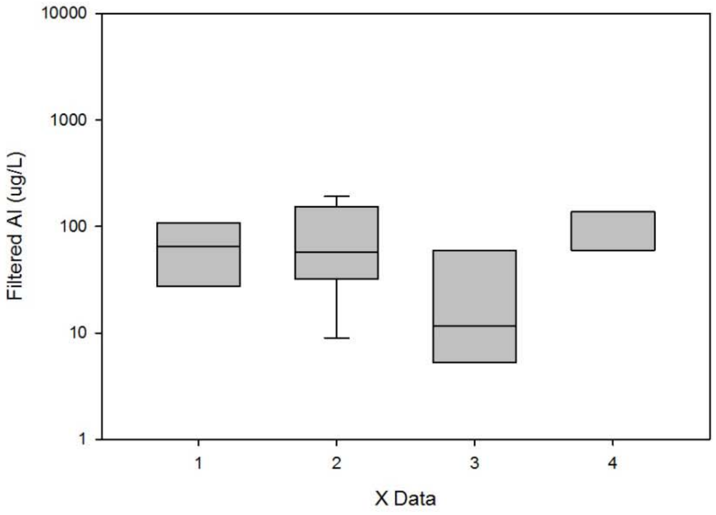


Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Total AL.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	6	0	174	62.75	2032.5
institutional	9	0	111	17.5	2395
residential	11	0	123	39	2040
H = 0.143 with 2 degrees of freedom. (P = 0.931)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.931)					

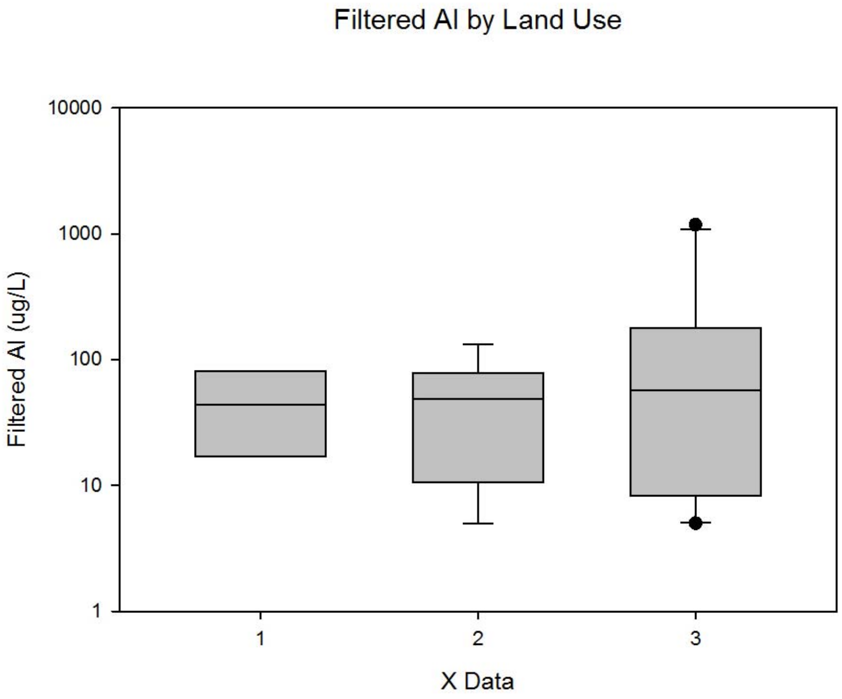
Filtered Al



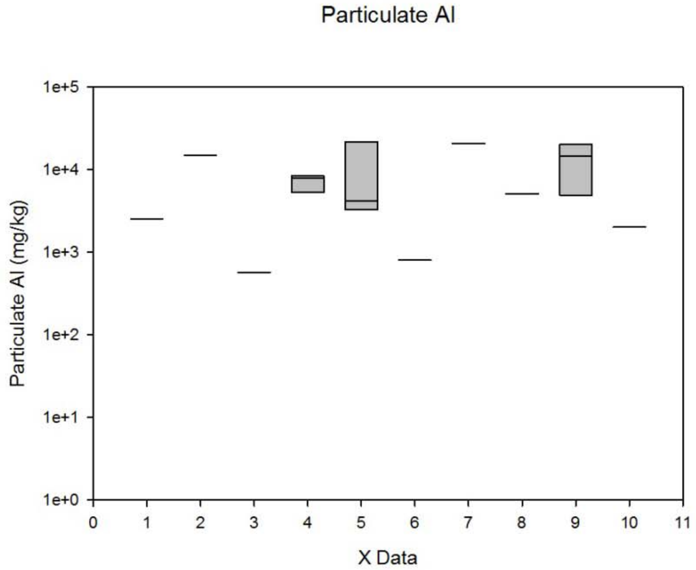
Filtered Al by Source Area

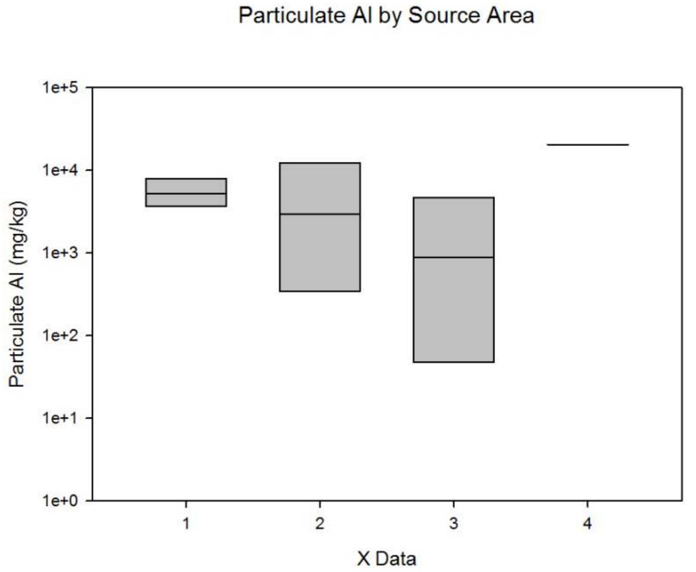


Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in filtered Al.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
lands	8	0	65	27.25	107
paved	9	0	57	32	153.5
roof	8	0	11.5	5.25	59.5
institOF	3	0	59	59	138
H = 6.510 with 3 degrees of freedom. (P = 0.089)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.089)					

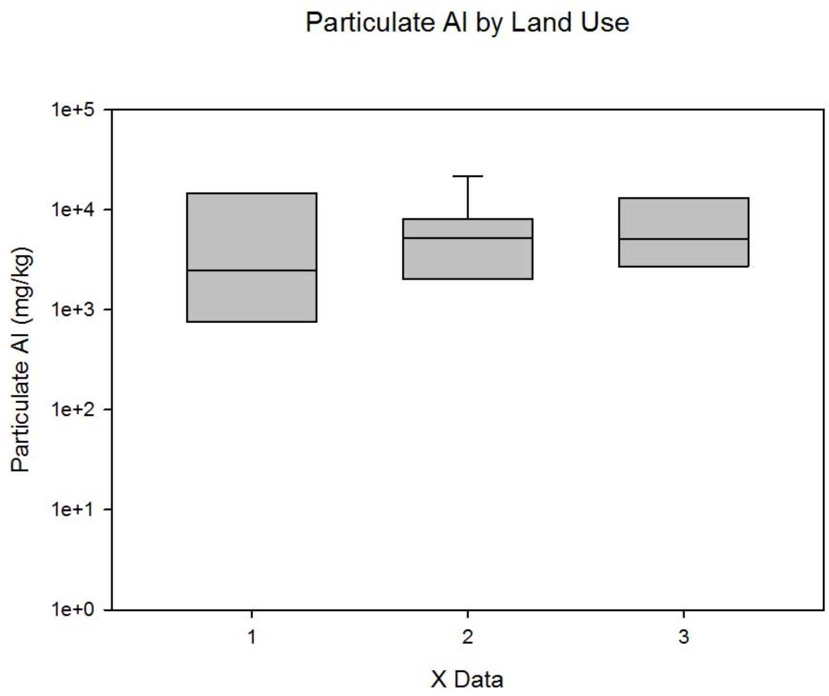

Filtered Al by Land Use
Filtered Al (ug/L)
10000
1000
100
10
1
1
2
3
X Data

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in filtered Al.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	6	0	44	17	80.25
institutional	9	0	49	10.5	77.5
residential	10	0	57	8.2	179
H = 0.392 with 2 degrees of freedom. (P = 0.822)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.822)					


Particulate Al
Particulate Al (mg/kg)
1e+5
1e+4
1e+3
1e+2
1e+1
1e+0
0
1
2
3
4
5
6
7
8
9
10
11
X Data


Particulate Al by Source Area
Particulate Al (mg/kg)
1e+5
1e+4
1e+3
1e+2
1e+1
1e+0
1
2
3
4
X Data

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in particulate Al.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
lands	7	0	5246.392	3696.581	7885.149
paved	8	0	2917.367	342.857	12200
roof	8	0	876.19	47.619	4700
institOF	2	0	20522.77	5445.545	35600
H = 5.119 with 3 degrees of freedom. (P = 0.163)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.163)					

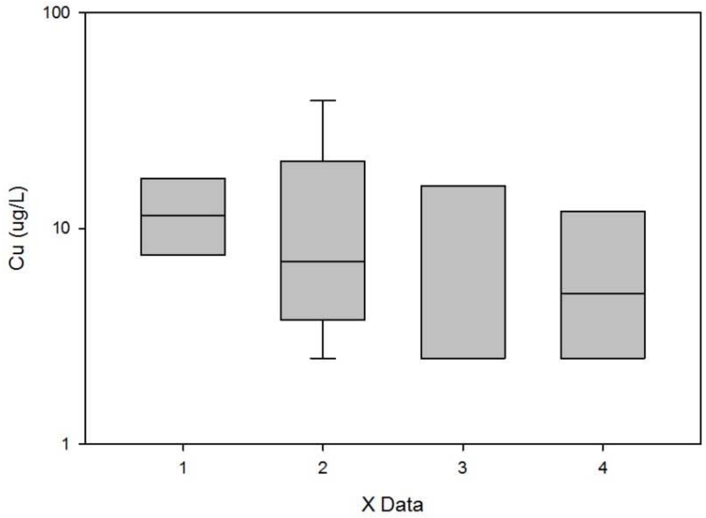


Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in particulate Al.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	6	0	2489.595	761.905	14700.41
institutional	9	0	5246.392	2038.889	8136.677

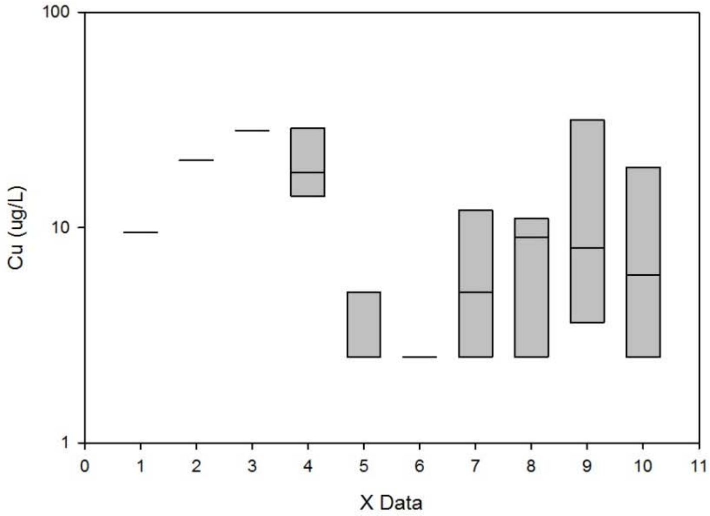
residential	8	0	5089.734	2720.588	13100
H = 0.429 with 2 degrees of freedom. (P = 0.807)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.807)					

Copper

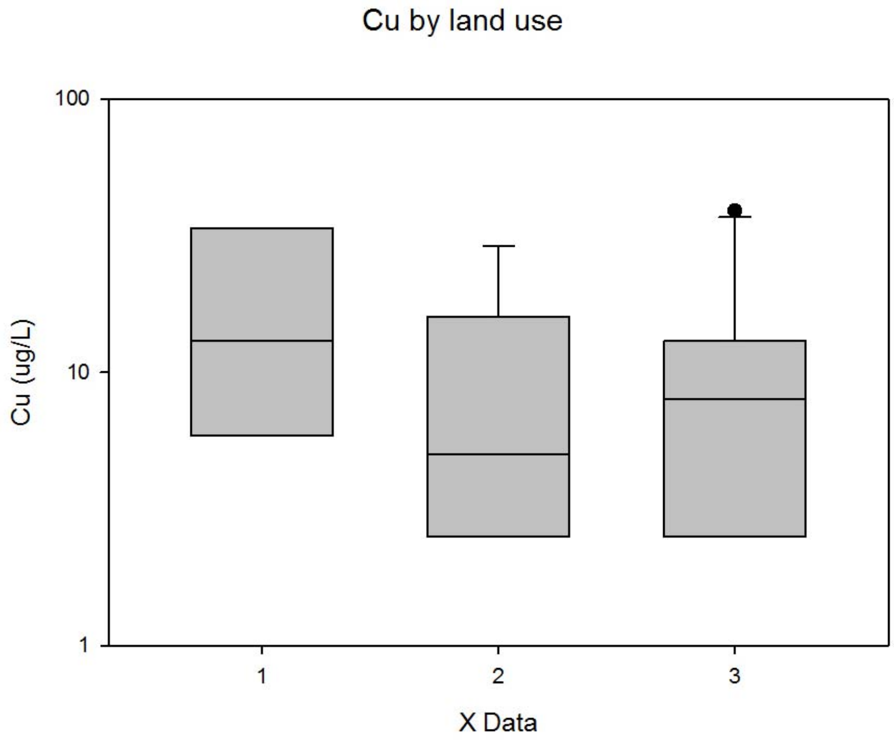
Total Copper by Source Area



Total Copper



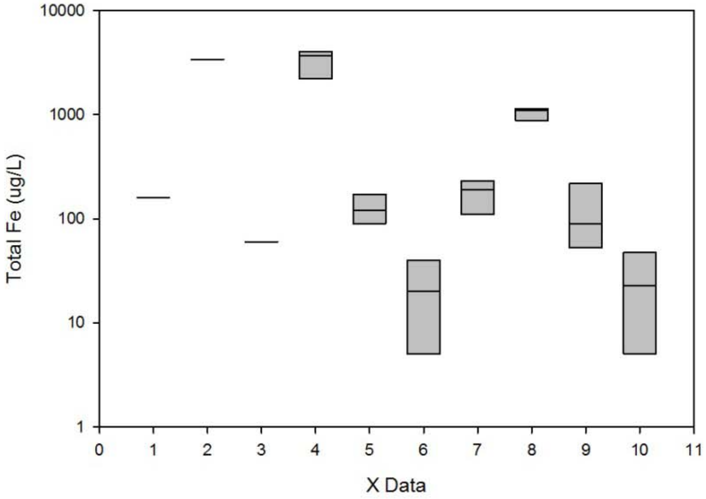
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Cu by source areas.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
lands	8	0	11.5	7.5	17
paved	9	0	7	3.75	20.5
roof	8	0	2.5	2.5	15.75
institOF	3	0	5	2.5	12
H = 3.183 with 3 degrees of freedom. (P = 0.364)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.364)					


Cu by land use
100
10
1
Cu (ug/L)
1
2
3
X Data

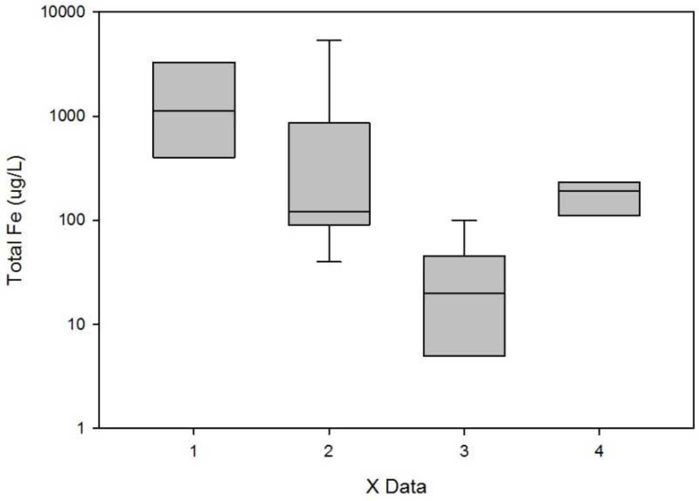
Kruskal-Wallis One Way Analysis of Variance on Ranks	Thursday, June 27, 2013, 12:42:51 AM				
Data source: Data 1 in Cu by source areas.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	6	0	13	5.875	33.75
institutional	9	0	5	2.5	16
residential	10	0	8	2.5	13
H = 2.216 with 2 degrees of freedom. (P = 0.330)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.330)					

Iron

Total Fe

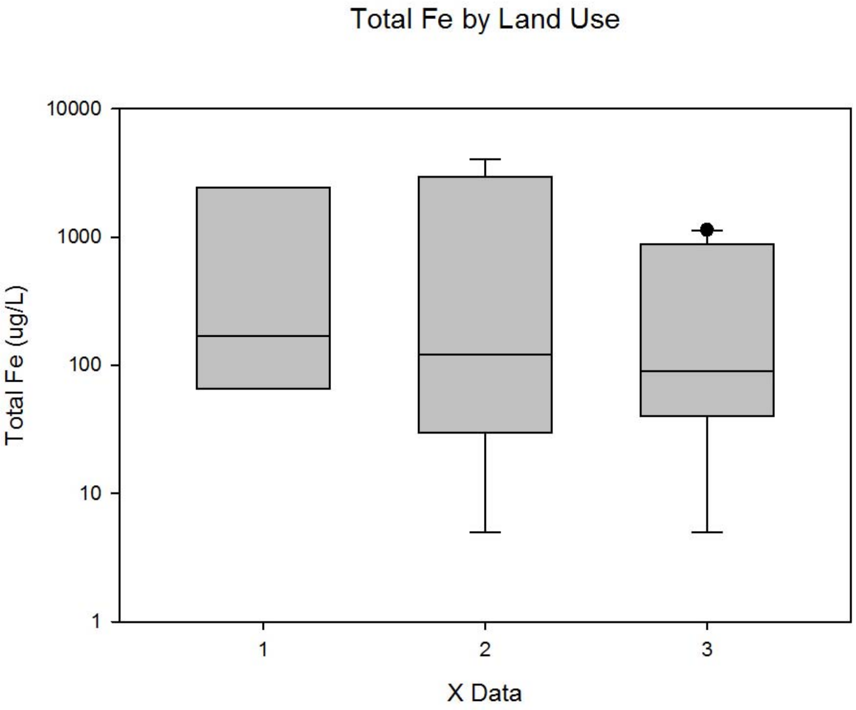


Total Fe by Source Areas



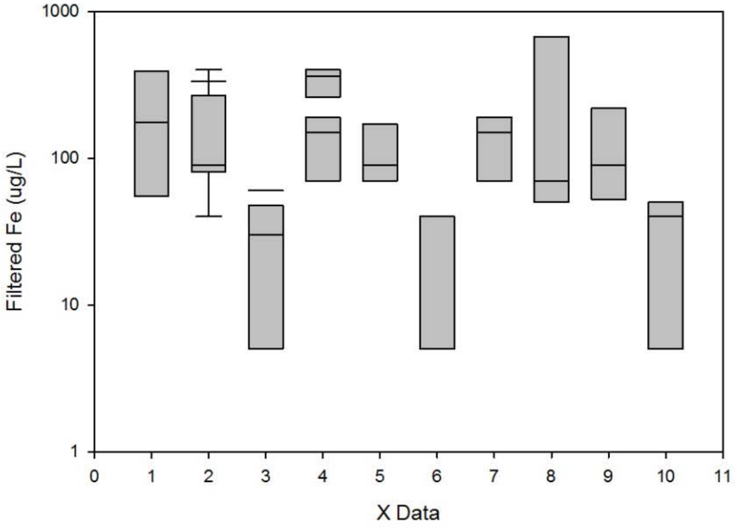
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Total Fe.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
lands	8	0	1120	400	3297.5
paved	9	0	120	90	860
roof	9	0	20	5	45
institOF	3	0	190	110	230
H = 17.438 with 3 degrees of freedom. (P = <0.001)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					
All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
lands vs roof	16.722	4.042	Yes		
lands vs paved	5.722	1.383	No		
lands vs institOF	5.167	0.896	Do Not Test		
institOF vs roof	11.556	2.036	No		
institOF vs paved	0.556	0.0979	Do Not Test		

paved vs roof	11	2.741	Do Not Test		
Note: The multiple comparisons on ranks do not include an adjustment for ties.					

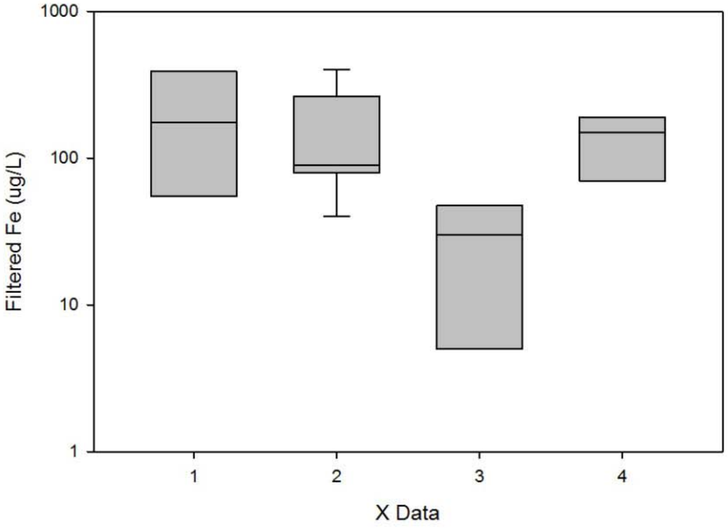


Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Total Fe.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	6	0	170	65	2425
institutional	9	0	120	30	2935
residential	11	0	90	40	880
H = 1.134 with 2 degrees of freedom. (P = 0.567)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.567)					

Filtered Fe

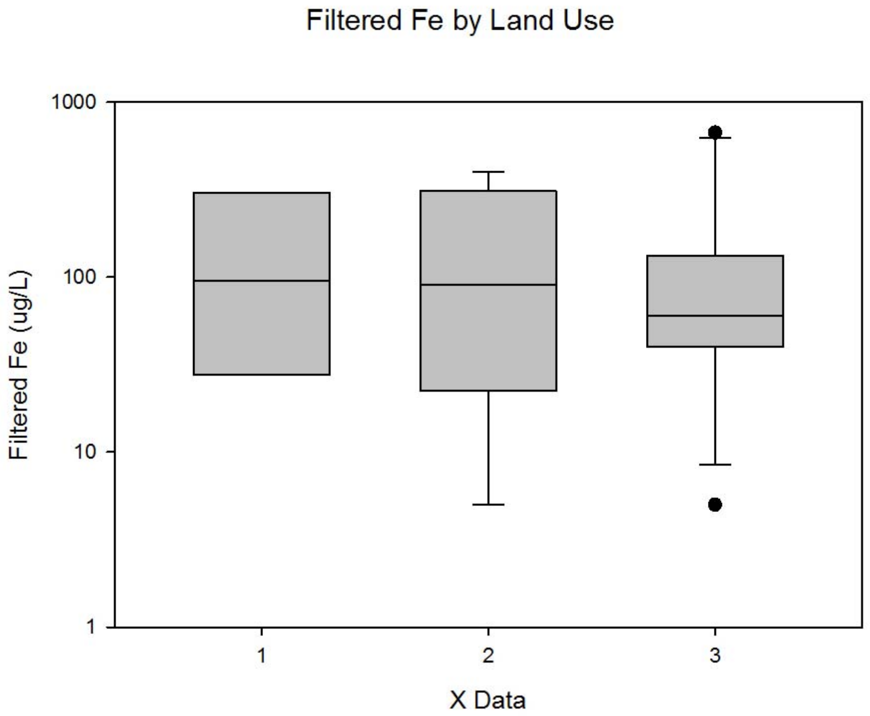


Filtered Fe by Source Areas



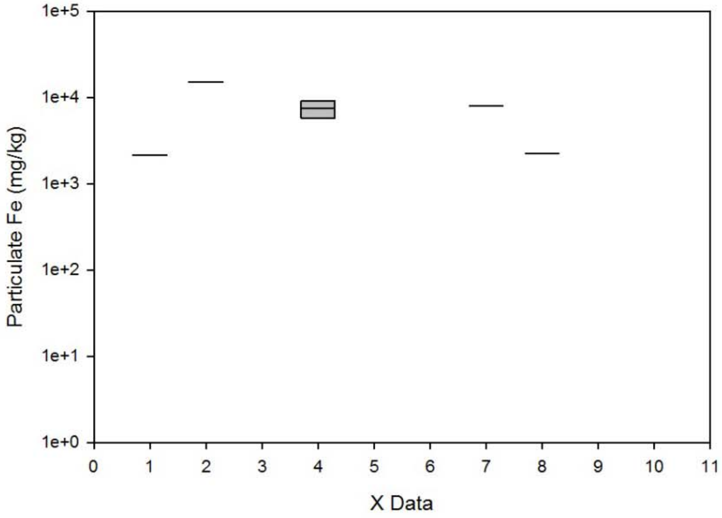
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in filtered Fe.JNB					
Normality Test (Shapiro-Wilk)	Passed	(P = 0.052)			
Equal Variance Test:	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
lands	8	0	175	55	390
paved	9	0	90	80	265
roof	8	0	30	5	47.5
institOF	3	0	150	70	190
H = 10.851 with 3 degrees of freedom. (P = 0.013)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.013)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					
All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
lands vs roof	11.563	2.811	Yes		

lands vs institOF	0.667	0.12	No		
lands vs paved	0.389	0.0973	Do Not Test		
paved vs roof	11.174	2.795	Yes		
paved vs institOF	0.278	0.0507	Do Not Test		
institOF vs roof	10.896	1.957	No		
Note: The multiple comparisons on ranks do not include an adjustment for ties.					

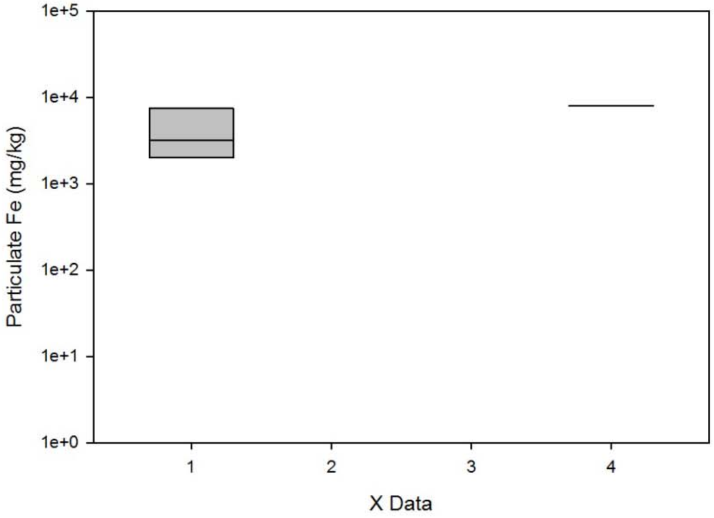


Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in filtered Fe.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	6	0	95	27.5	302.5
institutional	9	0	90	22.5	310
residential	10	0	60	40	132.5
H = 0.357 with 2 degrees of freedom. (P = 0.837)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.837)					

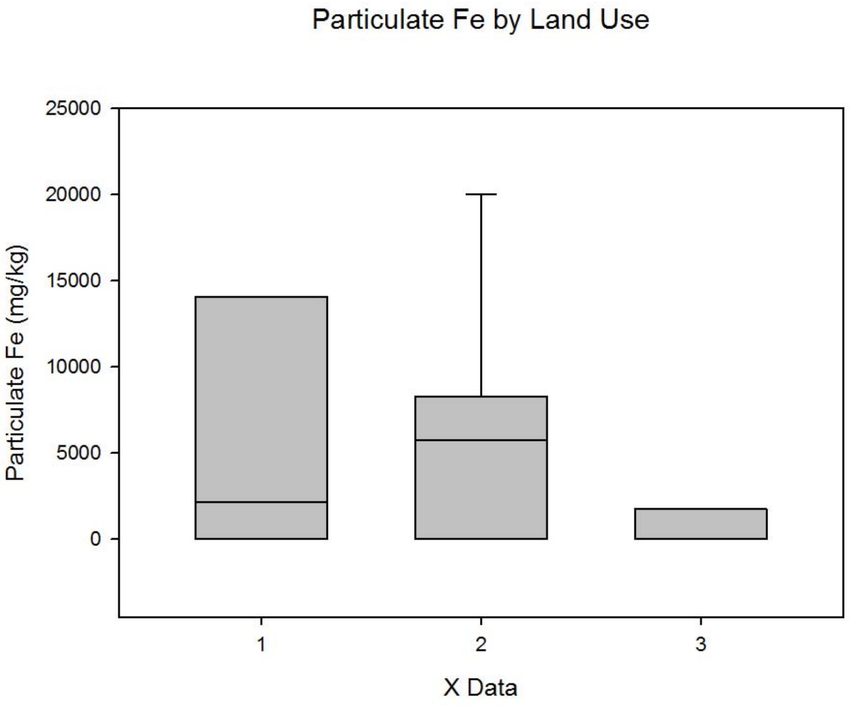
Particulate Fe



Particulate Fe by Source Area

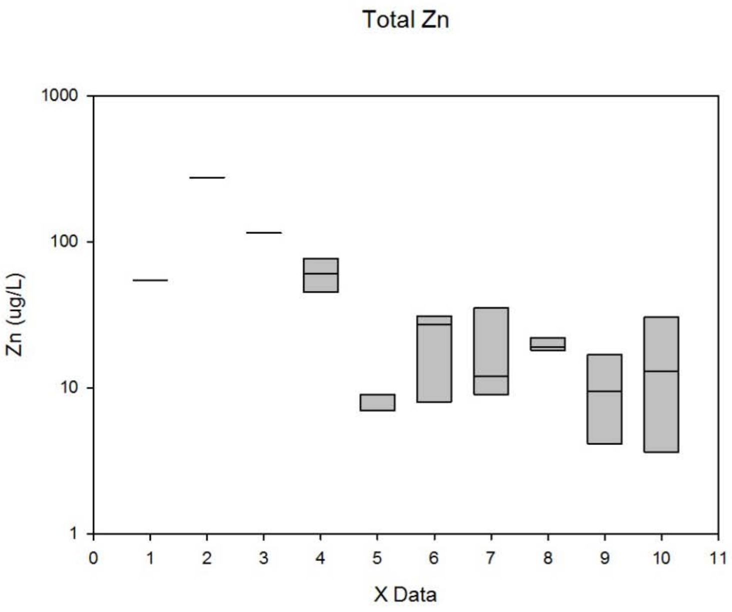


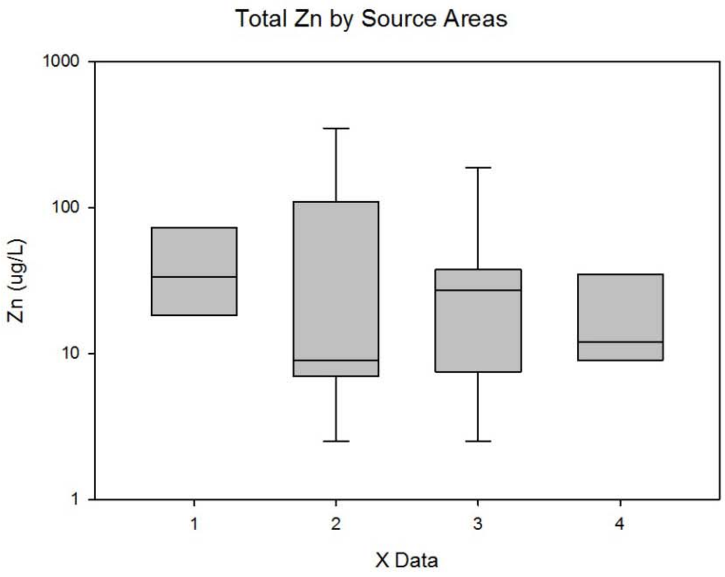
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in part Fe.JNB					
Normality Test (Shapiro-Wilk)	Passed	(P = 0.059)			
Equal Variance Test:	Passed	(P = 0.185)			
Group	N	Missing	Median	25%	75%
lands	7	0	3205.128	2002.413	7465.347
paved	8	0	0	0	16088.86
roof	8	0	0	0	681.818
institOF	2	0	8000	0	16000
H = 5.618 with 3 degrees of freedom. (P = 0.132)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.132)					


Particulate Fe by Land Use
Particulate Fe (mg/kg)
25000
20000
15000
10000
5000
0
1
2
3
X Data

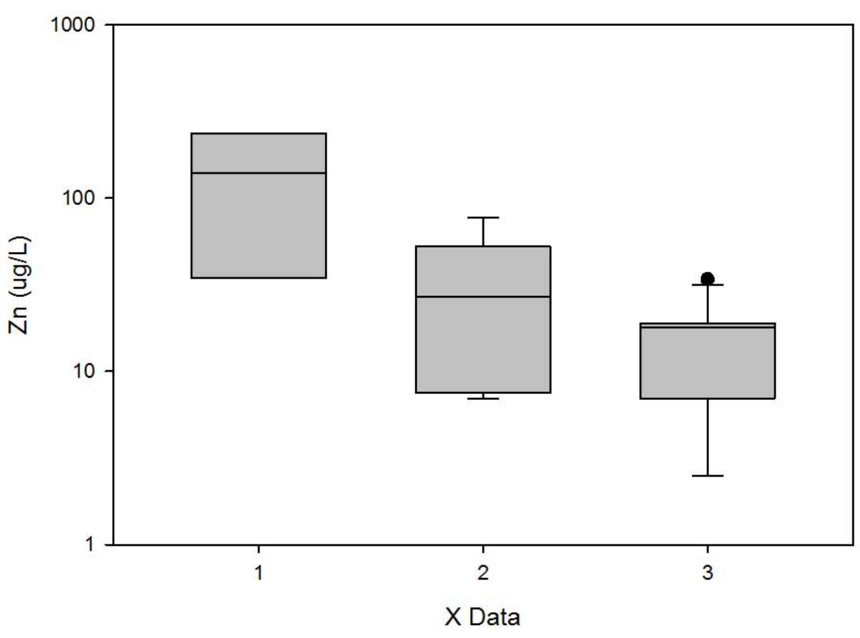
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in part Fe.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	6	0	2146.042	0	14087.23
institutional	9	0	5737.416	0	8278.128
residential	8	0	0	0	1729.082
H = 2.949 with 2 degrees of freedom. (P = 0.229)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.229)					

Zinc


Total Zn


Total Zn by Source Areas

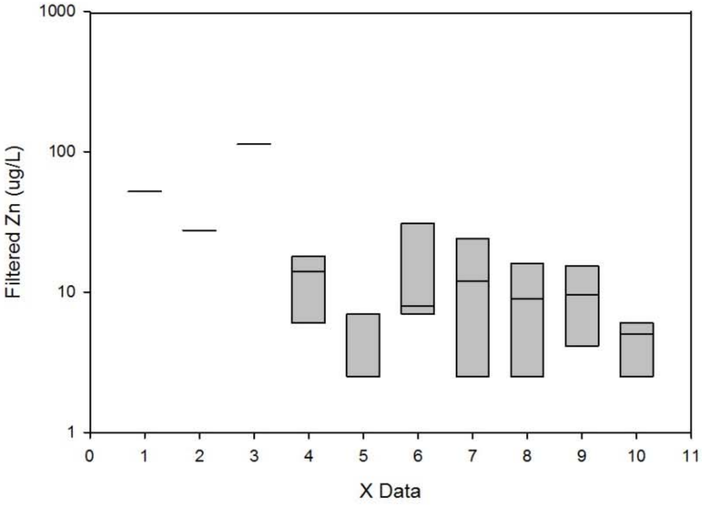
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Total Zn.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
lands	8	0	33.5	18.25	72.75
paved	9	0	9	7	109.5
roof	9	0	27	7.5	37.5
institOF	3	0	12	9	35
H = 3.407 with 3 degrees of freedom. (P = 0.333)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.333)					



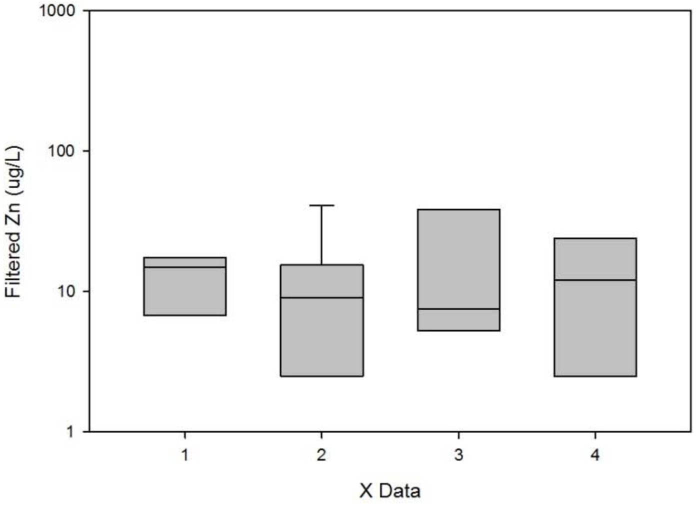
Total Zn by Land Use

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in Total Zn.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	6	0	140	34.75	237.5
institutional	9	0	27	7.5	52.5
residential	11	0	18	7	19
H = 8.830 with 2 degrees of freedom. (P = 0.012)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.012)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					
All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
commercial vs residential	11.485	2.959	Yes		
commercial vs institutional	8.111	2.012	No		
institutional vs residential	3.374	0.981	No		
Note: The multiple comparisons on ranks do not include an adjustment for ties.					

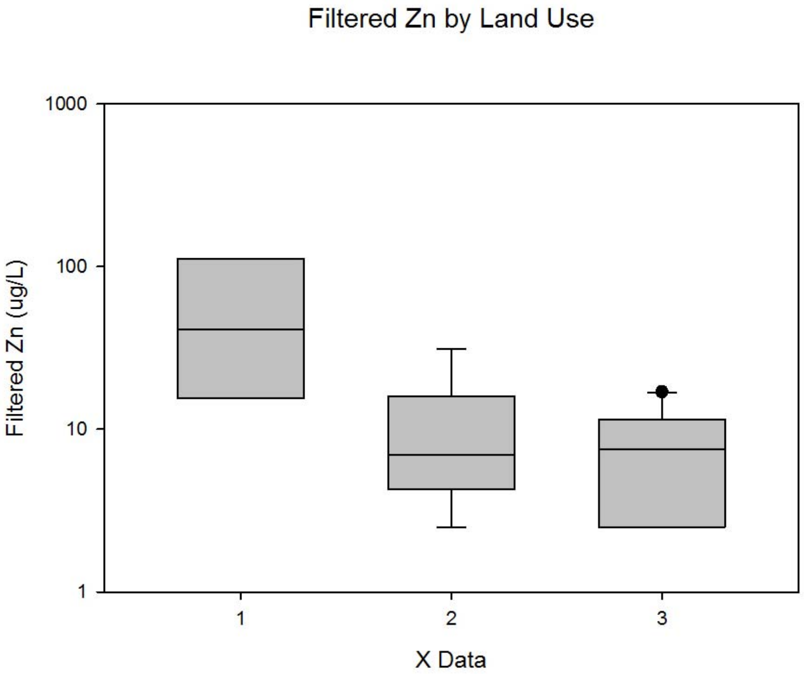
Filtered Zn



Filtered Zn by Source Area

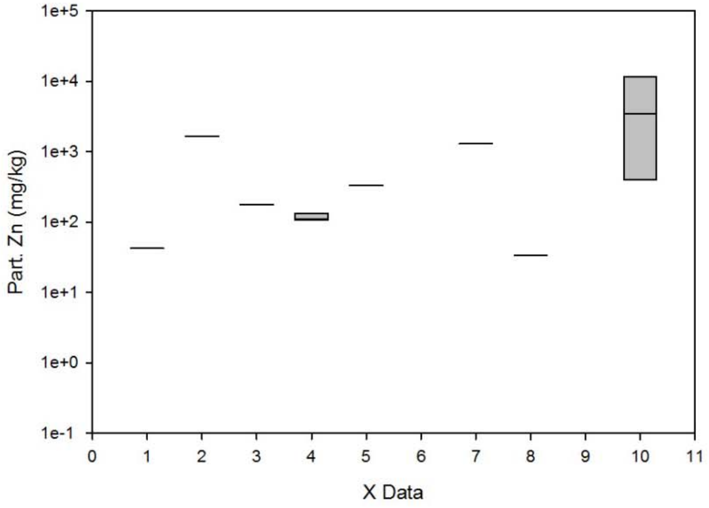


Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in filtered Zn.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
lands	8	0	15	6.75	17.5
paved	9	0	9	2.5	15.5
roof	8	0	7.5	5.25	38.5
institOF	3	0	12	2.5	24
H = 0.922 with 3 degrees of freedom. (P = 0.820)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.820)					

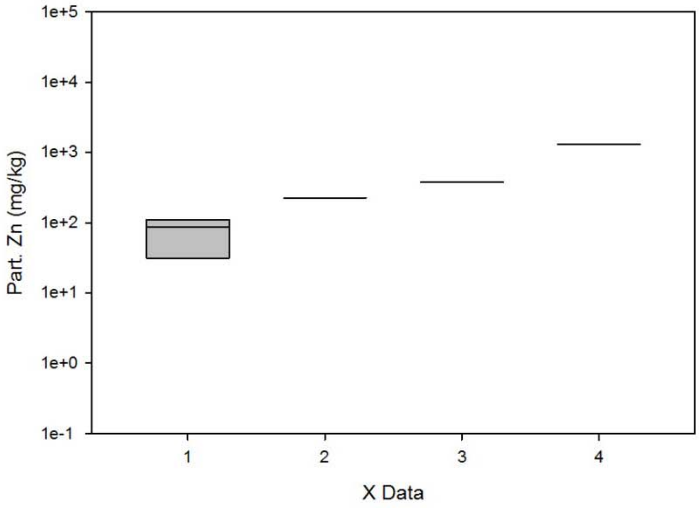

Filtered Zn by Land Use
Filtered Zn (ug/L)
1000
100
10
1
1
2
3
X Data

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in filtered Zn.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	6	0	41	15.5	112.25
institutional	9	0	7	4.25	16
residential	10	0	7.5	2.5	11.5
H = 9.971 with 2 degrees of freedom. (P = 0.007)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.007)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					
All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
commercial vs residential	11.367	2.991	Yes		
commercial vs institutional	10.056	2.592	Yes		
institutional vs residential	1.311	0.388	No		
Note: The multiple comparisons on ranks do not include an adjustment for ties.					

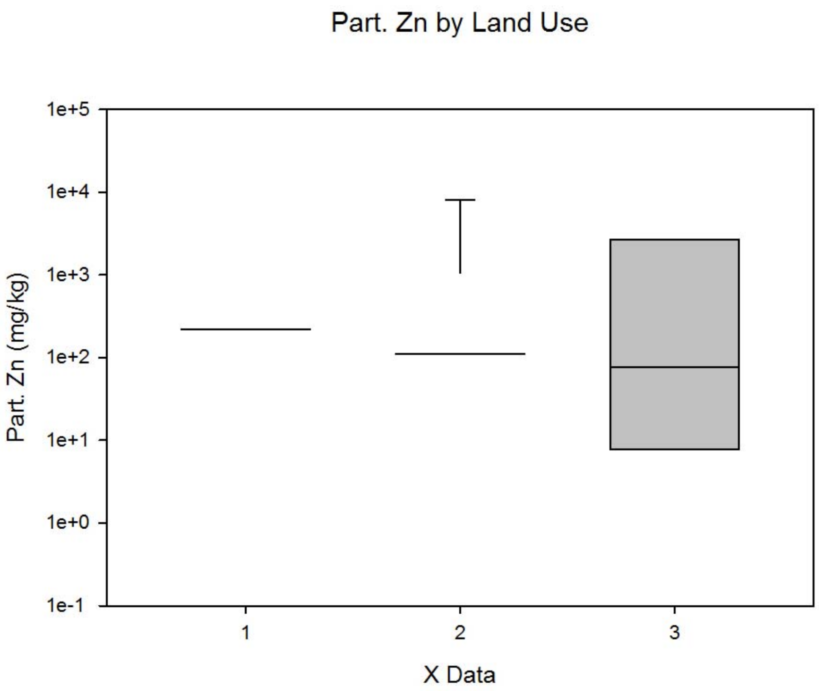
Particulate Zn



Particulate Zn by Source Areas



Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in part Zn.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
lands	7	0	85.47	30.733	110.876
paved	8	0	225.49	0	1611.421
roofs	8	0	378.571	0	6863.636
institOF	2	0	1300	0	2600
H = 1.394 with 3 degrees of freedom. (P = 0.707)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.707)					


Part. Zn by Land Use
Part. Zn (mg/kg)
1e+5
1e+4
1e+3
1e+2
1e+1
1e+0
1e-1
1
2
3
X Data

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in part Zn.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	6	0	221.306	0	1358.338
institutional	9	0	110.876	0	1066.667
residential	8	0	77.521	7.683	2690.909
H = 0.0475 with 2 degrees of freedom. (P = 0.977)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.977)					

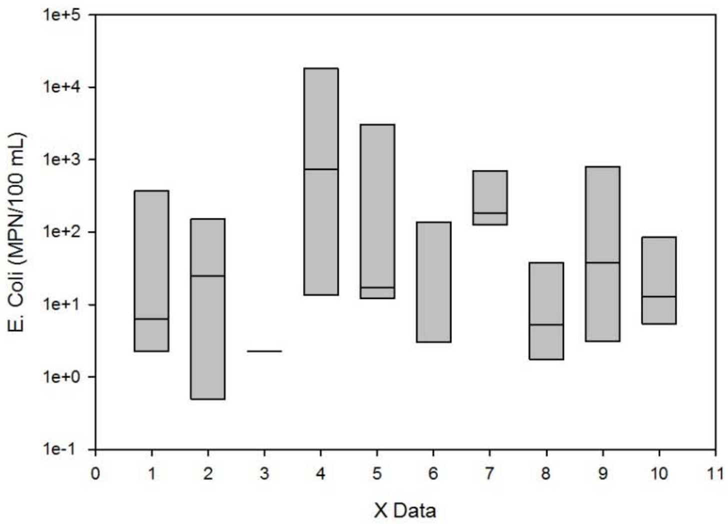
Bacteria in Stormwater Sheetflows

Site (values by MPN/100 mL)	Sample Date	Time	Land Use	Surface	E coli	Enterococci
9Mar11 Fairfax Office Pk Landsc	3/9/2011	755	Commercial	Landscaped	6	214
9Mar11 Evangelines Landsc	3/9/2011	815	Commercial	Landscaped	1	1,986
9Mar11 Ruby Tuesday Landsc	3/9/2011	820	Commercial	Landscaped	48	293
28Jun11 Galleria Grass	6/28/2011	1430	Commercial	Landscaped	691	1,300
23Mar12 Galleria Landsc	3/22/2012	900	Commercial	Landscaped	4	10,240
9Mar11 Evangelines Paved	3/9/2011	815	Commercial	Paved	1	13
22Jun11 Galleria Paved	6/22/2011	1610	Commercial	Paved	25	1,986
23Mar12 Galleria Paved	3/22/2012	900	Commercial	Paved	152	2,200
22Jun11 Galleria Roof	6/22/2011	1610	Commercial	Roof	4	1,203
23Mar12 Galleria Roof	3/22/2012	900	Commercial	Roof	1	8
5Sep11 Bama Belle Grass	9/5/2011	1115	Institutional	Landscaped	727	21,430
26Jan12 Bama Belle Landsc	1/26/2012	945	Institutional	Landscaped	13	610
17Aug12BamaBelleLandsc	8/17/2012	700	Institutional	Landscaped	18,350	241,960
28Jun Bama Belle Paved	6/28/2011	1430	Institutional	Paved	17	410
26Jan12 Bama Belle Paved	1/26/2012	1005	Institutional	Paved	12	228
17Aug12BamaBellePaved	8/17/2012	700	Institutional	Paved	3,070	1,300
28Jun11 Bama Belle Roof	6/28/2011	1430	Institutional	Roof	3	115
26Jan12 Bama Belle Roof	1/26/2012	1005	Institutional	Roof	3	2
17Aug12BamaBelleRoof	8/17/2012	700	Institutional	Roof	137	1,533
28Jun11 Bama Belle FilterInfluent	6/28/2011	1430	Institutional	yOutfall	169	4,130
26Jan12 Bama BelleFilterInfluent	1/26/2012	1010	Institutional	yOutfall	111	30,440
17Aug12BamaBelleRoofFilterInfluent	8/17/2012	700	Institutional	yOutfall	194	1,046
17Aug12BamaBelleFilterEffluent	8/17/2012	700	Institutional	zOutfall	866	29,090
9Mar11 Acad Dr. Lawn	3/9/2011	625	Residential	Landscaped	68	24,196
9Mar11 NorthridgeHigh Landsc	3/9/2011	730	Residential	Landscaped	5	816
9Mar11 Waterford Pl Lawn	3/9/2011	740	Residential	Landscaped	3	980
5Sep11 Acad Dr. Landsc	9/5/2011	1010	Residential	Landscaped	8	4,838
20Sep11 Acad Dr. Grass	9/20/2011	940	Residential	Landscaped	1	6,450
9Mar11 Acad Dr. Paved	3/9/2011	620	Residential	Paved	3	2,420
9Mar11 Waterford Pl Street	3/9/2011	740	Residential	Paved	1,553	2,500

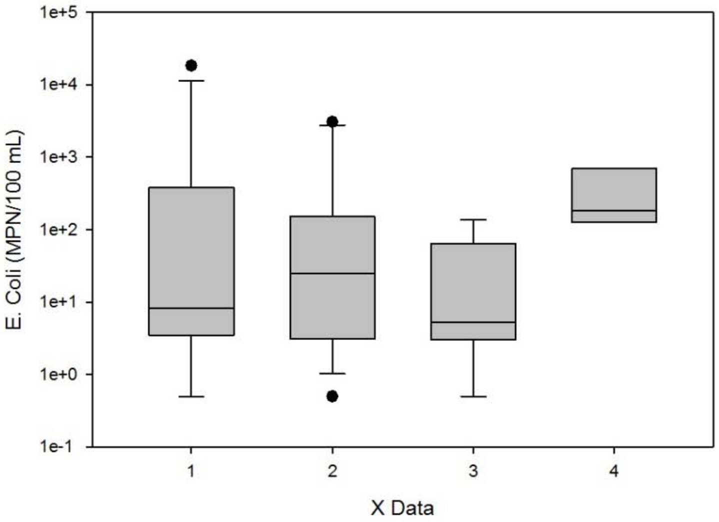
28Jun11 Acad Dr. Paved	6/28/2011	1430	Residential	Paved	38	613
20Sep11 Acad Dr. Paved	9/20/2011	715	Residential	Paved	44	409
30Sep12 Acad Dr. Paved	9/30/2012	1315	Residential	Paved	3	326
9Mar11 Acad Dr. Roof	3/9/2011	615	Residential	Roof	20	5
28Jun11 Acad Dr. Roof	6/28/2011	1430	Residential	Roof	5	60
20Sep11 Acad Dr. Roof	9/20/2011	715	Residential	Roof	6	4
30Sep12 Acad Dr. Roof	9/30/2012	1335	Residential	Roof	108	158
				count	37	37
				% detected	100	100
				maximum	18,350	241,960

E. Coli

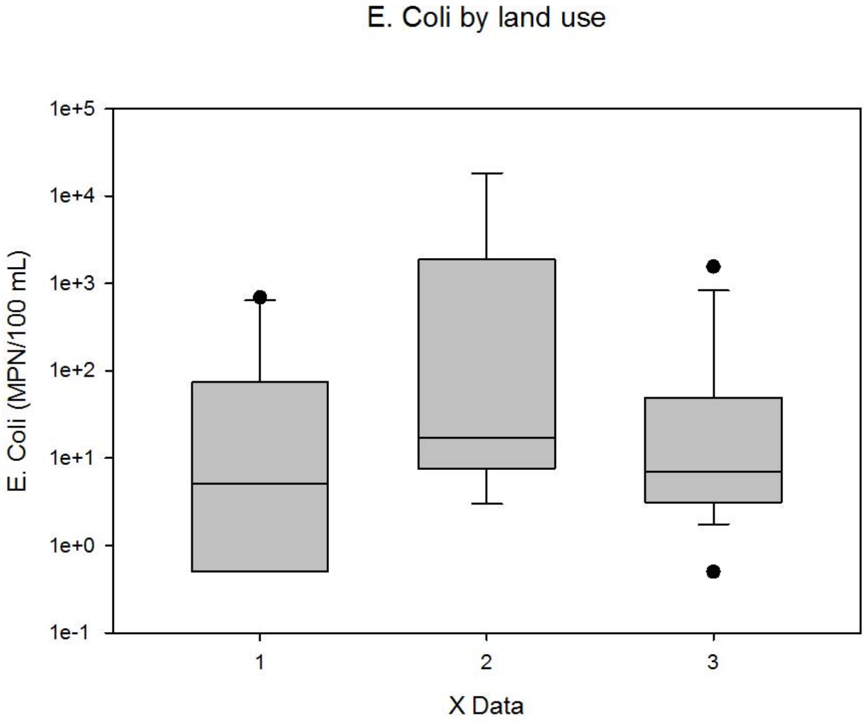
E. Coli



E. Coli by source area



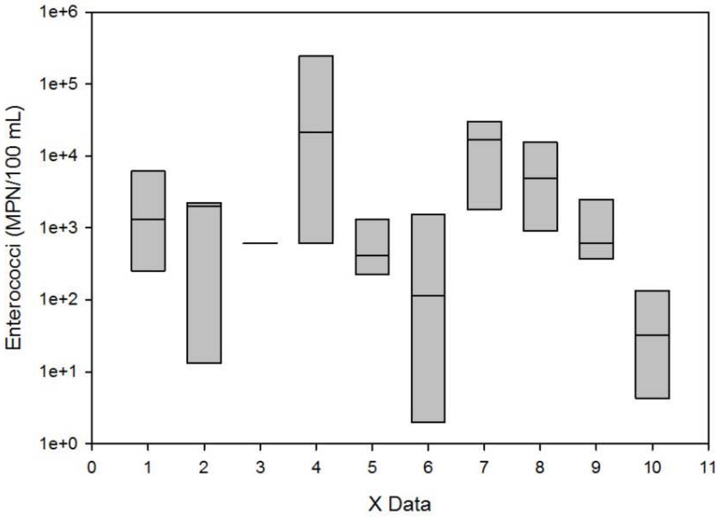
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in EColi by area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
lands	13	0	8.2	3.5	379.3
paved	11	0	24.8	3.1	151.8
roofs	9	0	5.2	3	63.75
institOF	4	0	181.1	125.55	698.2
H = 6.724 with 3 degrees of freedom. (P = 0.081)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.081)					



Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in EColi by area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%

commercial	10	0	5.15	0.5	74.175
institutional	9	0	17.1	7.55	1898.5
residential	14	0	7.1	3.1	49.6
H = 2.188 with 2 degrees of freedom. (P = 0.335)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.335)					

Enterococci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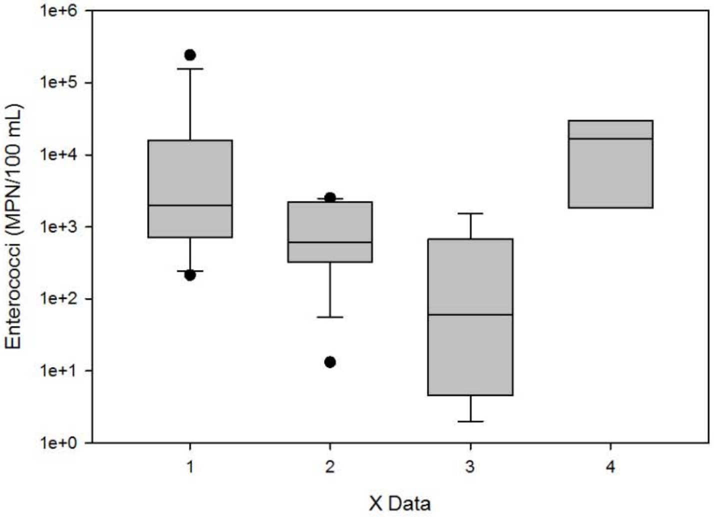
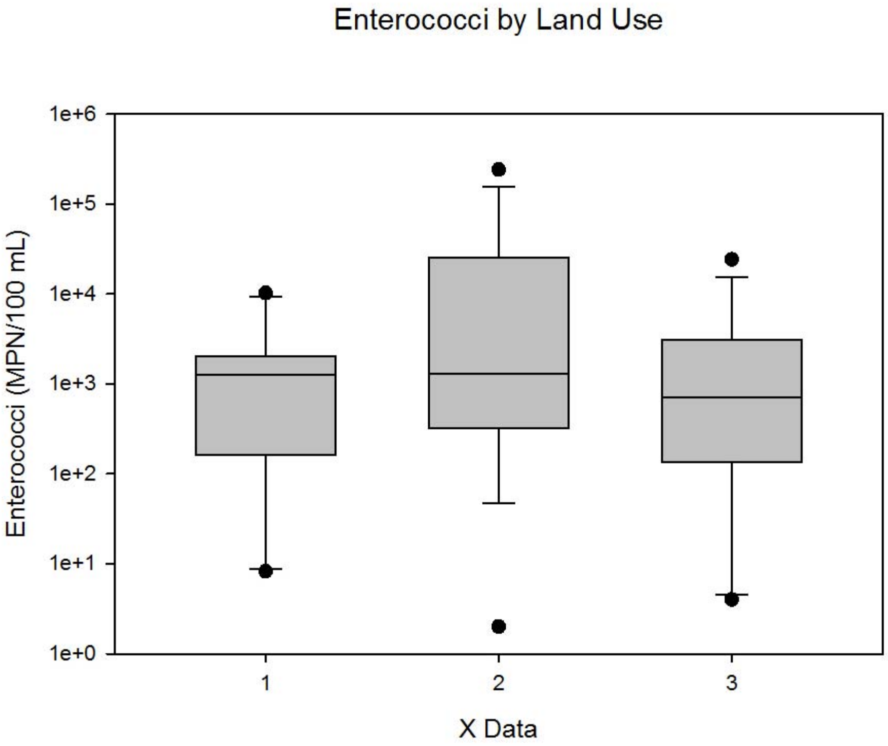

Enterococci by source areas

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in entero by area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
lands	13	0	1986.28	713.2	15835
paved	11	0	613.1	325.5	2200
roofs	9	0	60.1	4.55	680.455
institOF	4	0	16610	1817.15	30102.5
H = 15.789 with 3 degrees of freedom. (P = 0.001)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.001)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					
All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
institOF vs roofs	21.528	3.31	Yes		
institOF vs paved	11.795	1.866	No		

institOF vs lands	5.712	0.923	Do Not Test		
lands vs roofs	15.816	3.37	Yes		
lands vs paved	6.084	1.372	Do Not Test		
paved vs roofs	9.732	2	No		
Note: The multiple comparisons on ranks do not include an adjustment for ties.					

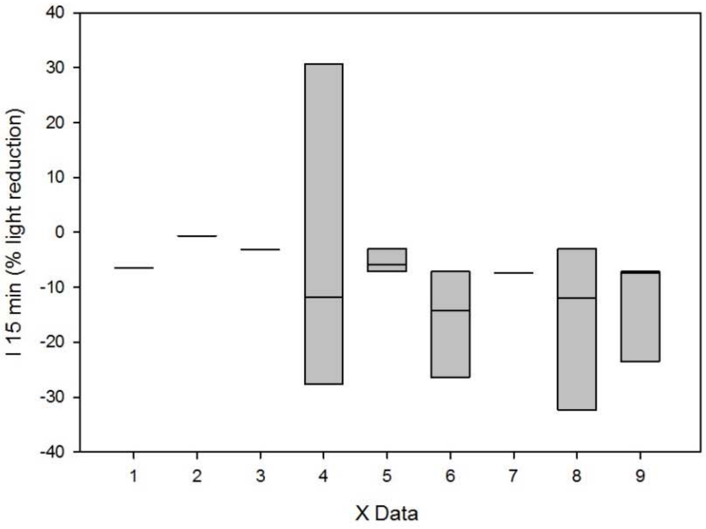


Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in entero by area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	10	0	1251.48	163.8	2039.71
institutional	13	0	1299.7	318.95	25260
residential	14	0	714.75	133.225	3084.585
H = 1.172 with 2 degrees of freedom. (P = 0.557)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.557)					

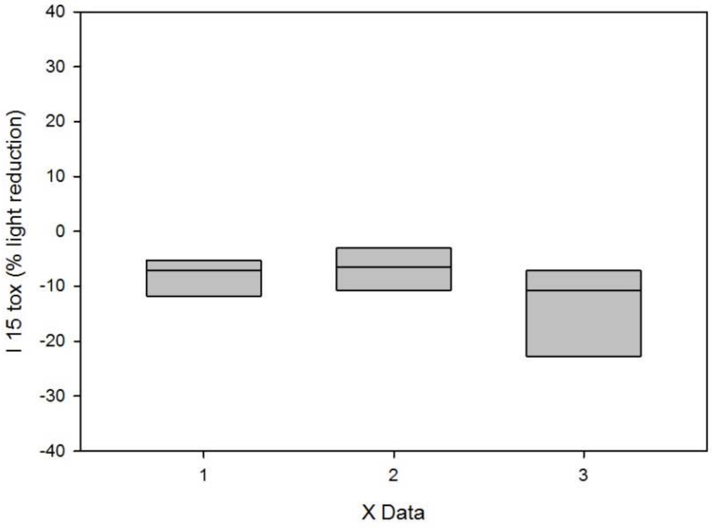
Toxicity of Stormwater Sheetflows

				%effect	%effect	%effect	%effect
Sample Date	Time	Land Use	Surface	5	15	25	45
6/28/2011	1430	Commercial	Landscaped	-8.7	-5.9	-0.9	-3.1
3/22/2012	900	Commercial	Landscaped	2.9	-7.1	-25.0	-36.4
6/22/2011	1610	Commercial	Paved	-5.0	5.9	9.5	15.6
3/22/2012	900	Commercial	Paved	11.8	-7.1	-25.0	-9.1
6/22/2011	1610	Commercial	Roof	11.8	14.3	0.0	18.2
3/22/2012	900	Commercial	Roof	-27.5	-20.6	-19.0	-19.5
9/5/2011	1115	Institutional	Landscaped	-11.7	-27.6	-27.7	-31.9
1/26/2012	945	Institutional	Landscaped	17.0	30.6	33.1	33.1
8/17/2012	700	Institutional	Landscaped	-12.5	-11.8	-13.8	-10.2
6/28/2011	1430	Institutional	Paved	-12.5	-5.9	-3.4	-0.8
1/26/2012	1005	Institutional	Paved	-21.3	-3.0	14.9	29.5
8/17/2012	700	Institutional	Paved	-5.9	-7.1	-25.0	-36.4
6/28/2011	1430	Institutional	Roof	11.8	-7.1	-25.0	-9.1
1/26/2012	1005	Institutional	Roof	-14.9	-14.2	-13.5	-17.5
8/17/2012	700	Institutional	Roof	-35.0	-26.5	-24.1	-24.2
9/5/2011	1010	Residential	Landscaped	-14.9	-9.7	-11.5	-13.9
9/20/2011	940	Residential	Landscaped	-11.7	-5.2	0.7	2.4
6/28/2011	1430	Residential	Paved	-42.5	-32.4	-26.7	-21.9
9/20/2011	715	Residential	Paved	-5.3	-3.0	-3.4	-4.8
9/30/2012	1315	Residential	Paved	-14.9	-11.9	-13.5	-15.7
6/28/2011	1430	Residential	Roof	-35.0	-23.5	-13.8	-10.2
9/20/2011	715	Residential	Roof	-11.7	-7.5	-1.4	11.4
9/30/2012	1335	Residential	Roof	11.8	-7.1	-25.0	-36.4

15 Minute Exposure Toxicity

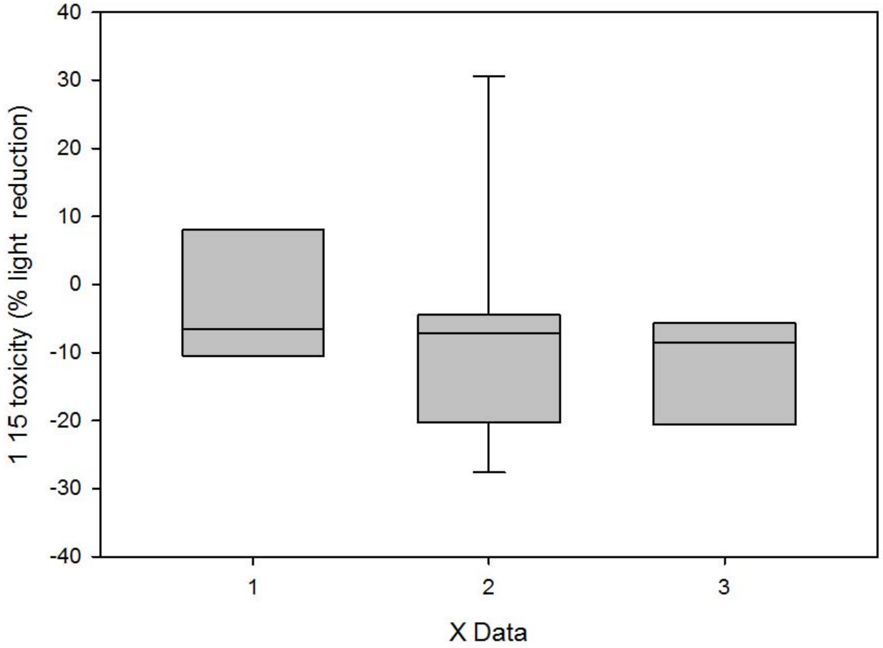


15 minute toxicity



I 15min tixicity by source areas

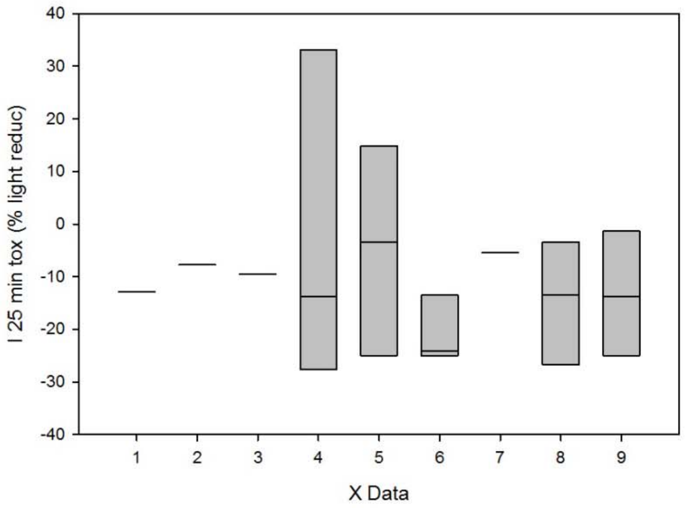
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in I 15mintox by area.JNB					
Normality Test (Shapiro-Wilk)	Passed	(P = 0.080)			
Equal Variance Test:	Passed	(P = 0.678)			
Group	N	Missing	Median	25%	75%
lands	7	0	-7.143	-11.765	-5.224
paved	8	0	-6.513	-10.741	-2.985
roofs	8	0	-10.821	-22.794	-7.143
H = 1.771 with 2 degrees of freedom. (P = 0.412)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.412)					



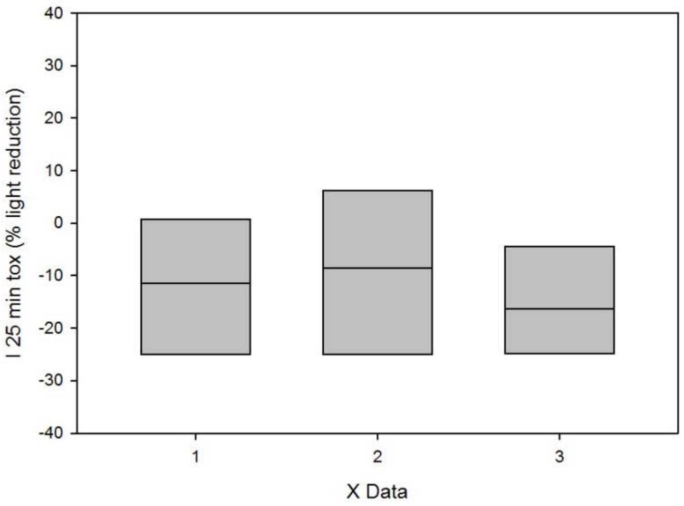
I 15 minute toxicity by land use

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in I 15mintox by area.JNB					
Normality Test (Shapiro-Wilk)	Passed	(P = 0.052)			
Equal Variance Test:	Passed	(P = 0.440)			
Group	N	Missing	Median	25%	75%
commercial	6	0	-6.513	-10.504	7.983
institutional	9	0	-7.143	-20.325	-4.434
residential	8	0	-8.582	-20.632	-5.704
H = 1.870 with 2 degrees of freedom. (P = 0.393)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.393)					

25 Minute Exposure Toxicity



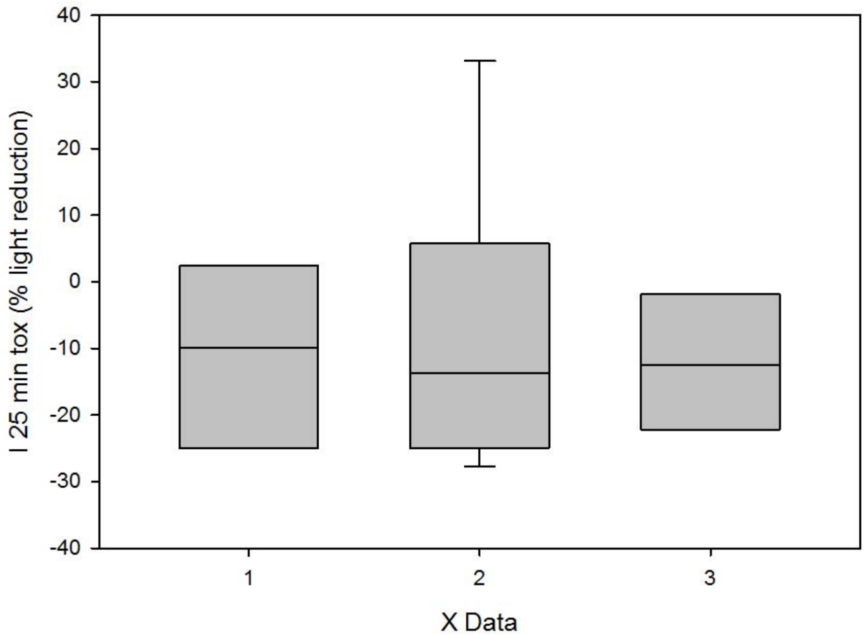
I 25 min toxicity



I 25 min toxicity by source area

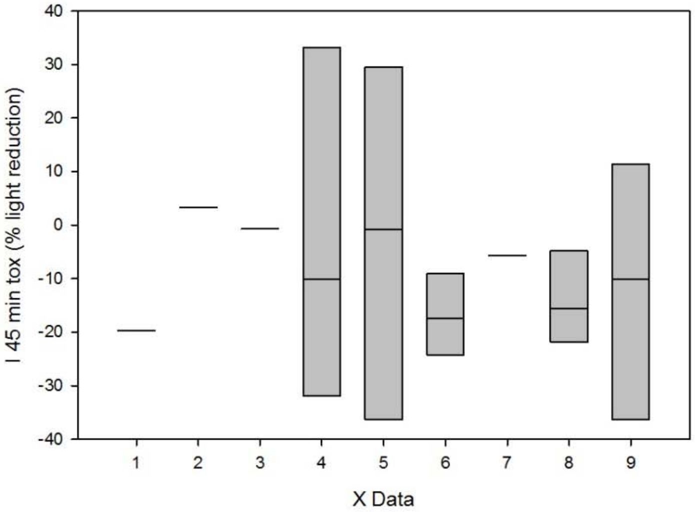
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in I 25mintox by areas.JNB					
Normality Test (Shapiro-Wilk)	Passed	(P = 0.269)			
Equal Variance Test:	Passed	(P = 0.240)			
Group	N	Missing	Median	25%	75%
lands	7	0	-11.486	-25	0.676
paved	8	0	-8.481	-25	6.267
roofs	8	0	-16.379	-24.784	-4.392
H = 0.469 with 2 degrees of freedom. (P = 0.791)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.791)					

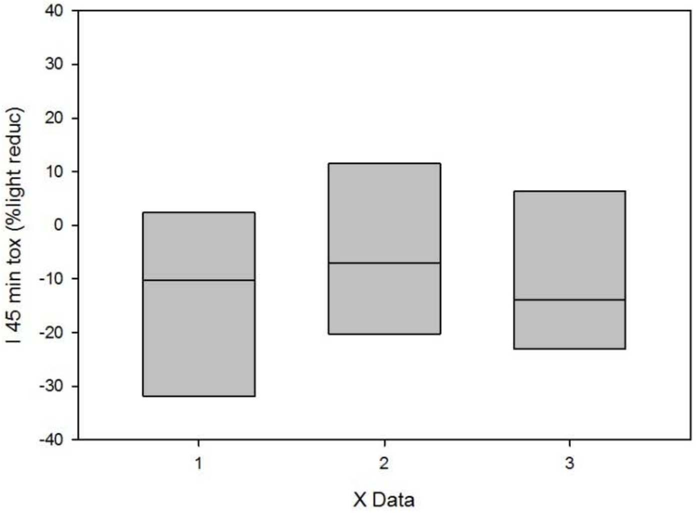
I 25 min toxicity by land use



Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in I 25mintox by areas.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
commercial	6	0	-9.914	-25	2.371
institutional	9	0	-13.793	-25	5.708
residential	8	0	-12.5	-22.198	-1.858
H = 0.182 with 2 degrees of freedom. (P = 0.913)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.913)					

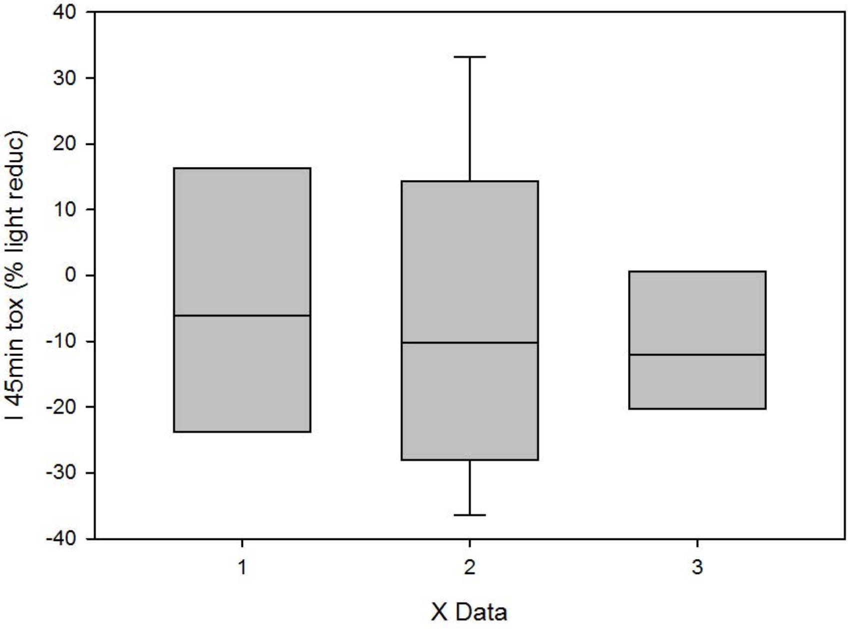
45 Minute Exposure Toxicity


I 45 minute toxicity


I 45 minute toxicity by source areas

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in I 45 mintox by areas.JNB					
Normality Test (Shapiro-Wilk)	Passed	(P = 0.503)			
Equal Variance Test:	Passed	(P = 0.723)			
Group	N	Missing	Median	25%	75%
lands	7	0	-10.156	-31.928	2.41
paved	8	0	-6.955	-20.322	11.523
roofs	8	0	-13.813	-23.047	6.312
H = 0.418 with 2 degrees of freedom. (P = 0.811)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.811)					

I 45 minute toxicity by land use

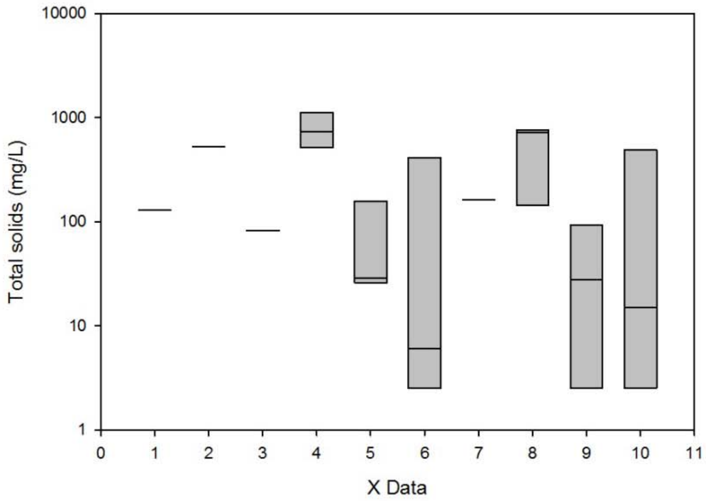


Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in I 45 mintox by areas.JNB					
Normality Test (Shapiro-Wilk)	Passed	(P = 0.513)			
Equal Variance Test:	Passed	(P = 0.323)			
Group	N	Missing	Median	25%	75%
commercial	6	0	-6.108	-23.739	16.264
institutional	9	0	-10.156	-28.073	14.368
residential	8	0	-12.006	-20.322	0.602
H = 0.297 with 2 degrees of freedom. (P = 0.862)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.862)					

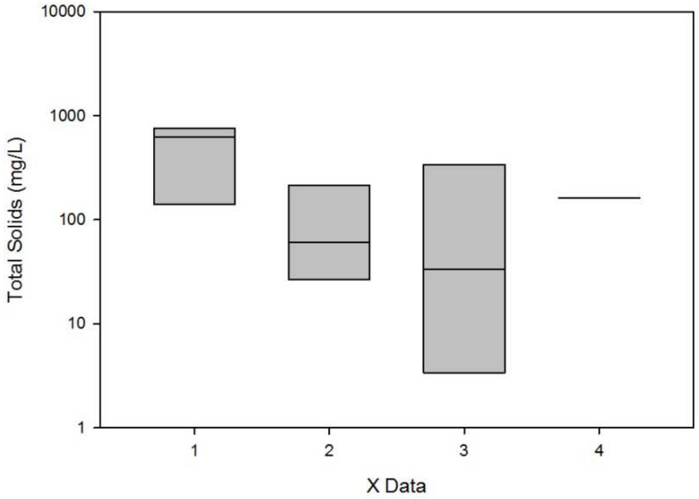
Particulates in Stormwater Sheetflows

Site	Sample Date	Time	Land Use	Surface	TDS	TS	SSC	TSS (0.45 - 250)
28Jun11 Galleria Grass	6/28/2011	1430	Commercial	Landscaped	65	139	74	47
23Mar12 Galleria Landsc	3/22/2012	900	Commercial	Landscaped	70	120	50	46
22Jun11 Galleria Paved	6/22/2011	1610	Commercial	Paved	93	231	138	81
23Mar12 Galleria Paved	3/22/2012	900	Commercial	Paved	59	816	757	296
22Jun11 Galleria Roof	6/22/2011	1610	Commercial	Roof	104	113	8	8
23Mar12 Galleria Roof	3/22/2012	900	Commercial	Roof	20	52	32	32
5Sep11 Bama Belle Grass	9/5/2011	1115	Institutional	Landscaped	199	516	317	203
26Jan12 Bama Belle Landsc	1/26/2012	945	Institutional	Landscaped	16	736	720	505
17Aug12BamaBelleLandsc	8/17/2012	700	Institutional	Landscaped	312	1,125	813	568
28Jun Bama Belle Paved	6/28/2011	1430	Institutional	Paved	135	157	22	20
26Jan12 Bama Belle Paved	1/26/2012	1005	Institutional	Paved	4	26	22	18
17Aug12BamaBellePaved	8/17/2012	700	Institutional	Paved	21	29	8	3
28Jun11 Bama Belle Roof	6/28/2011	1430	Institutional	Roof	3	6	3	3
26Jan12 Bama Belle Roof	1/26/2012	1005	Institutional	Roof	3	3	3	3
17Aug12BamaBelleRoof	8/17/2012	700	Institutional	Roof	7	414	408	3
26Jan12 Bama BelleFilterInfluent	1/26/2012	1010	Institutional	treated Outfall	122	132	11	10
17Aug12BamaBelleRoofFilterInfluent	8/17/2012	700	Institutional	treated Outfall	85	191	106	3
5Sep11 Acad Dr. Landsc	9/5/2011	1010	Residential	Landscaped	10	721	711	423
20Sep11 Acad Dr. Grass	9/20/2011	940	Residential	Landscaped	47	754	707	415
14OctAcadDrLandsc	14/10/12	1125	Residential	Landscaped	3	143	143	84
28Jun11 Acad Dr. Paved	6/28/2011	1430	Residential	Paved	74	93	19	17
20Sep11 Acad Dr. Paved	9/20/2011	715	Residential	Paved	25	28	3	2
30Sep12 Acad Dr. Paved	9/30/2012	1315	Residential	Paved	3	3	3	3
28Jun11 Acad Dr. Roof	6/28/2011	1430	Residential	Roof	3	489	489	5
20Sep11 Acad Dr. Roof	9/20/2011	715	Residential	Roof	15	15	3	3
30Sep12 Acad Dr. Roof	9/30/2012	1335	Residential	Roof	3	3	3	3

Total Solids (TS)



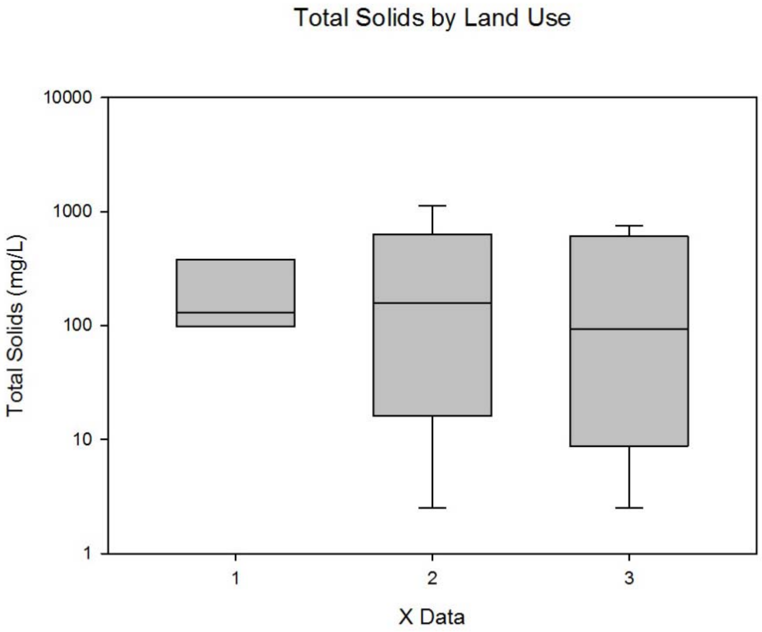
Total Solids



Source Areas

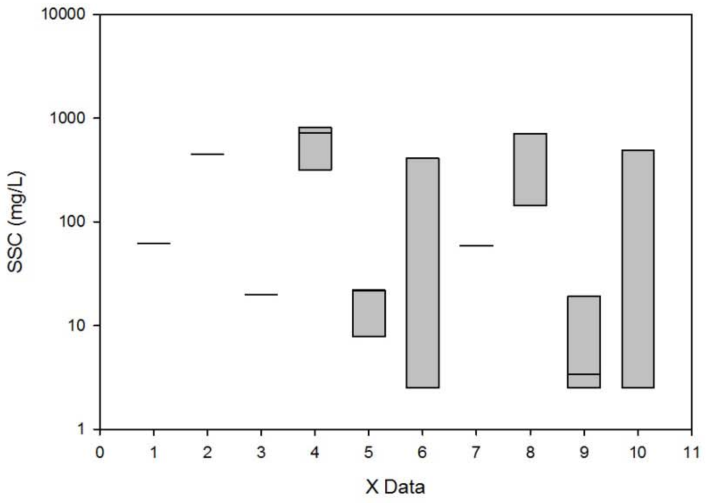
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in TS by area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
Lands	8	0	618.75	139.84	749.517
Paved	8	0	60.958	26.466	212.325
Roofs	8	0	33.25	3.38	339.09
Treated outfall	2	0	161.932	132.4	191.465
H = 8.535 with 3 degrees of freedom. (P = 0.036)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.036)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					
All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
Lands vs Roofs	10.625	2.778	Yes		
Lands vs Paved	8.125	2.125	No		
Lands vs Treated outfall	4.625	0.765	Do Not Test		

Treated outfall vs Roofs	6	0.992	No		
Treated outfall vs Paved	3.5	0.579	Do Not Test		
Paved vs Roofs	2.5	0.654	Do Not Test		
Note: The multiple comparisons on ranks do not include an adjustment for ties.					

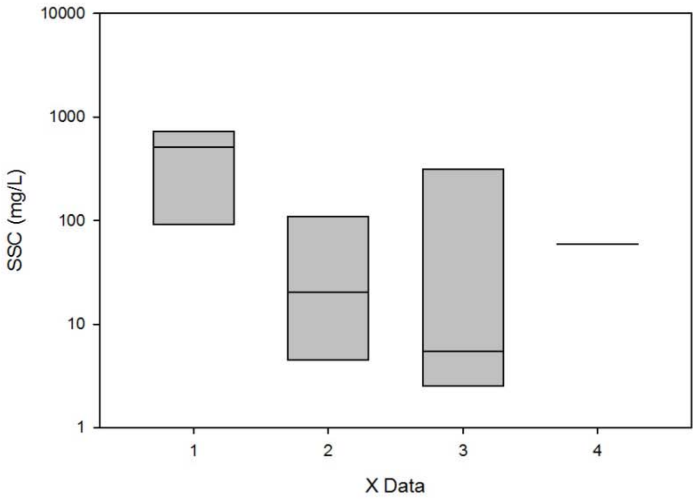


Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in TS by area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
Commercial	6	0	129.443	97.52	377.2
Institutional	9	0	156.6	16.011	626.25
Residential	9	0	93.1	8.75	604.75
H = 0.646 with 2 degrees of freedom. (P = 0.724)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.724)					

Suspended Solids Concentrations (SSC)



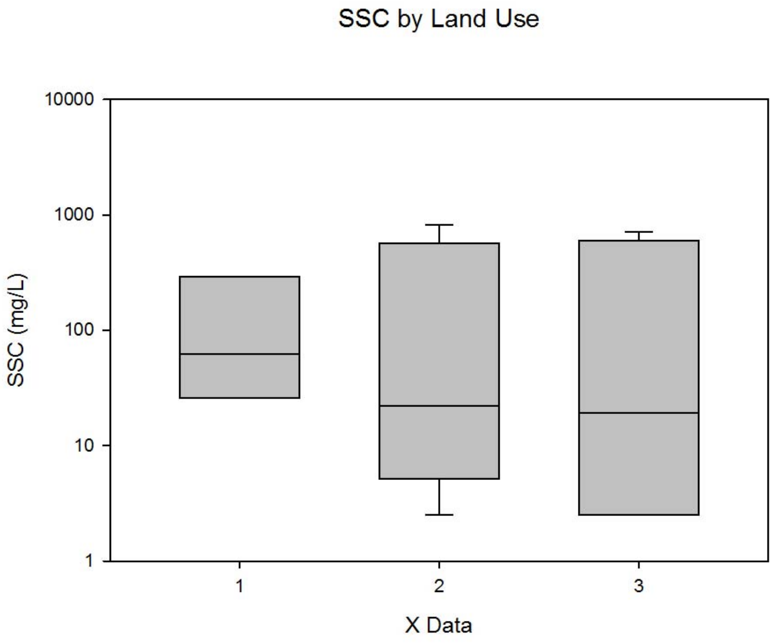
SSC



Source Areas

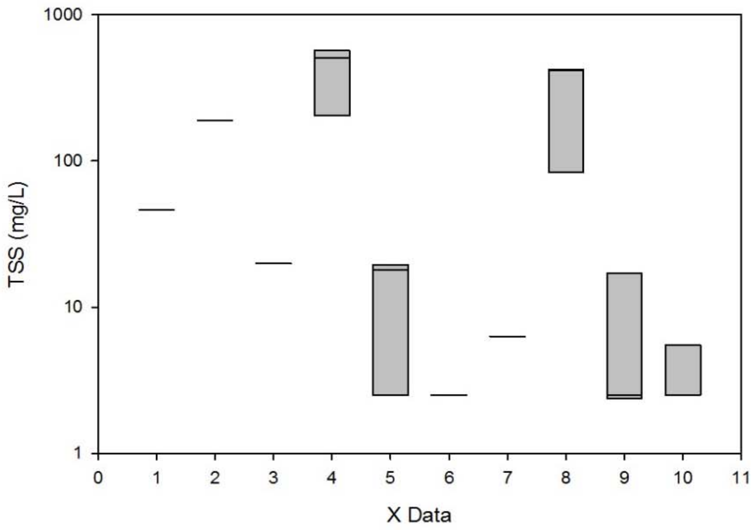
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in SSC by area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
Lands	8	0	512.261	91.465	717.875
Paved	8	0	20.35	4.477	109.3
Roofs	8	0	5.441	2.5	313.875
Treated outfall	2	0	58.682	10.9	106.465
H = 9.120 with 3 degrees of freedom. (P = 0.028)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.028)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					
All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
Lands vs Roofs	10.813	2.827	Yes		
Lands vs Paved	8.813	2.304	No		
Lands vs Treated outfall	7.625	1.261	Do Not Test		

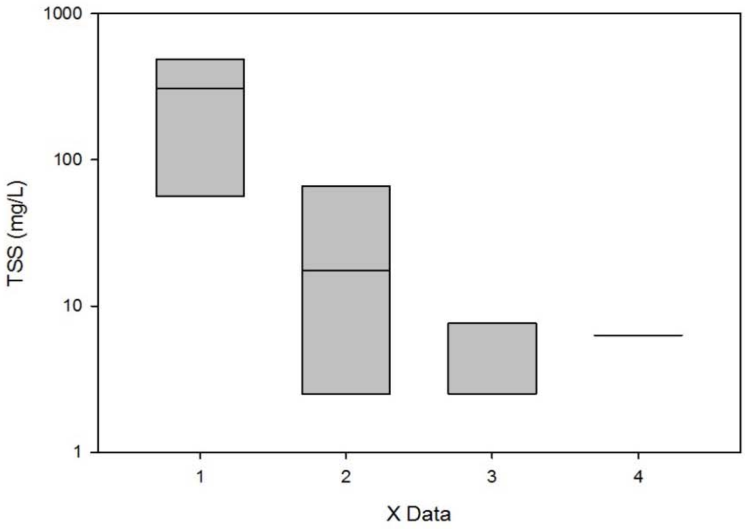
Treated outfall vs Roofs	3.188	0.527	No		
Treated outfall vs Paved	1.188	0.196	Do Not Test		
Paved vs Roofs	2	0.523	Do Not Test		
Note: The multiple comparisons on ranks do not include an adjustment for ties.					



Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in SSC by area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
Commercial	6	0	62.193	25.715	293.075
Institutional	9	0	22	5.169	564
Residential	9	0	19.1	2.5	597.761
H = 0.808 with 2 degrees of freedom. (P = 0.668)					

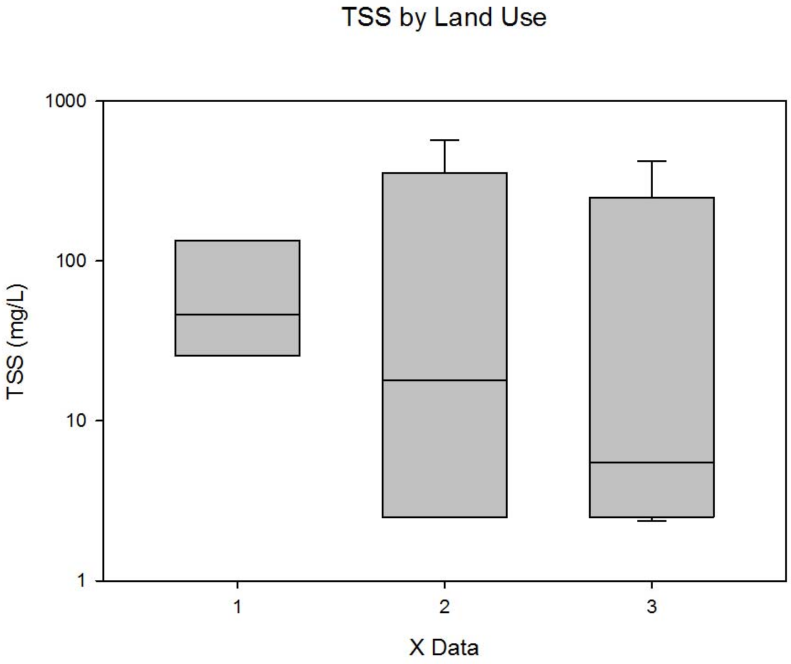
Total Suspended Solids (TSS; 0.45 to 250 µm)


TSS


Source Area

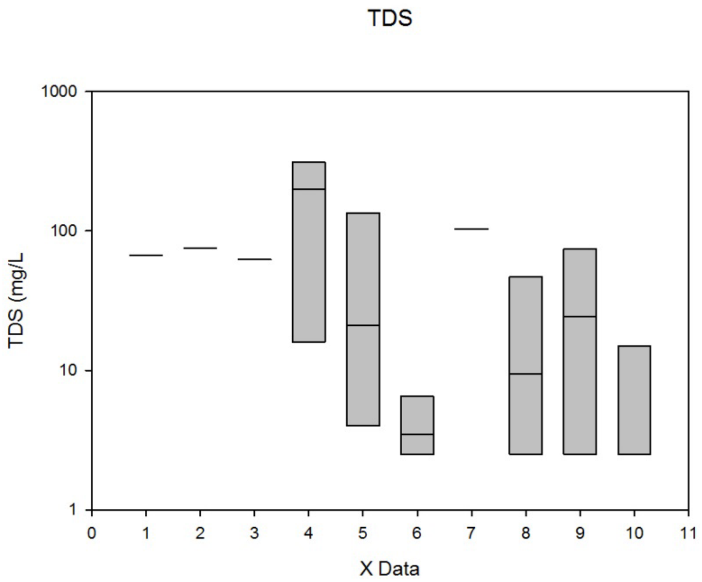
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in TSS by area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
Lands	8	0	309.011	55.965	484.5
Paved	8	0	17.5	2.5	65.625
Roofs	8	0	2.5	2.5	7.645
treated outfall	2	0	6.3	2.5	10.1
H = 14.912 with 3 degrees of freedom. (P = 0.002)					
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.002)					
To isolate the group or groups that differ from the others use a multiple comparison procedure.					
All Pairwise Multiple Comparison Procedures (Dunn's Method) :					
Comparison	Diff of Ranks	Q	P<0.05		
Lands vs Roofs	13.688	3.579	Yes		
Lands vs treated outfall	13	2.15	No		
Lands vs Paved	9.875	2.582	Do Not Test		

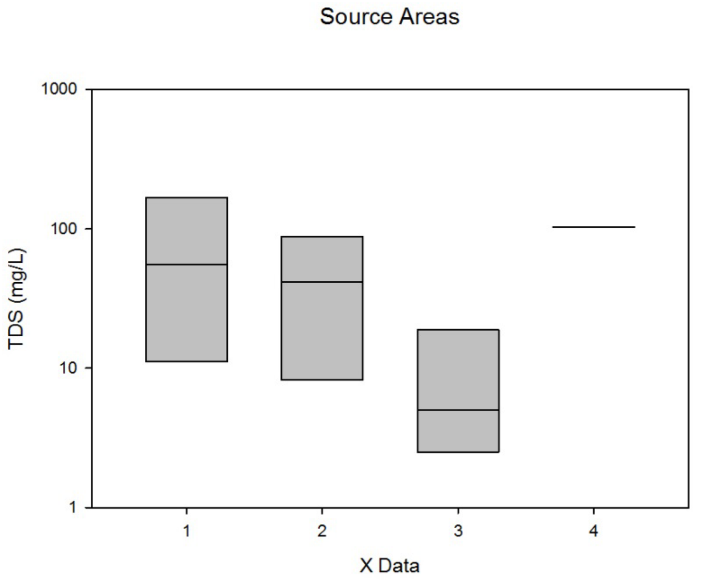
Paved vs Roofs	3.813	0.997	No		
Paved vs treated outfall	3.125	0.517	Do Not Test		
treated outfall vs Roofs	0.688	0.114	Do Not Test		
Note: The multiple comparisons on ranks do not include an adjustment for ties.					



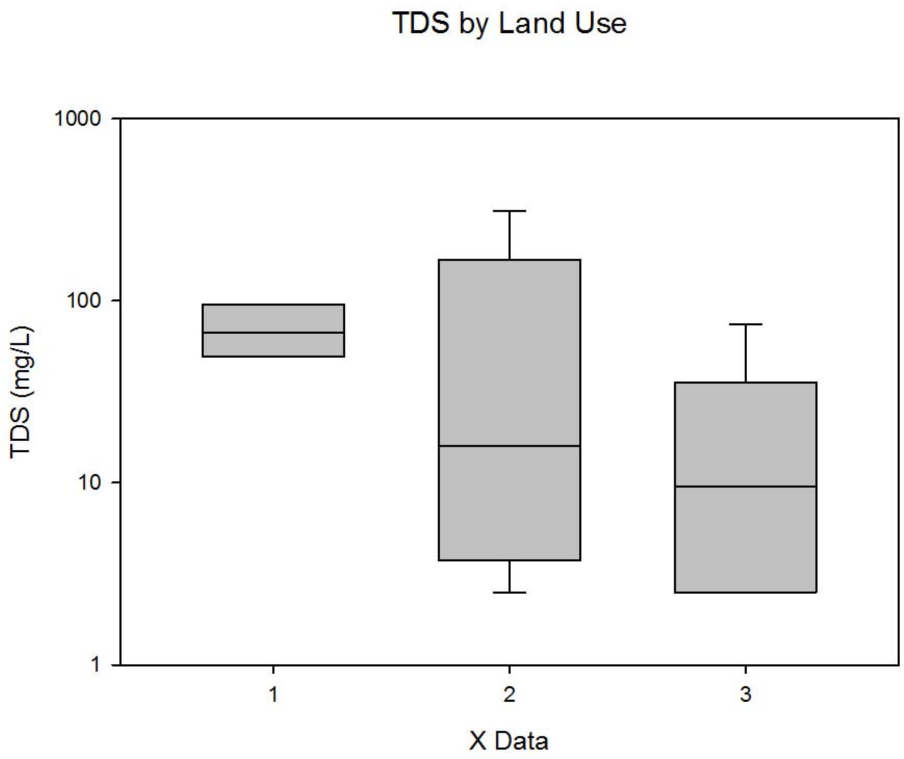
Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in TSS by area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
Commercial	6	0	46.393	25.715	134.625
Institutional	9	0	18	2.5	354.25
Residential	9	0	5.5	2.5	249.011
H = 1.540 with 2 degrees of freedom. (P = 0.463)					

Total Dissolved Solids (TDS)


TDS
1000
100
10
1
TDS (mg/L)
0
1
2
3
4
5
6
7
8
9
10
11
X Data


Source Areas
1000
100
10
1
TDS (mg/L)
1
2
3
4
X Data

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in TDS by area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
Lands	8	0	55.75	11.125	166.75
Paved	8	0	41.75	8.25	87.875
Roofs	8	0	5	2.5	18.75
Treated outfall	2	0	103.25	85	121.5
H = 6.545 with 3 degrees of freedom. (P = 0.088)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.088)					


TDS by Land Use
1000
100
10
1
TDS (mg/L)
1
2
3
X Data

Kruskal-Wallis One Way Analysis of Variance on Ranks					
Data source: Data 1 in TDS by area.JNB					
Normality Test (Shapiro-Wilk)	Failed	(P < 0.050)			
Group	N	Missing	Median	25%	75%
Commercial	6	0	67.25	49.25	95.5
Institutional	9	0	16	3.75	167
Residential	9	0	9.5	2.5	35.75
H = 5.389 with 2 degrees of freedom. (P = 0.068)					
The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.068)					

Appendix H. HPLC and GCMSD Chromatographs for Sheetflow Samples

Chromatographs for selected sheetflow samples

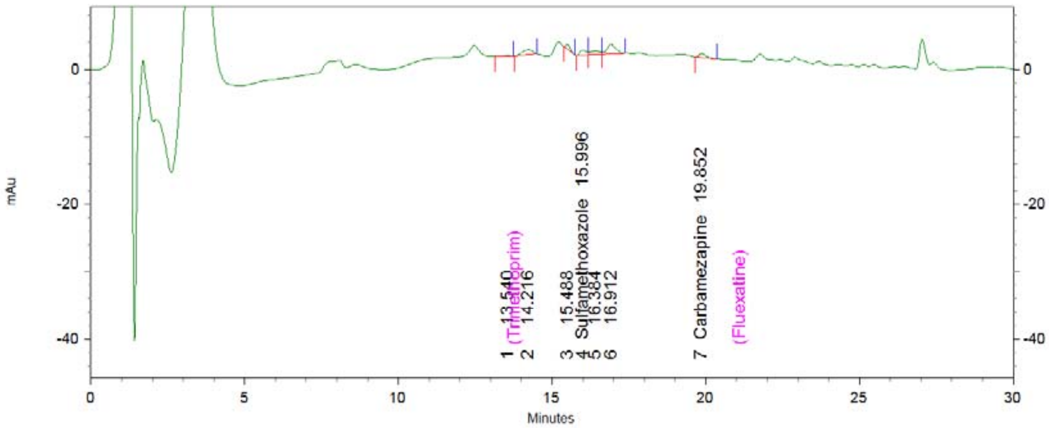
HPLC Pharmaceutical and Personal Care Products Chromatographs

110920AcademyDriveRoof20x2mlCarb121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met

C:\EZStart\Projects\Default\Data\Brads\110920AcademyDriveRoof20x2mlCarb121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met



1: 260 nm, 4 nm Results

Pk #	Name	Retention Time	ESTD concentration	Area
	Trimethoprim		0.000 BDL	
4	Sulfamethoxazole	15.996	236.093	10792
7	Carbamezapine	19.852	52.527	8752
	Fluexatine		0.000 BDL	
Totals			288.620	19544

Trim 0 ppb
Sulf 9. ppb
Carb 2 ppb
Fluox 0 ppb

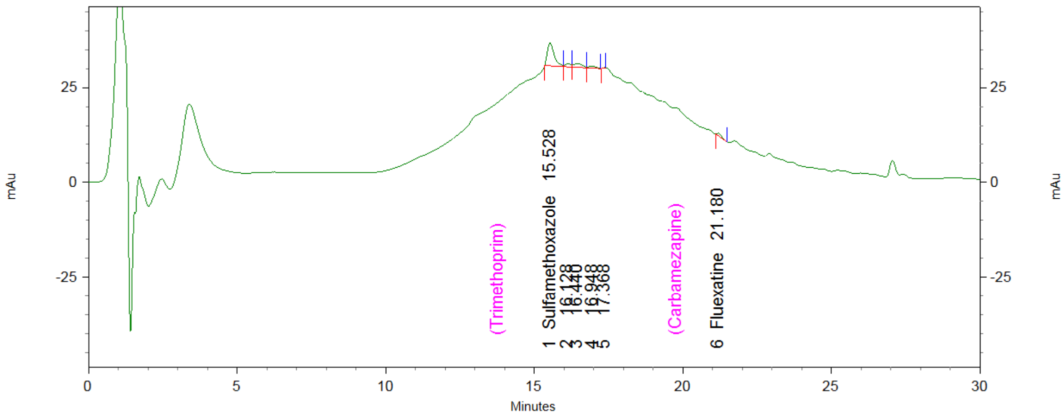
9/20/11, Residential Roof

141012AcadDriveLandsc20x2mlCarb121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met

C:\EZStart\Projects\Default\Data\Brads\141012AcadDriveLandsc20x2mlCarb121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met



1: 260 nm, 4 nm Results

Pk #	Name	Retention Time	ESTD concentration	Area
	Trimethoprim		0.000 BDL	
1	Sulfamethoxazole	15.528	319.380	95597
	Carbamezapine		0.000 BDL	
6	Fluexatine	21.180	154.711	7186
Totals			474.091	102783

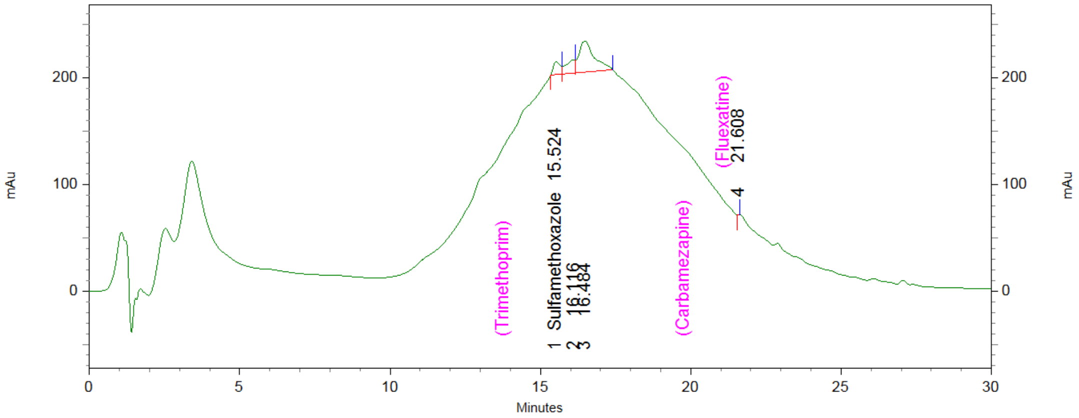
Trim 0 ppb
Sulf 13 ppb
Carb 0 ppb
Fluox 6 ppb

10/14/12, Residential Landscaped

```
090511RoofAcademyDr20x2mlCarb121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met

C:\EZStart\Projects\Default\Data\Brads\090511RoofAcademyDr20x2mlCarb121812
C:\EZStart\Projects\Default\Method\C121012Sulf.met
```



1: 260 nm, 4
nm Results

Pk #	Name	Retention Time	ESTD concentration	Area
	Trimethoprim		0.000 BDL	
1	Sulfamethoxazole	15.524	418.017	196032
	Carbamezapine		0.000 BDL	
	Fluexatine		0.000 BDL	
Totals			418.017	196032

Sulf 17 ppb

9/5/11, Residential Landscape

```
081712BamaBelleOpenSpace20X2121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met

C:\EZStart\Projects\Default\Data\Brads\081712BamaBelleOpenSpace20X2121812
C:\EZStart\Projects\Default\Method\C121012Sulf.met
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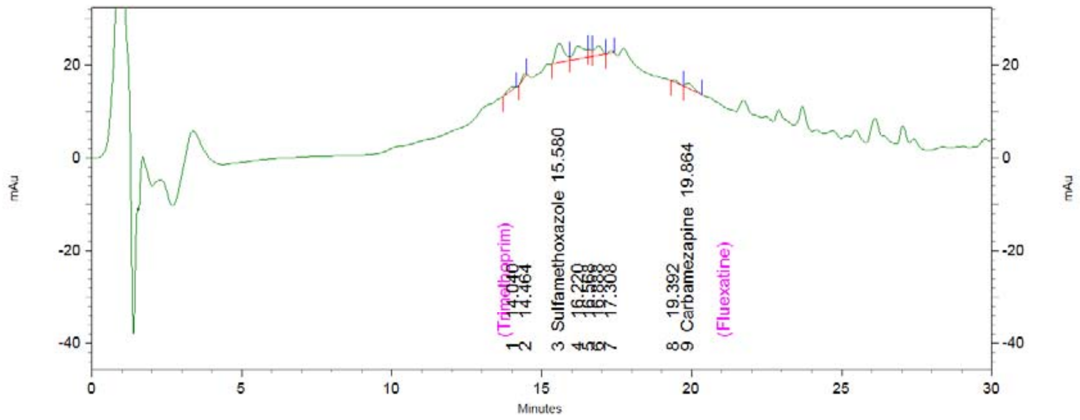


```
1: 260 nm, 4
nm Results
         Pk #  Name                 Retention          ESTD          Area
                                         Time  concentration
               Trimethoprim                          0.000 BDL
            3  Sulfamethoxaz           15.580          303.148         79069
               ole
            9  Carbamezapine           19.864           78.892         21173
               Fluexatine                            0.000 BDL

        Totals                                         382.039        100242
```

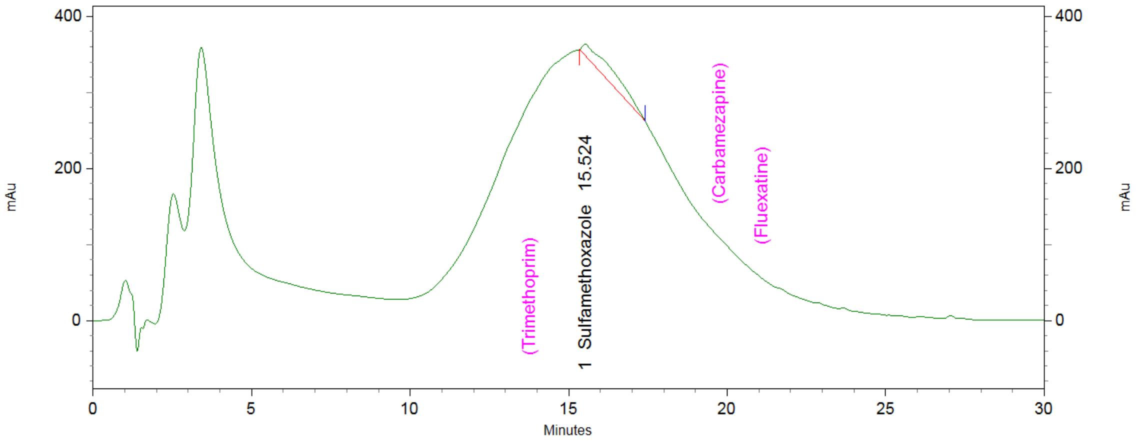
Trim 0 ppb
Sulf 12 ppb
Carb 3.1 ppb
Fluox 0 ppb

8/17/12, Institutional Landscaped

081712BamaBelleLandScaped20X2121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met

C:\EZStart\Projects\Default\Data\Brads\081712BamaBelleLandScaped20X2121812
C:\EZStart\Projects\Default\Method\C121012Sulf.met



1: 260 nm, 4
nm Results

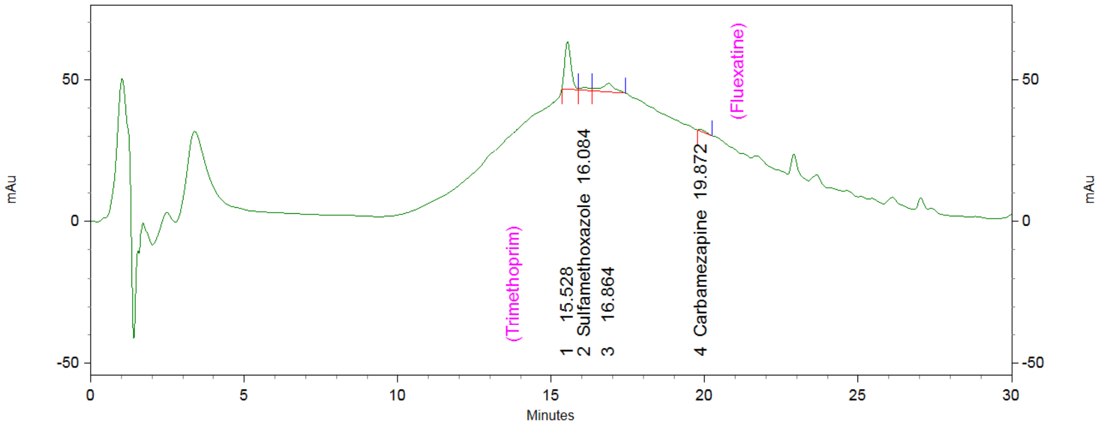
Pk #	Name	Retention Time	ESTD concentration	Area
	Trimethoprim		0.000 BDL	
1	Sulfamethoxazole	15.524	1942.780	1748590
	Carbamezapine		0.000 BDL	
	Fluexatine		0.000 BDL	
Totals			1942.780	1748590

8/17/12, Institutional Landscaped

062811CommGrass20x2mlCarb121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met

C:\EZStart\Projects\Default\Data\Brads\062811CommGrass20x2mlCarb121812
C:\EZStart\Projects\Default\Method\C121012Sulf.met



1: 260 nm, 4
nm Results

Pk #	Name	Retention Time	ESTD concentration	Area
	Trimethoprim		0.000 BDL	
2	Sulfamethoxazole	16.084	246.502	21391
4	Carbamezapine	19.872	57.744	11210
	Fluexatine		0.000 BDL	
Totals			304.246	32601

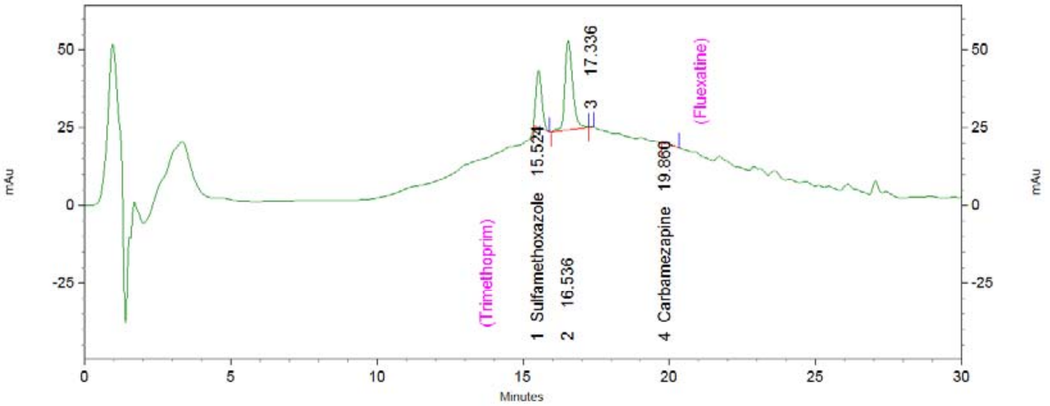
Trim 0 ppb
Sulf 9 ppb
Carb 2.3 ppb
Fluox 0 ppb

6/28/11, Commercial Landscaped

090511Grass20x2mlCarb121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met

C:\EZStart\Projects\Default\Data\Brads\090511Grass20x2mlCarb121812
C:\EZStart\Projects\Default\Method\C121012Sulf.met



1: 260 nm, 4
nm Results

Pk #	Name	Retention Time	ESTD concentration	Area
	Trimethoprim		0.000 BDL	
1	Sulfamethoxazole	15.524	472.561	251571
4	Carbamezapine	19.860	54.650	9752
	Fluexatine		0.000 BDL	
Totals			527.211	261323

Trim 0 ppb
Sulf 19 ppb
Carb 2 ppb
Fluox 0 ppb

9/5/11, Institutional Landscaped

```
062211CommPave20x2mlCarb121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met

C:\EZStart\Projects\Default\Data\Brads\062211CommPave20x2mlCarb121812
C:\EZStart\Projects\Default\Method\C121012Sulf.met
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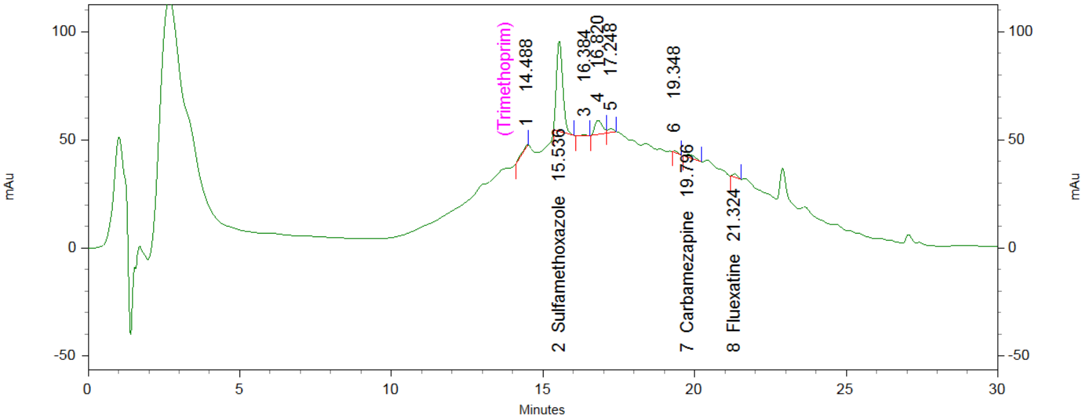


1: 260 nm, 4 nm Results

Pk #	Name	Retention Time	ESTD concentration	Area
	Trimethoprim		0.000 BDL	
2	Sulfamethoxazole	15.536	808.534	593668
7	Carbamezapine	19.796	100.782	31486
8	Fluexatine	21.324	223.097	17697
Totals			1132.413	642851

Trim 0 ppb
Sulf 32 ppb
Carb 4 ppb
Floux 9 ppb

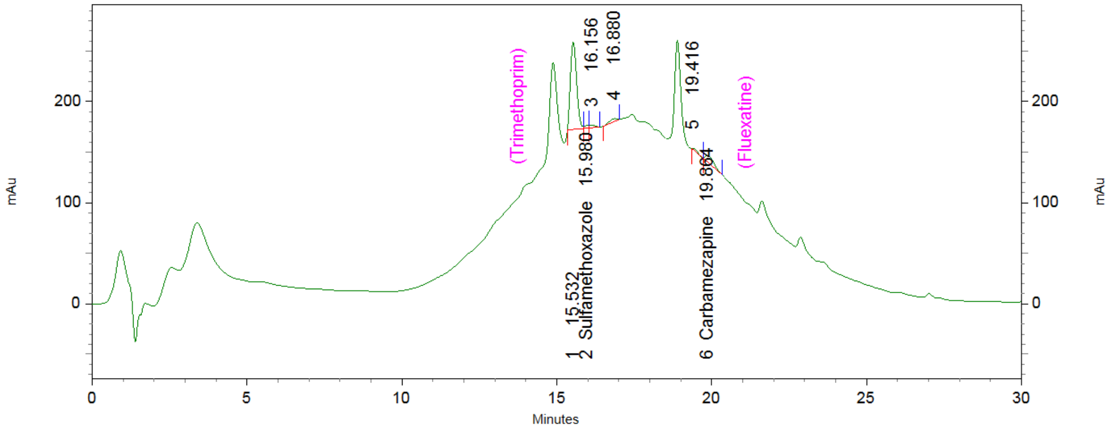
6/22/11, Commercial Paved

```
062211GallerRoofComm20x2mlCarb121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met

C:\EZStart\Projects\Default\Data\Brads\062211GallerRoofComm20x2mlCarb121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met
```



1: 260 nm, 4 nm Results

Pk #	Name	Retention Time	ESTD concentration	Area
	Trimethoprim		0.000 BDL	
2	Sulfamethoxazole	15.980	250.329	25288
6	Carbamezapine	19.864	319.659	134603
	Fluexatine		0.000 BDL	
Totals			569.989	159891

Trim 0 ppn
Sulf 10 ppb
Carb 13 ppb
Flu 0 ppb

6/22/11, Commercial Roof

```
062811OpenPaved20x2mlCarb121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met

C:\EZStart\Projects\Default\Data\Brads\062811OpenPaved20x2mlCarb121812
C:\EZStart\Projects\Default\Method\C121012Sulf.met
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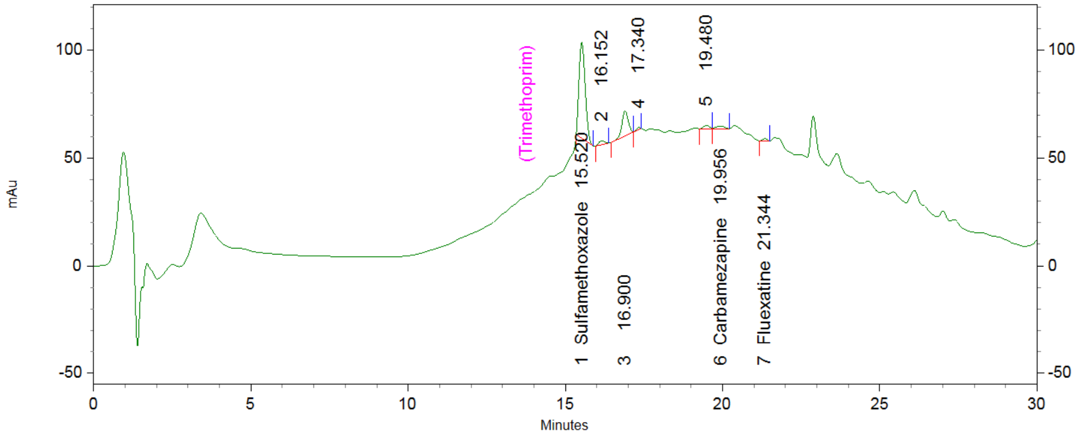

```
1: 260 nm, 4
nm Results
          Pk #  Name                Retention          ESTD          Area
                                         Time  concentration
-------------------------------------------------------------------------
                Trimethoprim                       0.000 BDL
             1  Sulfamethoxaz          15.520        821.997       607377
                ole
             6  Carbamezapine          19.956         82.413        22832
             7  Fluexatine             21.344        181.614        11321

        Totals
                                                    1086.024       641530
```

Trim 0 ppb
Sulf 33 ppb
Carb 3.3
Fluox 7 ppb

6/28/11, Institutional Paved

```
092011Paved20x2mlCarb121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met

C:\EZStart\Projects\Default\Data\Brads\092011Paved20x2mlCarb121812
C:\EZStart\Projects\Default\Method\C121012Sulf.met
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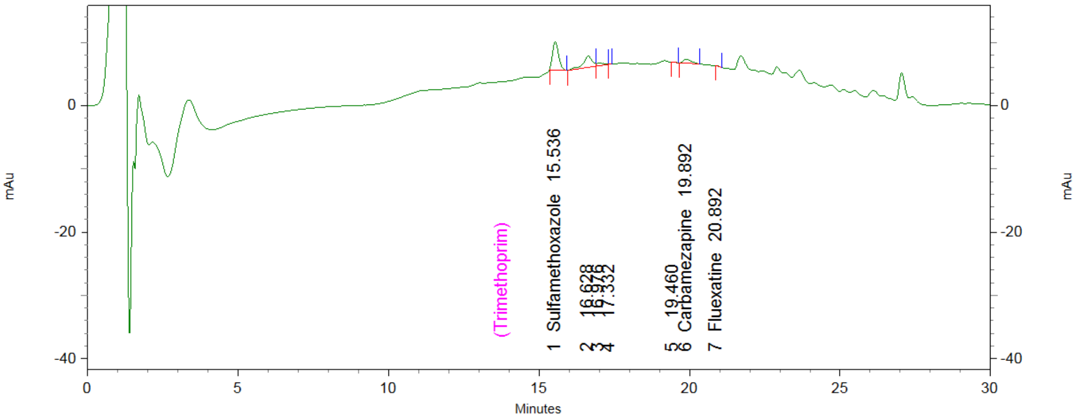


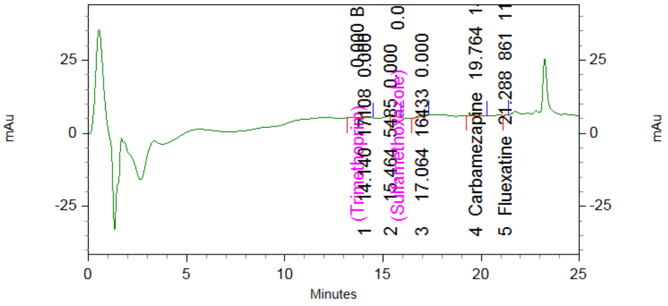
1: 260 nm, 4 nm Results

Pk #	Name	Retention Time	ESTD concentration	Area
	Trimethoprim		0.000 BDL	
1	Sulfamethoxazole	15.536	285.842	61448
6	Carbamezapine	19.892	57.479	11085
7	Fluexatine	20.892	112.851	752
Totals			456.172	73285

Trim 0 ppb
Sulf 11 ppb
Carbme 4.5 ppn

9/20/11, Residential Paved

01Blank04022013



C:\EZStart\Projects\Default\Data\Brads\04022013\01Blank04022013

1: 260 nm,
4 nm
Results

Pk #	Name	Retention Time	Area	ESTD concentration	Units
	Trimethoprim			0.000 BDL	ppb
	Sulfamethoxazole			0.000 BDL	ppb
4	Carbamezapine	19.764	14763	65.286	ppb
5	Fluexatine	21.288	861	113.560	ppb
Totals			15624	178.846	

01Blank04022013

C:\EZStart\Projects\Default\Method\010913SulfCarbCalib.met

1/26/12, Institutional (unknown surface) QA

```
CheckCarb121812

C:\EZStart\Projects\Default\Method\C121012Sulf.met

C:\EZStart\Projects\Default\Data\CheckCarb121812
C:\EZStart\Projects\Default\Method\C121012Sulf.met
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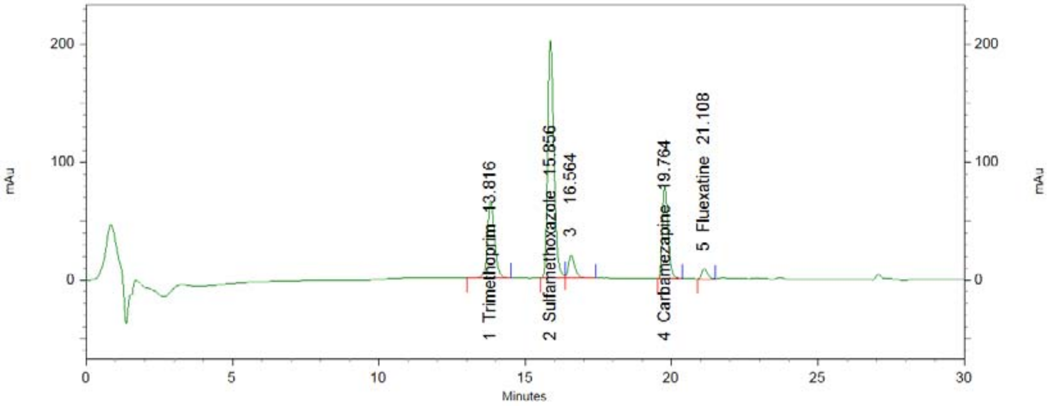


```
1: 260 nm, 4
nm Results
          Pk #  Name                Retention          ESTD          Area
                                         Time  concentration
-------------------------------------------------------------------------
             1  Trimethoprim           13.816      3661.056       1089407
             2  Sulfamethoxaz          15.856      3168.050       2996196
                ole
             4  Carbamezapine          19.764      2325.926       1079793
             5  Fluexatine             21.108       904.082        122366

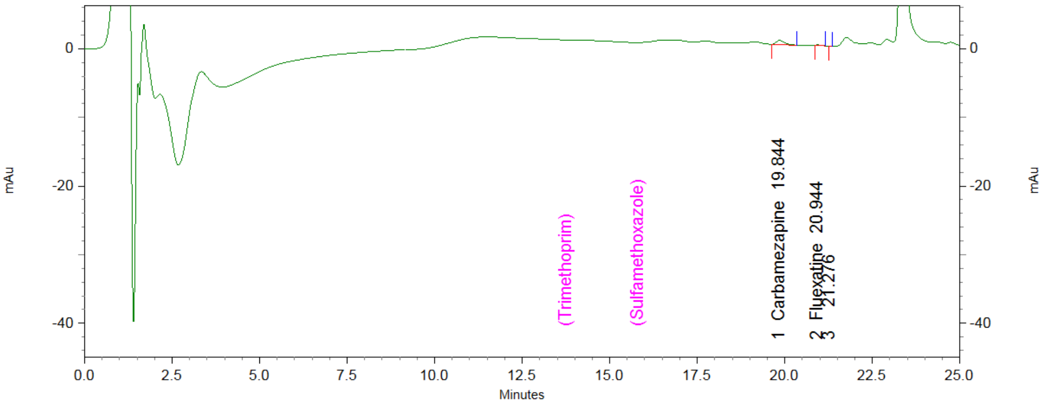
 ------------------------------------------------------------------------
|       Totals |              |              |              |             |
|              |              |              |    10059.114 |     5287762 |
 ------------------------------------------------------------------------
```

QA

02Blank04012013StdISulf

C:\EZStart\Projects\Default\Method\C121012Sulf.met

C:\EZStart\Projects\Default\Data\Brads\04012013\02Blank04012013StdISulf
C:\EZStart\Projects\Default\Method\C121012Sulf.met

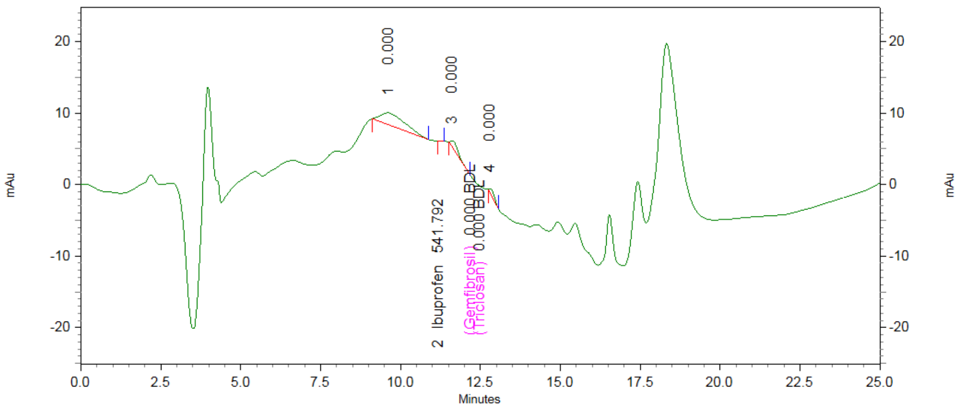


1

1: 260 nm, 4
nm Results

Pk #	Name	Retention Time	ESTD concentration	Area
	Trimethoprim		0.000 BDL	
	Sulfamethoxazole		0.000 BDL	
1	Carbamezapine	19.844	55.144	9985
2	Fluexatine	20.944	112.988	773
Totals			168.132	10758

QA



```
   C:\EZStart\Projects\Default\Method\04122013TCS.met

 C:\EZStart\Projects\Default\Data\Brads\TCS041113Brad\01Blank04112013TCS


 2: 240 nm, 4 nm
 Results
              Pk #  Name                   Retention Time          ESTD
                                                          concentration
                 2  Ibuprofen                      11.184       541.792
                    Gemfibrosil                               0.000 BDL
                    Triclosan                                 0.000 BDL

             Totals
                                                                541.792
 n/a

 n/a
Ibuprofen        BDL      0 ppb

Gemfibrozil      BDL      0 ppb

Triclosan        BDL      0 ppb
```

QA

PAH GCMSD Chromatographs

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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:Unknown
: 1
; AcadDrivlOxl40112
; AcadDrivlOx140112
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; 1.000
: 1.000
:21
: 1.000
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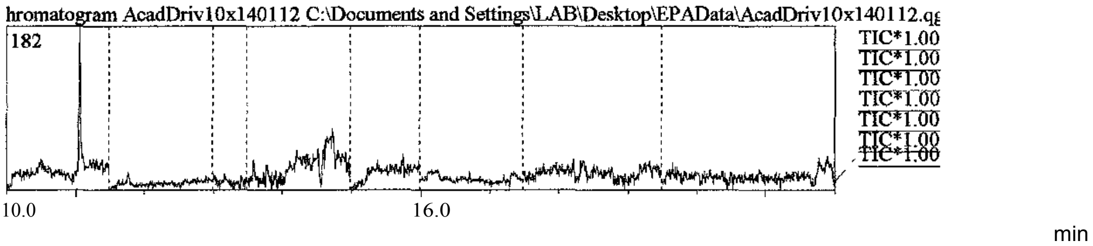
: C:\Documents and Settings\LAB\Desktop\EPAData\AcadDriv1Oxl40112.qgd
: C:\Documents and Settings\LAB\Desktop\IPAHCalll2011.qgm
: C:\Documents and Settings\LAB\Desktop\IPAHCalll2011.qgm

: C:\GCMSsolution\System\1105 1ITune
:Admin
: 11130/2012 7:33:26 AM



Quantitative Result Table

ID#	RTime	m/z	Area	Height	Cone.	Conc	.1 Recovery	Name
1	5.057	TIC	306	171	0.000	ppb	0.00	Naphthalene
2	6.596	TIC	36	9	0.000	ppb	0.00	Acenaphthvlene
3	6.751	TIC	34	5	0.000	ppb	0.00	Acenaphthene
4	7.365	TIC	15	8	0.000	ppb	0.00	Fluorene
5	8.117	TIC	12	9	0.000	ppb	0.00	Phenanthrene
6	8.300	TIC	63	11	0.000	ppb	0.00	Anthracene
7	9.375	TIC	89	23	0.000	ppb	0.00	Flouranthene
8	9.560	TIC	79	17	0.000	ppb	0.00	Pvrene
9	10.875	TIC	10	4	0.000	ppb	0.00	Benzo(a)anthracene
10	10.875	TIC	10	4	0.000	ppb	0.00	Chrysene
11	12.208	TIC	38	21	0.000	ppb	0.00	Benzo(b)fluoranthene
12	12.208	TIC	38	21	0.000	ppb	0.00	Benzo(k)fluoranthene
13	12.717	TIC	90	19	0.000	ppb	0.00	Benzo(a)pyrene
14	12.610	TIC	34	15	0.000	ppb	0.00	Indeno(1,2,3-cd)pyrene
15	14.615	TIC	52	15	0.000	ppb	0.00	Benzo(a,h)anthracene
16	15.008	TIC	50	13	0.000	ppb	0.00	Benzo(ghi)perylene

10/14/12 Residential Landscaped

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

: 7/9/2012 11:02:13 AM
:Unknown
: 1
: l20312GalleriaRoof050112
: 120312GalleriaRoof050102
: [1]=1.000
: 1.000
: 1.000
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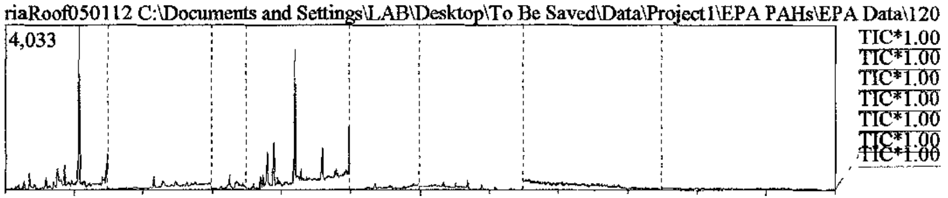

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3/22/12 Commercial Roof (no quantitative data, not charted)

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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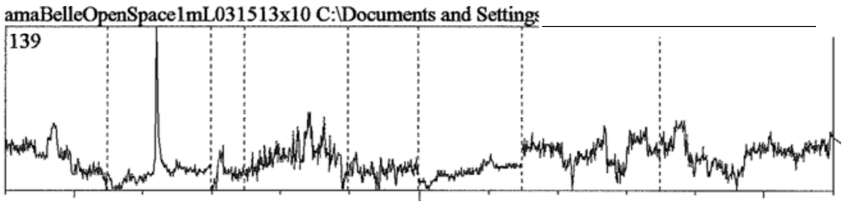

Quantitative Result Table

ID#	RTime	m/z	Area	Height	Cone. Conc	.l Recovery	Name
1	5.244	TIC	34	10	0.000 ppb	0.00	Naphthalene
2	6.533	TIC	17	6	0.000 ppb	0.00	Acenaphthylene
3	6.692	TIC	4	4	0.000 ppb	0.00	Acenaphthene
4	7.290	TIC	68	14	0.000 ppb	0.00	Fluorene
5	8.184	TIC	31	32	0.000 ppb	0.00	Phenanthrene
6	8.266	TIC	85	32	0.000 ppb	0.00	Anthracene
7	9.329	TIC	45	16	0.000 ppb	0.00	Flouranthene
8	9.621	TIC	144	23	0.000 ppb	0.00	Pyrene
9	10.893	TIC	9	9	0.000 ppb	0.00	Benzo(a)antbracene
10	10.893	TIC	10	9	0.000 ppb	0.00	Chrysene
11	12.258	TIC	52	15	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.258	TIC	58	16	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.687	TIC	166	42	3.278 ppb	0.00	Benzo(a)pyrene
14	12.558	TIC	160	27	97.507 ppb	0.00	Indeno(l,2,3-cd)pyrene
15	14.617	TIC	63	16	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.099	TIC	386	36	38.066 ppb	0.00	Benzo(ghi)perylene

8/17/12 Institutional Roof

Sample Infonnation

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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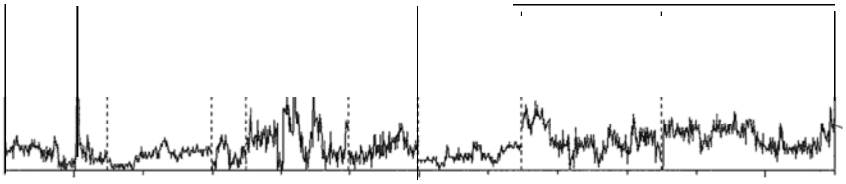

0712BamaBelle?2mL031512x10 C:\Documents and Settin

Quantitative Result Table

ID#	R.Time	mlz	Area	Height	Cone.	Conc	.l Recovery	Name
1	5.058	TIC	167	111	0.000	ppb	0.00	Naphthalene
2	6.571	TIC	18	9	0.000	ppb	0.00	Acenaphthylene
3	6.776	TIC	10	7	0.000	ppb	0.00	Acenaphthene
4	7.217	TIC	37	17	0.000	ppb	0.00	Fluorene
5	8.192	TIC	188	64	0.000	ppb	0.00	Phenanthrene
6	8.192	TIC	188	64	0.000	ppb	0.00	Anthracene
7	9.408	TIC	79	10	0.000	ppb	0.00	Flouranthene
8	9.608	TIC	71	15	0.000	ppb	0.00	Pvrene
9	10.792	TIC	15	8	0.000	ppb	0.00	Benzo(a)anthracene
10	10.792	TIC	15	8	0.000	ppb	0.00	Chrysene
11	12.192	TIC	35	9	0.000	ppb	0.00	Benzo(b)fluoranthene
12	12.300	TIC	79	20	0.000	ppb	0.00	Benzo(k)fluoranthene
13	12.725	TIC	28	19	0.000	ppb	0.00	Benzo(a)pyrene
14	12.558	TIC	39	13	0.000	ppb	0.00	Indeno(1,2,3-cd)pyrene
15	14.659	TIC	28	11	0.000	ppb	0.00	Benzo(a,h)anthracene
16	15.075	TIC	25	11	0.000	ppb	0.00	Benzo(ghi)perylene

Institutional

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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: 3/15/2013 4:24:54 PM

Quantitative Result Table

ID#	R.Time	m/z	Area	Height	Cone. Conc	.l Recovery	Name
1	5.057	TIC	588	368	10.241 ppb	0.00	Naphthalene
2	6.568	TIC	55	9	0.000 ppb	0.00	Acenaphthylene
3	6.779	TIC	52	12	0.000 ppb	0.00	Acenaphthene
4	7.244	TIC	127	32	0.000 ppb	0.00	Fluorene
5	8.184	TIC	49	31	0.000 ppb	0.00	Phenanthrene
6	8.241	TIC	43	23	0.000 ppb	0.00	Anthracene
7	9.350	TIC	61	26	0.000 ppb	0.00	Flouranthene
8	9.576	TIC	58	20	0.000 ppb	0.00	Pvrene
9	10.796	TIC	17	7	0.000 ppb	0.00	Benzo(a)anthracene
10	10.796	TIC	17	7	0.000 ppb	0.00	Chrysene
11	12.193	TIC	191	27	0.000 ppb	0.00	Benzo(b)tluorantbene
12	12.257	TIC	20	10	0.000 ppb	0.00	Benzo(k)tluoranthene
13	12.666	TIC	53	19	0.000 ppb	0.00	Benzo(a)pyrene
14	12.567	TIC	51	13	6.944 ppb	0.00	Indeno(1,2,3-cd)pyrene
15	14.760	TIC	82	14	0.000 ppb	0.00	Benzo(a,h)anthracene
16	14.986	TIC	23	4	0.000 ppb	0.00	Benzo(ghi)perylene

6/28/11, Commercial Landscaped

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File Report File Tuning File Modified by Modified

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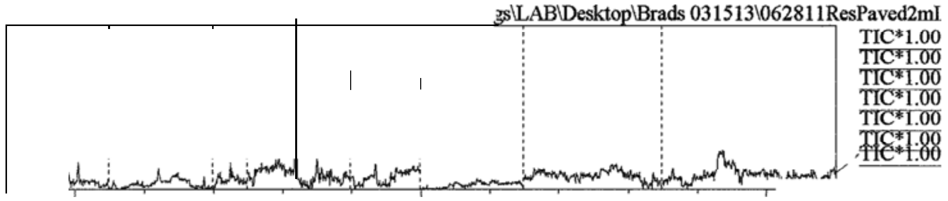

162811ResPaved2mL031513x10 C:\Documents and Settin
296

10.0 16.0
min

Quantitative Result Table

ID#	R.Time	m/z	Area	Height	Cone. Conc	.l Recovery	Name
1	5.092	TIC	20	14	0.000 ppb	0.00	Naphthalene
2	6.479	TIC	83	14	0.000 ppb	0.00	Acenaphthylene
3	6.866	TIC	26	23	0.000 ppb	0.00	Acenaphthene
4	7.275	TIC	96	26	0.000 ppb	0.00	Fluorene
5	8.183	TIC	297	275	0.000 ppb	0.00	Phenanthrene
6	8.299	TIC	27	13	0.000 ppb	0.00	Anthracene
7	9.345	TIC	69	42	0.000 ppb	0.00	Flouranthene
8	9.568	TIC	59	24	0.000 ppb	0.00	Pvrene
9	10.818	TIC	21	13	0.000 ppb	0.00	Benzo(a)anthracene
10	10.867	TIC	26	10	0.000 ppb	0.00	Chrysene
11	12.232	TIC	91	15	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.232	TIC	91	15	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.768	TIC	206	27	9.123 ppb	0.00	Benzo(a)p'yTene
14	12.768	TIC	198	26	129.080 ppb	0.00	Indeno(l,2,3-cd)pyrene
15	14.700	TIC	23	13	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.083	TIC	14	5	0.000 ppb	0.00	Benzo(ghi)perylene

6/28/11, residential paved

```
Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified


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:Admin
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Quantitative Result Table
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                   2    6.592    TIC     10        5          0.000 ppb      0.00  Acenaphthylene
                   3    6.592    TIC     10        5          0.000 ppb      0.00  Acenaphthene
                   4    7.308    TIC     24        9          0.000 ppb      0.00  Fluorene
                   5    8.207    TIC     140       27         0.000 ppb      0.00  Phenanthrene
                   6    8.275    TIC     25        12         0.000 ppb      0.00  Anthracene
                   7    9.308    TIC     34        7          0.000 ppb      0.00  Flouranthene
                   8    9.567    TIC     86        14         0.000 ppb      0.00  Pyrene
                   9    10.858   TIC     6         5          0.000 ppb      0.00  Benzo(a)anthracene
                  10    10.858   TIC     6         5          0.000 ppb      0.00  Chrysene
                  11    12.294   TIC     38        18         0.000 ppb      0.00  Benzo(b)fluoranthene
                  12    12.294   TIC     38        18         0.000 ppb      0.00  Benzo(k)fluoranthene
                  13    12.692   TIC     140       28         0.000 ppb      0.00  Benzo(a)pyrene
                  14    12.558   TIC     11        9          0.000 ppb      0.00  Indeno(l,2,3-cd)pyrene
                  15    14.650   TIC     36        21         0.000 ppb      0.00  Benzo(a,h)anthracene
                  16    15.068   TIC     53        8          0.000 ppb      0.00  Benzo(ghi)perylene
```

6/28/11, Institutional Outfall

Sample Information

Analyzed Sample Type Level# Sample Name Sample ID
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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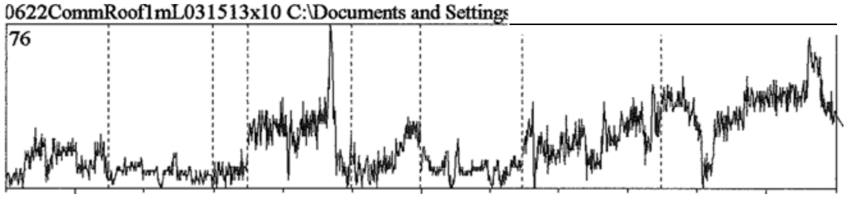

Quantitative Result Table

ID#	RTime	m/z	Area	Height	Cone.	Conc	.l Recovery	Name
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2	6.463	TIC	56	13	0.000	ppb	0.00	Acenaphthylene
3	6.750	TIC	20	6	0.000	ppb	0.00	Acenaphthene
4	7.217	TIC	53	10	0.000	ppb	0.00	Fluorene
5	8.150	TIC	47	19	0.000	ppb	0.00	Phenanthrene
6	8.250	TIC	98	22	0.000	ppb	0.00	Anthracene
7	9.458	TIC	69	16	0.000	ppb	0.00	Flouranthene
8	9.569	TIC	40	11	0.000	ppb	0.00	Pyrene
9	10.540	TIC	34	19	0.000	ppb	0.00	Benzo(a)anthracene
10	10.540	TIC	34	19	0.000	ppb	0.00	Chrysene
11	12.250	TIC	72	21	0.000	ppb	0.00	Benzo(b)fluoranthene
12	12.250	TIC	72	21	0.000	ppb	0.00	Benzo(k)fluoranthene
13	12.732	TIC	50	14	0.000	ppb	0.00	Benzo(a)pyrene
14	12.533	TIC	30	3	0.000	ppb	0.00	Indeno(1,2,3-cd)pyrene
15	14.678	TIC	46	24	0.000	ppb	0.00	Benzo(a,h)anthracene
16	15.075	TIC	83	12	0.000	ppb	0.00	Benzo(ghi)perylene

6/22/11, Commercial Roof

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
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Org Method File
Report File
Tuning File Modified by Modified

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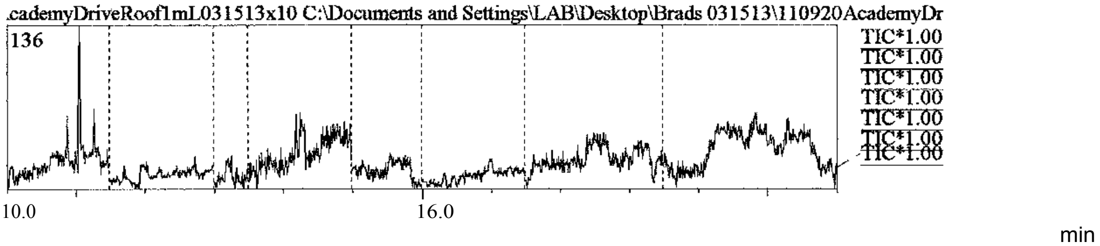

Quantitative Result Table

ID#	R.Time	m/z	Area	Height	Cone. Conc	.1 Recovery	Name
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2	6.610	TIC	17	8	0.000 ppb	0.00	Acenaphthylene
3	6.716	TIC	28	15	0.000 ppb	0.00	Acenaphthene
4	7.245	TIC	26	17	0.000 ppb	0.00	Fluorene
5	8.184	TIC	87	48	0.000 ppb	0.00	Phenanthrene
6	8.263	TIC	133	43	0.000 ppb	0.00	Anthracene
7	9.344	TIC	50	9	0.000 ppb	0.00	Flouranthene
8	9.544	TIC	76	18	0.000 ppb	0.00	Pvrene
9	10.833	TIC	17	7	0.000 ppb	0.00	Benzo(a)anthracene
10	10.833	TIC	17	7	0.000 ppb	0.00	Chrysene
11	12.201	TIC	20	13	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.275	TIC	39	11	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.667	TIC	115	30	0.000 ppb	0.00	Benzo(a)pyrene
14	12.625	TIC	105	32	51.810 ppb	0.00	Indeno(l,2,3·cd)pvrene
15	14.617	TIC	83	22	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.042	TIC	32	15	0.000 ppb	0.00	Benzo(ghi)perylene

9/20/11 Residential Roof

```
Sample Infonnation

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
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: 3/15/2013 6:05:09 PM

Quantitative  Result Table
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                      2    6.576    TIC     43        9         0.000  ppb   0.00  Aceuaphthylene
                    3      6.792    TIC     4         4         0.000  ppb   0.00  Aceuaphthene
                      4    7.252    TIC     74        35        0.000  ppb   0.00  Fluorene
                      5    8.190    TIC     195       98        0.000  ppb   0.00  Phenanthrene
                    6      8.190    TIC     197       98        0.000  ppb   0.00  Anthracene
                      7    9.350    TIC     35        28        0.000  ppb   0.00  Flouranthene
                    8      9.560    TIC     66        17        0.000  ppb   0.00  Pyrene
                      9    10.788   TIC     37        13        0.000  ppb   0.00  Benzo(a)anthracene
                    10     10.867   TIC     15        8         0.000  ppb   0.00  Chrysene
                    11     12.149   TIC     43        8         0.000  ppb   0.00  Benzo(b)fluoranthene
                    12     12.149   TIC     43        8         0.000  ppb   0.00  Benzo(k)fluoranthene
                    13     12.701   TIC     113       20        0.000  ppb   0.00  Benzo(a)pyrene
                    14     12.527   TIC     18        7         0.000  ppb   0.00  Indeno(1,2,3-cd)pyrene
                    15     14.675   TIC     63        11        0.000  ppb   0.00  Benzo(a,h)anthracene
                    16     15.068   TIC     93        22        0.000  ppb   0.00  Benzo(ghi)perylene
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3/22/12 Commercial Landscaped

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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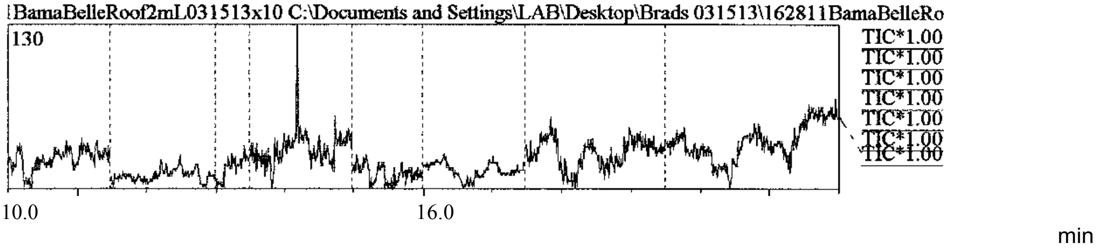

Quantitative Result Table

ID#	RTime	m/z	Area	Height	Cone. Conc	.l Recovery	Name
1	5.083	TIC	99	19	0.000 ppb	0.00	Naphthalene
2	6.642	TIC	40	9	0.000 ppb	0.00	Acenaphthvlene
3	6.901	TIC	25	8	0.000 ppb	0.00	Acenaphthene
4	7.242	TIC	55	17	0.000 ppb	0.00	Fluorene
5	8.180	TIC	311	121	0.000 ppb	0.00	Phenanthrene
6	8.180	TIC	311	121	0.000 ppb	0.00	Anthracene
7	9.358	TIC	80	21	0.000 ppb	0.00	Flouranthene
8	9.600	TIC	23	9	0.000 ppb	0.00	Pyrene
9	10.754	TIC	13	9	0.000 ppb	0.00	Benzo(a)anthracene
10	10.754	TIC	13	9	0.000 ppb	0.00	Chrysene
11	12.207	TIC	17	13	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.276	TIC	70	27	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.663	TIC	37	15	0.000 ppb	0.00	Benzo(a)pyrene
14	12.592	TIC	48	17	4.451 ppb	0.00	Indeno(l,2,3·cd)pvrene
15	14.642	TIC	234	30	4.022 ppb	0.00	Benzo(a,h)anthracene
16	14.975	TIC	41	11	0.000 ppb	0.00	Benzo(ghi)perylene

6/28/11 Institutional Roof

```
Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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: 3/15/2013 2:20:13 PM

Quantitative Result Table
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                 2    6.608    TIC    21     11       0.000 ppb    0.00  Acenaphthvlene
                 3    6.725    TIC    52     7        0.000 ppb    0.00  Acenaphthene
                 4    7.196    TIC    49     14       0.000 ppb    0.00  Fluorene
                 5    8.192    TIC    45     26       0.000 ppb    0.00  Phenanthrene
                 6    8.275    TIC    96     21       0.000 ppb    0.00  Anthracene
                 7    9.367    TIC    31     15       0.000 ppb    0.00  Flouranthene
                 8    9.575    TIC    42     16       0.000 ppb    0.00  Pvrene
                 9    10.783   TIC    40     8        0.000 ppb    0.00  Benzo(a)anthracene
                10    10.783   TIC    40     8        0.000 ppb    0.00  Chrysene
                11    12.215   TIC    49     24       0.000 ppb    0.00  Benzo(b)fluoranthene
                12    12.215   TIC    49     24       0.000 ppb    0.00  Benzo(k)fluoranthene
                13    12.667   TIC    42     12       0.000 ppb    0.00  Benzo(a)pyrene
                14    12.667   TIC    36     11       0.000 ppb    0.00  Indeno(l,2,3-cd)pyrene
                15    14.666   TIC    57     27       0.000 ppb    0.00  Benzo(a,h)anthracene
                16    14.978   TIC    75     14       0.000 ppb    0.00  Benzo(ghi)perylene
```

QA

```
Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File
Modified by
Modified


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: C:\GCMSsolution\System\1l0511Tune
:Admin
: 3/15/2013 6:55:20 PM

Quantitative Result Table
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                 1     5.046    TIC   2556   1990     85.075 ppb    0.00  Naphthalene
                   2   6.566    TIC   1712   1732     72.157 ppb    0.00  Acenaphthylene
                   3   6.734    TIC   707    720      96.417ppb     0.00  Acenaphthene
                   4   7.236    TIC   2227   1895     81.299 ppb    0.00  Fluorene
                   5   8.175    TIC   3225   3304     120.892 ppb   0.00  Phenanthrene
                   6   8.226    TIC   3307   2742     69.363 ppb    0.00  Anthracene
                   7   9.341    TIC   3245   2948     103.251 ppb   0.00  Flouranthene
                 8     9.562    TIC   3438   2737     100.548 ppb   0.00  Pvrene
                   9   10.833   TIC   1122   875      170.420 ppb   0.00  Benzo(a)anthracene
                 10    10.833   TIC   1122   875      72.968 ppb    0.00  Chrysene
                 11    12.224   TIC   853    462      152.626 ppb   0.00  Benzo(b)fluoranthene
                 12    12.224   TIC   853    462      58.501 ppb    0.00  Benzo(k)fluoranthene
                 13    12.674   TIC   497    277      51.649 ppb    0.00  Benzo(a)pyrene
                 14    12.558   TIC   39     15       0.000 ppb     0.00  Indeno(l,2,3-cd)pyrene
                 15    14.675   TIC   82     12       0.000 ppb     0.00  Benzo(a.h)anthracene
                 16    15.001   TIC   619    256      70.916 ppb    0.00  Benzo(ghi)perylene
```

QA

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
T . File
M edby
Modified

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: C:\GCMSsolution\System\110511Tune
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: 3/15/2013 7:20:23 PM

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Cone. Conc.l Recovery Name
                        1   5.052    TIC   2590   2295   86.368 ppb    0.00  Naphthalene
                        2   6.572    TIC   1776   1504   75.287 ppb    0.00  Acenaphthylene
                        3   6.741    TIC   763    715    104.981 ppb   0.00  Acenaphthene
                        4   7.242    TIC   2322   2354   85.182 ppb    0.00  Fluorene
                        5   8.182    TIC   3255   3312   122.155 ppb   0.00  Phenanthrene
                        6   8.232    TIC   3069   2700   63.778 ppb    0.00  Anthracene
                        7   9.345    TIC   3466   2762   111.296 ppb   0.00  Flouranthene
                        8   9.567    TIC   3740   3365   110.410 ppb   0.00  Pvrene
                        9   10.796   TIC   1006   731    151.092 ppb   0.00  Benzo(a)anthracene
                        10  10.837   TIC   1472   862    99.846 ppb    0.00  Chrysene
                        11  12.229   TIC   916    489    168.906 ppb   0.00  Benzo(b)fluoranthene
                        12  12.229   TIC   916    489    64.250 ppb    0.00  Benzo(k)fluoranthene
                        13  12.679   TIC   508    282    53.257 ppb    0.00  Benzo(a)pyrene
                        14  12.604   TIC   48     18     4.451 ppb     0.00  Indeno(1,2,3-cd)pvrene
                        15  14.571   TIC   611    246    32.668 ppb    0.00  Benzo(a,h)anthracene
                        16  15.007   TIC   617    263    70.634 ppb    0.00  Benzo(ghi)perylene
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QA

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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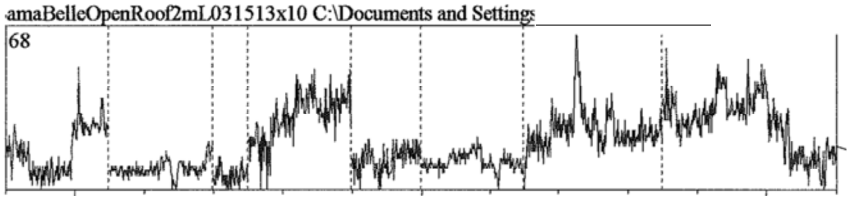
:Admin
: 3/15/2013 3:34:47 PM



Quantitative Result Table

ID#	R.Time	m/z	Area	Height	Cone. Conc	.l Recovery	Name
1	5.058	TIC	59	37	0.000 ppb	0.00	Naphthalene
2	6.565	TIC	61	10	0.000 ppb	0.00	Acenaphthylene
3	6.725	TIC	31	5	0.000 ppb	0.00	Acenaphthene
4	7.282	TIC	11	10	0.000 ppb	0.00	Fluorene
5	8.254	TIC	183	27	0.000 ppb	0.00	Phenanthrene
6	8.254	TIC	183	27	0.000 ppb	0.00	Anthracene
7	9.287	TIC	83	15	0.000 ppb	0.00	Flouranthene
8	9.508	TIC	17	12	0.000 ppb	0.00	Pyrene
9	10.626	TIC	22	6	0.000 ppb	0.00	Benzo(a)anthracene
10	11.002	TIC	47	11	0.000 ppb	0.00	Chrysene
11	12.260	TIC	166	53	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.260	TIC	166	53	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.768	TIC	124	23	0.000 ppb	0.00	Benzo(a)pyrene
14	12.558	TIC	27	13	0.000 ppb	0.00	Indeno(l,2,3-cd)pyrene
15	14.667	TIC	29	10	0.000 ppb	0.00	Benzo(a,h)anthracene
16	14.982	TIC	224	26	15.227 ppb	0.00	Benzo(ghi)perylene

8/17/12 Institutional Roof

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
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Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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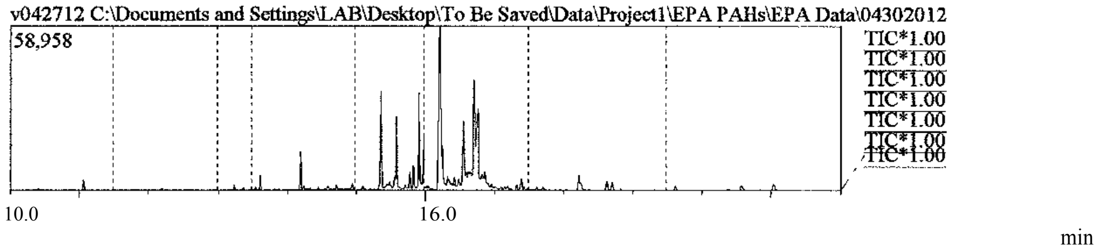

Quantitative Result Table

ID#	R.Time	m/z	Area	Height	Cone. Conc	.l Recovery	Name
1	5.061	TIC	3588	3435	124.317 ppb	0.00	Naphthalene
2	6.581	TIC	437	388	9.799 ppb	0.00	Acenaphthy1ene
3	6.749	TIC	270	94	29.590 ppb	0.00	Acenaphthene
4	7.233	TIC	2452	1973	90.495 ppb	0.00	Fluorene
5	8.192	TIC	13228	13750	542.039 ppb	0.00	Phenanthrene
6	8.242	TIC	1745	1574	32.709 ppb	0.00	Anthracene
7	9.358	TIC	38012	35331	1368.985 ppb	0.00	Flouranthene
8	9.581	TIC	28934	26126	933.119 ppb	0.00	Pyrene
9	10.817	TIC	8817	4450	1452.538 ppb	0.00	Benzo(a)anthracene
10	10.864	TIC	11555	5368	874.185 ppb	0.00	Chrvsene
11	12.216	TIC	14018	5396	3554.749 ppb	0.00	Benzo(b)fluoranthene
12	12.216	TIC	14018	5396	1259.804 ppb	0.00	Benzo(k)tluoranthene
13	12.700	TIC	4689	2721	664.259 ppb	0.00	Benzo(a)p)Tene
14	12.566	TIC	34	28	0.000 ppb	0.00	Indeno(l,2,3-cd)pyrene
15	14.674	TIC	116	61	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.038	TIC	5348	2118	737.644 ppb	0.00	Benzo(ghi)perylene

3/22/12 Commercial Paved

```
Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
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Method File
Org Method File
Report File
Tuning File Modified by Modified

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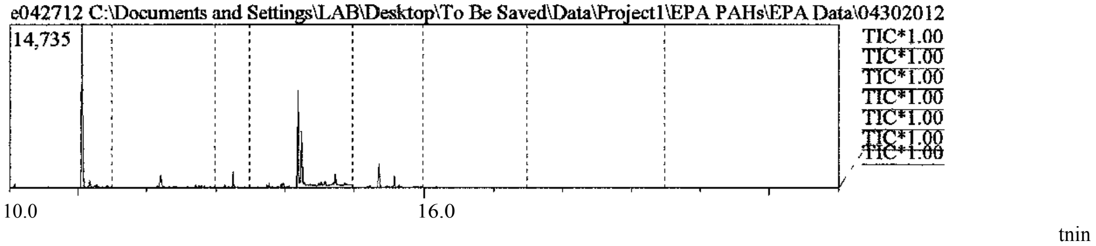

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Quantitative Result Table
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            2   6.580    TIC    142     88       0.000 ppb      0.00  Acenaphthylene
          3     6.756    TIC    260     187      28.061 ppb     0.00  Acenaphthene
            4   7.250    TIC    1680    1461     58.943 ppb     0.00  Fluorene
            5   8.193    TIC    8752    8700     353.590 ppb    0.00  Phenanthrene
          6     8.243    TIC    6838    5060     152.223 ppb    0.00  Anthracene
            7   9.356    TIC    2387    2095     72.014 ppb     0.00  Flouranthene
            8   9.578    TIC    1269    1061     29.720 ppb     0.00  Pvrene
            9   10.810   TIC    96      51       0.000 ppb      0.00  Benzo(a)anthracene
          10    10.849   TIC    205     111      2.545 ppb      0.00  Chrysene
          11    12.213   TIC    271     75       2.224ppb       0.00  Benzo(b)fluoranthene
          12    12.213   TIC    271     75       5.394 ppb      0.00  Benzo(k)fluoranthene
          13    12.717   TIC    235     40       13.361 ppb     0.00  Benzo(a)pyrene
          14    12.622   TIC    123     58       66.766 ppb     0.00  Indeno(1,2,3-cd)pyrene
          15    14.629   TIC    121     32       0.000 ppb      0.00  Benzo(a,h)anthracene
          16    15.042   TIC    180     37       9.023 ppb      0.00  Benzo(ghi)perylene
```

Institutional sample

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
IJ:Yection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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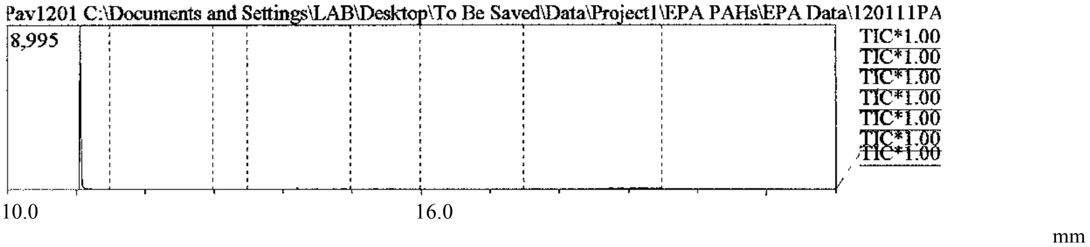

Quantitative Result Table

ID#	R.Time	mlz	Area	Height	Cone.	Conc.l Recovery	Name
1	5.059	TIC	9648	8983	354.751 ppb	0.00	Naphthalene
2	6.583	TIC	17	8	0.000 ppb	0.00	Acenaphthvlene
3	6.775	TIC	29	9	0.000 ppb	0.00	Acenaphthene
4	7.217	TIC	13	11	0.000 ppb	0.00	Fluorene
5	8.194	TIC	177	86	0.000 ppb	0.00	Phenanthrene
6	8.293	TIC	67	19	0.000 ppb	0.00	Anthracene
7	9.359	TIC	139	65	0.000 ppb	0.00	Flouranthene
8	9.579	TIC	83	41	0.000 ppb	0.00	Pyrene
9	10.808	TIC	50	7	0.000 ppb	0.00	Benzo(a)anthracene
10	10.808	TIC	50	7	0.000 ppb	0.00	Chrvsene
11	12.242	TIC	42	19	0.000 ppb	0.00	BenzO(b)fluoranthene
12	12.242	TIC	42	19	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.750	TIC	101	13	0.000 ppb	0.00	Benzo(a)pyrene
14	12.543	TIC	112	23	57.626 ppb	0.00	Indeno(l,2,3-cd)pvrene
15	14.683	TIC	39	12	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.107	TIC	25	17	0.000 ppb	0.00	Benzo(ghi)perylene

6/28/11 Institutional Paved

```
Sample Information

Analyzed Sample Type Level# Sample Name Sample ID
IS Amount Sample Amount Dilution Factor
Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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Quantitative  Result Table
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                    3    6.708     TIC      26         8          0.000  ppb      0.00  Acenaphthene
                    4    7.348     TIC      16         12         0.000  ppb      0.00  Fluorene
                    5    8.200     TIC      119        44         0.000  ppb      0.00  Phenanthrene
                    6    8.283     TIC      95         26         0.000  ppb      0.00  Anthracene
                    7    9.418     TIC      198        30         0.000  ppb      0.00  Flouranthene
                    8    9.585     TIC      207        32         0.000  ppb      0.00  Pvrene
                    9    10.875    TIC      44         8          0.000  ppb      0.00  Benzo(a)anthracene
                  10     10.875    TIC      13         5          0.000  ppb      0.00  Chrysene
                  11     12.225    TIC      33         18         0.000  ppb      0.00  Benzo(b)fluoranthene
                  12     12.225    TIC      33         18         0.000  ppb      0.00  Benzo(k)fluoranthene
                  13     12.762    TIC      31         22         0.000  ppb      0.00  Benzo(a)pyrene
                  14     12.633    TIC      85         19         35.193  ppb     0.00  Indeno(1,2,3·cd)pyrene
                  15     14.742    TIC      42         14         0.000  ppb      0.00  Benzo(a,h)anthracene
                  16     15.059    TIC      10         8          0.000  ppb      0.00  Benzo(ghi)perylene
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6/28/11 Institutional Roof

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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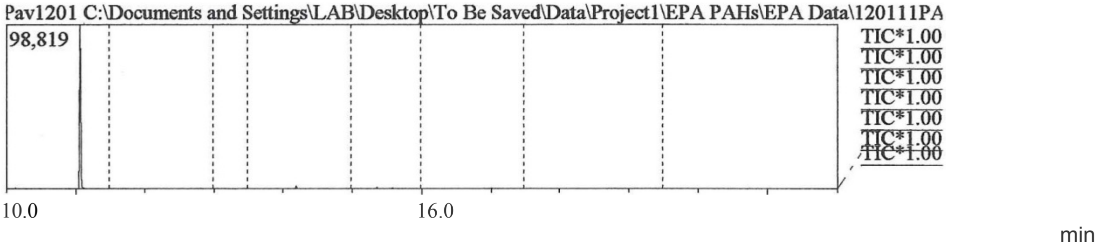

ID#	R.Time	m/z	Area	Height	Cone. Conc.l	Recovery	Name
1	5.060	TIC	103715	98766	3931.686 ppb	0.00	Naphthalene
2	6.582	TIC	22	21	O.OOOpp	0.00	Acenaphthylene
3	6.758	TIC	123	64	7.111 ppb	0.00	Acenaphthene
4	7.251	TIC	220	215	O.OOOpp	0.00	Fluorene
5	8.192	TIC	1853	1678	63.128 ppb	0.00	Phenanthrene
6	8.284	TIC	154	74	O.OOOpp	0.00	Anthracene
7	9.357	TIC	916	789	18.461 ppb	0.00	Flouranthene
8	9.578	TIC	754	507	12.902 ppb	0.00	Pvrene
9	10.849	TIC	198	82	16.465 ppb	0.00	Benzo(a)anthracene
10	10.849	TIC	198	82	2.008ppb	0.00	Chrvsene
11	12.213	TIC	135	57	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.213	TIC	135	57	0.OOOppb	0.00	Benzo(k)fluoranthene
13	12.704	TIC	97	27	O.OOOpp	0.00	Benzo(a)Q!jrene
14	12.641	TIC	162	32	99.169 ppb	0.00	Indeno(,3-cd)pvrene
15	14.617	TIC	15	9	O.OOOpp	0.00	Benzo(a, thracene
16	15.044	TIC	I11	41	O.OOOpp h	0.00	Benzo(erylene

Quantitative Result Table

6/28/11 Institutional Paved

```
Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
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Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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Quantitative Result Table
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                   1     5.061     TIC    1614    1368      49.255 ppb    0.00  Naphthalene
                     2   6.675     TIC    5       4         0.000 ppb     0.00  Acenaphthylene
                     3   6.742     TIC    37      6         0.000 ppb     0.00  Acenaphthene
                     4   7.366     TIC    34      28        0.000 ppb     0.00  Fluorene
                     5   8.195     TIC    150     83        0.000 ppb     0.00  Phenanthrene
                   6     8.242     TIC    90      42        0.000 wb      0.00  Anthracene
                     7   9.357     TIC    193     139       0.000 ppb     0.00  Flouranthene
                   8     9.578     TIC    244     131       0.000 ppb     0.00  Pyrene
                     9   10.775    TIC    21      7         0.000 ppb     0.00  Benzo(a)anthracene
                   10    10.860    TIC    113     41        0.000 ppb     0.00  Chrvsene
                   11    12.219    TIC    98      26        0.000 ppb     0.00  Benzo(b)fluoranthene
                   12    12.268    TIC    34      20        0.000 ppb     0.00  Benzo(k)fluoranthene
                   13    12.792    TIC    51      22        0.000 ppb     0.00  Benzo(a)pyrene
                   14    12.567    TIC    95      12        43.501 ppb    0.00  Indeno(1,2,3-cd)pyrene
                   15    14.609    TIC    80      13        0.000 ppb     0.00  Benzo(a,h)anthracene
                   16    15.039    TIC    21      11        0.000 ppb     0.00  Benzo(ghi)perylene
```

6/22/11 Commercial Paved

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
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Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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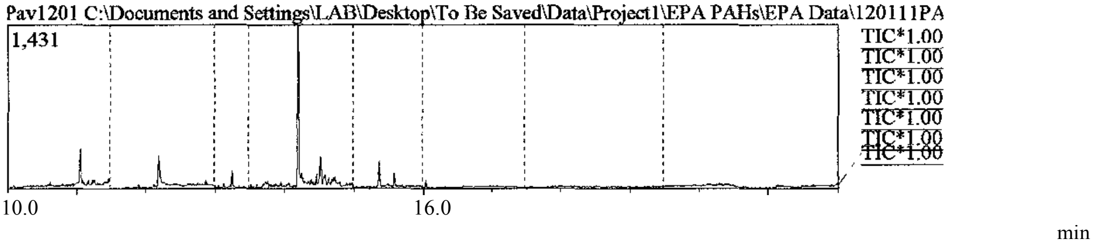

Quantitative Result Table

ID#	RTime	m/z	Area	Height	Cone. Conc	.l Recovery	Name
1	5.092	TIC	64	36	0.000 ppb	0.00	Naphthalene
2	6.571	TIC	22	14	0.000 ppb	0.00	Acenaphthylene
3	6.748	TIC	48	18	0.000 ppb	0.00	Acenaphthene
4	7.244	TIC	186	146	0.000 ppb	0.00	Fluorene
5	8.185	TIC	1995	1417	69.106 ppb	0.00	Phenanthrene
6	8.185	TIC	1995	1417	38.575 ppb	0.00	Anthracene
7	9.350	TIC	282	230	0.000 ppb	0.00	Flouranthene
8	9.573	TIC	196	130	0.000 ppb	0.00	Pyrene
9	10.783	TIC	32	9	0.000 ppb	0.00	Benzo(a)anthracene
10	10.860	TIC	35	10	0.000 ppb	0.00	Chrvsene
11	12.194	TIC	139	17	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.194	TIC	151	18	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.725	TIC	18	8	0.000 ppb	0.00	Benzo(a)pyrene
14	12.526	TIC	8	8	0.000 ppb	0.00	Indeno(1,2,3-cd)pyrene
15	14.644	TIC	91	17	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.075	TIC	26	12	0.000 ppb	0.00	Benzo(ghi)perylene

6/28/11 Residential Paved

```
Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File
Modified by
Modified

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: C:\GCMSsolution\System\110511Tune
:Admin
: 12/2/2011 12:31:39 AM

Quantitative Result Table

         ID#   R.Time   m/z   Area    Height   Cone. Conc    .l Recovery Name
         1     5.062    TIC   10514   8490     387.681 ppb   0.00  Naphthalene
           2   6.492    TIC   8       6        0.000 ppb     0.00  Acenaphthylene
         3     6.758    TIC   24      8        0.000 ppb     0.00  Acenaphthene
           4   7.254    TIC   78      18       0.000 ppb     0.00  Fluorene
           5   8.198    TIC   236     93       0.000 ppb     0.00  Phenanthrene
           6   8.198    TIC   236     93       0.000 ppb     0.00  Anthracene
           7   9.359    TIC   69      52       0.000 ppb     0.00  Flouranthene
         8     9.580    TIC   88      48       0.000 ppb     0.00  Pyrene
           9   10.858   TIC   19      8        0.000 ppb     0.00  Benzo(a)anthracene
         10    10.858   TIC   19      8        0.000 ppb     0.00  Chrvsene
         11    12.225   TIC   20      16       0.000 ppb     0.00  Benzo(b)fluoranthene
         12    12.275   TIC   40      15       0.000 ppb     0.00  Benzo(k)fluoranthene
         13    12.708   TIC   38      9        0.000 ppb     0.00  Benzo(a)pyrene
         14    12.542   TIC   143     21       83.383 ppb    0.00  Indeno(l,2,3-cd)pyrene
         15    14.659   TIC   47      12       0.000 ppb     0.00  Benzo(a,h)anthracene
         16    15.097   TIC   92      12       0.000 ppb     0.00  Benzo(ghi)perylene
```

Institutional Sample

Sample Information

Analyzed Sample Type Level# Sample Name Sample ID
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
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Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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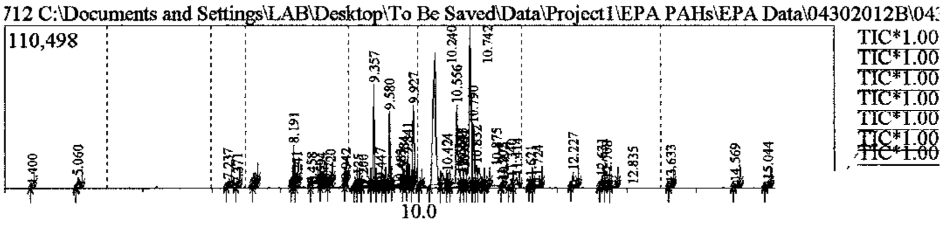

Quantitative Result Table

ID#	R.Time	m/z	Area	Height	Cone. Conc	.l Recovery	Name
1	5.060	TIC	7839	7457	285.963 ppb	0.00	Naphthalene
2	6.581	TIC	784	704	26.770 ppb	0.00	Acenaphthylene
3	6.750	TIC	445	158	56.352 ppb	0.00	Acenaphtbene
4	7.237	TIC	7181	5012	283.769 ppb	0.00	Fluorene
5	8.191	TIC	26439	29113	1098.250 ppb	0.00	Phenanthrene
6	8.241	TIC	3761	3217	80.017ppb	0.00	Anthracene
7	9.357	TIC	74286	70737	2689.583 ppb	0.00	Flourantbene
8	9.580	TIC	70859	51664	2302.179ppb	0.00	Pyrene
9	10.832	TIC	17989	12982	2980.750 ppb	0.00	Benzo(a)antbracene
10	10.875	TIC	25635	11043	1955.480 ppb	0.00	Chrysene
11	12.227	TIC	27945	10667	7153.789 ppb	0.00	Benzo(b)fluorantbene
12	12.227	TIC	27945	10667	2530.640 ppb	0.00	Benzo(k)fluorantbene
13	12.708	TIC	8732	5437	1255.094 ppb	0.00	Benzo(a)pyrene
14	12.577	TIC	39	36	0.000 ppb	0.00	lndeno(l,2,3-cd)pyrene
15	14.680	TIC	707	232	39.962 ppb	0.00	Benzo(a,h)anthracene
16	15.044	TIC	11374	4939	1587.231 ppb	0.00	Benzo(ghi)perylene

1/26/12 Institutional Paved

```
Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
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Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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Quantitative Result Table

          ID#   R.Time   rnlz   Area     Height   Cone. Conc     .l Recovery Name
          1     5.058    TIC    111811   118959   4239.540 ppb   0.00  Naphthalene
            2   6.576    TIC    38       29       0.000 ppb      0.00  Acenaphthvlene
            3   6.755    TIC    129      59       8.028 ppb      0.00  Acenaphthene
            4   7.248    TIC    374      228      5.567 ppb      0.00  Fluorene
            5   8.189    TIC    1662     1352     55.086 ppb     0.00  Phenanthrene
          6     8.300    TIC    401      75       1.170 ppb      0.00  Anthracene
            7   9.352    TIC    1029     796      22.574 ppb     0.00  Flouranthene
          8     9.575    TIC    798      653      14.339 ppb     0.00  Pvrene
            9   10.846   TIC    338      88       39.792 ppb     0.00  Benzo(a)anthracene
          10    10.846   TIC    338      88       12.759 ppb     0.00  Chrysene
          11    12.208   TIC    202      71       0.000 ppb      0.00  Benzo(b)fluoranthene
          12    12.208   TIC    202      71       0.000 ppb      0.00  Benzo(k)fluoranthene
          13    12.694   TIC    116      28       0.000 ppb      0.00  Benzo(a)pyrene
          14    12.615   TIC    172      60       107.478 ppb    0.00  Indeno(l,2,3-cd)pyrene
          15    14.657   TIC    52       18       0.000 ppb      0.00  Benzo(a,h)anthracene
          16    15.040   TIC    72       34       0.000 ppb      0.00  Benzo(ghi)perylene
```

Unknown Institutional Sample

```
Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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Quantitative Result Table

                ID#   R.Time    rnlz   Area     Height   Cone. Conc      .l Recovery Name
                1     5.058     TIC    111811   118959   4239.540 ppb    0.00  Naphthalene
                  2   6.576     TIC    38       29       0.000 ppb       0.00  Acenaphthvlene
                  3   6.755     TIC    129      59       8.028 ppb       0.00  Acenaphthene
                  4   7.248     TIC    374      228      5.567 ppb       0.00  Fluorene
                  5   8.189     TIC    1662     1352     55.086 ppb      0.00  Phenanthrene
                6     8.300     TIC    401      75       1.170 ppb       0.00  Anthracene
                  7   9.352     TIC    1029     796      22.574 ppb      0.00  Flouranthene
                8     9.575     TIC    798      653      14.339 ppb      0.00  Pvrene
                  9   10.846    TIC    338      88       39.792 ppb      0.00  Benzo(a)anthracene
                10    10.846    TIC    338      88       12.759 ppb      0.00  Chrysene
                11    12.208    TIC    202      71       0.000 ppb       0.00  Benzo(b)fluoranthene
                12    12.208    TIC    202      71       0.000 ppb       0.00  Benzo(k)fluoranthene
                13    12.694    TIC    116      28       0.000 ppb       0.00  Benzo(a)pyrene
                14    12.615    TIC    172      60       107.478 ppb     0.00  Indeno(l,2,3-cd)pyrene
                15    14.657    TIC    52       18       0.000 ppb       0.00  Benzo(a,h)anthracene
                16    15.040    TIC    72       34       0.000 ppb       0.00  Benzo(ghi)perylene
```

6/28/11 Institutional Roof

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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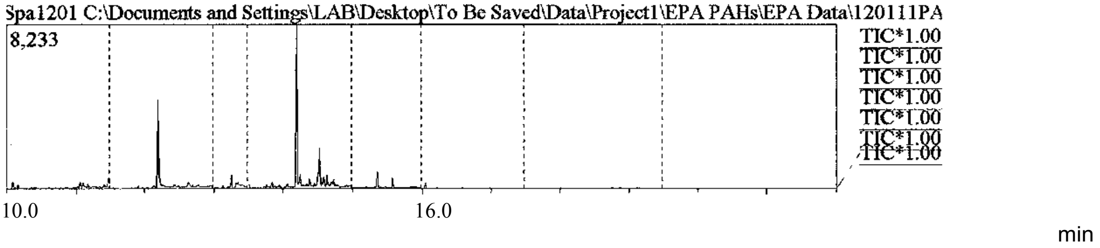

Quantitative Result Table

ID#	R.Time	m/z	Area	Height	Cone. Conc	.1 Recovery	Name
1	5.060	TIC	340	280	0.811 ppb	0.00	Naphthalene
2	6.583	TIC	108	49	0.000 ppb	0.00	Acenaphthylene
3	6.754	TIC	106	68	4.511 ppb	0.00	Acenaphthene
4	7.249	TIC	779	640	22.119 ppb	0.00	Fluorene
5	8.190	TIC	7990	8168	321.508 ppb	0.00	Phenanthrene
6	8.241	TIC	824	635	11.096 ppb	0.00	Anthracene
7	9.354	TIC	1118	843	25.815 ppb	0.00	Flouranthene
8	9.576	TIC	713	515	11.563 ppb	0.00	Pyrene
9	10.779	TIC	14	7	0.000 ppb	0.00	Benzo(a)anthracene
10	10.858	TIC	41	13	0.000 ppb	0.00	Chrysene
11	12.203	TIC	47	15	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.250	TIC	23	11	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.754	TIC	258	33	16.722 ppb	0.00	Benzo(a)pyrene
14	12.589	TIC	47	20	3.620 ppb	0.00	Indeno(1,2,3-cd)pyrene
15	14.731	TIC	57	12	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.025	TIC	85	16	0.000 ppb	0.00	Benzo(ghi)perylene

6/28/11 Institutional unknown surface

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor
Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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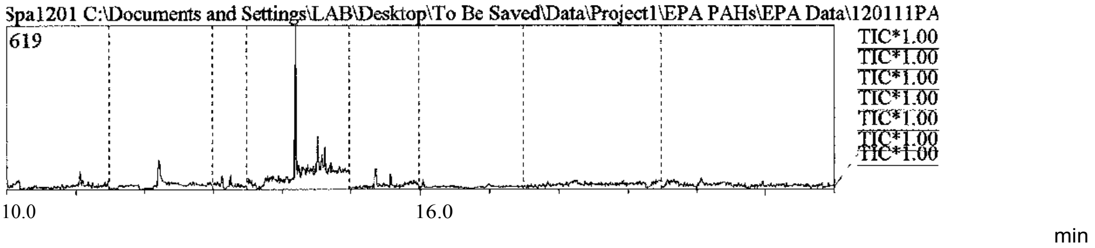

Quantitative Result Table

ID#	R.Time	m/z	Area	Height	Cone.	Conc	.1 Recovery	Name
1	5.059	TIC	137	65	0.000	ppb	0.00	Naphthalene
2	6.665	TIC	98	15	0.000	ppb	0.00	Acenaphthylene
3	6.752	TIC	19	10	0.000	ppb	0.00	Acenaphthene
4	7.248	TIC	129	54	0.000	ppb	0.00	Fluorene
5	8.191	TIC	696	587	14.415	ppb	0.00	Phenanthrene
6	8.241	TIC	87	60	0.000	ppb	0.00	Anthracene
7	9.354	TIC	123	74	0.000	ppb	0.00	Flouranthene
8	9.576	TIC	84	52	0.000	ppb	0.00	Pvrene
9	10.908	TIC	8	4	0.000	ppb	0.00	Benzo(a)anthracene
10	10.908	TIC	8	4	0.000	ppb	0.00	Chrysene
11	12.217	TIC	102	23	0.000	ppb	0.00	Benzo(b)f!uoranthene
12	12.259	TIC	37	25	0.000	ppb	0.00	Benzo(k)f!uoranthene
13	12.625	TIC	27	7	0.000	ppb	0.00	Benzo(a)pyrene
14	12.575	TIC	12	8	0.000	ppb	0.00	Indeno(1,2,3-cd)pyrene
15	14.652	TIC	23	16	0.000	ppb	0.00	Benzo(a,h)anthracene
16	15.033	TIC	47	15	0.000	ppb	0.00	Benzo(ghi)perylene

6/28/11 Institutional unknown surface

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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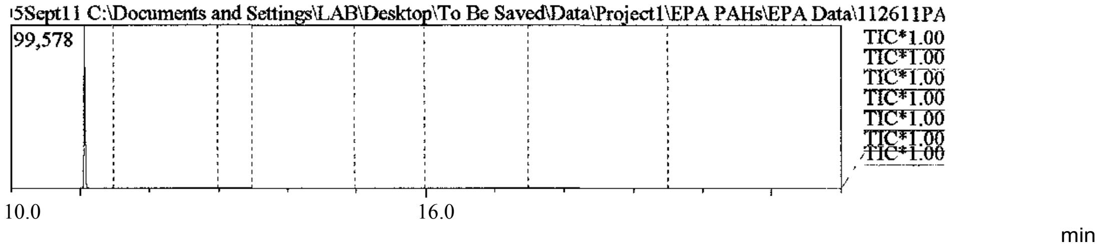

Quantitative Result Table

ID#	R.Time	m/z	Area	Height	Cone. Conc	.l Recovery	Name
1	5.067	TIC	97956	99464	3712.698 ppb	0.00	Naphthalene
2	6.583	TIC	15	15	0.000 ppb	0.00	Acenaphthylene
3	6.706	TIC	105	40	4.358 ppb	0.00	Acenaphthene
4	7.257	TIC	219	110	0.000 ppb	0.00	Fluorene
5	8.195	TIC	815	564	19.426 ppb	0.00	Phenanthrene
6	8.244	TIC	293	116	0.000 ppb	0.00	Anthracene
7	9.358	TIC	219	196	0.000 ppb	0.00	Flouranthene
8	9.581	TIC	303	114	0.000 ppb	0.00	Pyrene
9	10.854	TIC	12	9	0.000 ppb	0.00	Benzo(a)anthracene
10	10.854	TIC	12	9	0.000 ppb	0.00	Chrysene
11	12.243	TIC	33	15	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.243	TIC	33	15	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.650	TIC	108	18	0.000 ppb	0.00	Benzo(a)pyrene
14	12.535	TIC	42	21	0.000 ppb	0.00	Indeno(l,2,3-cd)pyrene
15	14.916	TIC	12	11	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.053	TIC	32	13	0.000 ppb	0.00	Benzo(ghi)perylene

9/5/11 Institutional Landscaped

Sample Infonnation

Analyzed Sample Type Level# Sample Name Sample **ill**
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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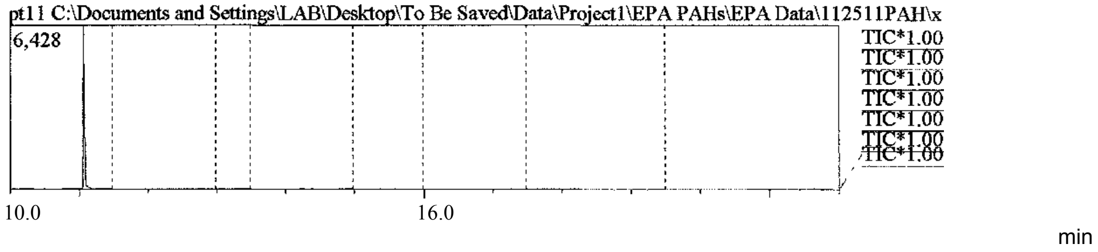

Quantitative Result Table

ID#	R.Time	m/z	Area	Height	Cone. Conc	.1 Recovery	Name
1	5.067	TIC	7102	6408	257.938 ppb	0.00	Naphthalene
2	6.457	TIC	12	8	0.000 ppb	0.00	Acenaphthvlene
3	6.457	TIC	12	8	0.000 ppb	0.00	Acenaphthene
4	7.333	TIC	11	7	0.000 ppb	0.00	Fluorene
5	8.142	TIC	45	13	0.000 ppb	0.00	Phenanthrene
6	8.250	TIC	122	28	0.000 ppb	0.00	Anthracene
7	9.365	TIC	34	22	0.000 ppb	0.00	Flouranthene
8	9.583	TIC	47	33	0.000 ppb	0.00	Pyrene
9	10.758	TIC	7	5	0.000 ppb	0.00	Benzo(a)anthracene
10	10.758	TIC	7	5	0.000 ppb	0.00	Chrysene
11	12.226	TIC	31	18	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.226	TIC	31	18	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.738	TIC	98	16	0.000 ppb	0.00	Benzo(a)pyrene
14	12.610	TIC	47	11	3.620 ppb	0.00	Indeno(l,2,3-cd)pyrene
15	14.742	TIC	87	17	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.046	TIC	101	23	0.000 ppb	0.00	Benzo(ghi)perylene

9/5/11 Institutional Landscaped

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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Quantitative Result Table
ID# R.Time *mlz*

Area

Height

Cone. Conc.l Recovery Name

1	5.061	TIC	18616	17057	695.763 ppb	0.00	Naphthalene
2	6.578	TIC	80	49	0.000 ppb	0.00	Acenaphthylene
3	6.751	TIC	210	164	20.415 ppb	0.00	Acenaphthene
4	7.250	TIC	1206	1103	39.571 ppb	0.00	Fluorene
5	8.192	TIC	8137	6580	327.697 ppb	0.00	Phenanthrene
6	8.284	TIC	124	113	0.000 ppb	0.00	Anthracene
7	9.354	TIC	1772	1377	49.624 ppb	0.00	Flouranthene
8	9.576	TIC	955	886	19.466 ppb	0.00	Pvrene
9	10.808	TIC	78	26	0.000 ppb	0.00	Benzo(a)anthracene
10	10.848	TIC	106	60	0.000 ppb	0.00	Chrvsene
11	12.218	TIC	181	46	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.218	TIC	181	46	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.740	TIC	168	42	3.570 ppb	0.00	Benzo(a)pyrene
14	12.618	TIC	53	31	8.605 ppb	0.00	Indeno(l,2,3-cd)pyrene
15	14.698	TIC	109	28	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.033	TIC	210	42	13.253 ppb	0.00	Benzo(ghi)pery!ene

1/26/12 Institutional Roof

```
Sample Infonnation

Analyzed Sample Type Level#  Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
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Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified


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Quantitative Result Table
ID#      RTime      m/z


Cone. Conc.l Recovery Name
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                     2   6.583     TIC     149       129       0.000 ppb        0.00  Acenaphthvlene
                     3   6.758     TIC     518       434       67.515 ppb       0.00  Acenaphthene
                     4   7.252     TIC     3073      2684      115.875 ppb      0.00  Fluorene
                     5   8.193     TIC     15625     14605     642.958 ppb      0.00  Phenanthrene
                     6   8.193     TIC     15625     14605     358.421 ppb      0.00  Anthracene
                     7   9.357     TIC     2920      2801      91.419 ppb       0.00  Flouranthene
                     8   9.580     TIC     1752      1282      45.492 ppb       0.00  Pvrene
                     9   10.849    TIC     223       97        20.631 ppb       0.00  Benzo(a)anthracene
                     10  10.849    TIC     223       97        3.928 ppb        0.00  Chrvsene
                     11  12.216    TIC     194       51        0.000 ppb        0.00  Benzo(b)fluoranthene
                     12  12.292    TIC     17        17        0.000 ppb        0.00  Benzo(k)fluoranthene
                     13  12.675    TIC     83        29        0.000 ppb        0.00  Benzo(a)pyrene
                     14  12.631    TIC     195       50        126.588 ppb      0.00  Indeno(1,2,3-cd)pyrene
                     15  14.701    TIC     33               9  0.000 ppb        0.00  Benzo(a,h)anthracene
                     16  15.041    TIC     96        39        0.000 ppb        0.00  Benzo(ghi)perylene
```

3/22/12 Commercial Landscaped

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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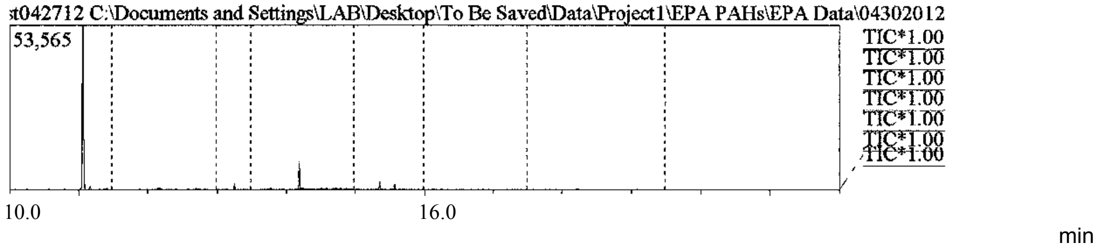

Quantitative Result Table
ID# R.Time m/z

Area

Height

Cone. Conc.l Recovery Name

1	5.059	TIC	52568	53517	1986.801 ppb	0.00	Naphthalene
2	6.580	TIC	243	200	0.311 ppb	0.00	Acenaphthylene
3	6.755	TIC	567	305	75.008 ppb	0.00	Acenaphthene
4	7.251	TIC	2348	2085	86.244 ppb	0.00	Fluorene
5	8.192	TIC	9166	9140	371.020 ppb	0.00	Phenanthrene
6	8.243	TIC	988	692	14.945 ppb	0.00	Anthracene
7	9.357	TIC	2794	2641	86.831 ppb	0.00	Flouranthene
8	9.578	TIC	2030	1619	54.570 ppb	0.00	Pvrene
9	10.810	TIC	260	187	26.796 ppb	0.00	Benzo(a)anthracene
10	10.850	TIC	427	241	19.594 ppb	0.00	Chrysene
11	12.215	TIC	688	217	109.986 ppb	0.00	Benzo(b)fluoranthene
12	12.215	TIC	690	217	43.627 ppb	0.00	Benzo(k)fluoranthene
13	12.701	TIC	242	106	14.384 ppb	0.00	Benzo(a)pyrene
14	12.618	TIC	275	155	193.056 ppb	0.00	Indeno(l,2,3-cd)pyrene
15	14.708	TIC	35	14	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.035	TIC	270	86	21.712 ppb	0.00	Benzo(ghi)perylene

1/26/12 Institutional Landscaped

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor
Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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Quantitative Result Table

ID#	R.Time	m/z	Area	Height	Cone. Conc	.l Recovery	Name
1	5.059	TIC	6926	6510	251.246 ppb	0.00	Naphthalene
2	6.575	TIC	353	220	5.691 ppb	0.00	Acenaphthylene
3	6.748	TIC	505	382	65.527 ppb	0.00	Acenaphthene
4	7.250	TIC	1341	1157	45.088 ppb	0.00	Fluorene
5	8.189	TIC	4688	3993	182.487 ppb	0.00	Phenanthrene
6	8.239	TIC	1302	769	22.313 ppb	0.00	Anthracene
7	9.358	TIC	1229	1308	29.856 ppb	0.00	Flouranthene
8	9.576	TIC	1028	795	21.850 ppb	0.00	Pyrene
9	10.808	TIC	71	52	0.000 ppb	0.00	Benzo(a)anthracene
10	10.847	TIC	191	123	1.470 ppb	0.00	Chrysene
11	12.200	TIC	204	52	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.200	TIC	204	52	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.683	TIC	552	130	59.687 ppb	0.00	Benzo(a)pyrene
14	12.583	TIC	200	25	130.742 ppb	0.00	Indeno(l,2,3-cd)pyrene
15	14.667	TIC	39	20	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.067	TIC	69	33	0.000 ppb	0.00	Benzo(ghi)perylene

9/5/11 Residential Landscaped

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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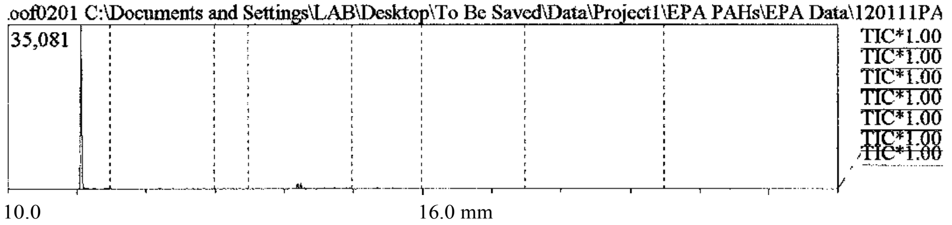

Quantitative Result Table

ID#	R.Time	m/z	Area	Height	Cone. Conc	.l Recovery	Name
1	5.059	TIC	34752	35037	1309.341 ppb	0.00	Naphthalene
2	6.578	TIC	35	25	0.000 ppb	0.00	Acenaphthylene
3	6.756	TIC	62	26	0.000 ppb	0.00	Acenaphthene
4	7.250	TIC	148	130	0.000 ppb	0.00	Fluorene
5	8.191	TIC	1250	1155	37.740 ppb	0.00	Phenanthrene
6	8.241	TIC	1175	1072	19.333 ppb	0.00	Anthracene
7	9.355	TIC	484	389	2.733 ppb	0.00	Flouranthene
8	9.576	TIC	361	316	0.069 ppb	0.00	Pyrene
9	10.835	TIC	66	34	0.000 ppb	0.00	Benzo(a)anthracene
10	10.835	TIC	66	34	0.000 ppb	0.00	Chrvsene
11	12.199	TIC	101	26	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.250	TIC	35	15	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.692	TIC	61	27	0.000 ppb	0.00	Benzo(a)pyrene
14	12.629	TIC	120	21	64.273 ppb	0.00	Indeno(1,2,3-cd)pyrene
15	14.718	TIC	109	17	0.000 ppb	0.00	Benzo(a,h)anthracene
16	14.992	TIC	185	18	9.728 ppb	0.00	Benzo(ghi)perylene

6/28/11 Residential Roof

Sample Information

Analyzed Sample Type Level# Sample Name SampleiD
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
Tuning File Modified by Modified

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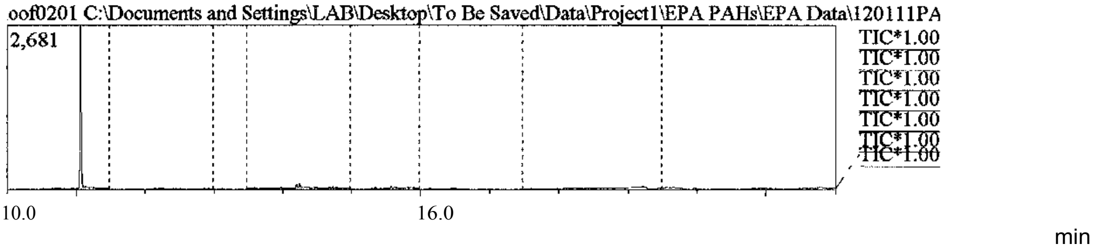

Quantitative Resuh Table

ID#	R.Time	mlz	Area	Height	Cone. Conc	.l Recovery	Name
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2	6.492	TIC	35	9	0.000 ppb	0.00	Acenaphthvlene
3	6.701	TIC	11	7	0.000 ppb	0.00	Acenaphthene
4	7.258	TIC	25	16	0.000 ppb	0.00	Fluorene
5	8.197	TIC	122	63	0.000 ppb	0.00	Phenanthrene
6	8.247	TIC	142	76	0.000 ppb	0.00	Anthracene
7	9.357	TIC	72	42	0.000 ppb	0.00	Flouranthene
8	9.582	TIC	124	40	0.000 ppb	0.00	Pyrene
9	10.868	TIC	62	11	0.000 ppb	0.00	Benzo(a)anthracene
10	10.868	TIC	62	11	0.000 ppb	0.00	Chrysene
11	12.242	TIC	73	30	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.242	TIC	73	30	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.733	TIC	18	9	0.000 ppb	0.00	Benzo(a)pyrene
14	12.533	TIC	14	14	0.000 ppb	0.00	Indeno(1,2,3-cd)pyrene
15	14.626	TIC	38	14	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.097	TIC	23	7	0.000 ppb	0.00	Benzo(ghi)perylene

6/28/11 Residential Roof

Sample Information

Analyzed Sample Type Level# Sample Name Sample i ll
IS Amount Sample Amount Dilution Factor Vial#
Injection Volume
Data File
Org Data File
Method File
Org Method File
Report File
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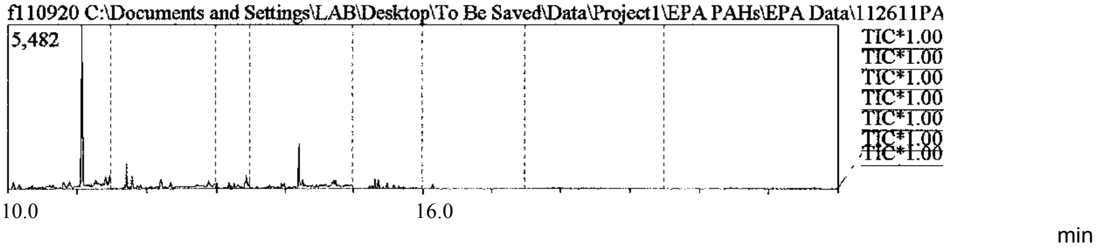

Quantitative Result Table

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3	6.707	TIC	359	85	43.200 ppb	0.00	Acenaphtbene
4	7.258	TIC	202	165	0.000 ppb	0.00	Fluorene
5	8.197	TIC	1685	1491	56.054 ppb	0.00	Phenanthrene
6	8.249	TIC	431	282	1.874 ppb	0.00	Anthracene
7	9.360	TIC	342	318	0.000 ppb	0.00	Flourantbene
8	9.583	TIC	256	154	0.000 ppb	0.00	Pvrene
9	10.843	TIC	76	29	0.000 ppb	0.00	Benzo(a)anthracene
10	10.843	TIC	76	29	0.000 ppb	0.00	Chrvsene
11	12.250	TIC	112	25	0.000 ppb	0.00	Benzo(b)fluorantbene
12	12.250	TIC	112	25	0.000 ppb	0.00	Benzo(k)fluorantbene
13	12.717	TIC	102	17	0.000 ppb	0.00	Benzo(a)pyrene
14	12.567	TIC	34	17	0.000 ppb	0.00	Indeno(l,2,3-cd)pyrene
15	14.658	TIC	35	16	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.036	TIC	101	15	0.000 ppb	0.00	Benzo(ghi)perylene

9/20/11 Residential Roof

Sample Information

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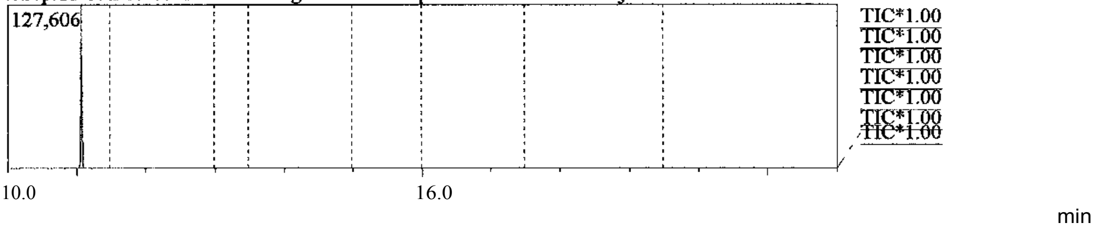

Quantitative Result Table

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2	6.581	TIC	30	26	0.000 ppb	0.00	Acenaphthylene
3	6.758	TIC	40	33	0.000 ppb	0.00	Acenaphthene
4	7.252	TIC	212	126	0.000 ppb	0.00	Fluorene
5	8.193	TIC	903	834	23.131 ppb	0.00	Phenanthrene
6	8.243	TIC	224	168	0.000 ppb	0.00	Anthracene
7	9.357	TIC	392	267	0.000 ppb	0.00	Flouranthene
8	9.579	TIC	230	147	0.000 ppb	0.00	Pvrene
9	10.850	TIC	35	12	0.000 ppb	0.00	Benzo(a)anthracene
10	10.850	TIC	35	12	0.000 ppb	0.00	Chrysene
11	12.241	TIC	239	53	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.241	TIC	239	53	2.474 ppb	0.00	Benzo(k)fluoranthene
13	12.667	TIC	10	9	O.OOOppb	0.00	Benzo(a)pyrene
14	12.569	TIC	57	18	11.929 ppb	0.00	Indeno(l,2,3-cd)pyrene
15	14.669	TIC	20	7	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.049	TIC	248	31	18.610 ppb	0.00	Benzo(ghi)perylene

9/20/11 Residential Landscaped

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Sample Information

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Method File
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                  3   6.758    TIC   55       32       0.000 ppb      0.00  Acenaphthene
                  4   7.257    TIC   210      157      0.000 ppb      0.00  Fluorene
                5     8.197    TIC   1007     765      27.509 ppb     0.00  Phenanthrene
                6     8.247    TIC   229      174      0.000 ppb      0.00  Anthracene
                7     9.359    TIC   399      337      0.000 ppb      0.00  Flouranthene
                8     9.582    TIC   263      215      0.000 ppb      0.00  Pyrene
                  9   10.847   TIC   41       18       0.000 ppb      0.00  Benzo(a)anthracene
                10    10.847   TIC   41       18       0.000 ppb      0.00  Chrvsene
                11    12.210   TIC   127      26       0.000 ppb      0.00  Benzo(b)fluoranthene
                12    12.210   TIC   138      28       0.000 ppb      0.00  Benzo(k)fluoranthene
                13    12.742   TIC   32       14       0.000 ppb      0.00  Benzo(a)pyrene
                14    12.592   TIC   37       17       0.000 ppb      0.00  Indeno(1,2,3-cd)pyrene
                15    14.717   TIC   21             6  0.000 ppb      0.00  Benzo(a,h)anthracene
                16    15.054   TIC   113      19       0.000 ppb      0.00  Benzo(ghi)perylene
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9/20/11 Residential Paved

Sample Information

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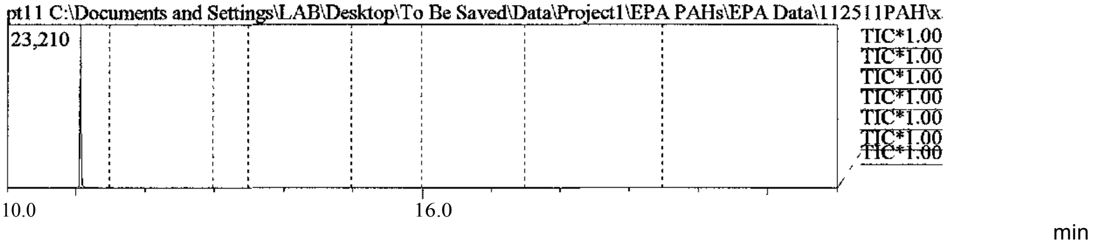

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2	6.584	TIC	38	11	0.000 ppb	0.00	Acenaphthylene
3	6.733	TIC	19	6	0.000 ppb	0.00	Acenaphthene
4	7.342	TIC	120	13	0.000 ppb	0.00	Fluorene
5	8.199	TIC	177	117	0.000 ppb	0.00	Phenanthrene
6	8.251	TIC	60	33	0.000 ppb	0.00	Anthracene
7	9.360	TIC	98	41	0.000 ppb	0.00	Flouranthene
8	9.598	TIC	108	18	0.000 ppb	0.00	Pvrene
9	10.833	TIC	40	11	0.000 ppb	0.00	Benzo(a)anthracene
10	10.833	TIC	40	11	0.000 ppb	0.00	Chrvsene
11	12.249	TIC	223	33	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.249	TIC	223	33	1.014 ppb	0.00	Benzo(k)fluoranthene
13	12.767	TIC	35	9	0.000 ppb	0.00	Benzo(a)pyrene
14	12.617	TIC	44	9	1.128 ppb	0.00	Indeno(1,2,3-cd)pyrene
15	14.668	TIC	59	13	0,000 ppb	0.00	Benzo(a,h)anthracene
16	15.075	TIC	46	13	0.000 ppb	0.00	Benzo(ghi)pezylene

9/20/11 Residential Landscaped

Sample Information

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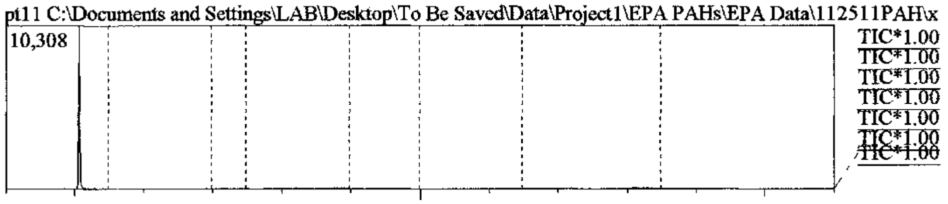

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3	6.758	TIC	34	7	0.000 ppb	0.00	Acenaphthene
4	7.258	TIC	117	22	0.000 ppb	0.00	Fluorene
5	8.201	TIC	150	53	0.000 ppb	0.00	Phenanthrene
6	8.201	TIC	120	49	0.000 ppb	0.00	Anthracene
7	9.261	TIC	22	13	0.000 ppb	0.00	Flouranthene
8	9.582	TIC	164	23	0.000 ppb	0.00	Pvrene
9	10.883	TIC	7	5	0.000 ppb	0.00	Benzo(a)anthracene
10	10.883	TIC	7	5	0.000 ppb	0.00	Chrysene
11	12.196	TIC	91	31	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.290	TIC	108	26	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.768	TIC	102	23	0.000 ppb	0.00	Benzo(a)pyrene
14	12.567	TIC	76	16	27.715 ppb	0.00	Indeno(1,2,3-cd)pyrene
15	14.625	TIC	7	0	0.000 ppb	0.00	Benzo(a,h)anthracene
16	14.983	TIC	21	5	0.000 ppb	0.00	Benzo(ghi)perylene

9/20/11 Residential Landscaped

Sample Information

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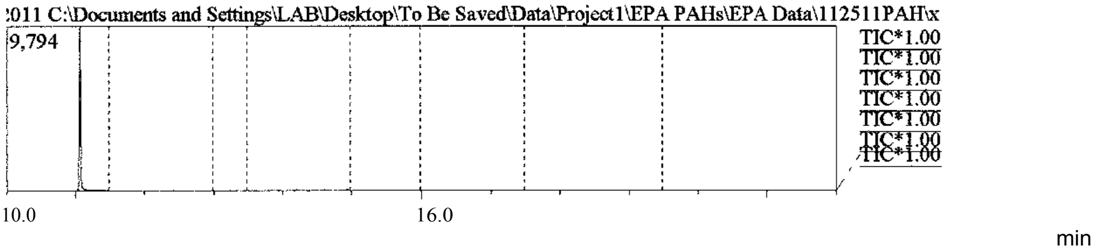

Quantitative Result Table

ID#	R.Time	m/z	Area	Height	Cone. Conc	.1 Recovery	Name
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2	6.509	TIC	10	9	0.000 ppb	0.00	Acenaplrthylene
3	6.792	TIC	5	4	0.000 ppb	0.00	Acenaphthene
4	7.313	TIC	42	11	0.000 ppb	0.00	Fluorene
5	8.200	TIC	75	47	0.000 ppb	0.00	Phenanthrene
6	8.249	TIC	68	24	0.000 ppb	0.00	Anthracene
7	9.365	TIC	23	18	0.000 ppb	0.00	Flouranthene
8	9.583	TIC	66	27	0.000 ppb	0.00	Pvrene
9	10.918	TIC	126	17	4.469 ppb	0.00	Benzo(a)anthracene
10	10.918	TIC	126	17	0.000 ppb	0.00	Chrvsene
11	12.217	TIC	60	15	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.217	TIC	60	15	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.708	TIC	63	14	0.000 ppb	0.00	Benzo(a)pyrene
14	12.661	TIC	126	13	69.258 ppb	0.00	Indeno(1,2,3-cd)pvrene
15	14.679	TIC	69	10	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.033	TIC	20	6	0.000 ppb	0.00	Benzo(ghi)perylene

9/20/11 Residential Paved

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Quantitative Result Table

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2	6.580	TIC	60	38	0.000 ppb	0.00	Acenaphthvlene
3	6.756	TIC	29	23	0.000 ppb	0.00	Acenaphthene
4	7.280	TIC	27	21	0.000 ppb	0.00	Fluorene
5	8.193	TIC	701	630	14.626 ppb	0.00	Phenanthrene
6	8.242	TIC	169	125	0.000 ppb	0.00	Anthracene
7	9.357	TIC	226	190	0.000 ppb	0.00	Flouranthene
8	9.579	TIC	235	125	0.000 ppb	0.00	Pvrene
9	10.854	TIC	98	19	0.000 ppb	0.00	Benzo(a)anthracene
10	10.854	TIC	98	19	0.000 ppb	0.00	Chrvsene
11	12.217	TIC	62	22	0.000 ppb	0.00	Benzo(b)fluoranthene
12	12.265	TIC	70	19	0.000 ppb	0.00	Benzo(k)fluoranthene
13	12.751	TIC	129	31	0.000 ppb	0.00	Benzo(a)pyrene
14	12.624	TIC	177	32	111.632 ppb	0.00	Indeno(1,2,3-cd)pvrene
15	14.592	TIC	119	27	0.000 ppb	0.00	Benzo(a,h)anthracene
16	15.046	TIC	70	23	0.000 ppb	0.00	Benzo(ghi)perylene

9/5/11 Residential Landscaped

Appendix I. Other PAH Sources and Fate Data

Pavement Leaching Test Data

Preparing Hot-Mix Asphalt Specimens (HMA) by Means of the Rolling Slab Compactor

Apparatus

1.1 Rolling Slab Compactor – A rolling compactor with a hydraulically lifted platform. The lift platform shall have a pressure gage capable of measuring pressure up to 3,000 psi. The platform shall be capable of being uniformly lifted (manually or automatically) across the bottom of the platform.
1.2 Specimen Mold – A rectangular, 2-piece, steel mold with walls at least 9 mm thick. When the mold is assembled it shall have inside dimensions of 510 mm by 507 mm. It shall have a height of 228 mm. The dimension perpendicular to the side marked “Front” is the length dimension specified in Section 3.1.
1.3 Base Insert Frame – A steel framed spacer with dimensions of 509 mm by 506 mm by 40 mm.
1.4 Thick Insert Plates – Steel plates with dimensions of 509 mm by 506 mm by 10 mm.
1.5 Thin Insert Plates – Steel plates with dimensions of 509 mm by 506 mm by 3 mm.
1.6 Vertical Kneading Plates – Steel plates that go on top of mix that are 105 mm by 10 mm by 505 mm. They are 105 mm tall when standing on their 10 mm side. There are 49 of the 10 mm kneading plates and one 3 mm thick plate.
1.7 Wax Paper – Paper coated with wax so the HMA will not stick to it.
1.8 Metal Partition – A metal partition capable of dividing the mix into four quadrants.
1.9 Mix Transfer Funnel – A metal device with a tapered end capable of transferring mix from pans into the four quadrants created by the splitter.
1.10 Thermometers – Armored, glass, or dial type thermometers with metal stems for determining the temperature of aggregates, binder, and HMA up to 204 °C and readable to 1°C.
1.11 Balance – A balance meeting the requirements of AASHTO M 231, Class G 5, for determining the mass of aggregates, binder, and HMA.
1.12 Oven – An oven thermostatically controlled to ±3°C, for heating aggregates, binder, HMA, and equipment as required. The oven shall be capable of maintaining the temperature required for mixture conditioning in accordance with AASHTO R 30.
1.13 Miscellaneous – Flat bottom scoop, large trowel, vice grips, rubber mallet, screw driver and mechanical jack.

Equipment Preparation

2.1 Determine the number of insert plates needed to achieve desired slab thickness. Table I-1 shows plates needed to achieve different thicknesses.

Table I-1: Number of base plates required to reach desired slab thickness

Slab Ht. (mm)	Frame	10 mm plates	3 mm plates
113.3	no	1	0
110.0	no	1	1
103.8	no	2	0
100.5	no	2	1
94.3	no	3	0
91.0	no	3	1
79.9	yes	0	1
73.7	yes	1	0
70.4	yes	1	1
64.2	yes	2	0
60.9	yes	2	1
54.7	yes	3	0
51.4	yes	3	1
45.2	yes	4	0
41.9	yes	4	1

2.2 Cut two pieces of wax paper, one for the top and one for the bottom, to fit in mold by using one of the insert base plates as a template.

2.3 Place assembled mold, base plates, and partition in an oven set to the desired compaction temperature a minimum of 30 minutes prior to compaction.

Material Preparation

3.1 Determine mass of total mix needed to achieve desired height and air voids (usually target 7%). Equation 1 shows how to calculate total mix mass.

$$m_T = (lwt)(G_{mm} * \rho_w)\left[\frac{(100 - \%V_a)}{100}\right]$$

where:

m_T = total mass of slab in g;
l = length of slab, 509.5 mm;
w = width of slab, 506.5 mm;
t = desired thickness of slab in mm;
G_{mm} = theoretical maximum specific gravity of the mix;
V_a = desired percent air voids of slab, usually 7%;
ρ_w = density of water, 0.001 g/mm^3.

3.2 Prepare four separate batches. Determine the total mass of each batch by dividing m_T by four.

3.3 Mix each batch separately and set aside.

3.4 Place all 4 pans in oven for two hours at 300°F, or the desired compaction temperature, in accordance with AASHTO R 30.

3.5 For specimens using field mix, sample according to AASHTO T 168. Reduce the mix to batch size using Method B in AASHTO T 328.

Procedure

4.1 When the compaction temperature of the mix is achieved, remove the heated mold and assemble it on the mechanical jack with the side marked “Front” facing the jack.
4.2 Place base frame in mold. Place base plates in mold.
4.3 On the top base plate, place a piece of pre-cut wax paper.
4.4 Place the metal partition on top of the wax paper. Pour mix from one pan into the mix transfer funnel, then into one quadrant. Pour the next into the mix transfer funnel and then into the quadrant diagonally across from the first quadrant. Repeat for the other two pans.
4.5 Carefully remove the metal partition from the mix.
4.6 Spade the mix with a large trowel until the mix is at a relatively uniform depth. Then level the mix out with the trowel, taking care not to segregate the mix. The mix should be kept in the vicinity of the quadrant in which it was poured.
4.7 Place the other piece of wax paper on top of the leveled mix.
4.8 Place 49 vertical kneading plates on the mix, taking care not to wrinkle the paper or move the mix. Put the plates in simultaneously from each side. The plates should be orientated perpendicular to the front of the compaction mold. The rubber mallet may be required to get the last plate in the mold.
4.9 Move specimen mold to the rolling compactor using the mechanical jack. Adjust the jack platform with the specimen mold until it is level with the compactor platform. Slide the mold onto the compactor’s platform with one person guiding from behind the compactor and one person pushing from the front. Do this in one uniform motion. Take care not to let the frame or bottom plate slip out of the bottom of the mold.
4.10 Once mold is set on the platform make sure the entire base of the mold is touching the platform. The rubber mallet may be needed here.
4.11 Turn hydraulic valves to the closed position and turn the roller on. Lift the mold and platform to the roller by pumping the hydraulic handle.
4.12 When the top of the kneading plates reaches the roller, stop pumping the handle and let the roller roll atop the kneading plates. Now only pump the handle when the roller is at the ends of the mold. This will pick up the other end of the mold. Slightly pump the handle each time the roller goes to the end without letting the pressure go above 1200 psi. If the pressure is increasing too rapidly, let out a small amount of pressure using the hydraulic valves. Continue gradually lifting the compaction platform until the kneading plates are level with the top of the mold.
4.13 Stop the roller and release the pressure so that the platform is lowered.
4.14 Slide specimen mold back onto the mechanical jack. One person should hold the jack against the compactor platform while the other pushes the mold from the back of the compactor at the same time.

4.15 Remove the kneading plates. A screw driver and vise grips shall be used to pull the first couple of plates out. The plates should be removed starting in the middle and working out to each side simultaneously.
4.16 Slide the mold onto a counter and let it cool in front of a fan for a minimum of one hour before removing the mold. Do not handle the slab before it reaches room temperature.
4.17 Once the slab has cooled to room temperature, flip the slab over and remove the wax paper from the bottom. The bottom of the slab is the ideal side for most testing.
4.18 The slab should be stored on a rigid plate such as a 1-inch thick piece of plywood to protect against deformation. Never stack slabs or leave on a non-flat surface.

Microtox Screening Procedure

The Microtox Screening Procedure makes use of a lyophilized preparation of bioluminescent marine bacteria, Vibrio fischeri, to measure the toxicity of a sample relative to a control sample. Readings are taken four times during the 45 minute run. At each of the four reading times, the light output of each sample and each control is measured on a scale of 0 to 100 and recorded (only the first three readings are recorded by the MicrotocOmni software).

V. fisheri emits light as a byproduct of respiration and if a water sample contains one or more components that interfere with the respiration, then the bacteria’s light output is reduced proportionally to the amount of interference with respiration, or toxicity. The light output reduction is proportional to the toxicity of the sample. The relative toxicity of a sample to the control can then be calculated. These relative toxicities can be compared to toxicity test results using standard reagents.

Apparatus

- Microtox Model 500 Analyzer and MicrotoxOmni software
- Eppendorf repeater 4780 pipettor (with tips) or 10 µl pipettor (with disposable tips)
- 500 µl pipettor or an adjustable 100-1000 µl pipettor (with disposable tips)
- Glass cuvettes
- Plastic weighing cups

Reagents

- Microtox bacterial reagent
- Microtox reconstitution solution
- Microtox diluent
- Reagent grade Sodium Chloride
- Hydrated Zinc Sulfate or crystalline Phenol standards

Sample preparation

Note: Microtox instrument has space in its incubator for 30 cuvettes. For a normal run, three of the cuvettes (A1, A2 and A3) are reserved for the control solution. The next three of the remaining 27 cuvettes is reserved for the 0.75 mg/l of $ZnSO_4 \cdot 7H_2O$ EC50 standard solution, followed by three cuvettes for 5 mg/l of Phenol EC50 standard solution. The EC50 values where the toxicities are reduced by 50% were determined during the calibration of the instrument. The remaining 23 cuvettes contain the samples to be tested.

1. Weighing cups were labels according to the samples.
2. 3 gms of Nacl was weighed into the weigh cups.
3. The sample vial was inverted several times before adding the adding sample to the weighing cups.
4. 10 ml of the sample was added to the respective weighing cup and using a separate eppendorf tip for each sample and the sample and salt were mixed using the eppendorf tip until the salt is completely dissolved.

Alternatively, your samples maybe stored in the 40 ml sample vials immediately after collection and stored for up to one week at 4°C. Do not add salt to the vials until you are ready to run the Microtox test. Fill the vial up completely so that there is no head space above the sample water. Then, when ready to run the Microtox procedure, invert the vial a few times, pour out some of the sample, and add 0.2 g of NaCl per 10 ml of sample.

Logging on to the computer program and database (optional):

1. On the computer desktop, open up the MicrotoxOmni program (icon is solid blue triangle).
2. Username: MANAGER
Password: MANAGER
Be sure to enter both in all capital letters.
3. On the next screen, choose cancel.
4. Choose “Data Capture Test” under the Options menu. This is to ensure the Analyzer and the computer is communicating with each other properly.
5. Select Acute mode and click READ.
6. If the screen says anything other than “Ready to Receive Data”, check the connections on the back of the computer.
7. Click cancel.
8. Under the Test menu or from the toolbar, choose “Run Test” and select the screen.mtt template based on the WET screening protocol.
9. Click NEXT.
10. Leave all default setting as they are unless you are specifically instructed to change them. Only the number of samples should need to be changed.
11. Click Next.
12. Enter your sample name and click OK.

13. Here you will see a display of the wells which are color-coded according to the number of controls and samples. The standards are also recognized by the program as samples. DO NOT press the space bar until you are ready to add the Microtox reagent to begin the test.

Preparation of Apparatus

1. Any cuvettes in the Incubator and REAGENT slots from earlier experiments were discarded.
2. New cuvettes were placed into the REAGENT slot and into the incubator slots (3 for controls and 6 for standards and the remaining for the samples). All the cuvettes were rinsed in 18 mega ohm water five time and air dried before use in the experiment.
3. 1 ml of the Reconstitution Solution was added to the cuvette in the REAGENT position.
4. A timer was set for 5 minutes to allow for temperature stabilization of the Reconstitution Solution.
5. Meanwhile 1 ml of Diluent was pipetted into the cuvettes in the positions A1, A2 and A3.
6. 1 ml of the standard solutions, 0.75 mg/l of Zinc Sulfate and 5mg/l of Phenol was pippetted into the cuvette in positions A4, A5, B1, B2, B3 and B4.
7. 1 ml of each of the samples (already adjusted for salinity, as specified above) were pipetted into the cuvettes in position B5 through F5 depending on the number of samples.
8. The Mictrotox Reagent bacterium was then removed from the freezer. (Must be stored prior to use in a freezer no warmer than -20°C).
9. The reagent vial was tapped gently on the countertop several times to break up the contents.
10. After the 5 minute temperature stabilization period has expired, the vial was opened.
11. The Reconstituion Solution was poured into the REAGENT slot into the reagent vial. The contents were swirled ensured its mixed (all solid reagent should go into solution).
12. The bacterium solution in the reagent vial was mixed using a 500 µl pipette, for 10 times.
13. A timer was set for 15 minutes.

Analysis of Samples

1. The reagent was then added to the controls, standards and samples, using a 10 µl repeating pipettor.
2. After the reagent is added to all the vials the solution in each of the vials was mixed 3 times, with a 500 µl pipettor, using a new pipette tip each time.
3. It takes approximately 5 min to finish with the mixing in each of the vials.
4. The cuvettes were then placed in the reading slot and the reading was noted for each of the cuvettes at the end of 5, 15, 25 and 45 minutes.
5. The values so recorded were then used to calculate the % toxicity.

Washoff Data

Nutrients in Pavement Runoff

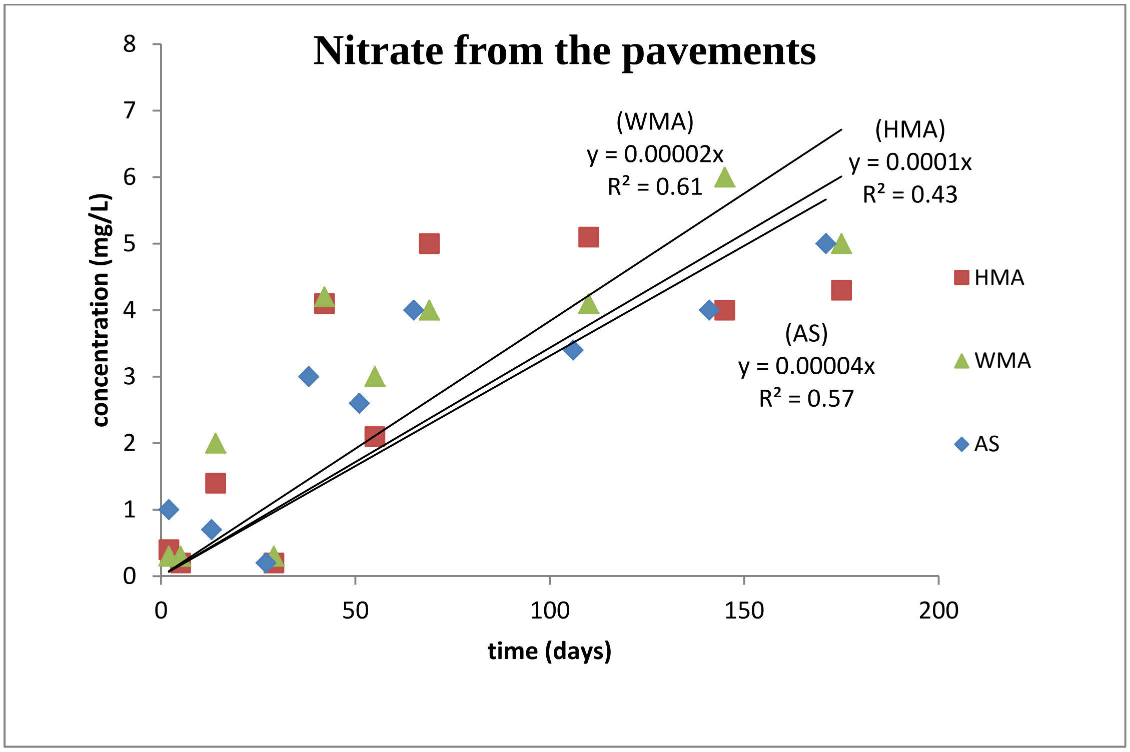


Figure I-1. Nitrate loss from the pavements with the aging of the pavements

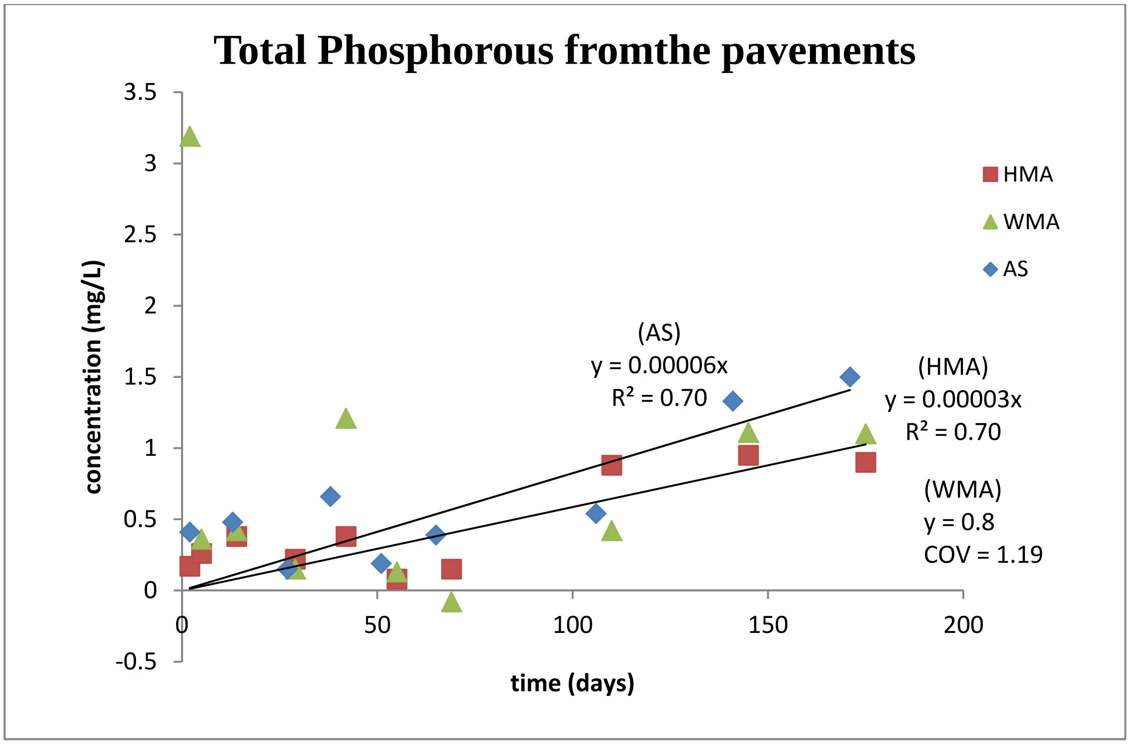


Figure I-2. Total Phosphorous from the pavements with time.

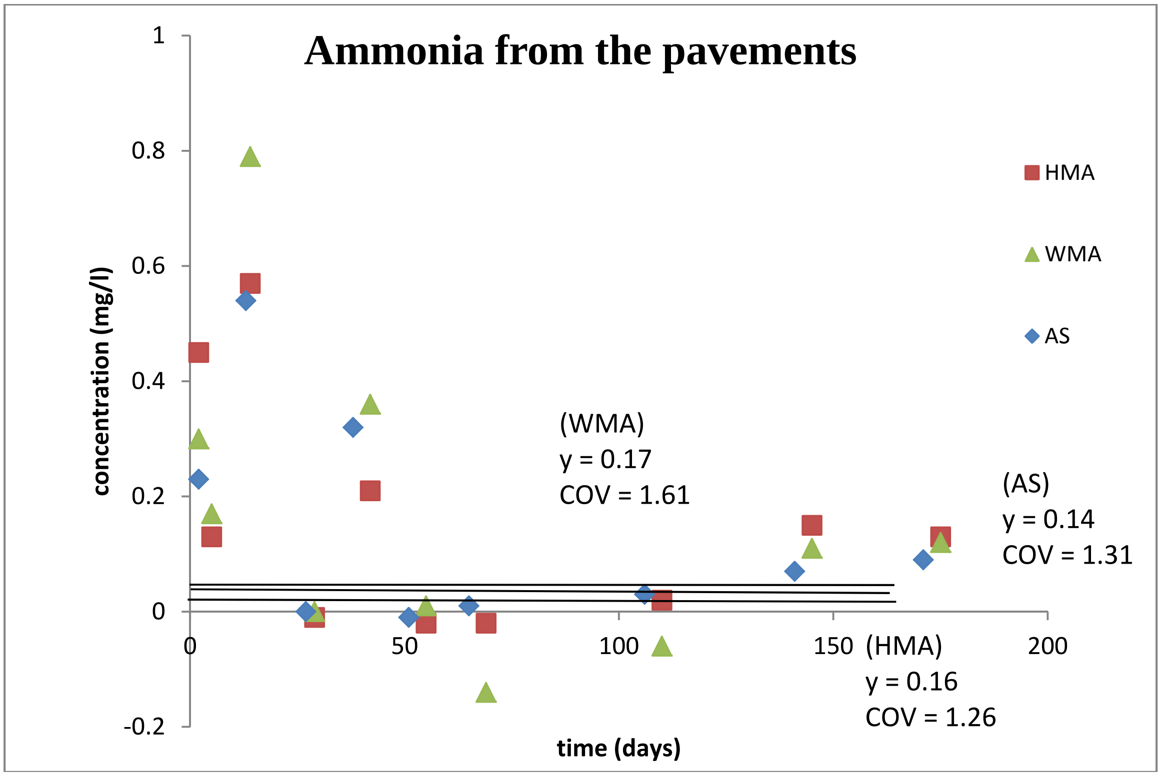


Figure I-3. Ammonia from the pavements with time.

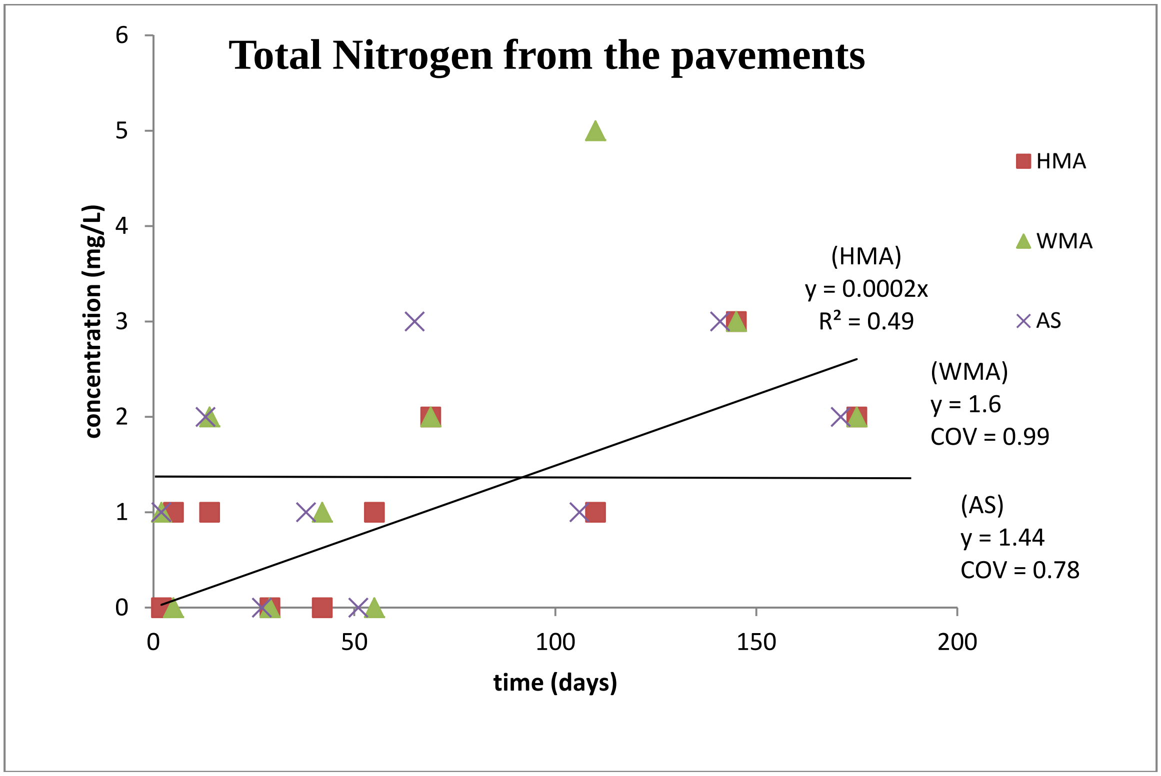


Figure I-4. Total Nitrogen from the pavements with time

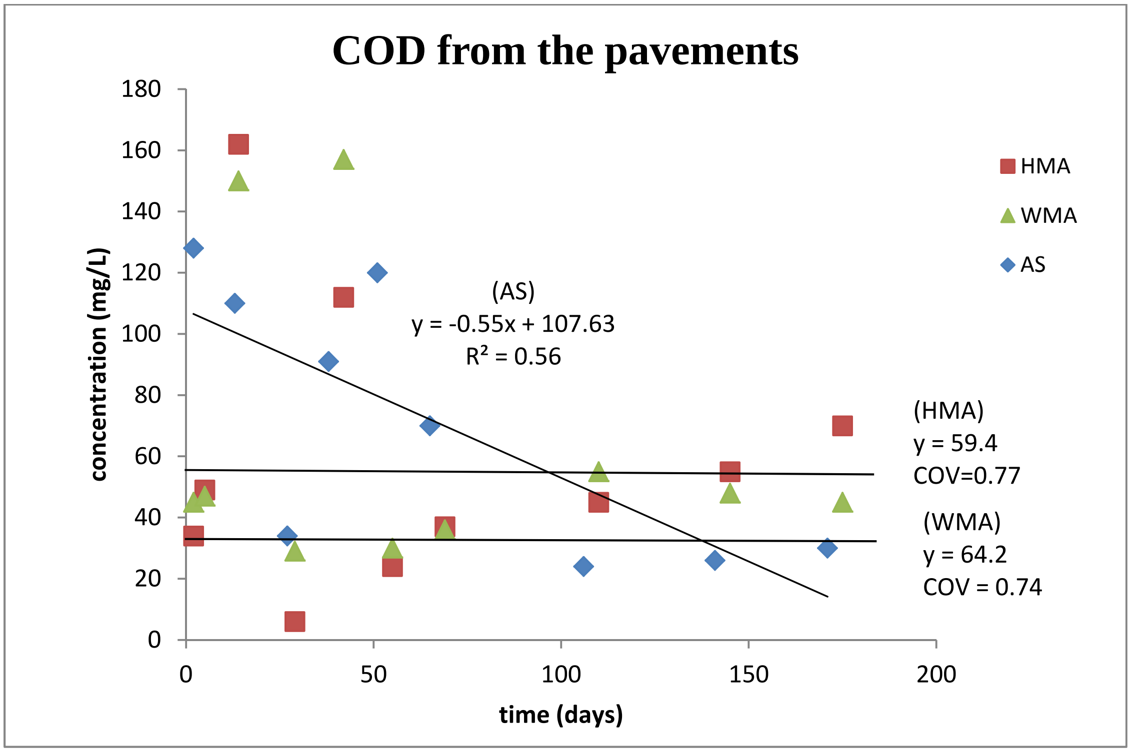


Figure I-5. COD from the pavements with time.

Detergents in Pavement Runoff

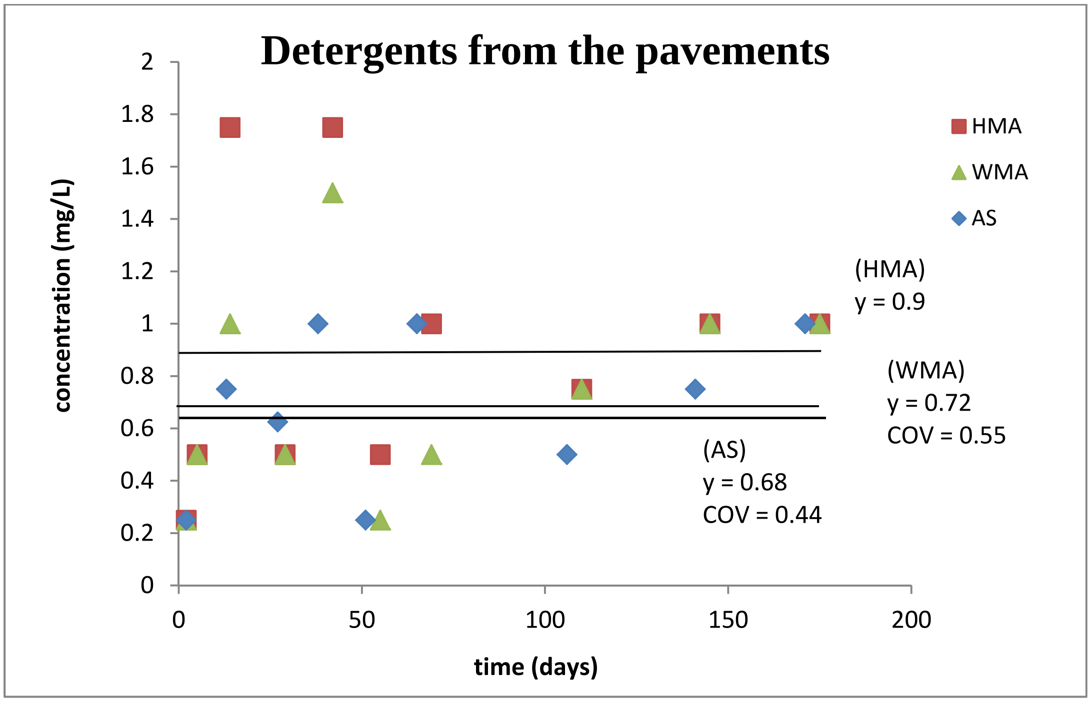


Figure I-6. Detergent release from the pavements with aging.

Heavy Metals in Pavement Runoff

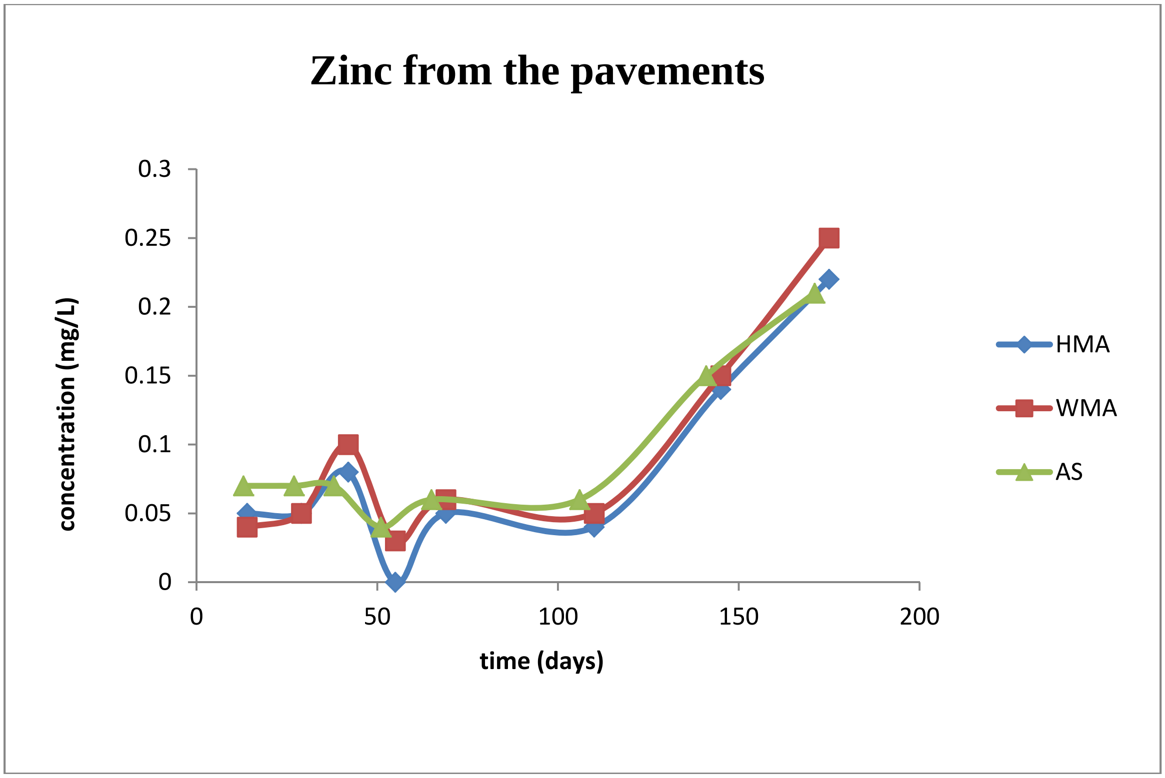


Figure I-7. Zinc from the pavements with time

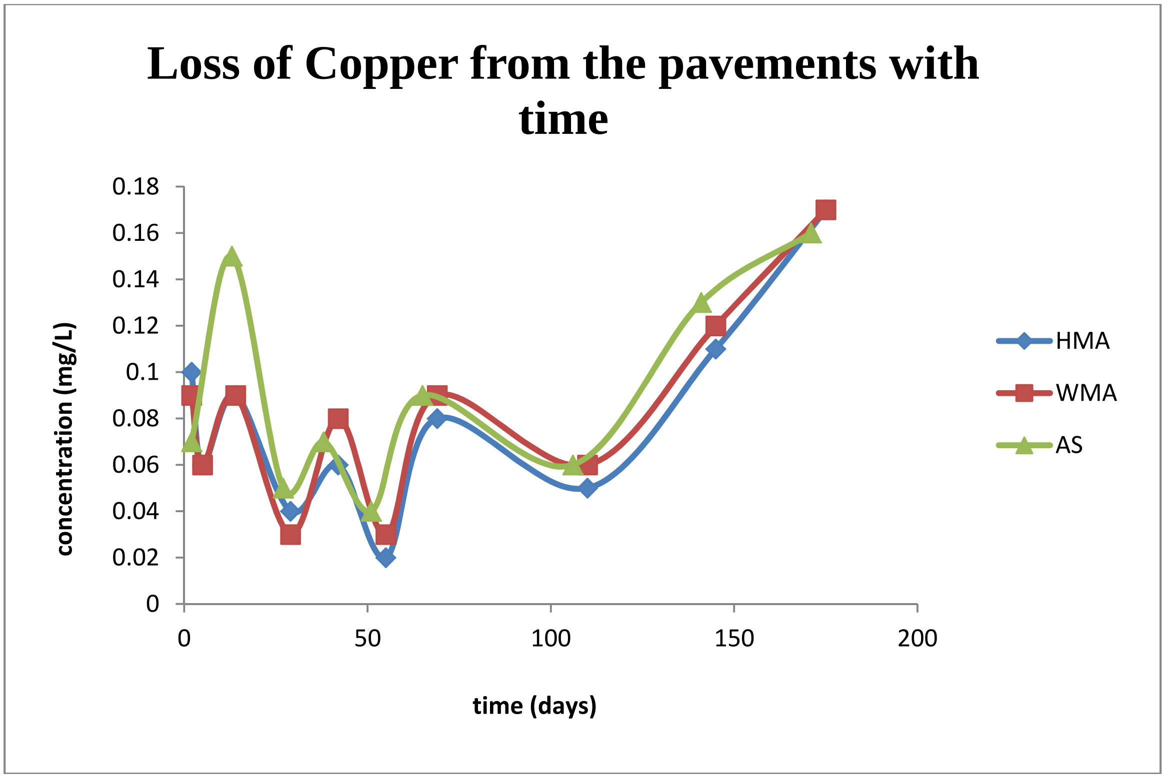


Figure I-8. Copper from the pavements with time.

Major Peaks and IR Scans of Crude Oil Samples

Wavelengths and transparencies of principle peaks for the analyzed samples

Fayetteville Crude Oil with sand at 0 hr.		
Sample ID	Wavelength (cm-1)	Transparency (%)
Crude Oil (0)	4322.9	43.54
	4249.6	49.19
	4050.4	60.53
	3610.2	80.10
	3180.5	59.57
	2887.0	0.04
	2729.8	26.3
	2656.4	39.20
	2402.9	72.40
	2195.3	79.75
	2038.3	82.05
	1940.4	82.18
	1893.2	79.70
	1741.3	70.38
	1704.6	65.76
	1605.0	38.56
	1453.0	0.04
	1374.4	0.08
Fayetteville Crude Oil sampled after 3hr UV light exposure with Acetone as the solvent.		
Sample ID	Wavelength (cm-1)	Transparency (%)
Crude Oil (1)	4185.8	42%
	3414.4	1.86
	3002.5	0.50
	2858.5	22.14
	2579.2	88.84
	2444.7	90.01
	2145.4	81.35
	1679.3	0.12
	1443.6	0.05
	1233.9	0.09
	1093.7	1.16

Fayetteville Crude Oil sampled after 24hr UV light exposure with Acetone as the solvent.

Sample ID	Wavelength (cm-1)	Transparency (%)
Crude Oil(2)	4259.0	86.60
	3595.9	17.38
	3396.4	56.69
	2911.8	3.24
	2857.7	4.80
	2729.5	83.47
	2547.5	89.87
	2391.3	90.45
	2178.5	90.40
	2042.7	86.44
	1755.0	74.36
	1698.2	30.15
	1640.9	49.56
	1376.1	43.40
	1276.2	94.55
	1147.3	89.63

Fayetteville Crude Oil sampled after 48hr UV light exposure with Acetone as the solvent.

Sample ID	Wavelength (cm-1)	Transparency (%)
Crude Oil(2)	4258.4	93.79
	3605.6	36.44
	3396.1	76.74
	2918.3	4.68
	2857.0	14.05
	2730.9	92.27
	2043.7	94.52
	1684.2	30.96
	1641.9	64.79
	1396.7	32.06
	1355.5	15.13
	1277.2	97.98
	1230.7	32.89
	1152.3	94.92

Fayetteville Crude Oil sampled after 72hr UV light exposure with Acetone as the solvent.

Sample ID	Wavelength (cm-1)	Transparency (%)
Crude Oil(3)	4261.6	95.24
	3606.8	74.01
	3387.2	92.83
	3000.6	63.32
	2928.7	2.94
	2192.4	97.73
	2043.2	96.87
	1757.6	33.08
	1640.4	91.62
	1340.3	20.03
	1282.3	99.84
	1148.9	97.53

Fayetteville Crude Oil sampled after 96 hr UV light exposure with Acetone as the solvent.

Sample ID	Wavelength (cm-1)	Transparency (%)
Crude Oil(4)	3601.1	58.25
	3006.4	40.40
	2952.6	90.29
	2916.1	75.31
	1755.0	24.02
	1727.9	62.47
	1454.0	51.05
	1452.4	45.31
	1427.5	32.03
	1219.5	71.37

Fayetteville Crude Oil sampled after 120 hr UV light exposure with Acetone as the solvent.

Sample ID	Wavelength (cm-1)	Transparency (%)
Crude Oil(5)	3595.1	79.45
	2856.9	37.61
	1752.0	22.37
	1699.4	32.34
	1427.8	32.60
	1228.7	19.42
	1090.2	46.51

Wavelength and Principle Peaks of the Crude Oil Standard Samples from Ontario, CA.

Sample ID	Wavelength (cm-1)	Transparency (%)
1001	4330.1	45.91
	4258.1	51.50
	4067.6	65.46
	2925.4	3.06
	2729.3	32.50
	2670.1	39.68
	2404.8	82.93
	2026.2	90.69
	1902.8	90.42
	1701.6	73.75
	1606.7	47.01
	1459.0	3.38
	1376.8	3.95
	1304.0	26.99
	1169.3	45.61
	1076.6	50.84
	1032.3	46.98
2001	4330.0	29.36
	4254.7	33.37
	3607.3	52.68
	2923.5	0.60
	2729.3	23.12
	2670.8	27.86
	2398.7	55.10
	2314.4	55.53
	1706.1	36.58
	1606.9	32.37
	1455.5	1.38
	1376.8	1.83
	1303.6	15.94
	1169.1	27.24
	1031.9	28.63
3001	4329.7	47.07
	4257.7	53.67
	4067.9	65.42
	2919.8	0.04
	2729.3	29.26
	2671.8	42.90
	2313.9	84.45
	1868.1	85.53
	1605.2	24.40
	1468.2	0.03

	1377.1	0.03
	1167.7	26.35
	1031.8	28.18
4001	4329.5	47.84
	4254.7	54.21
	4066.5	65.30
	2930.7	0.99
	2728.9	31.03
	2669.7	42.39
	2313.9	82.45
	1906.6	82.73
	1604.2	20.92
	1459.5	1.18
	1376.7	1.25
	1169.0	25.19
	1032.3	27.46
1002	4330.2	43.22
	4258.4	48.93
	4068.1	63.91
	2849.4	0.01
	2729.4	30.54
	2670.3	38.14
	2401.7	83.25
	2308.7	85.35
	2027.1	89.02
	1902.0	88.32
	1701.9	71.12
	1606.8	44.21
	1446.6	0.03
	1377.2	0.07
	1304.0	24.47
	1169.3	44.49
	1076.9	50.28
	1032.3	46.25
	965.9	35.66
	885.6	36.80
2002	4330.4	42.63
	4258.2	48.14
	2921.7	0.46
	2729.3	30.64
	2671.0	37.51
	2401.5	82.47
	2314.3	83.46
	2027.0	87.80

	1902.4	88.21
	1706.9	58.96
	1606.3	47.35
	1456.4	0.75
	1377.2	0.97
	1303.8	23.66
	1169.2	43.53
	1076.8	48.66
	1031.9	47.08
3002	4329.7	47.78
	4257.7	54.02
	4068.3	65.33
	2924.8	2.24
	2729.2	32.26
	2671.8	45.45
	2402.1	81.74
	2312.7	84.35
	2027.6	88.81
	1867.9	82.75
	1601.9	26.8
	1455.5	2.87
	1377.4	3.34
	1167.6	29.16
4002	4329.4	46.50
	4257.6	52.40
	4067.4	64.40
	2925.4	0.01
	2728.8	31.01
	2670.2	42.58
	2027.2	87.98
	1905.6	80.41
	1604.1	18.38
	1468.8	0.01
	1376.5	0.07
	1168.9	24.34
1003	4329.9	41.06
	4258.1	46.05
	4067.0	57.13
	2882.1	0.00
	2728.9	25.97
	2670.0	34.28
	1900.1	79.59
	1707.6	62.50
	1606.2	36.32

	1448.1	0.04
	1377.2	0.09
	1304.6	20.16
	1168.8	25.75
2003	4329.7	47.78
	4257.7	54.02
	4068.3	65.33
	2924.8	2.24
	2729.2	32.36
	2671.8	45.45
	2402.1	81.74
	2312.7	84.35
	2027.6	88.81
	1867.9	82.75
	1605.1	25.91
	1455.5	2.87
	1377.4	3.34
	1167.6	29.16
	1377.4	3.34
	1167.6	29.16
	1031.9	30.65
3003	4330.3	40.74
	4258.1	47.04
	4068.1	57.49
	2974.0	0.03
	2729.7	26.77
	2671.1	37.94
	2033.9	81.02
	1903.8	76.52
	1604.5	25.94
	1458.2	0.02
	1376.9	0.02
	1307.0	13.21
	1155.7	19.80
4003	4329.5	42.83
	4258.0	47.96
	4067.6	58.10
	2890.0	0.06
	2728.4	25.56
	2669.6	35.27
	1903.8	77.42
	1708.3	44.20
	1605.4	29.32
	1449.7	0.02

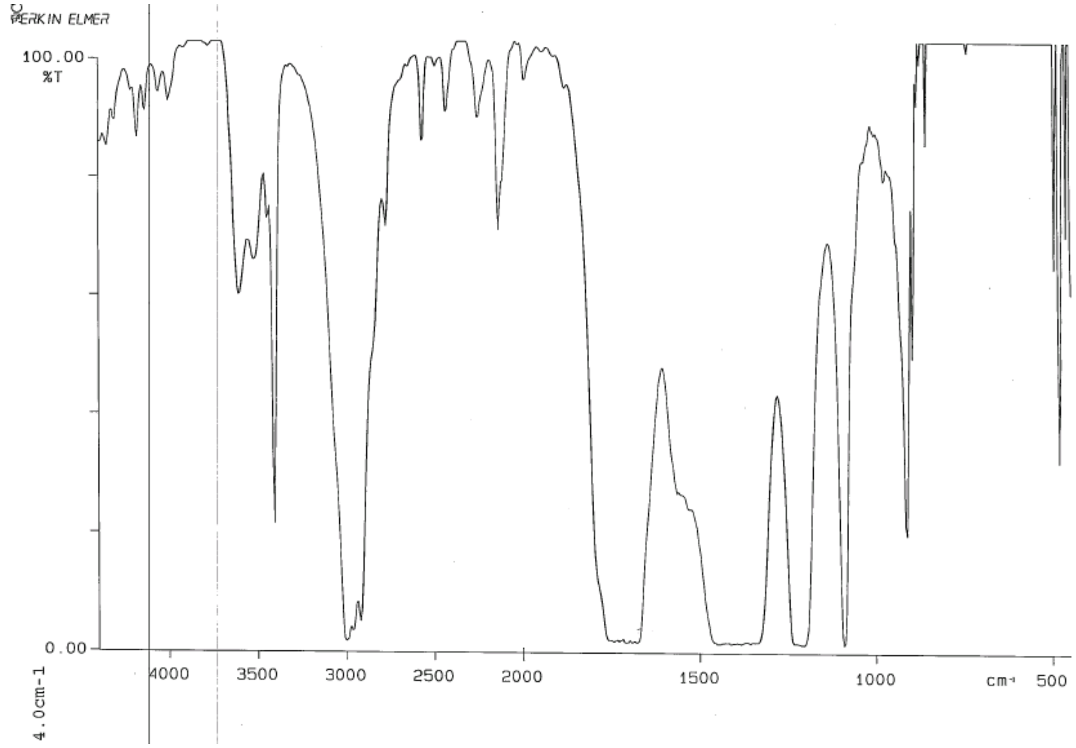
	1376.6	0.06
	1168.4	20.87
1004	4330	40.98
	4258.1	46.06
	4067.3	57.04
	3902.9	70.65
	3854.1	69.64
	3839.2	71.02
	3821.8	71.22
	3802.3	72.65
	3751.6	72.99
	3735.7	73.84
	3712.0	75.75
	3690.1	75.81
	3676.0	75.43
	3649.9	75.21
	3629.8	76.40
	3567.7	81.72
	2868.3	0.10
	2729.0	25.88
	2669.9	34.21
	2366.1	71.65
	1890.1	78.64
	1772.0	74.05
	1734.0	69.07
	1700.6	60.09
	1684.4	63.55
	1653.8	63.13
	1606.5	35.83
	1559.4	55.73
	1540.1	53.64
	1444.1	0.07
	1376.6	0.10
	1304.7	20.48
	1169.0	25.69
2004	4329.4	41.87
	4258.2	46.66
	4067.6	57.62
	3903.0	70.68
	3854.1	69.59
	3839.1	71.07
	3821.8	71.25
	3802.3	72.84
	3751.6	73.04

	3735.8	73.98
	3712.0	75.51
	3690.2	76.05
	3676.0	75.65
	3649.9	75.41
	3619.6	75.51
	3567.5	80.26
	2882.0	0.00
	2728.5	26.78
	2668.7	34.58
	2407.5	71.51
	1890.1	77.75
	1734.1	67.14
	1700.4	59.34
	1684.2	61.51
	1670.0	62.89
	1653.8	59.74
	1605.9	30.17
	1559.6	53.21
	1540.2	51.77
	1450.5	0.02
	1376.5	0.05
	1305.4	19.52
	1169.2	23.33
3004	4330.2	40.65
	4257.7	46.95
	4068.0	57.62
	3903.0	70.55
	2904.0	0.02
	2729.6	26.54
	2671.8	37.54
	2028.3	80.60
	1907.9	75.63
	1734.0	67.48
	1684.1	56.13
	1604.4	24.75
	1461.3	0.01
	1377.5	0.08
	1155.9	19.34
4004	4329.4	42.93
	4257.8	48.00
	4067.1	58.21
	2914.1	0.01
	2728.4	25.50

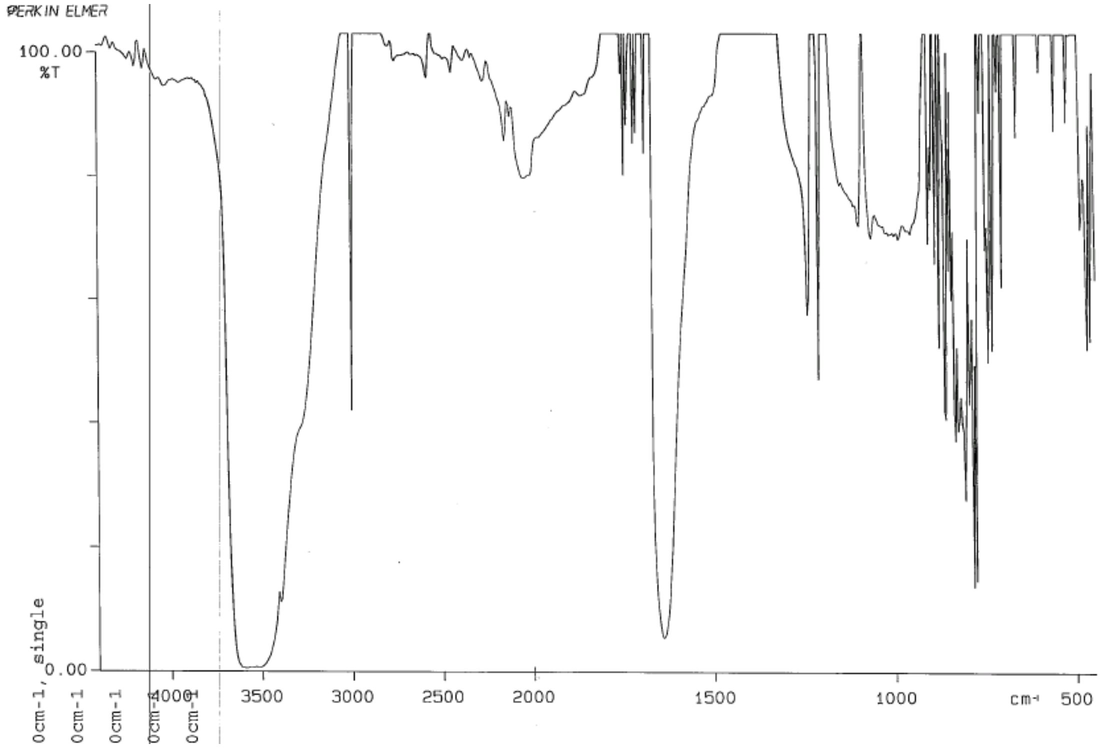
	1890.0	76.55
	1706.9	43.03
	1605.6	29.13
	1459.6	0.04
	1376.8	0.10
	1168.6	20.92
1005	4329.4	42.31
	2558.5	47.09
	3619.9	77.83
	2924.6	0.51
	2828.4	27.95
	2363.4	70.58
	1892.4	78.22
	1708.1	62.18
	1605.8	30.73
	1458.7	1.37
	1376.7	1.79
	1305.2	20.47
	1169.0	24.06
2005	4329.1	42.31
	4252.8	46.73
	2924.6	0.51
	2729.1	27.73
	2406.7	72.73
	1900.9	78.94
	1605.7	33.38
	1457.9	0.90
	1376.9	1.03
	1156.1	27.84
3005	4329.6	42.74
	4257.4	47.83
	2944.4	0.00
	2728.4	25.47
	1708.1	44.52
	1605.4	29.06
	1446.1	0.00
	1376.5	0.01
	1168.4	20.85
4005	4330.1	38.49
	4257.8	44.59
	2929.9	0.00
	2031.6	79.99
	1904.7	75.67
	1604.9	23.08

	1469.5	0.00
	1376.6	0.04
	1306.4	11.86
	1156.1	18.79
5005	4328.5	40.45
	4256.8	45.46
	3177.1	44.15
	2865.7	0.00
	2670.0	33.98
	1696.5	44.10
	1604.0	14.28
	1451.3	0.01
	1374.3	0.02
	1168.3	15.84

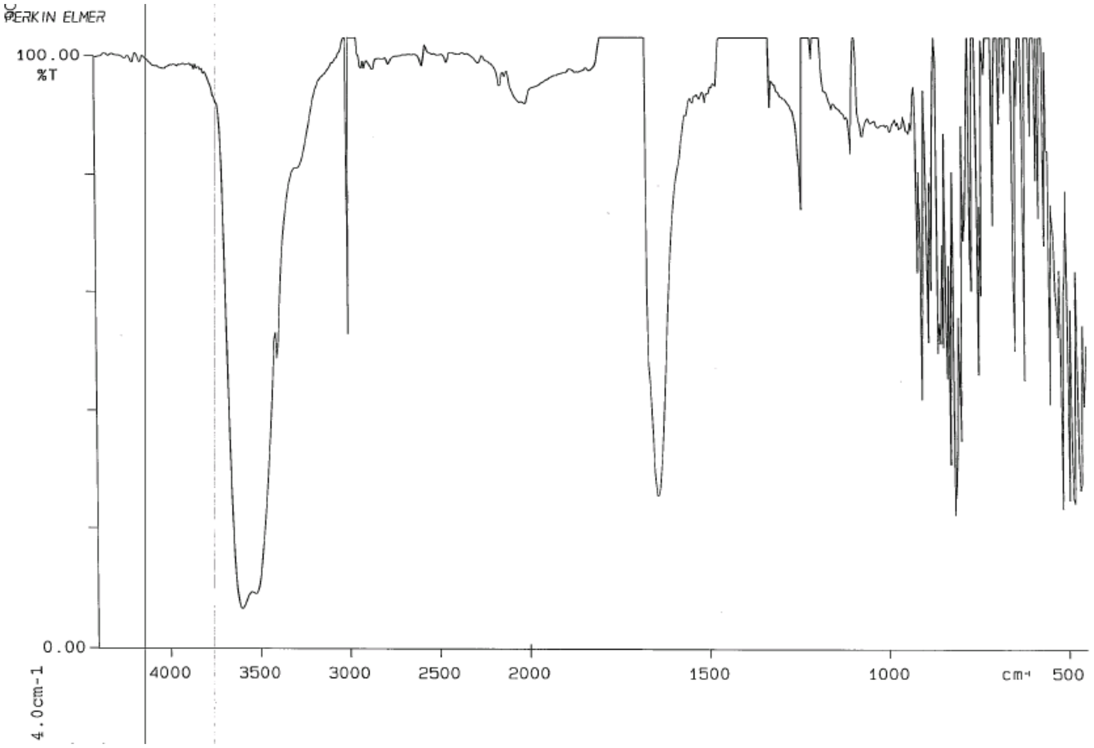
Acetone



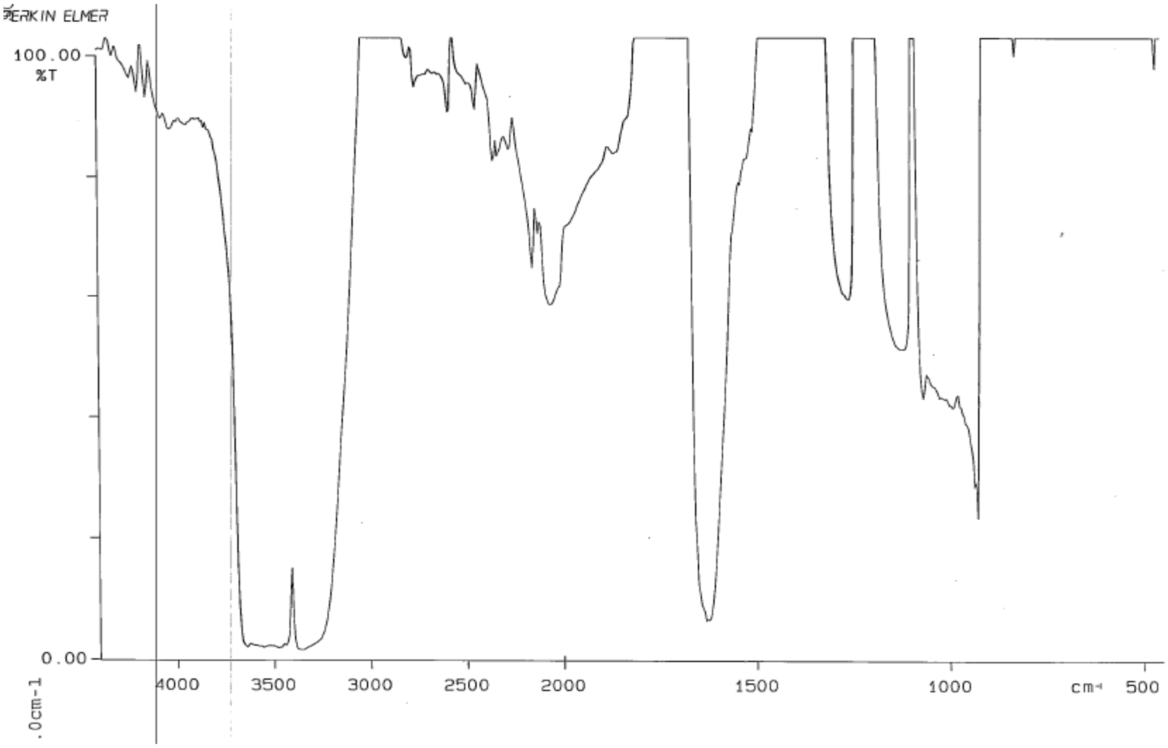
Scan 1: Scan of Acetone as the solvent



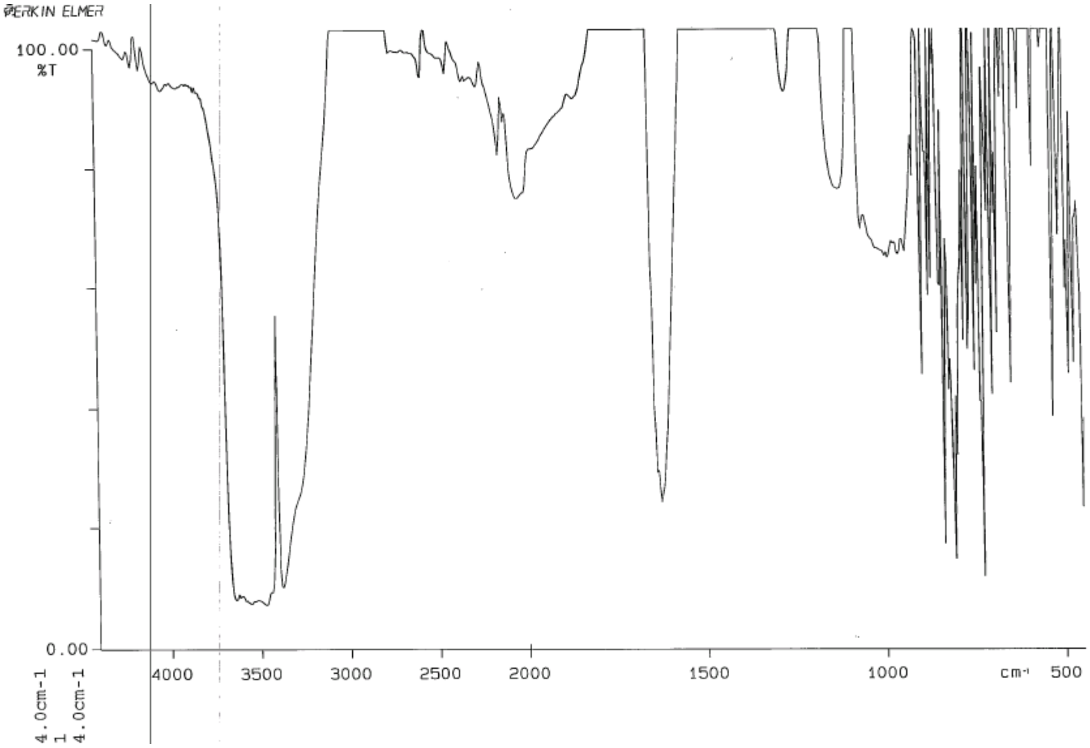
Scan 2: Scan of sample 3 after the Acetone background was subtracted.



Scan 3: Scan of sample 4 after the Acetone background was subtracted.

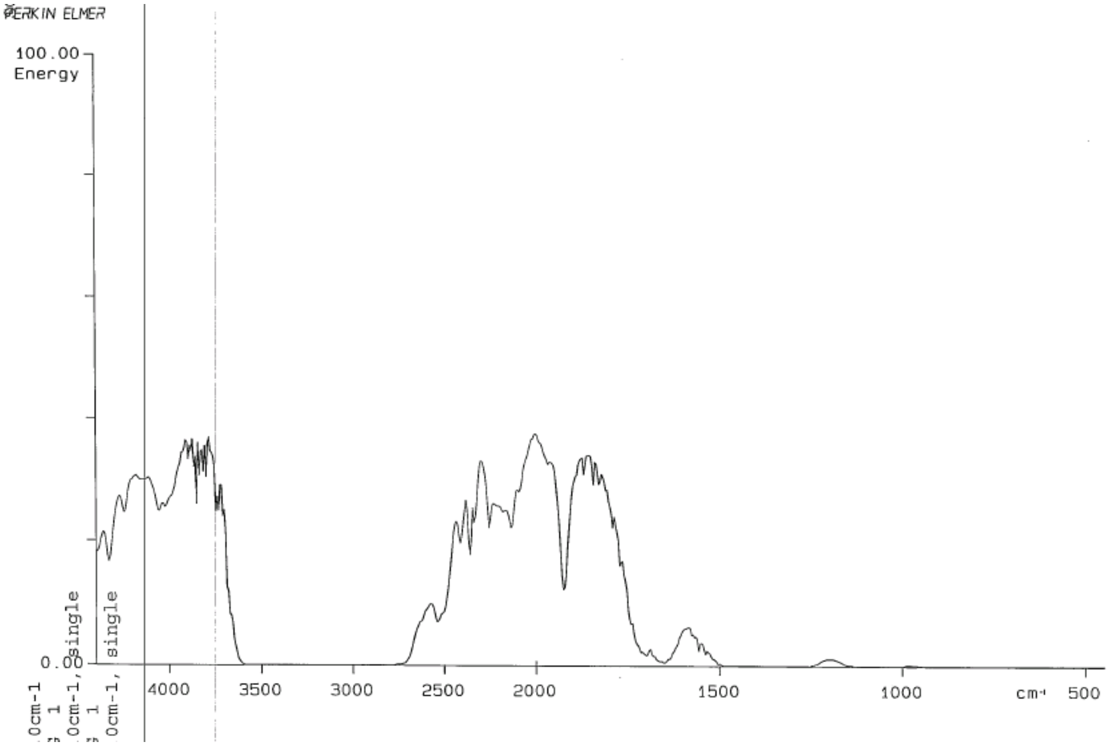


Scan 4: Scan of sample 5 after the Acetone background was subtracted.

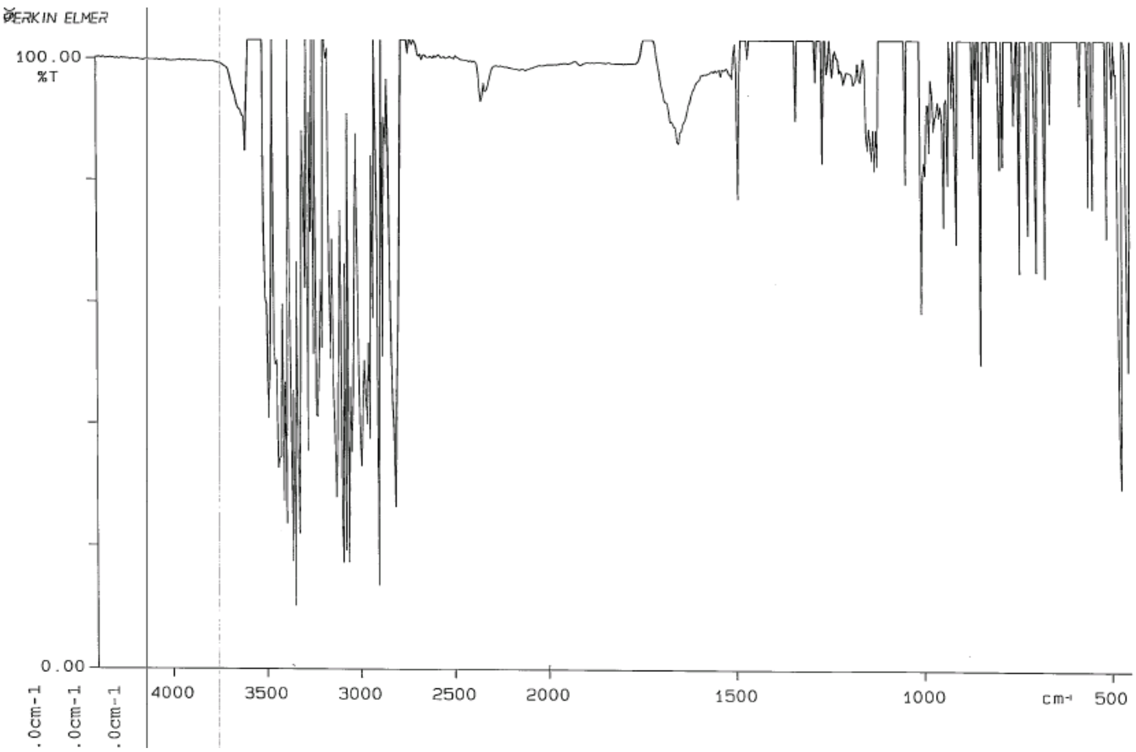


Scan 5: Scan of sample 6 after the Acetone background was subtracted.

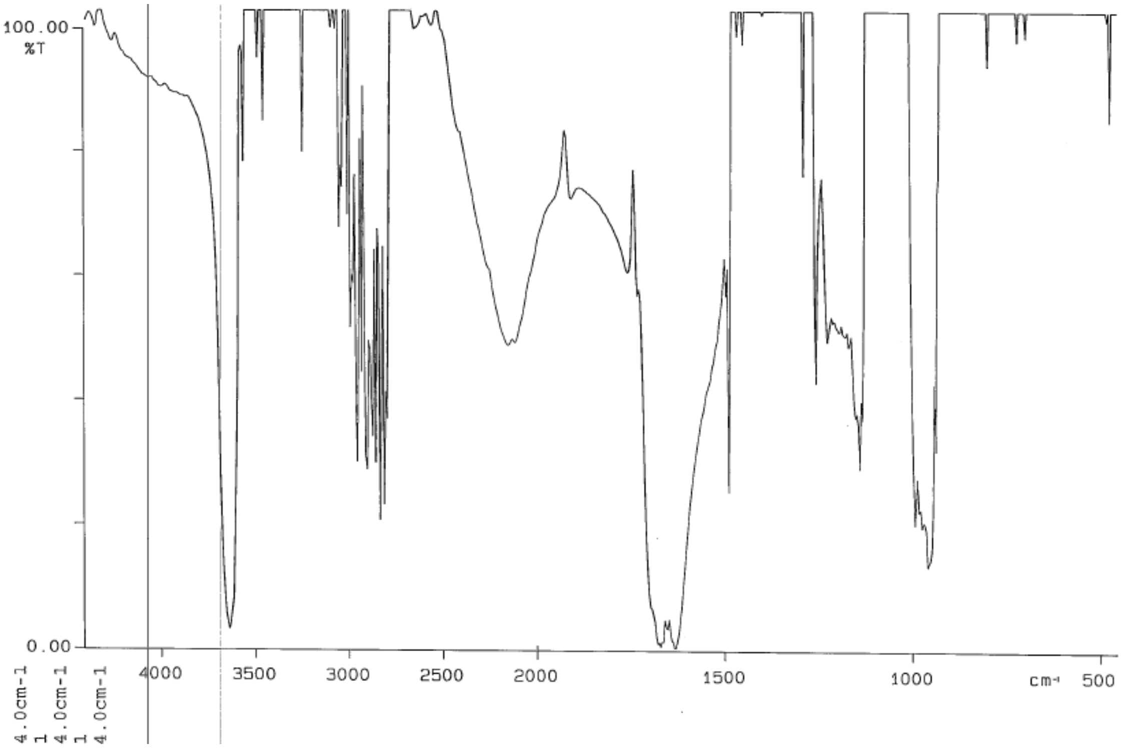
Denatured Alcohol



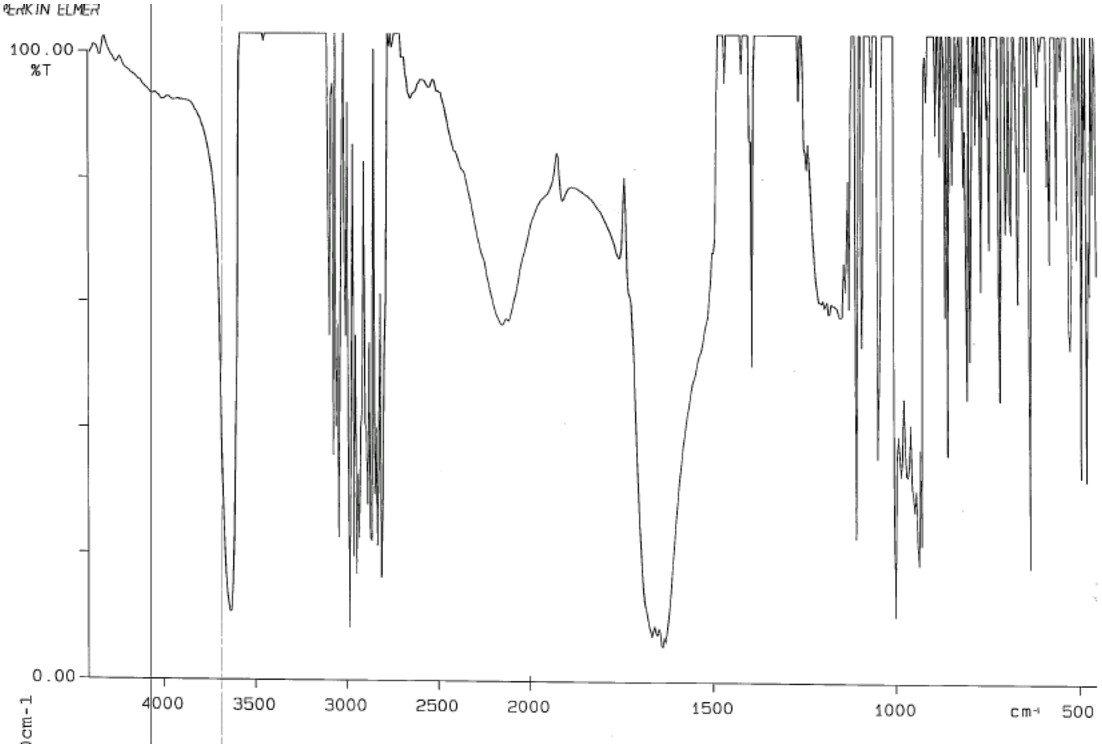
Scan 5: Denatured alcohol as the background.



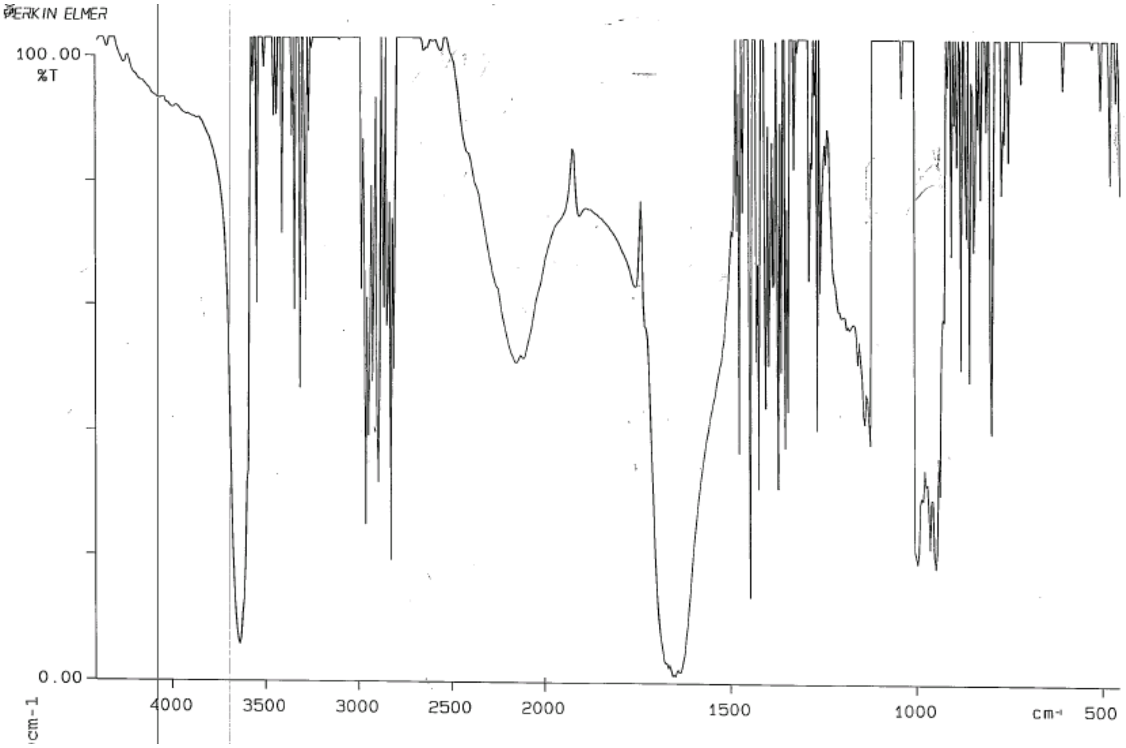
Scan 6: Denatured alcohol.



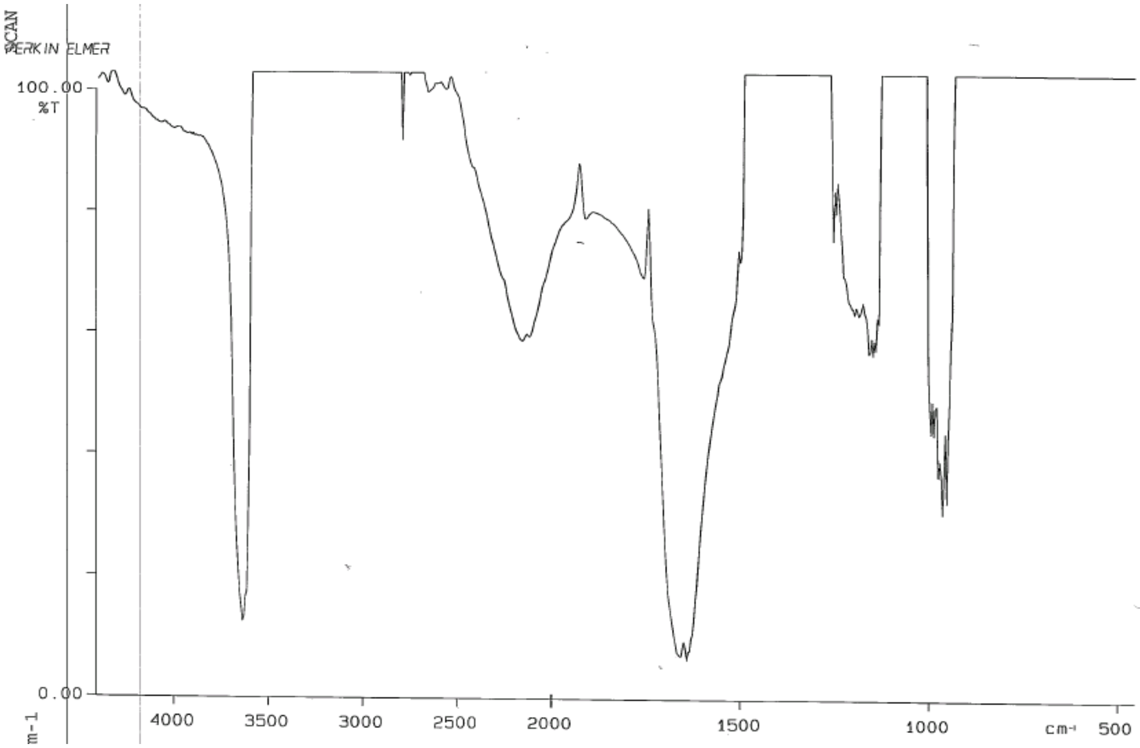
Scan 7: Scan of sample 1 after the Denatured Alcohol background was subtracted.



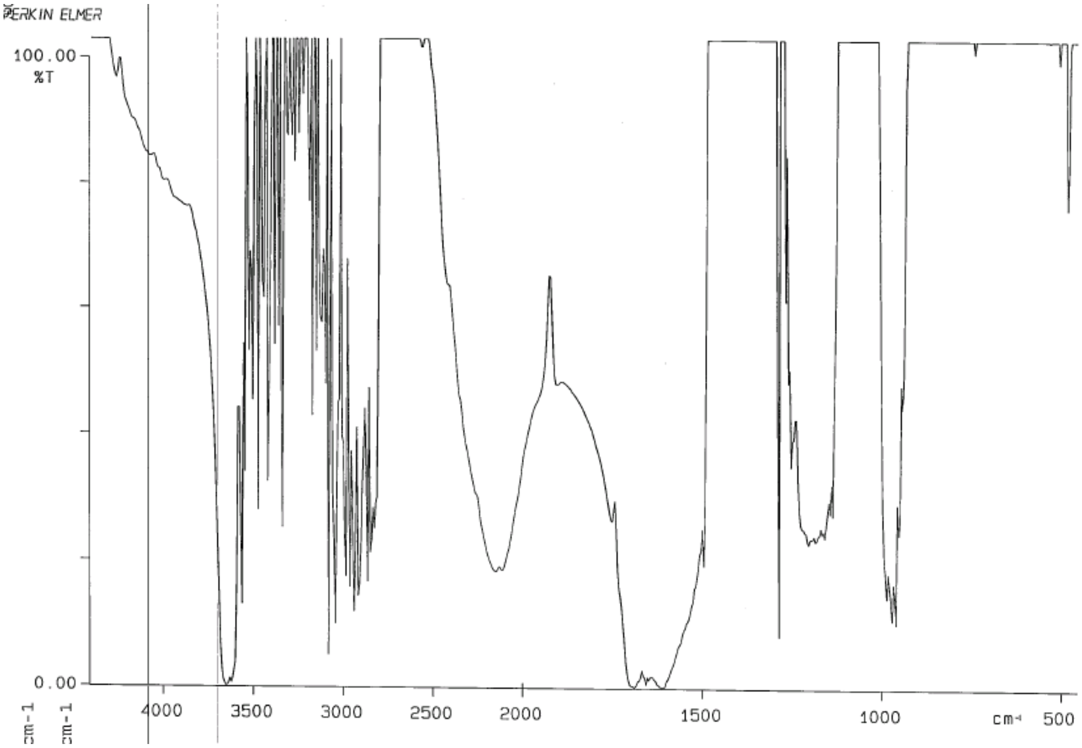
Scan 8: Scan of sample 2 after the Denatured Alcohol background was subtracted.



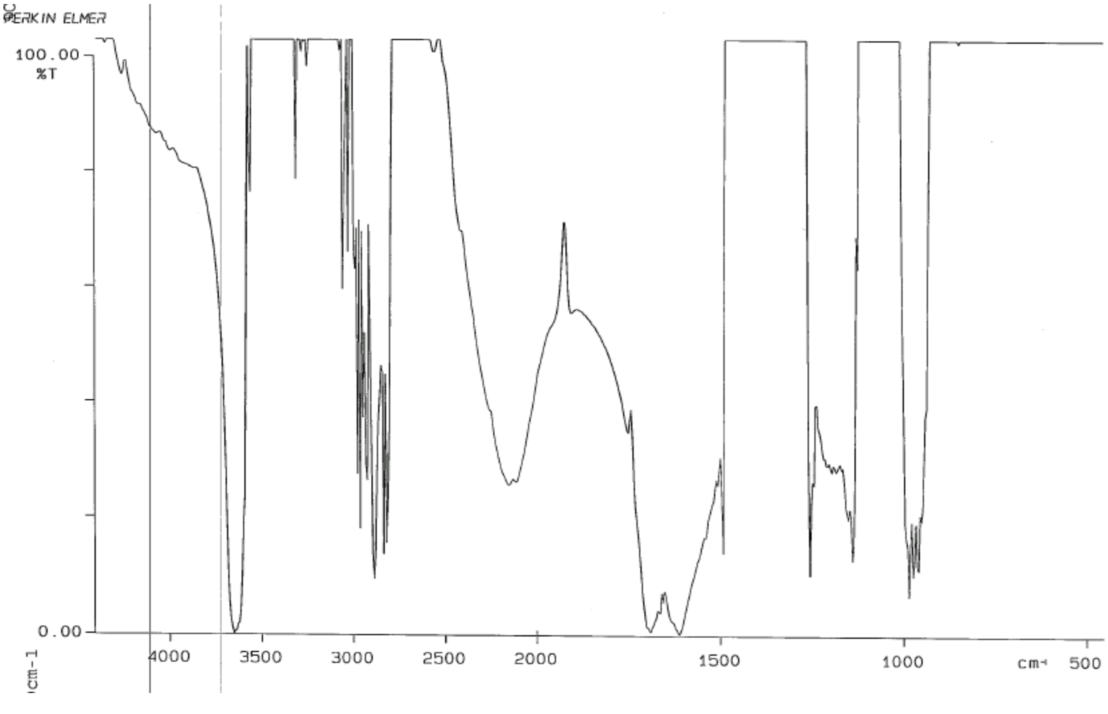
Scan 9: Scan of sample 3 after the Denatured Alcohol background was subtracted.



Scan 10: Scan of sample 4 after the Denatured Alcohol background was subtracted.

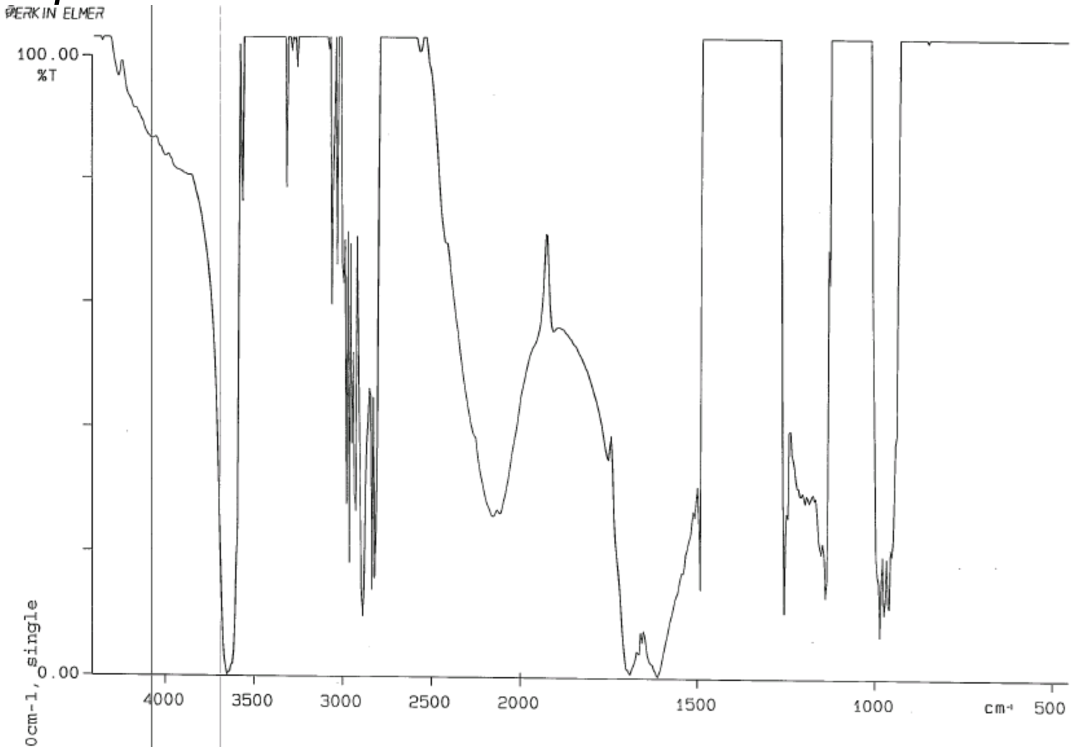


Scan 11: Scan of sample 5 after the Denatured Alcohol background was subtracted.

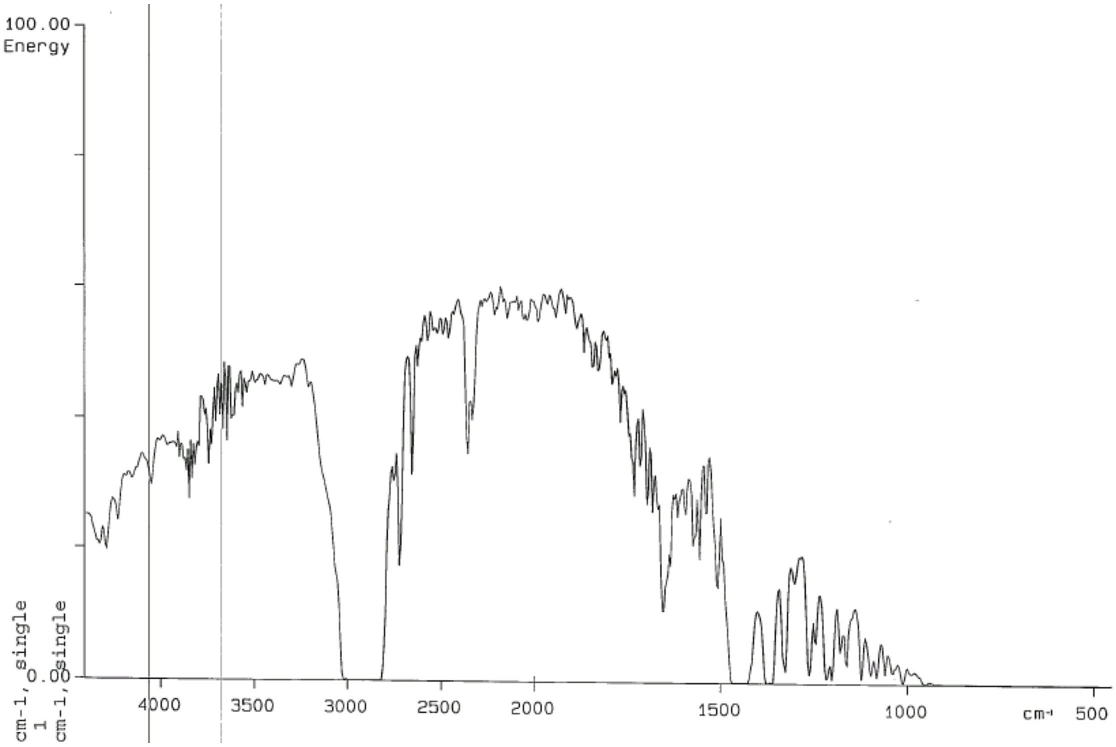


Scan 12: Scan of sample 6 after the Denatured Alcohol background was subtracted.

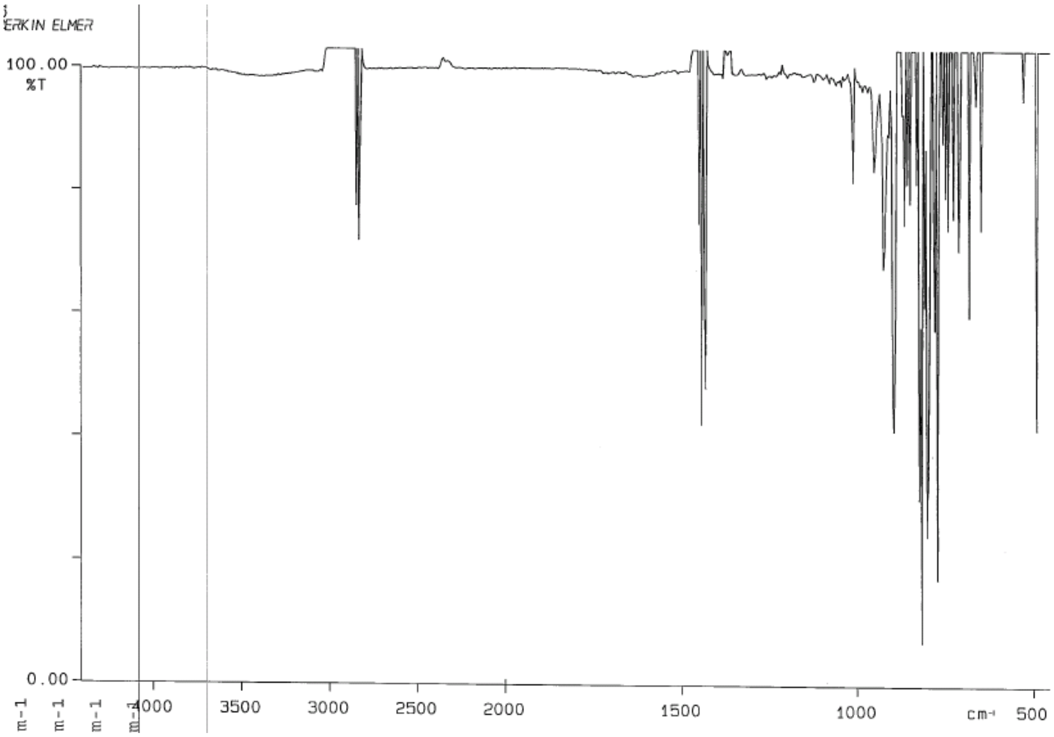
Turpentine



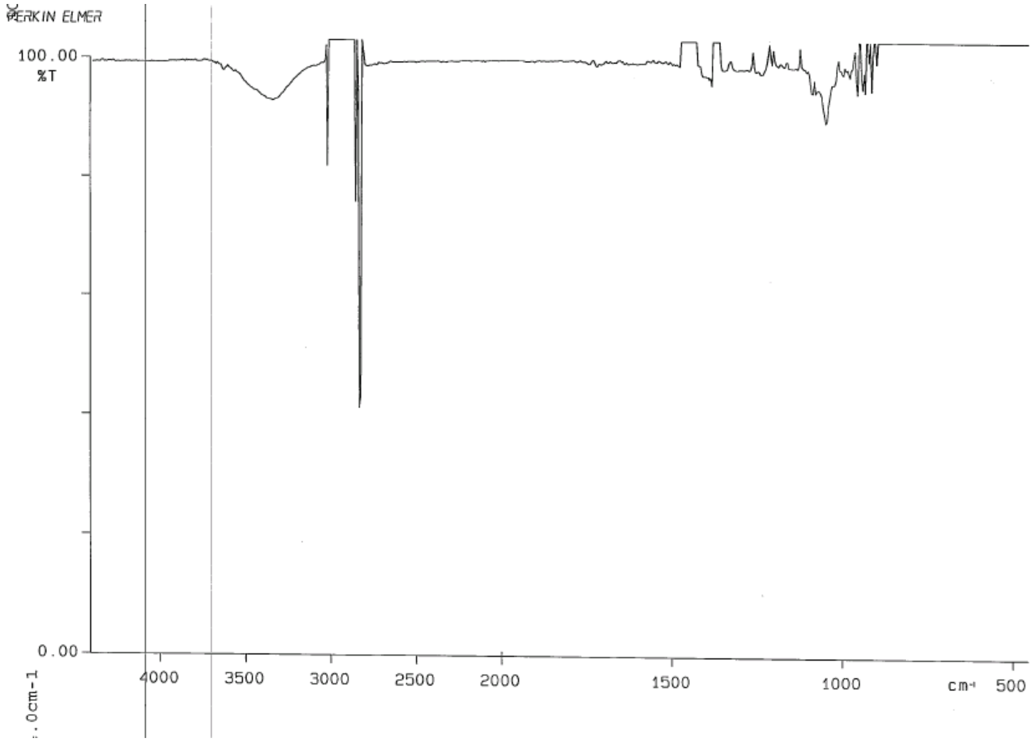
Scan 13: Turpentine with air as the background.



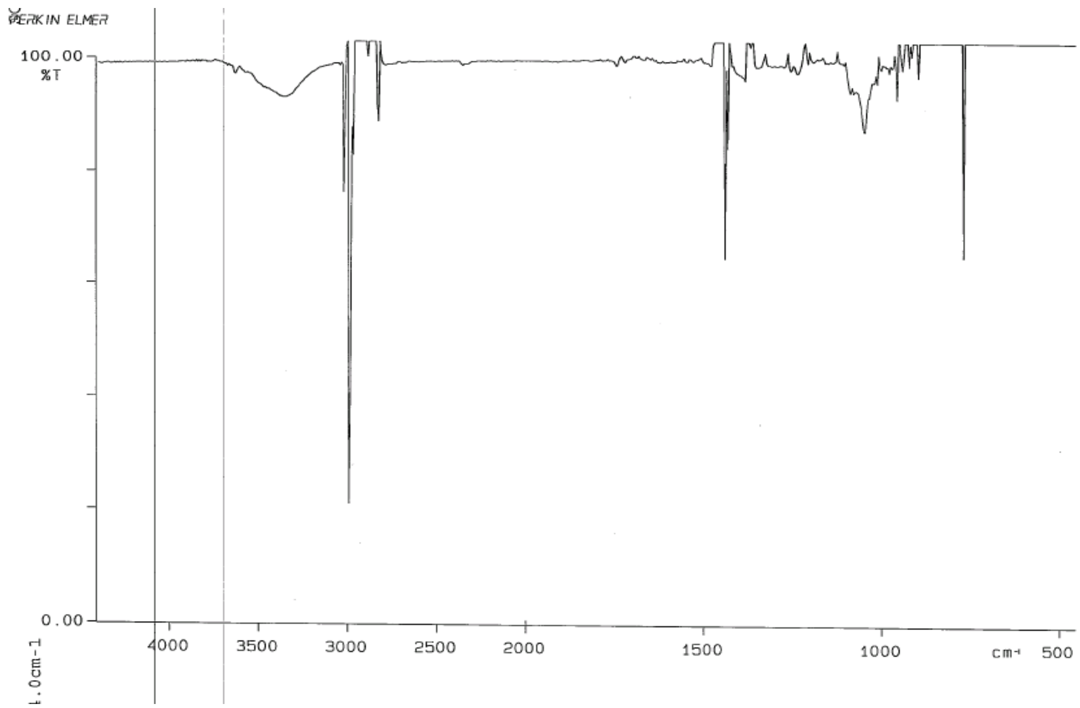
Scan 14: Turpentine as the background.



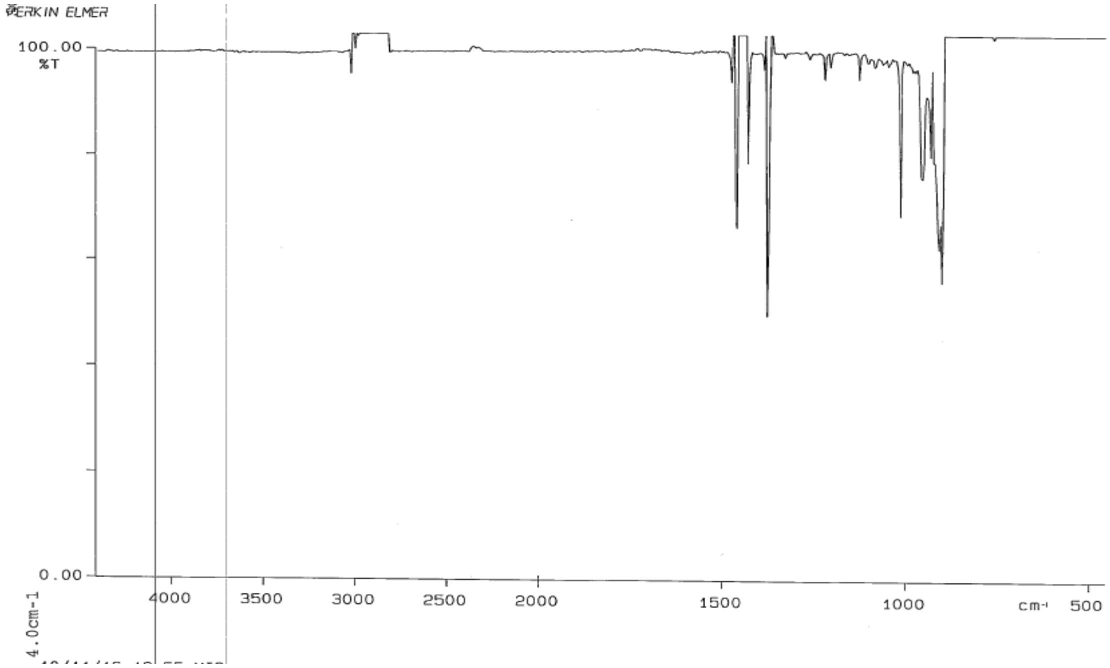
Scan 15: Scan of sample 1 after the Turpentine background was subtracted.



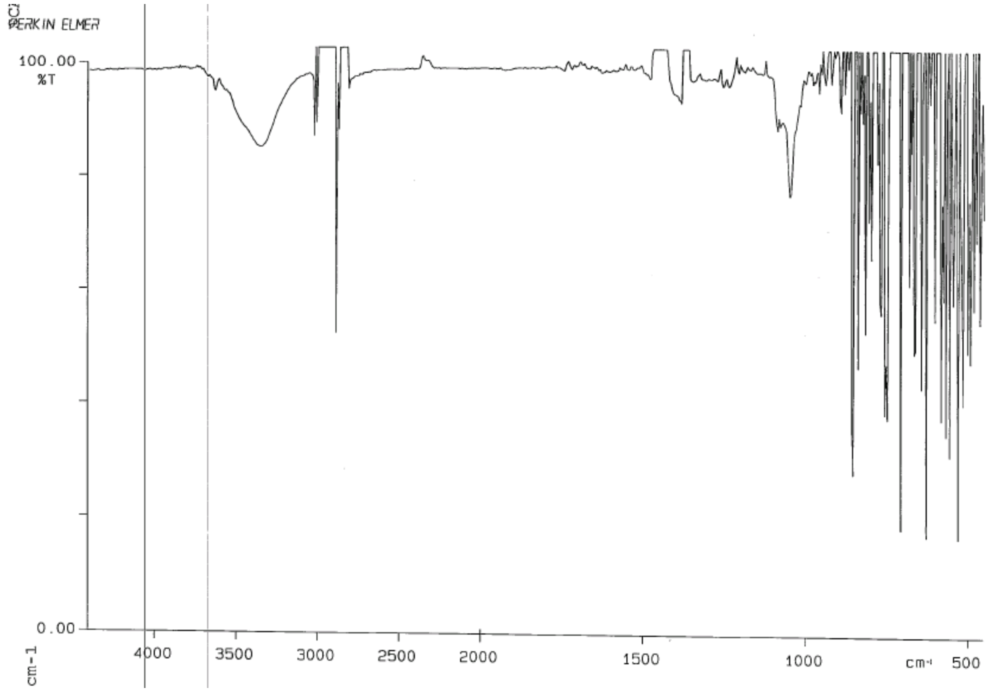
Scan 16: Scan of sample 2 after the Turpentine background was subtracted.



Scan 17: Scan of sample 3 after the Turpentine background was subtracted.

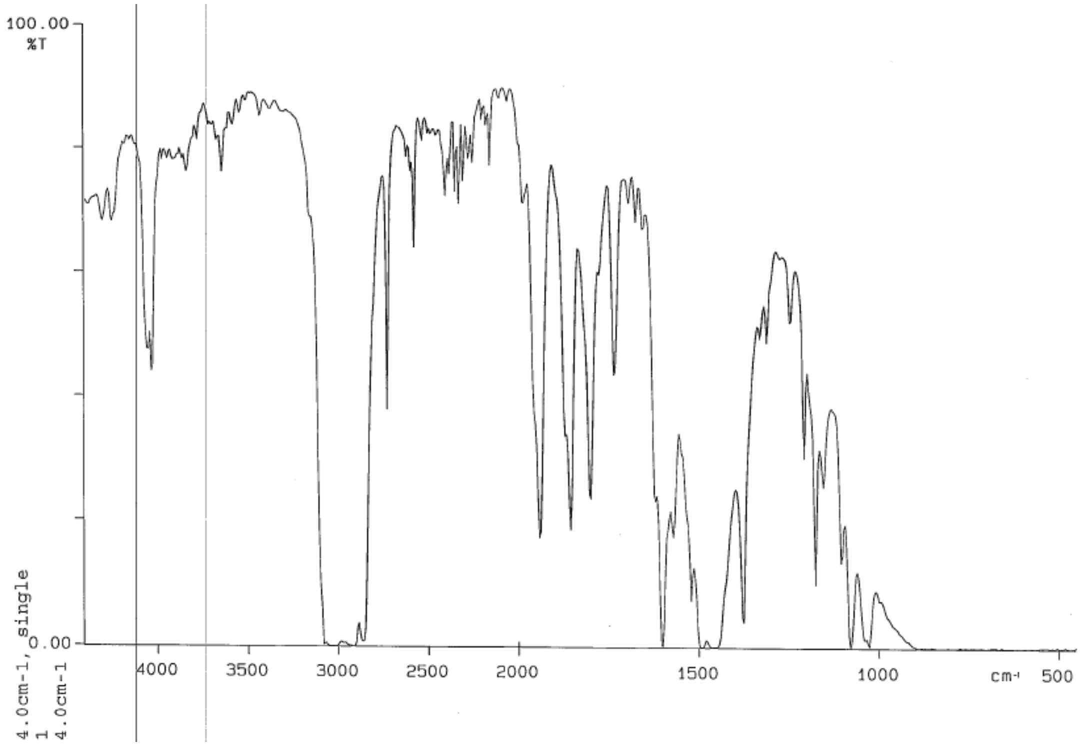


Scan 18: Scan of sample 5 after the Turpentine background was subtracted.

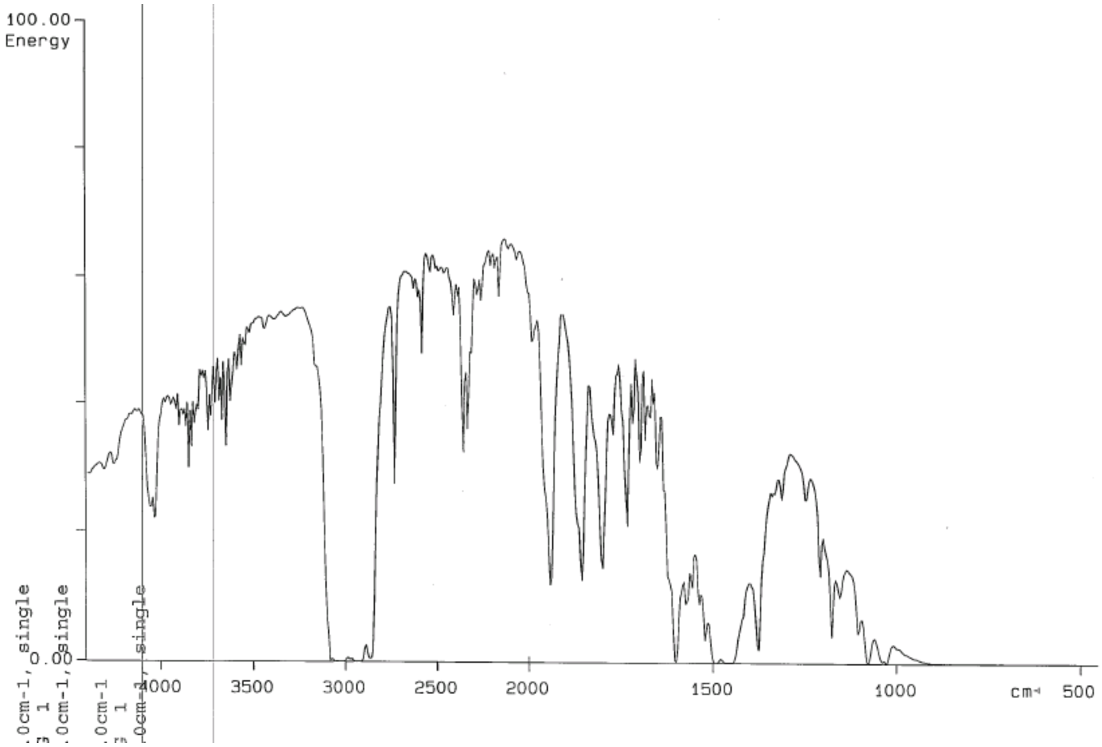


Scan 19: Scan of sample 6 after the Turpentine background was subtracted.

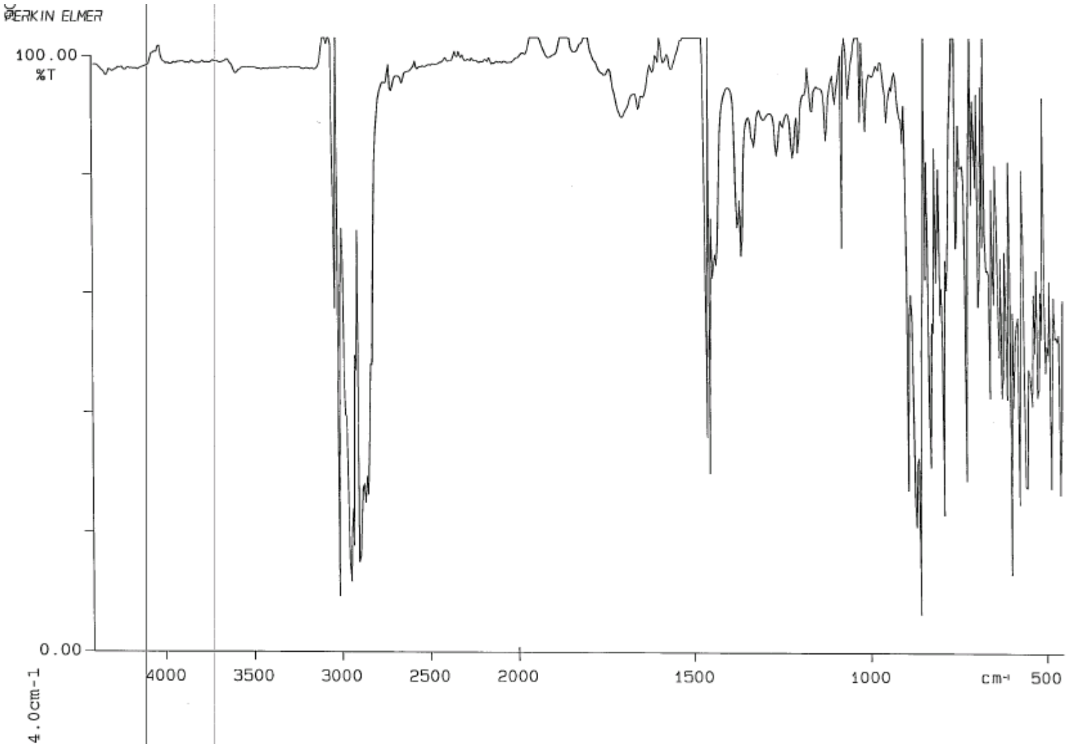
Toluene



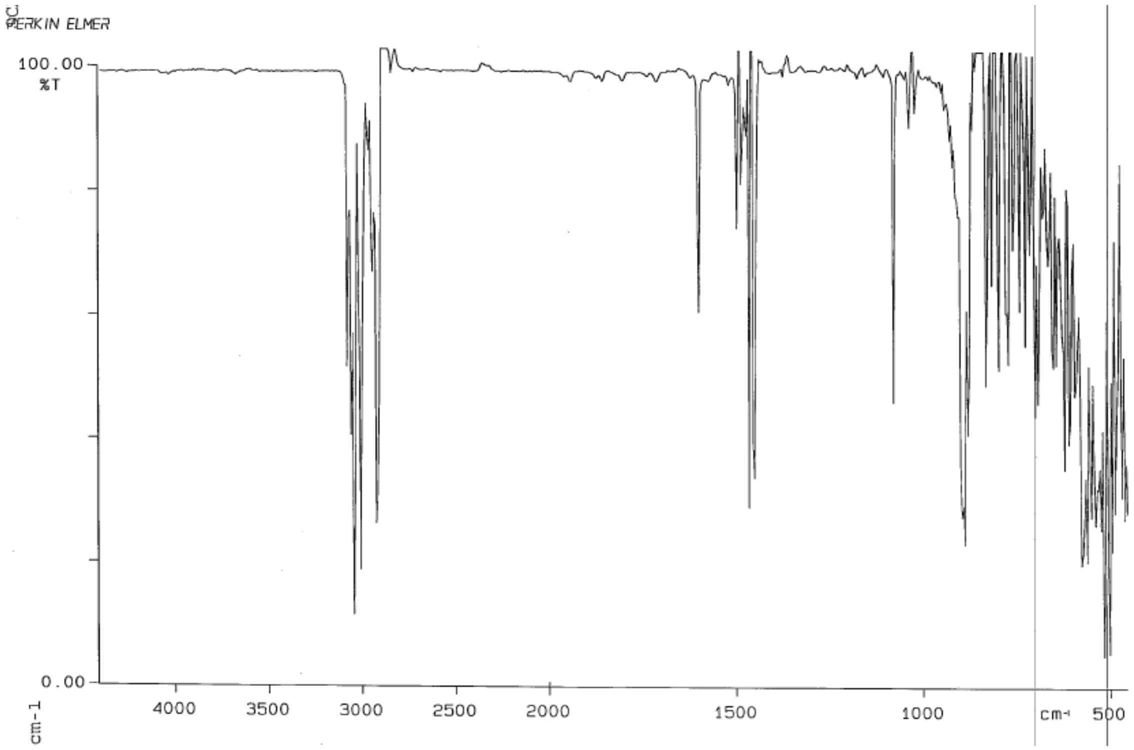
Scan 19: Toluene with air as the background.



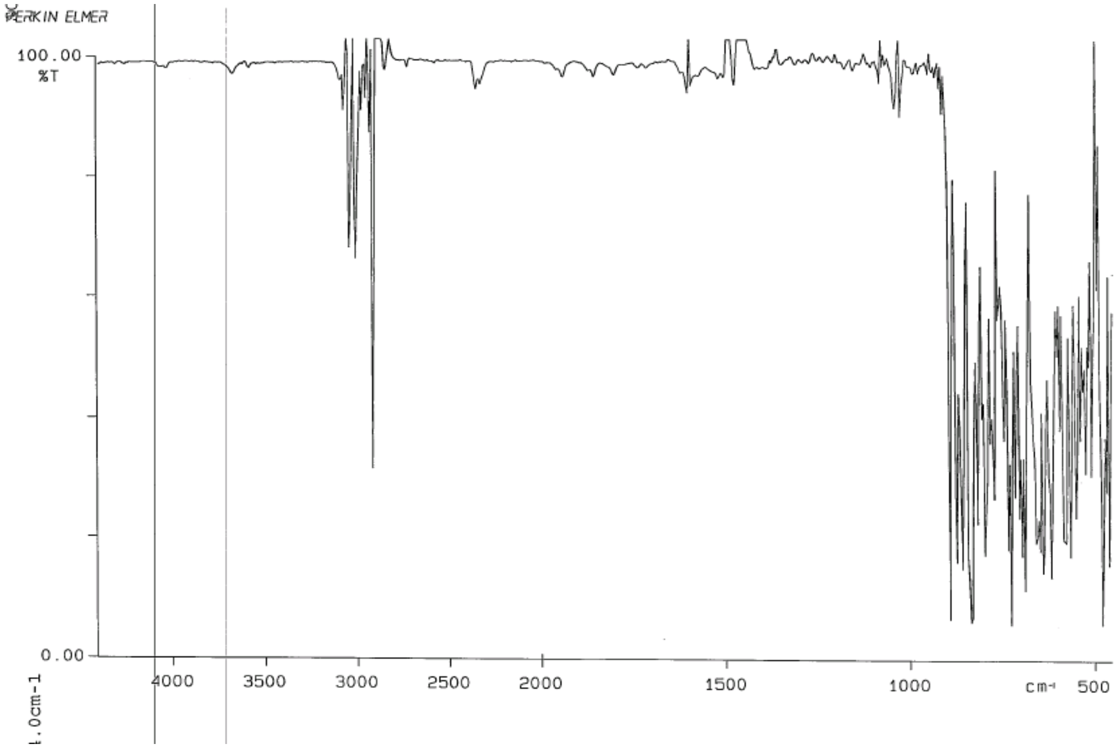
Scan 20: Toluene as the background.



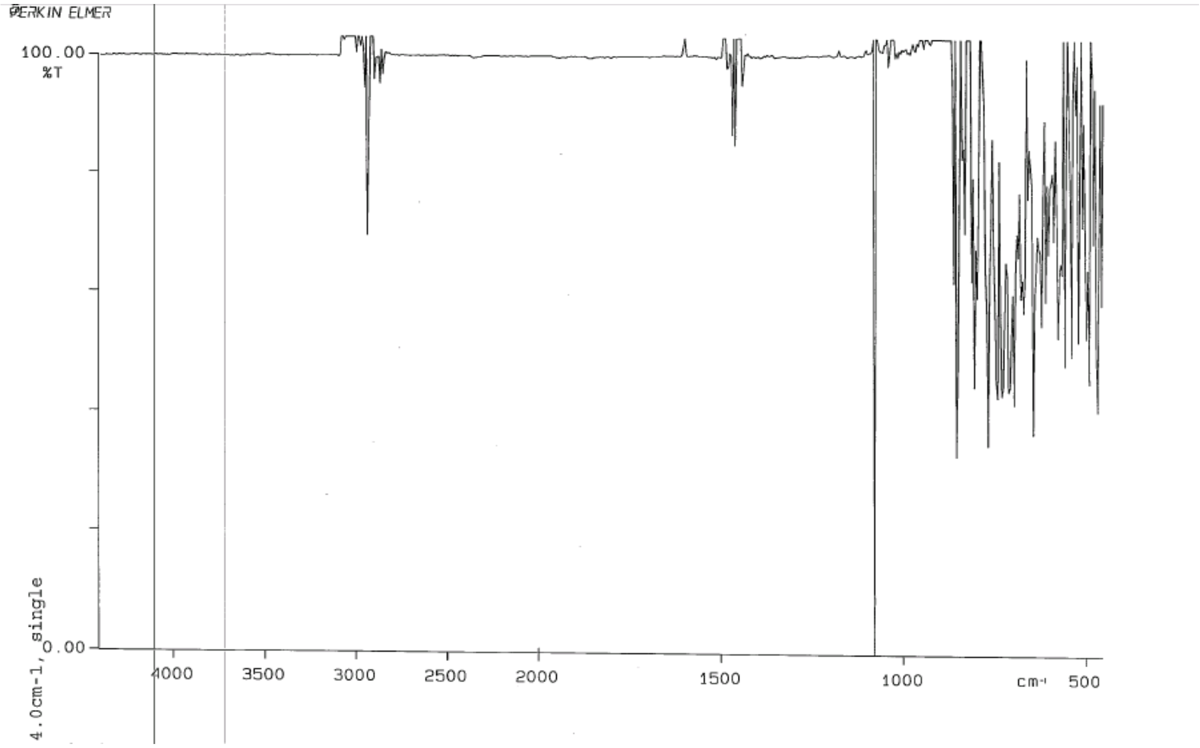
Scan 21: Scan of sample 1 after the Toluene background was subtracted.



Scan 22: Scan of sample 2 after the Toluene background was subtracted.

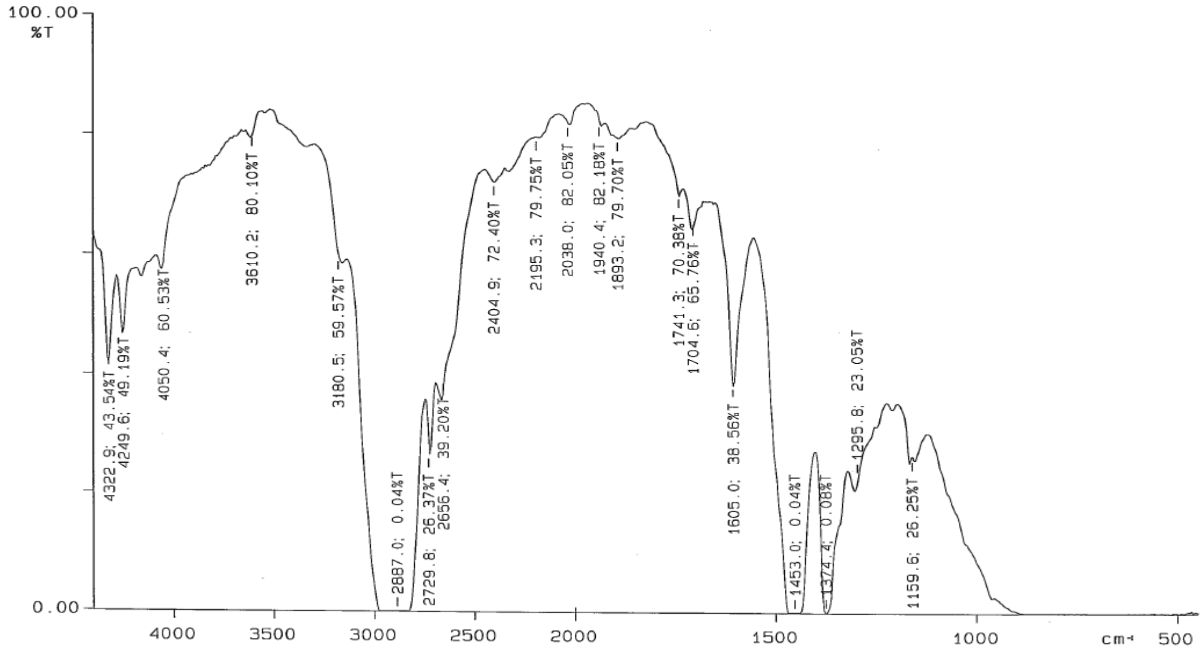


Scan 23: Scan of sample 3 after the Toluene background was subtracted.

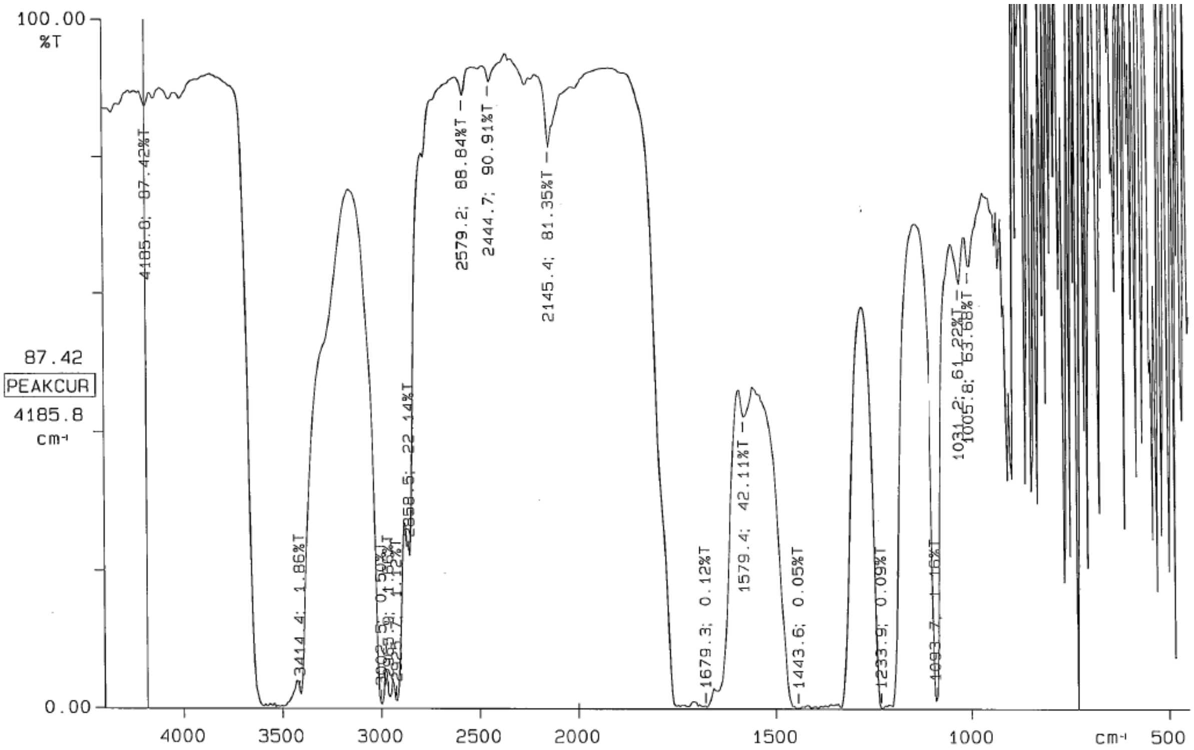


Scan 24: Scan of sample 5 after the Toluene background was subtracted.

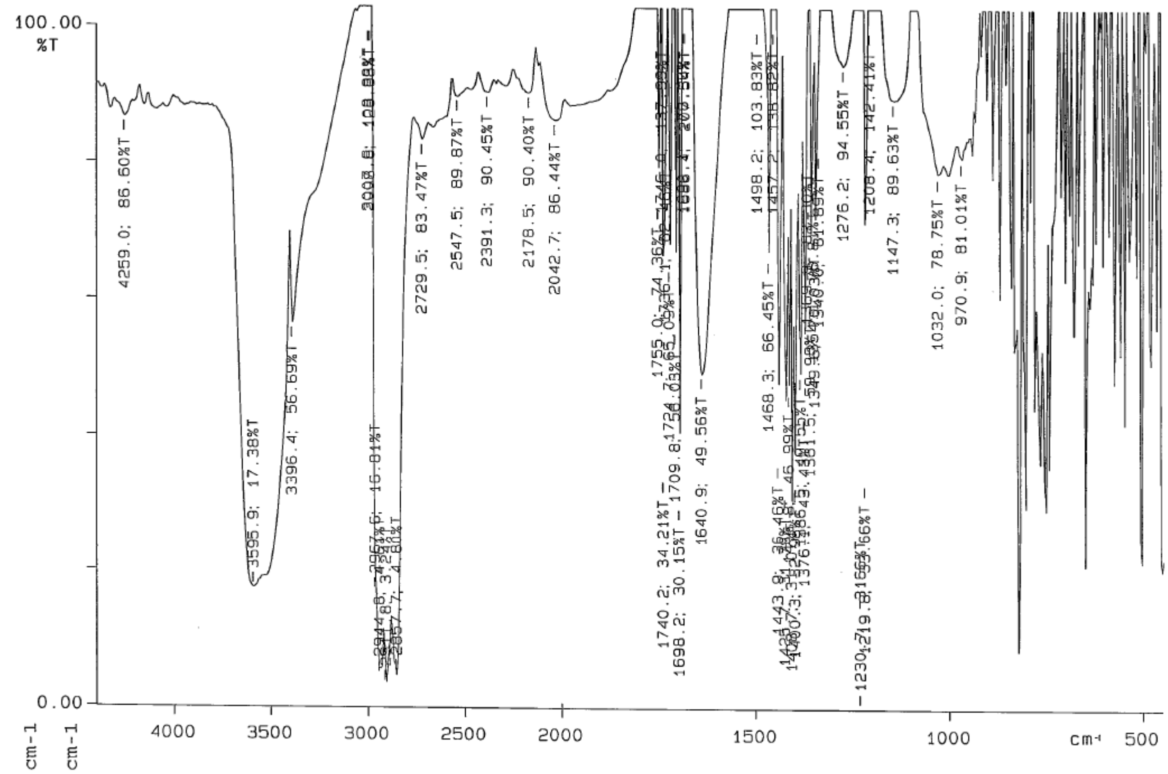
IR Spectrophotometry Scans of Deepwater Horizon Oil and Sand Mixtures with Degradation



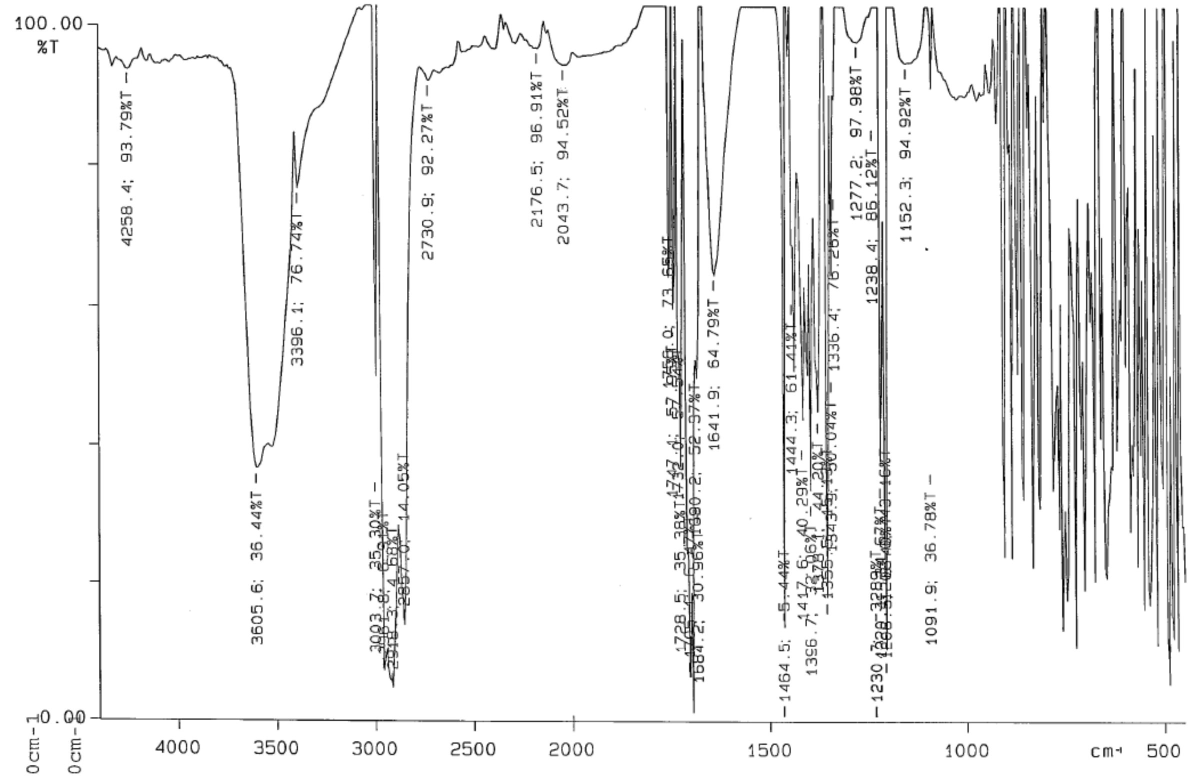
Scan 25: Crude Oil with air as the background, before aging.



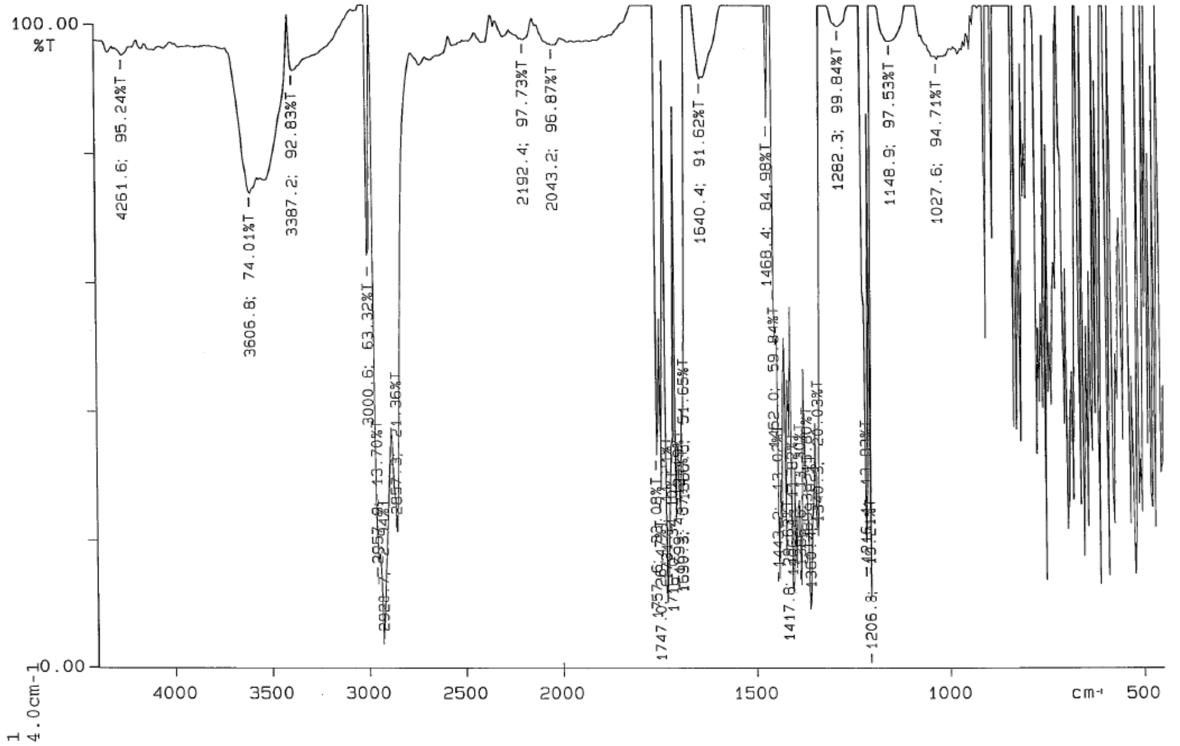
Scan 26: Crude oil sample after 24hr aging with UV radiation, with Acetone solvent.



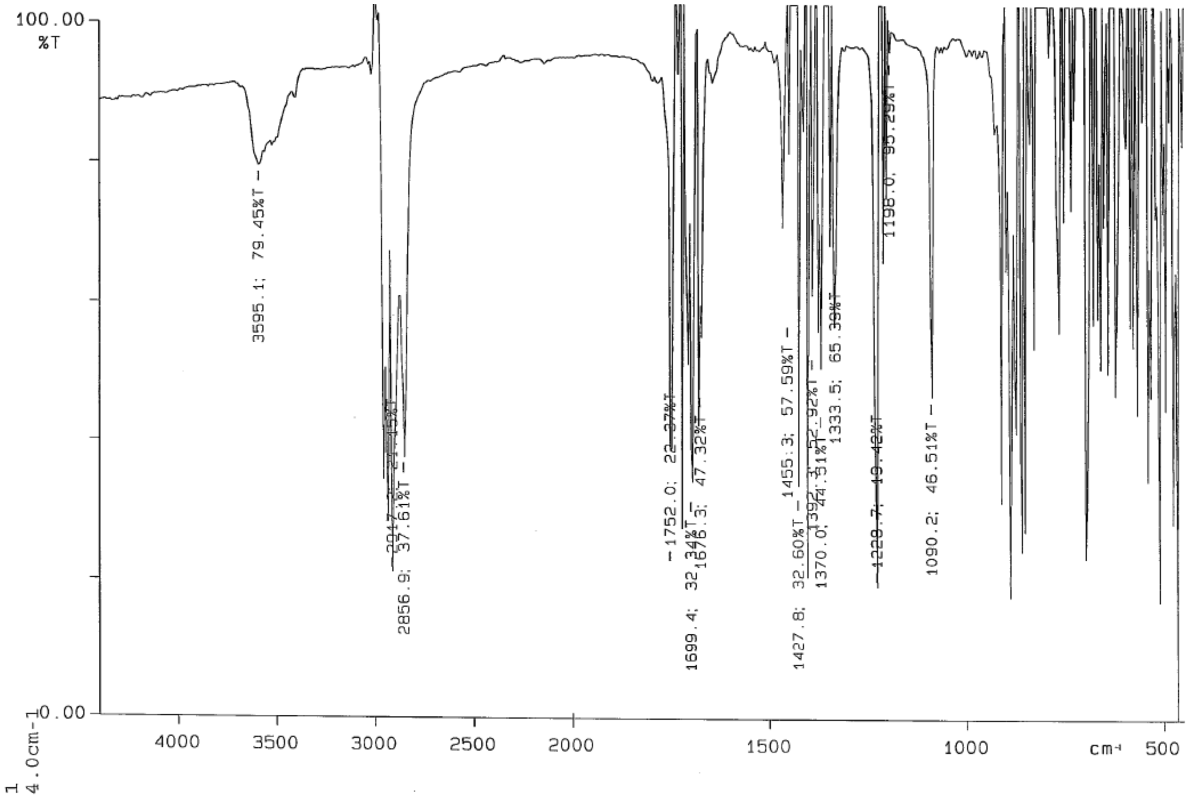
Scan27: Crude oil sample after 24hr aging with UV radiation with Acetone solvent.



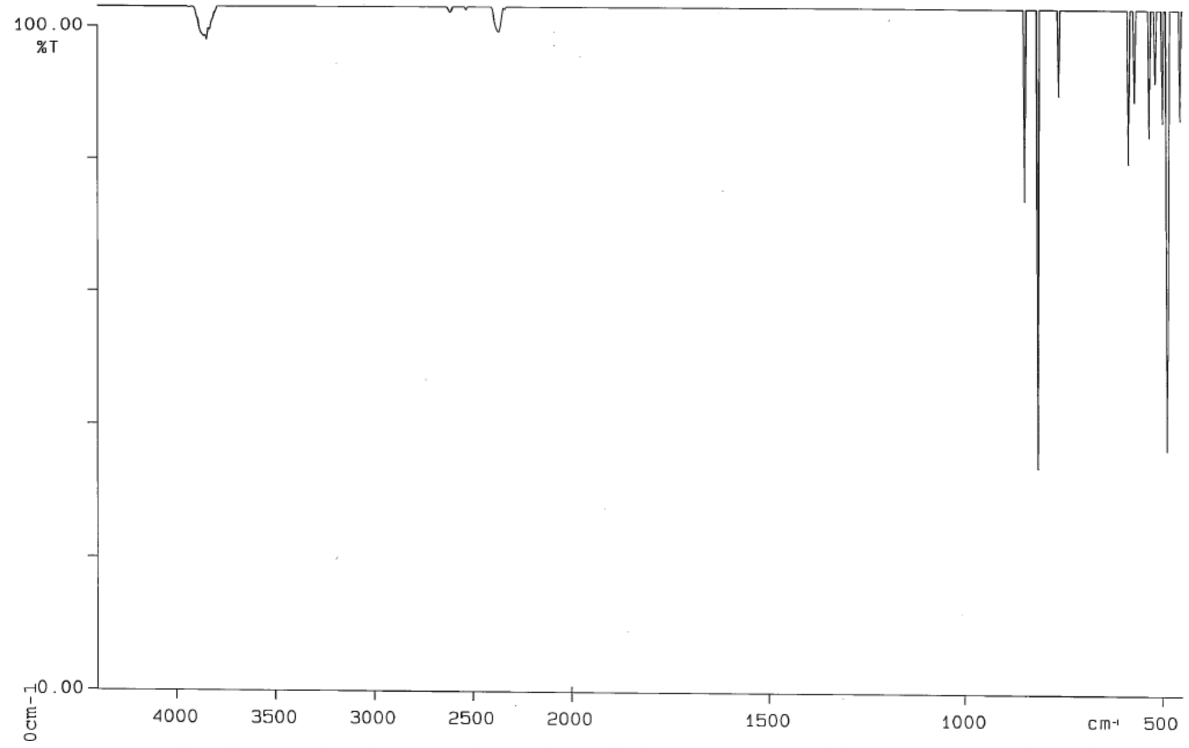
Scan 28: Crude oil sample after 48hrs of UV light exposure with Acetone.



Scan 29: Crude oil sample after 72hrs of UV light exposure with Acetone as solvent.

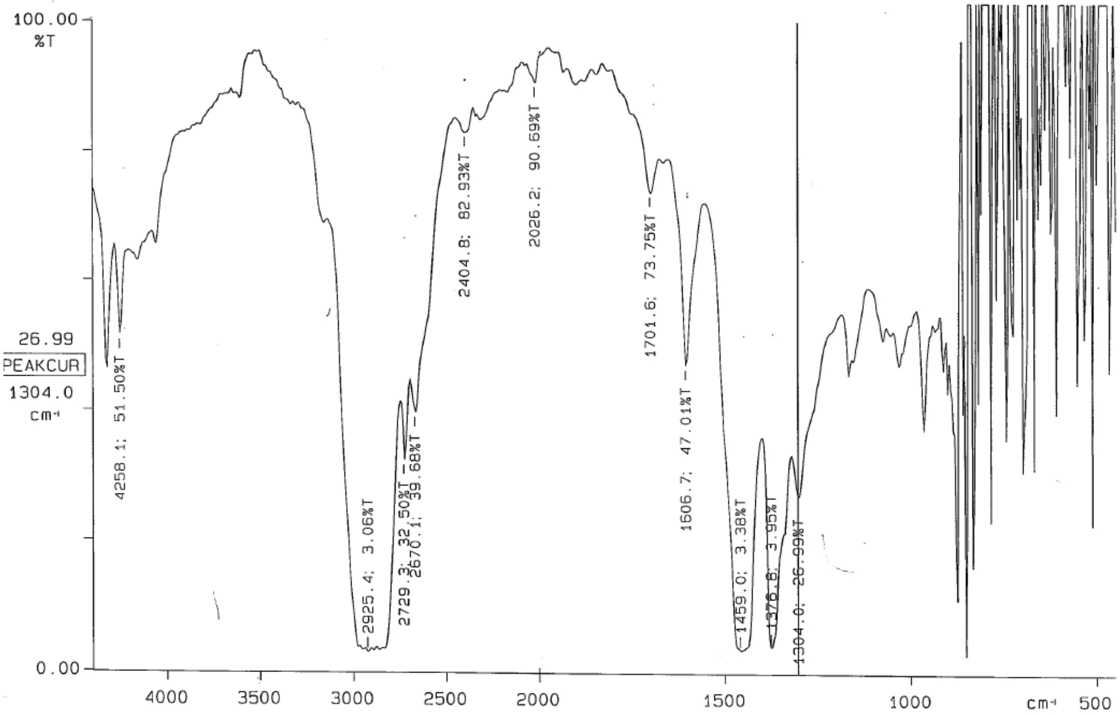


Scan 30: Crude oil sample after 120hrs of UV light exposure with Acetone as the solvent.

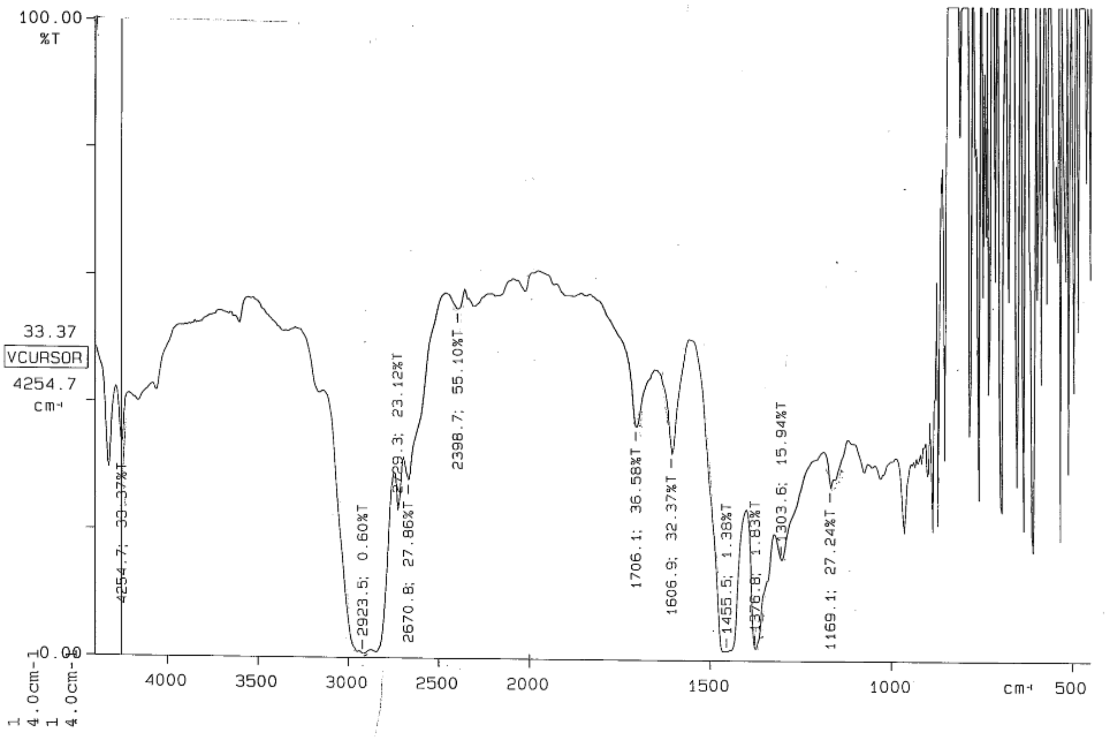


Scan 31: Crude oil sample after 124 hrs of UV light exposure with Acetone as the solvent.

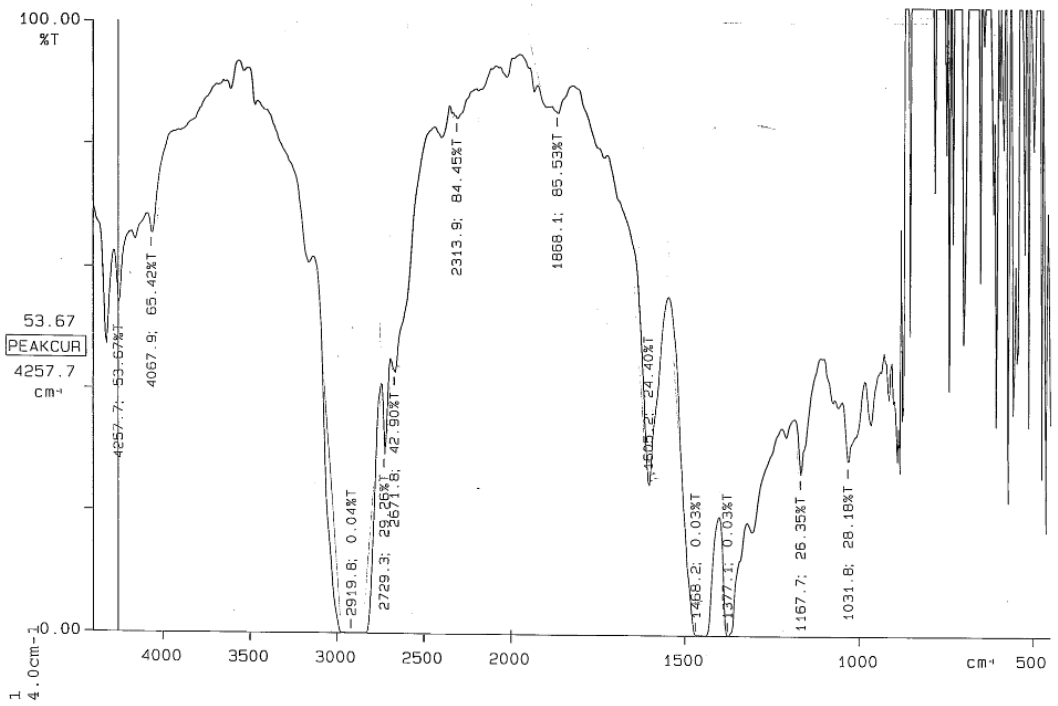
IR Spectrophotometry Scans of Selected Crude Oils



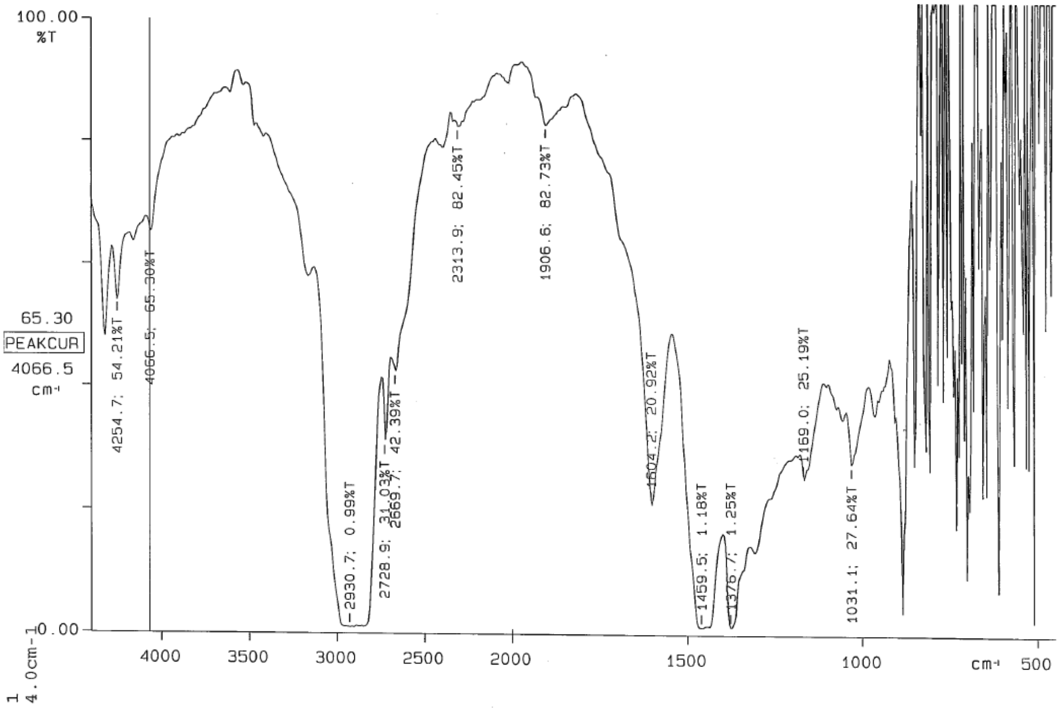
Scan 32: Crude oil sample 1001 sampled at Oxford County.



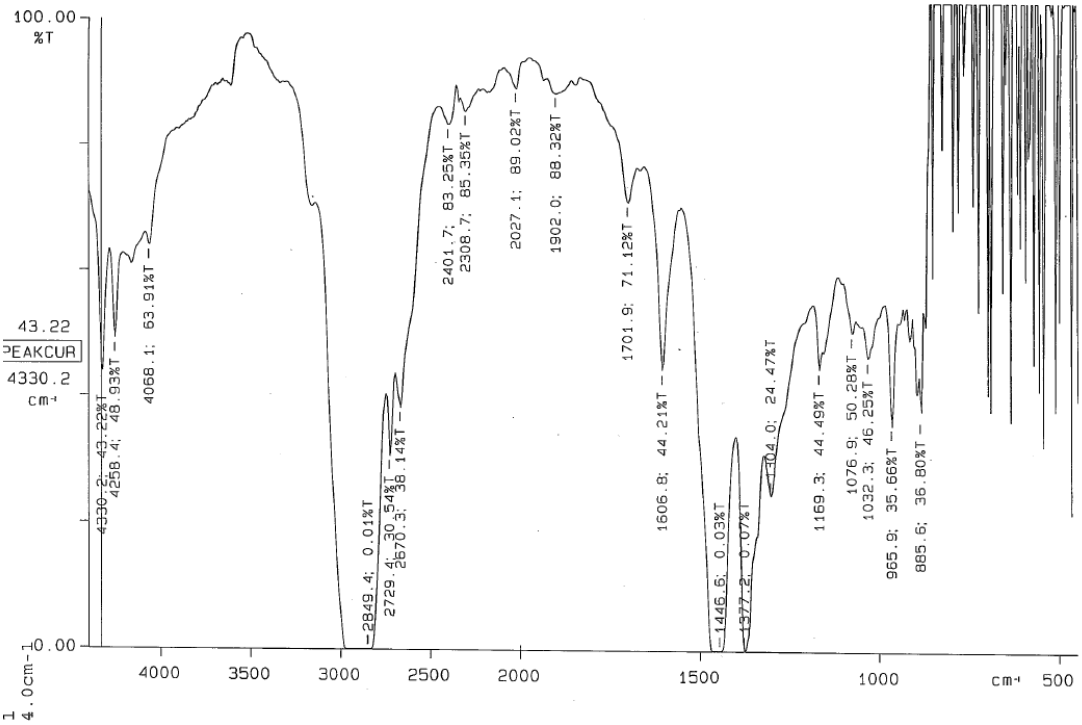
Scan 33: Crude oil sample 2001 sampled at Brount County.



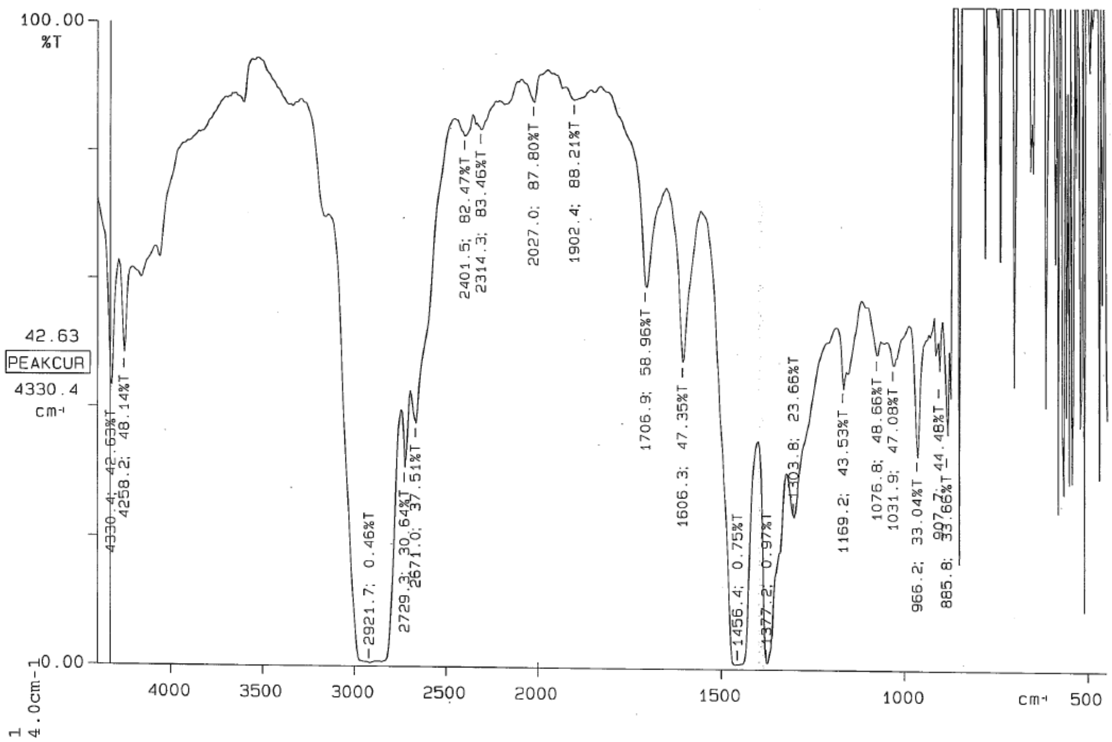
Scan 34: Crude oil sample 3001 sampled at Enniskillen well.



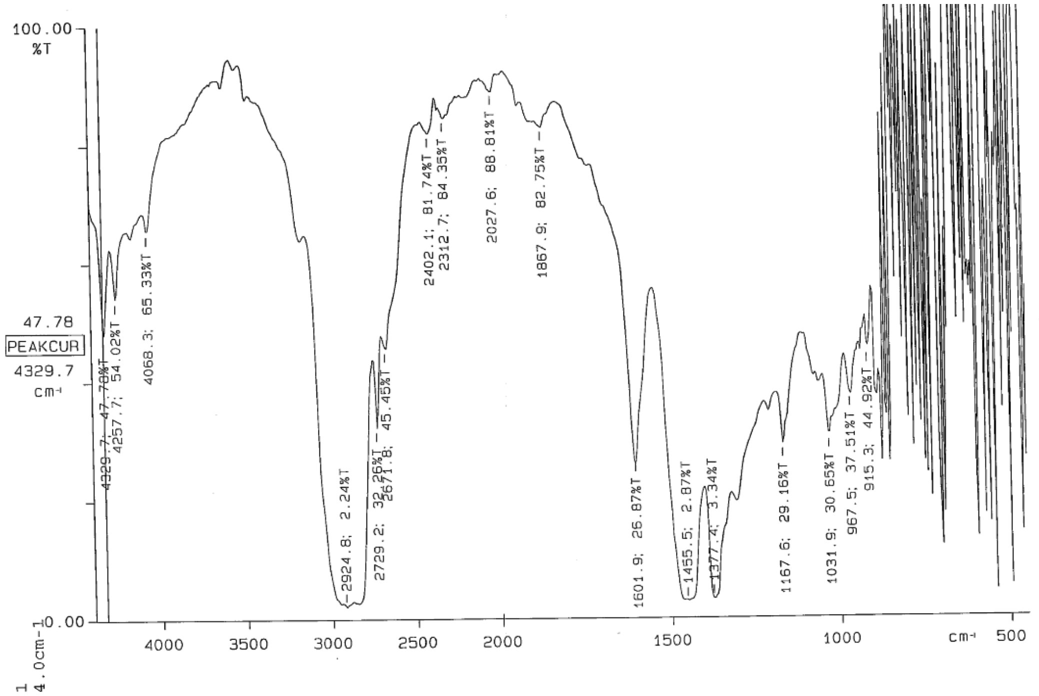
Scan 35: Crude oil sample 4001 sampled at Lambton County.



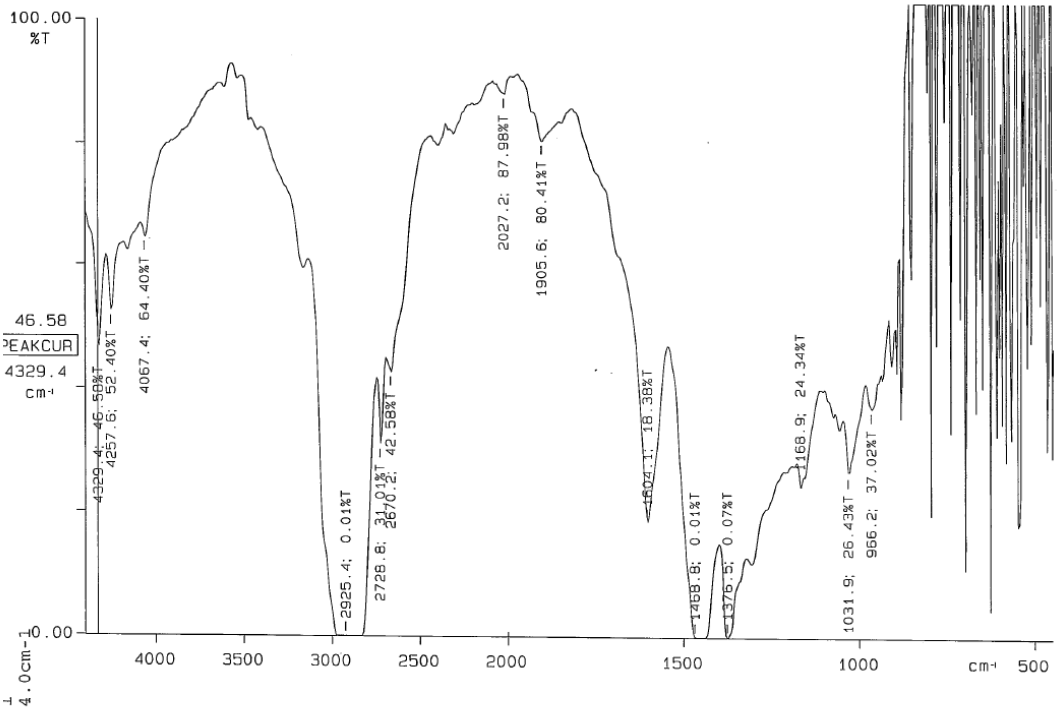
Scan 36: Crude oil sample 1002 sampled at Oxford County (replicate of 1001).



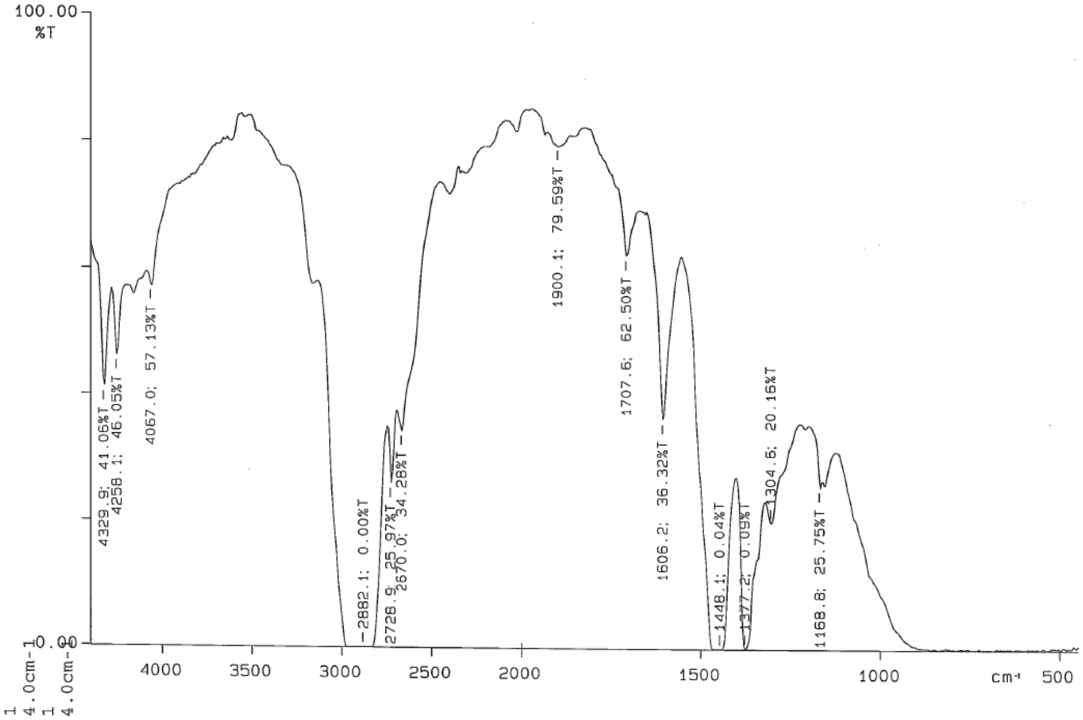
Scan 37: Crude oil sample 2002 sampled at Brount County (replicate of 2001).



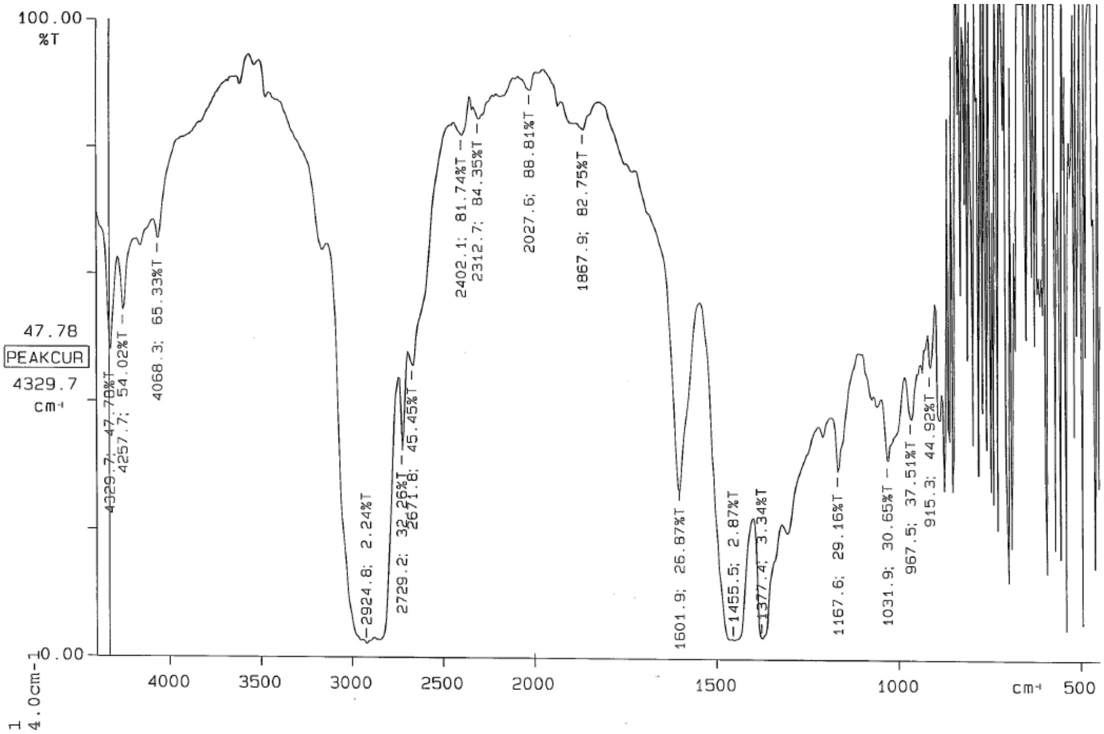
Scan 38: Crude oil sample 3002 sampled at Enniskillen well (replicate of 3001).



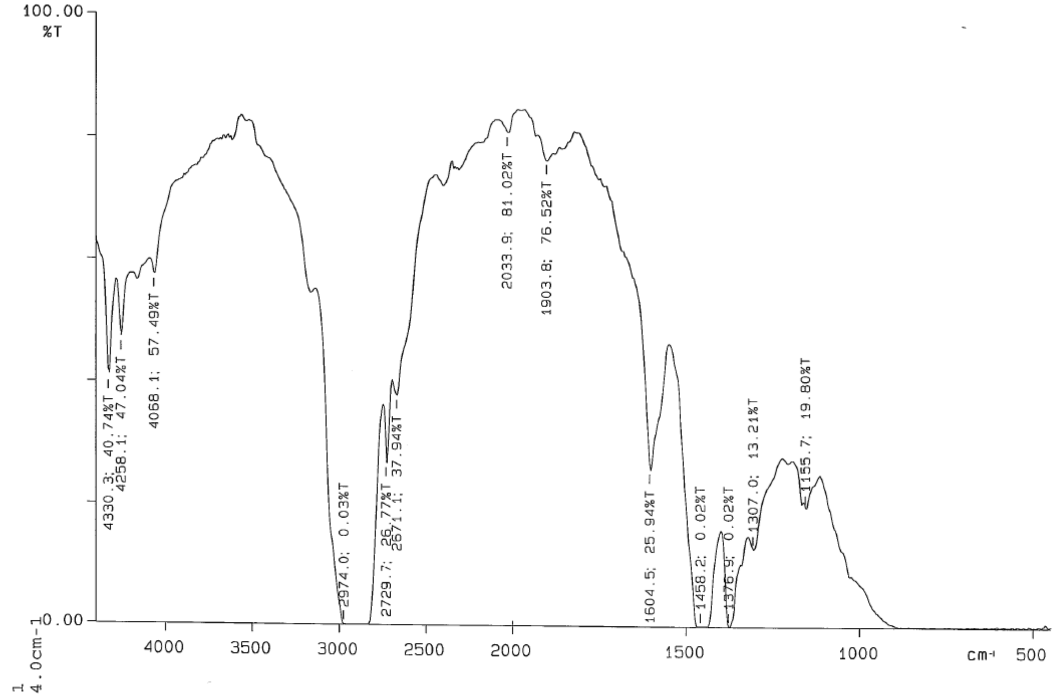
Scan 39: Crude oil sample 4002 sampled at Lambton County (replicate of 4001).



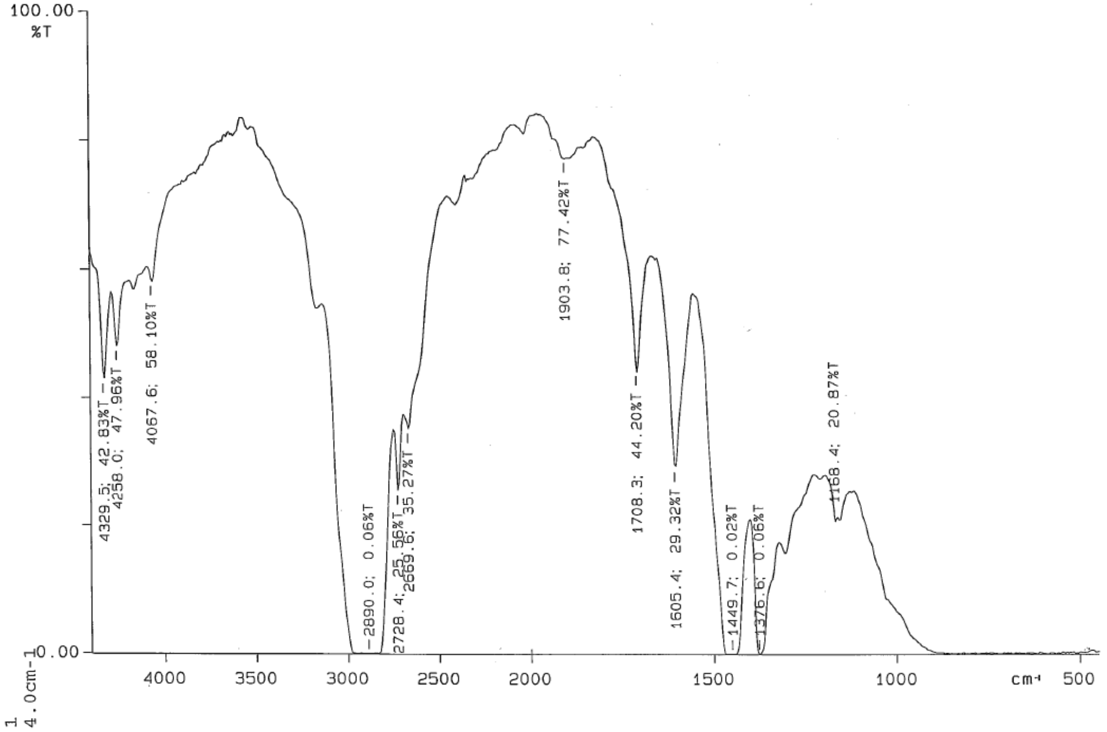
Scan 40: Crude oil sample 1003 sampled at Louisiana, USA.



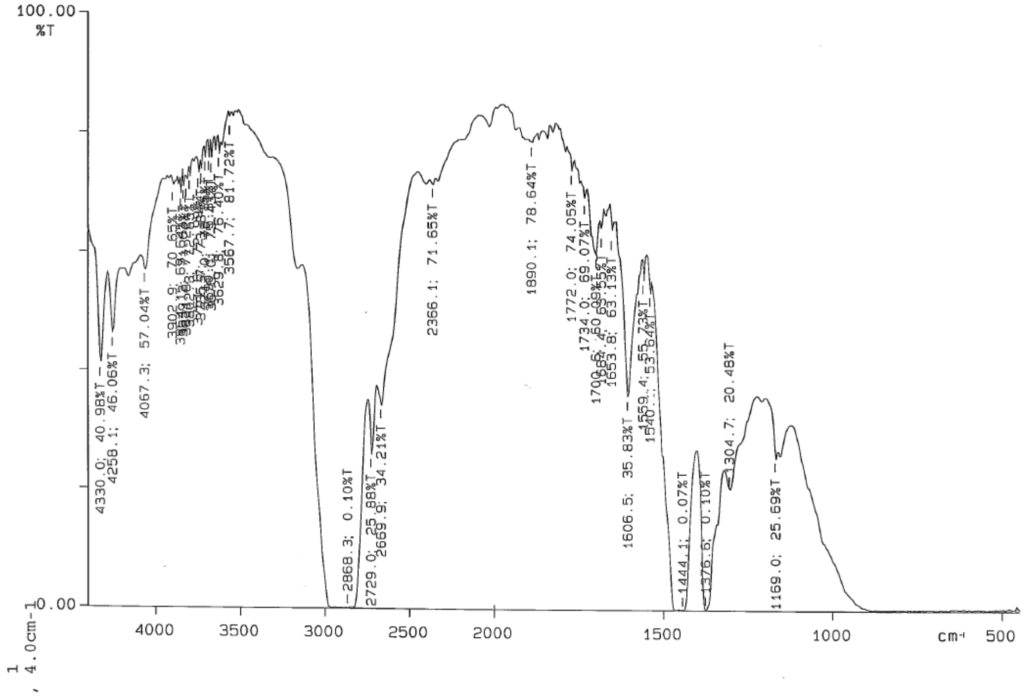
Scan 41: Crude oil sample 2003 sampled at Qua Iboe, Nigeria.



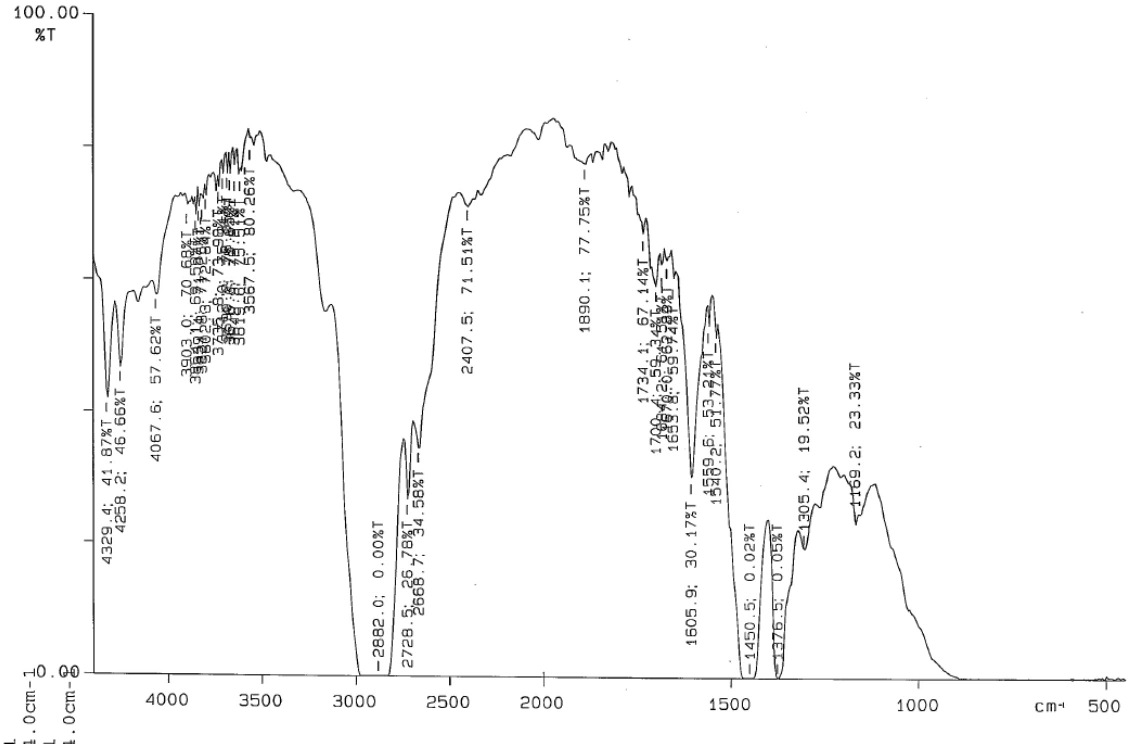
Scan 42: Crude oil sample 3003 sampled at Iraq (Basra Light).



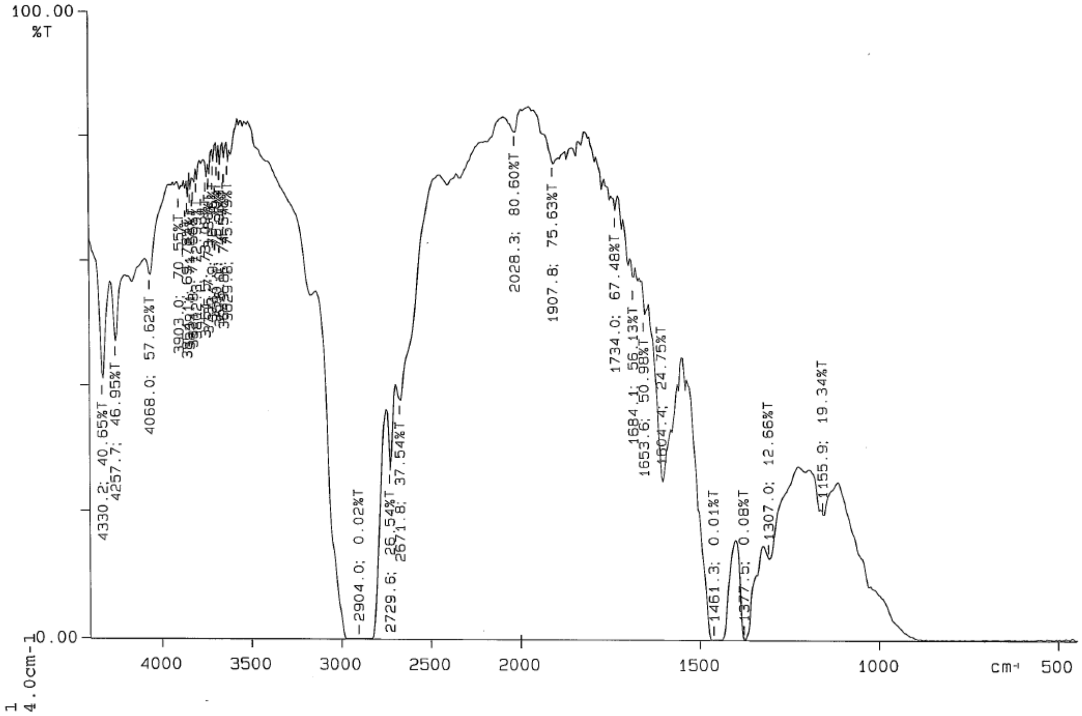
Scan 43: Crude oil sample 4003 which is a Hoops blend.



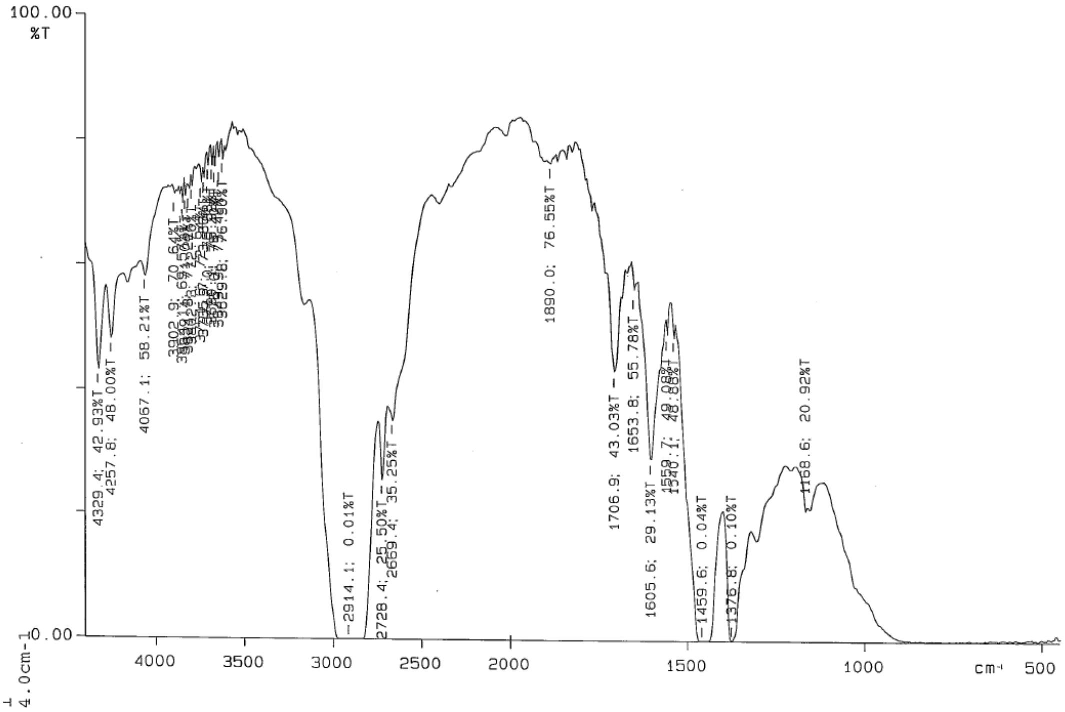
Scan 44: Crude oil sample 1004 sampled at Louisiana, USA (replicate of 1003).



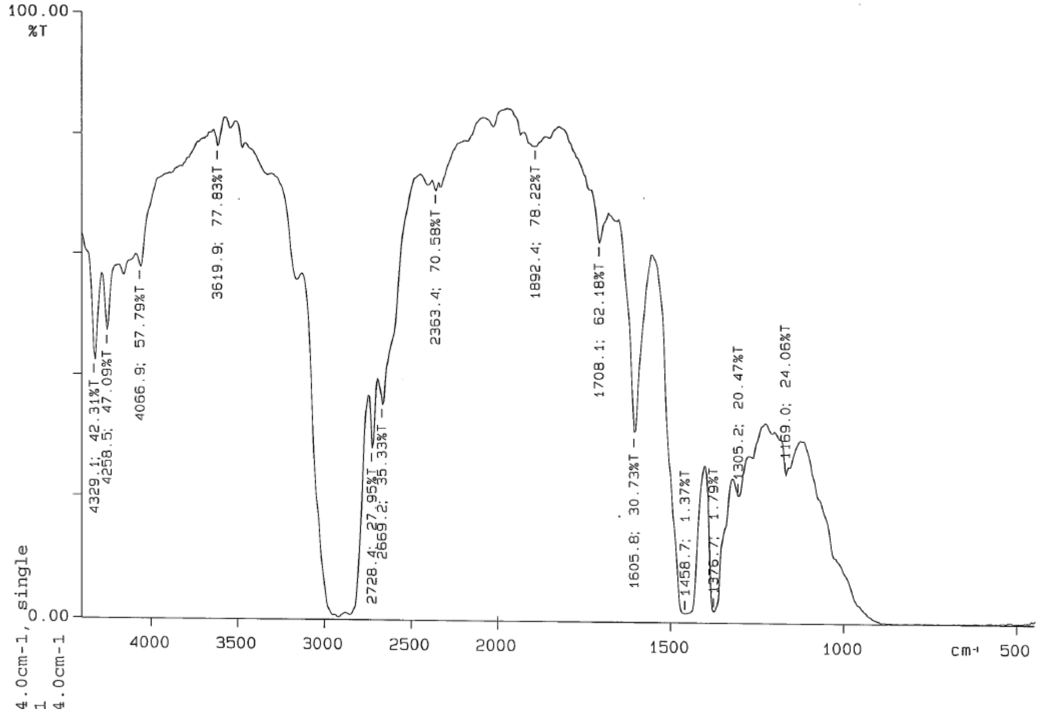
Scan 45: Crude oil sample 2004 sampled at Nigeria (replicate of 2003).



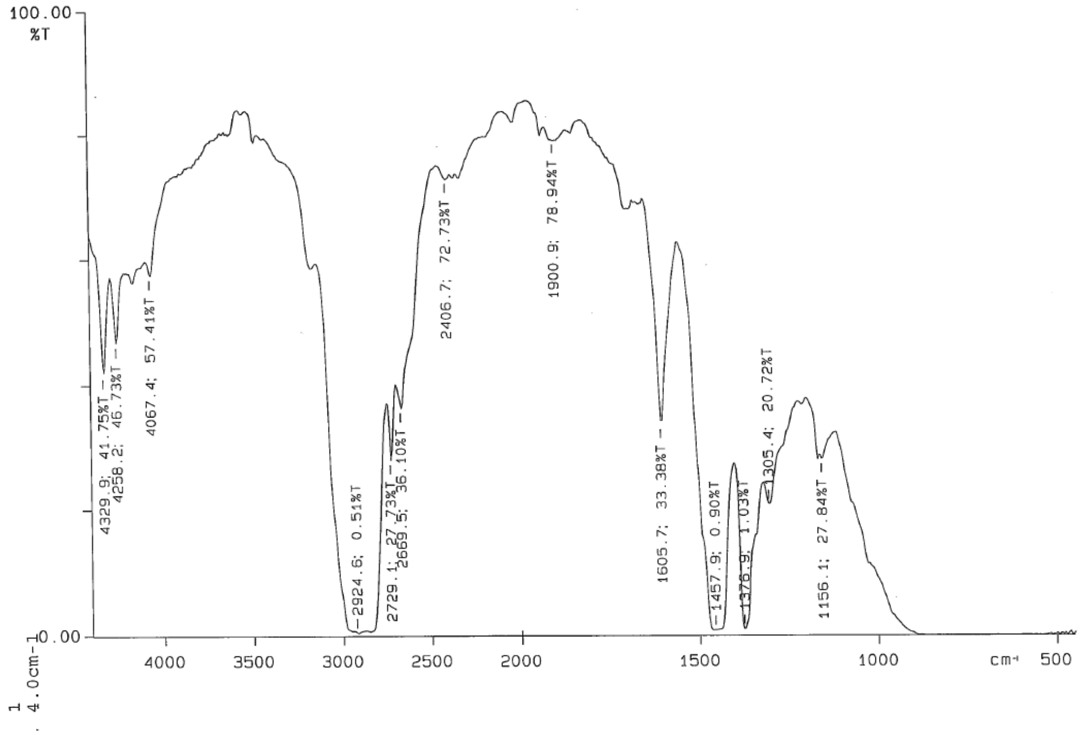
Scan 46: Crude oil sample 3004 sampled at Iraq (replicate of 3003).



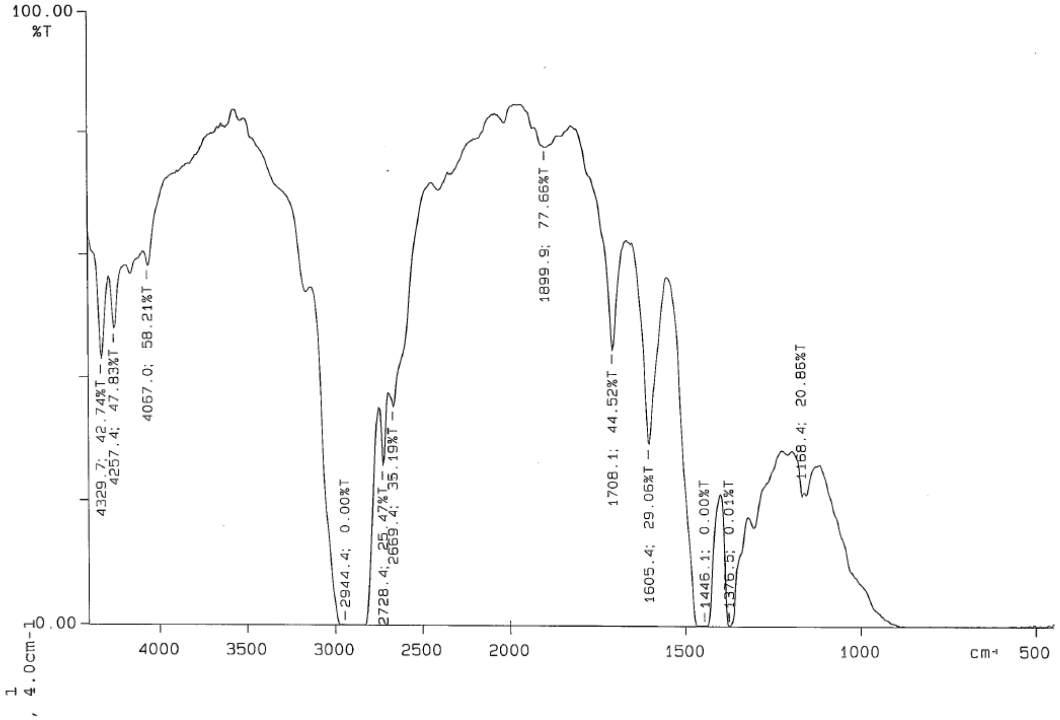
Scan 47: Crude oil sample 4004 which is a Hoops blend (replicate of 3003).



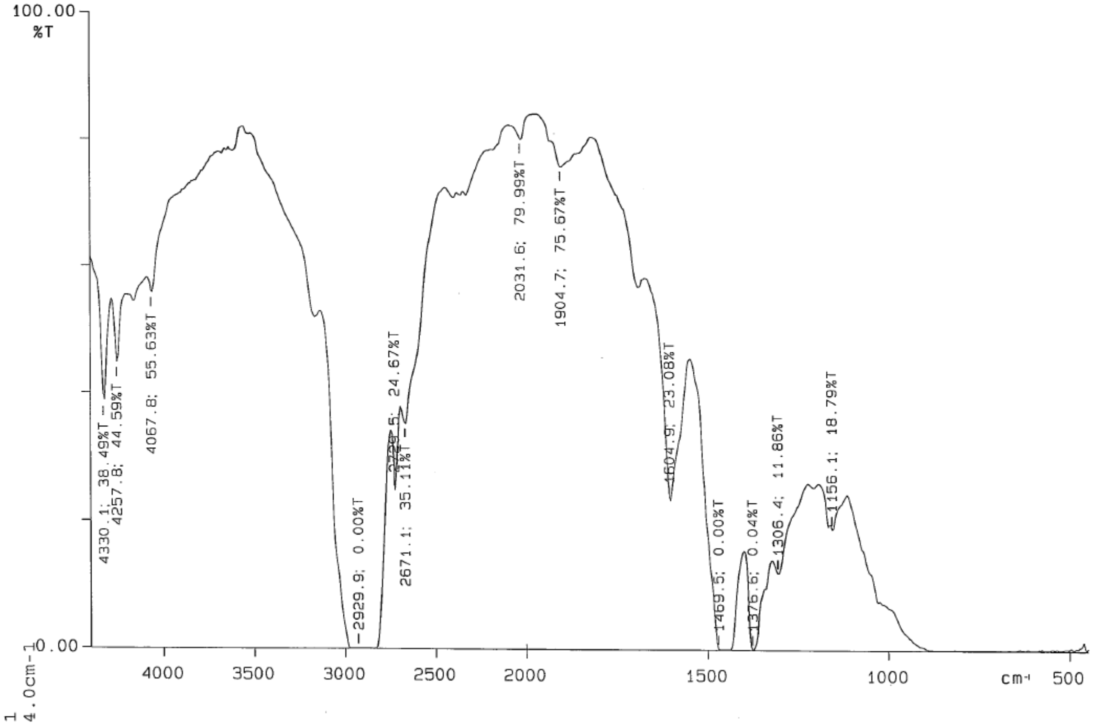
Scan 48: Crude oil sample 1005 sampled from unknown location.



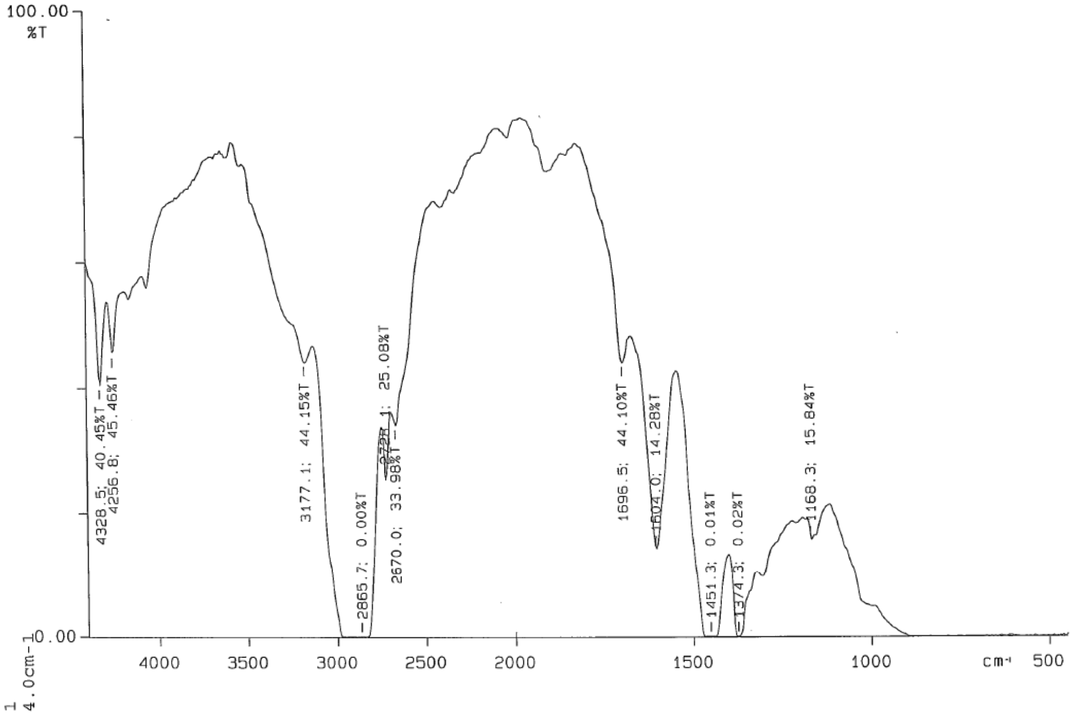
Scan 49: Crude oil sample 2005 sampled from unknown location.



Scan 50: Crude oil sample 3005 sampled from unknown location.



Scan 51: Crude oil sample 4005 sampled from unknown location.



Scan 52: Crude oil sample 5005 sampled from unknown location.