

TREATABILITY OF EMERGING CONTAMINANTS IN WASTEWATER
TREATMENT PLANTS DURING WET WEATHER FLOWS

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A DISSERTATION

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in the Department of Civil, Construction and
Environmental Engineering
in the Graduate School of
The University of Alabama

TUSCALOOSA, AL

2013

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ABSTRACT

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. Emerging contaminants (ECs) have been identified in surface waters receiving wastewater effluents and have been found to potentially cause adverse effects on aquatic wildlife. These materials are produced by industry in very large quantities and are disposed of in toilets and in industrial effluent where partial treatment occurs before their discharge. 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 focuses on the effects of stormwater infiltration, the inflow into sanitary systems and the amounts and treatability of targeted pharmaceuticals. Stormwater is a known source of many contaminants and could mix with wastewater through stormwater infiltration and inflow (I & I). Several dry and wet weather series of samples were obtained from the city of Tuscaloosa's wastewater treatment plant. Samples were examined from four locations within the treatment plant in order to determine if there are significant differences between influent quantities and removal characteristics during periods of increased flows associated with

wet weather compared to normal flow periods. The data generally show treatability appears to remain similar during both wet and dry weather conditions under a wide range of flow conditions. Changes in hydraulic retention times and hourly flow variations were also observed to determine treatment plant performance.

Emphasis was placed on the following pesticides: aldrin, chlordane, dieldrin, endrin, gamma-BHC, heptachlor, heptachlor epoxide, hexachlorobenzene, hexachlorocyclopentadiene, methoxychlor, and toxaphene. As expected, not all compounds were quantified in the samples, with many being below the detection limits.

DEDICATION

This dissertation is dedicated to the generations before me who did not have the resources or opportunity to receive a post-secondary education. I want to particularly dedicate this work to my grandmother, Martha Goodson, who worked in housekeeping for over 15 years at the University of Alabama.

LIST OF ABBREVIATIONS

PCBs- polycyclic biphenyls (Arochlor)

CBZ-carbamazepine

CSOs-Combined sewer overflows

CAS-conventional activated sludge

ECs-Emerging contaminants

ECOC-Emerging contaminants of concern

EDCs endocrine disruptor compounds

FLX-fluoxetine

GFB-Gemfibrozil

HMW-High molecular weight

HRT-hydraulic retention time

IBP-Ibuprofen

LMW-Low molecular weight

MBR-membrane bioreactor

OCP-Organochlorine Pesticides

PPs-Pharmaceutical products

PhACs-Pharmaceutically Active Compounds

PPCPs-Pharmaceuticals and personal care products

PAHs-polyaromatic hydrocarbons

PEs-population equivalents

POP-Persistent Organic Pollutant

STPs- Sewage treatment plants

SRT-solids retention time

SMZ-sulfamethoxazole

TCL-Triclosan

TRM-trimethoprim

WWTP-Wastewater treatment plant

BQ-Below quantification

BDL-Below detection limit

MDL-Method Detection limit

ACKNOWLEDGEMENTS

I am thankful for what I believe was a divine journey. There were several individuals who assisted me through this process. I would like to thank the Department of Civil, Construction and Environmental Engineering for giving me the opportunity to obtain a PhD. Dr. Pauline Johnson was instrumental in my acceptance and I appreciate that tremendously. I also want to thank my advisor and dissertation chair, Dr. Robert Pitt. I am appreciative to him for giving me the opportunity to work with him on the EPA project. Through him, I have learned about patience, perseverance and having a passion for scholarly work. Thank you for being so patient and understanding with me through this process. I would not have finished this process if it were not for your diligence and quick thinking when several roadblocks came my way. I would also like to thank all my committee members for your thoughtful insight and recommendations to make my dissertation a better scholarly work. I would like to thank two of my committee members in particular for the analysis of my data: Dr. Sam Subramaniam from Miles College and Dr. Shirley Clark from Penn State Harrisburg. Thank you to the Environmental Protection Agency and the National Science Foundation (EPSCoR) for the funding received to complete this project. I thank my colleagues, Redi, Olga, Leila and Brad for their insight and encouragement through my journey. John Harden was also a great encouragement to me. You are more than a colleague: you are a great friend!

When obtaining my PhD, it was important for me to have a support system. Without these individuals, I would have given up the journey. I would like to thank my friends who I met through the African-American Graduate Student Association for encouraging me when things got really difficult. Ebony Johnson and Nadia Richardson were two of my closest friends who walked with me through my ups and downs. They also obtained their PhDs through rough waters

and have encouraged me to do the same. I would like to thank Kathy Echols, BJ Guenther and the Women's Dissertation Support group for their love, support and encouragement when all I wanted to do was procrastinate. Accountability is important in this process.

I would like to thank my chair, Dr. Robert Pitt; the department chair, Dr. Ken Fridley and Dr. John Schmitt from the Graduate School for helping me through the challenges that I faced toward the end of my matriculation. I would not be finished if it were not for you.

Lastly, I would like to thank my family for their prayers, support and encouragement then I had many doubts and fears. Mom, thanks for supporting me at my defense! Marilyn, thank you for your help! I love you guys tremendously! I offer a VERY special thank you to Angela Mitchell! She provoked me with a strong tongue to stop talking about graduate school and DO IT! I would not be a PhD if it were not for you!

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1.0 INTRODUCTION

The U.S. Environmental Protection Agency (EPA) 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, Gonzalez, and Barceló 2003, 685-696). These pollutants have recently 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 PCBs and DDTs (Snyder et al. 2006). Researchers such as 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, 4526-4534). The EPA works in conjunction with the U.S. Geological Survey to compile a list of these contaminants found in the U.S. waterways (A National Reconnaissance). Samples have been obtained from 139 U.S. streams and waterways to analyze ninety five organic wastewater contaminants (Kolpin et al. 2002, 1202-1211). These emerging contaminants are employed in large quantities during daily consumption. Yet many have no maximum concentration limits in discharge permits. Research on several contaminants investigated during the Reconnaissance Study is being conducted to decipher the potential effect of these compounds on aquatic wildlife and the environment. Campbell (2006) conducted a study as an example 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, 1265-1280). 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, 14-21).

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. Studies are performed to determine 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 glucuronides) or even unchanged (Heberer 2002, 5-17). Some of these conjugates can pass through the treatment plant untreated and enter into the waterways. 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 (Heberer 2002, 5-17).

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. Pharmaceuticals enter the treatment system either directly, or through fecal matter or urine. Personal care products could possibly enter the treatment plant through direct disposal or by shower or bath water. 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.

Some emerging contaminants may not be adequately removed by wastewater treatment facilities. Recent studies demonstrate wastewater treatment plant removal of personal care products and pharmaceutical can range between 60% and 90% for a variety of polar compounds (Carballa et al. 2004, 2918-2926). The removal rate is mostly contingent on the physical and chemical nature of the pollutant and the effect of the wastewater matrix. It also depends on the treatment plant itself, the retention time through each unit process and the specific unit processes used at the treatment facility (Mohapatra et al. 2010, 923-941). 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.

1.1 OBJECTIVES

The purpose 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 were therefore to:

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

During this research, several 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.

1.2 RESEARCH QUESTIONS

The questions addressed during this research include:

1. Do infiltration and inflow affect the EC concentrations of the influent entering the treatment plant?
2. What quantities of ECs are being discharged to the treatment plant during large rain events due to stormwater inflow or infiltration (I&I)?
3. How significant is stormwater I&I in affecting the treatment of the ECs; which stormwater characteristics (such as increased flows or modified concentrations) affect the treatment processes of the wastewater treatment plant?

2.0 LITERATURE REVIEW

Much of the literature concerning emerging contaminant removal involves advanced treatment of sanitary wastewater. Typical conventional treatment involves sedimentation and biological treatment processes; advanced treatment systems (usually chemical) can be costly and are not commonly used. This review discusses treatability of ECs using conventional wastewater treatment under normal conditions, although advanced treatment processes are briefly discussed, along with available information pertaining to wet weather flow conditions.

Most current WWTPs are not designed to treat substances such as human and veterinary pharmaceuticals, personal care products, surfactants and surfactant residues, plasticizers and various industrial additives (Petrovic, Gonzalez, and Barceló 2003, 685-696). Also, pollutants polar in nature are more difficult to remove by sedimentation processes, as they are usually more soluble. Therefore, treatment results for ECs at wastewater systems are varied depending on the unit processes available and the characteristics of the pollutants. Some ECs entering the treatment plants are unaltered through use, while others are conjugates of parent compounds, which may be more resistant to treatment.

Due to the complexity of wastewater characteristics, proper analyses and analytical equipment are necessary. Some emerging contaminants are absorbed onto particulates and require effective extractions as part of the analytical methods. However, if certain chemicals have low sorption onto particulates, pollutant removal is more likely to be effective in the biological secondary treatment processes at the treatment plant.

2.1 TREATMENT AND PHYSICO-CHEMICAL PROPERTIES OF EMERGING CONTAMINANTS

Emerging contaminants include a broad range of pollutants with varying characteristics and effects on the environment. In order to gain some understanding of how these pollutants are removed by different unit processes, it is possible to compare them to other contaminants having similar characteristics. Yet not all pollutants in the same category behave similarly. For example, one may ask if all hormones are removed at the same rate during the secondary treatment process?

There are many physicochemical properties known for emerging contaminants, but only some are important when estimating EC behavior in treatment systems (Mauricio et al. 2006, 75-87). 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, Schäfer, and Elimelech 2005, 7698-7705). 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, Gros, and Barcelo 2006, 68-81). 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, 229-246).

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, 5095-5124).

2.1.1 Pharmaceuticals and personal care products (PPCPs)

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, 753-761). 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, Yang, and Metcalfe 2005, 7469-7475). Polarity, photo-stability and volatility determine the fate and transport of PhACs in the wastewater system (Miao, Yang, and Metcalfe 2005, 7469-7475). 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, 135-149).

Pharmaceuticals are separated into three categories according to their functional groups: carboxylic, hydroxyl and amide (Nakada et al. 2006, 3297-3303). The biological and chemical activities of pharmaceuticals are strongly influenced by their functional groups (Nghiem, Schäfer, and Elimelech 2005, 7698-7705). 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, Tuhkanen, and Kronberg 2005, 2219-2228). 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.

Table 2.1. Selected Chemical Properties of Pharmaceuticals

Pharmaceutical	Log k_{ow}	Solubility (mg/L)	pKa	Toxicity ($\mu\text{g/L}$)	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 $\mu\text{g/L}$	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 $\mu\text{g/L}$	Phenol
Trimethoprim	0.79	400	7.2	P. subcapitata. IC ₅₀ 80- 130 mg/L	Diamine

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, 2677-2682). Sulfamethoxazole contains two functional moieties (-NH-S(O₂)) at both sides of the sulfonamide linkage (Nghiem, Schäfer, and Elimelech 2005, 7698-7705). Sulfamethoxazole is shown to dissociate twice, once with the protonation of the primary amine group -NH₂ and then with the deprotonation of the sulfanomide (-NH) (Nghiem, Schäfer, and Elimelech 2005, 7698-7705). 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, Schäfer, and Elimelech 2005, 7698-7705). 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 (Pérez, Eichhorn, and Aga 2009, 1361-1367). 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, 7069-7076).

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, 7069-7076). Toxicity of the freshwater green alga *P. subcapitata* has an IC 50 of 1.5 mg/L (Yang et al. 2009, 1201-1208). 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, 3533-3541). 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, 1-6). 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, 1-6). 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, 1-6). 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 (Hazardous Substance Database 2012; 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 trifluorine 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 glucuronide and norfluoxetine from the human body. Some of the glucuronides are reactivated in wastewater treatment plants by cleavage (Nentwig 2007, 163-170). 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-007mmHg (Nentwig 2007, 163-170). 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 predominately protonated at neutral pH and only partially adsorb to sludge (Bedner and MacCrehan 2006, 2130-2137). The lethal concentration at 50% (IC 50) for *P. subcapitata* was found to be 24 μ g/L (Brooks et al. 2003, 169-183). 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, 1-10). Seventy-two percent of the compound is released in urine, and various metabolites are excreted from urine into the wastewater system (Zhang, Geißen, and Gal 2008, 1151-1161). 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, Schäfer, and Elimelech 2005, 7698-7705). Carbamazepine has a low octanol-water coefficient (K_{ow}) and a water solubility of 17.7 mg/L (25°C) (Nakada et al. 2006, 3297-3303; Sethia and Squillante 2004, 1-10; Zhang, Geißen, and Gal 2008, 1151-1161). 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, Geißen, and Gal 2008, 1151-1161). Carbamazepine is frequently detected in groundwater up to concentrations of 610 ng/L and in other water bodies (Zhang, Geißen, and Gal 2008, 1151-1161). 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 (Hazardous Substance Database 2012; 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, Geißen, and Gal 2008, 1151-1161). 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, Geißen, and Gal 2008, 1151-1161). 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 metabolites 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, 370-375).

Table 2.2 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, 517-525). 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, 4998-5004). Triclosan, a polychlorinated diphenyl ether, has similar chemical properties to hydroxylated metabolites of ortho-substituted PCBs and PBDEs (Cherednichenko et al. 2012, 14158-14163). 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 $\mu\text{g/L}$ 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, 4998-5004; Heidler and Halden 2007, 362-369). 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 Substance Database 2012). Even though its dissociated form tends to degrade in sunlight, triclosan is quite resistant to hydrolysis (Singer et al. 2002, 4998-5004). It is converted, either by UV radiation or photohydrolysis, into 2, 8-dichlorodibenzo-p-dioxin (2, 8-DCDD, a dioxin) (Latch et al. 2005, 517-525). 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, 452-456). Also, exposure of triclosan to freshwater green alga *P. subcapitata* yielded an IC 50 of $1.4 \mu\text{g/L}$ (Yang et al. 2009, 1201-1208). In aerobic water-sediment systems maintained in darkness at $20 \pm 2^\circ\text{C}$, 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 (U.S. Environmental Protection Agency 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 Substance Database 2012). Exposure of *Daphnia* to ibuprofen yielded an EC 50 of 108 mg/L (Cleuvers 2003, 185-194).

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, sunlit, lake water and reservoir water to have half-lives of 120 ± 16 days and 288 ± 61 days, respectively (Araujo et al. 2011, 13-18).

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.

2.1.2 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, 104-115). 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 will help 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 (Buseti et al. 2006, 104-115).

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 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, 1447-1463). 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 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 2.3. Characteristics of PAHs

Compound	Molecular weight (g/mol)	Solubility (water)(mg/L)	Log kow	Volativity 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 x 10 ⁻³ *	
acenaphthene	154.2	1.93*	4.02**	7.91 x 10 ⁻⁵ *	LC50 Salmo gairdneri 1570 µg/L
fluorene	166.2	1.68-1.98 *	4.12**	1.0 x 10 ⁻⁴ *	EC 50 V. fischeri 4.10 µg/mL
anthracene	178.2	0.076 *	4.53**	1.77 x 10 ⁻⁵ *	D.magna EC 50=211 µg/L
phenanthrene	178.2	1.20 *	4.48**	2.56 x 10 ⁻⁵ *	EC50; Daphnia magna 678.41 µg/L
pyrene	202.2	0.077 *	5.12**	1.14 x 10 ⁻⁵ *	D.magna EC 50=67000 µg/L

fluoranthene	202.2	0.20-0.26 *	5.14**	6.5 x 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 x 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 x 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 volatilized 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).

Sorption onto particulates is directly related to sorption coefficients, solubility and the amount of organic material, but biodegradation of PAHs vary considerably. The study by 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 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.

2.1.3 Pesticides and Herbicides

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, 231-271); 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 (Katsoyiannis and Samara 2004, 2685-2698). 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. 1995, pp. 964-970).

The major types of pesticides are organochlorine pesticides and organophosphorus pesticides. Of these categories, they are divided into four types: insecticides, fungicides, herbicides and bactericides (Badawy, Ghaly, and Gad-Allah 2006, 166-175). Chlorinated phenoxy acid herbicides, which account for the majority of pesticides worldwide, are characterized by high polarity and thermal lability (Petrovic, Gonzalez, and Barceló 2003, 685-696).

Organochlorine pesticides are known for their persistence in the environment and their bioaccumulation in the food chain (Jiries, Al-Nasir, and Beese 2002, 97-107) .

Organophosphorus pesticides degrade faster in the environment than organochlorine pesticides (Jiries, Al-Nasir, and Beese 2002, 97-107). 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, 7193-7200). 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, Lee, and Wolf 1980, 19-28). In the Selah study, total 2,4D was found in the Dallas wastewater treatment plant study. 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 (U.S. EPA 2001).

Table 2.4. Properties of Pesticides

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 treatment 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 (U.S. 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, Vallero, and Lewis 1999, 4373-4378). It is an isomer and can be conformed to other more toxic compounds. Theoretically, the sorption onto particulate matter is a method employed 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, 792-797). 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 (U.S. Environmental Protection Agency). Chlordane has an environmental half-life of ten to twenty years (Bondy et al. 2000, 386-398). Because it is fat soluble, it can enter animal tissue and accumulate, causing harmful effects in 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-Jørgensen et al. 2001, 141-153). The hormone 17β -estradiol is important for stimulating breast cell proliferation in mature breast tissue (Bonefeld-Jørgensen et al. 2001, 141-153). 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. 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 it is 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. It binds to soil and is 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 Labour Organisation, United Nations Environment Programme, and World Health Organization 1988). Aldrin breaks down into dieldrin which kills disease carrying insects, such as the tsetse fly. Since the early 1970s, the two compounds are severely restricted or banned in several countries, especially in agriculture (International Labour Organisation, United Nations Environment Programme, and World Health Organization 1988). Nevertheless, they are still used in some other countries for termite control (International Labour Organisation, United Nations Environment Programme, and World Health Organization 1988). 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 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 2.5. Physical and Chemical Properties of Aroclors (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 x 10 ⁻⁴	2.9 x 10 ⁻⁴	5.6
1221	200.7	0.59 (24°C)	6.7 x 10 ⁻³	3.5 x 10 ⁻³	4.7
1232	232.2	0.45	4.06 x 10 ⁻³	No data	5.1
1242	266.5	0.34	4.06 x 10 ⁻³	5.2 x 10 ⁻⁴	5.6
1248	No data	No data	No data	No data	No data
1254	328	0.012	7.71 x 10 ⁻⁵	2.0 x 10 ⁻³	6.5
1260	357.7	0.0027	4.06 x 10 ⁻⁵	4.6 x 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 on to particulate matter rather than dissolve in aqueous solutions and are therefore likely to be removed at wastewater treatment plants by sedimentation.

2.1.4 Endocrine disruptors

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, 1265-1280).

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, 1265-1280). In their sediment associations, there is the potential for biological uptake, degradation and transformations to less or more mobile forms (Campbell et al. 2006, 1265-1280). The solubility values suggest they would not stay in solution; however, most EDCs are identified in water samples (Campbell et al. 2006, 1265-1280). 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, 753-761). Synthetic compounds with estrogenic activity include 17 α -ethynylestradiol (EE2), and alkylphenol polyethoxylates (NPnEO) (Teske and Arnold 2008, 107-124). In the Teske literature review, chemical and biological characteristics such as chemical structure, molecular weight,

water solubility at 20C 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.

Table 2.6. Properties of Endocrine Disruption Chemicals

EDC	Molecular weight (g/mol)	Water solubility at 20C (mg/L)	Log K_{ow}
Estrone (E1)	270.4	13	3.43
17 β -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 ($n \geq 3-5$)	352.0-440.0	5.88-9.48	4.2-4.3
Nonylphenoxy ethoxy acetic acid	322	soluble	1.34

(Teske and Arnold 2008, 107-124)

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 17 β -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.

2.2 WASTEWATER TREATABILITY IN CONVENTIONAL WWTP

2.2.1 Description of wastewater 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 dissertation research, 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).

2.2.2 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 dissertation research, 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.

2.2.2.1 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 (Göbel et al. 2007, 361-371). The average inflow (dry weather) is 16,500 m³/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 ($V=2,500 \text{ m}^3$). The main conventional activated sludge treatment (CAS-K) includes denitrification ($V=1,900 \text{ m}^3$) and nitrification ($V=3,700 \text{ m}^3$) 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 ($V=4 \text{ m}^3$) and nitrification ($V=6 \text{ m}^3$) 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 (Göbel et al. 2007, 361-371). Both systems are designed for nitrification and denitrification. Conventional activated sludge treatment includes a denitrifying volume (anoxic, mixed) of $2,300 \text{ m}^3$ and nitrifying (aerobic) volume of $6,800 \text{ m}^3$. 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 gives a list of the reduction rates for the primary treatment process.

Table 2.7. 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	21312-10-7	9 to 21
	SMX + N4AcSMX		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

(Göbel et al. 2007, 361-371)

The Gobel study showed a high degree of variability in the removal of each of the ECs during primary treatment. 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 (Göbel et al. 2007, 361-371). 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 2.8. 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

(Göbel et al. 2007, 361-371)

In the Castiglioni (2006) study, six different wastewater treatment plants were observed with varying flow rates and population. Table 8 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 2.9. 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, 357-363)

The Castiglioni research 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.

Table 2.10. 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	+
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(Castiglioni et al. 2006, 357-363) *presence or absence of pharmaceutical (qualitative)

The wastewater treatment plant in the Rosal (2010) study is located in Alcala de Henares in Madrid, Spain. This plant treats a mixture of domestic and industrial wastewater with a capacity of 3,000 m³/h (33,020 gpd) (Rosal et al. 2010, 578-588). 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, 578-588). 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 2.11. Dissociation Constants, Influent and Effluent Concentrations of ECs

Compound	Caffeine	<i>Carbamazepine</i>	<i>Gemfibrozil</i>	Naproxen	<i>Sulfamethoxazole</i>	<i>Triclosan</i>	<i>Trimethoprim</i>
pKa	10.4	13.9	4.7	4.2	5.7	7.8	6.8
Influent (ng/L)	65 x 10 ³	173	17 x 10 ³	5228	530	2417	197
Max	5 x 10 ³	106	415	1196	162	<LOQ	78
Min							
Avg	23 x 10 ³	129	3.5 x 10 ³	2363	279	860	104
Effluent (ng/L)	1589	173	5233	2208	370	512	148
Max	<LOQ	69	3	359	104	<LOQ	<LOQ
Min							
Avg	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, 578-588)

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 m³/d to 105,300 m³/d. All activated sludge systems studied used primary clarification. Table 11 is a compilation of the plant systems' influent and effluent concentrations. Table 12 shows the percent reductions of activated sludge treatment systems for this study.

Table 2.12. 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 (%)
<i>Ibuprofen</i>	0.061	Influent	8.84	8.45	16.5	
		Effluent	0.353	0.384	0.773	95.4%
<i>Gemfibrozil</i>	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%
<i>Triclosan</i>	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, 544-558)

The Lishman study 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, 544-558) and 69 percent (Ternes 1998, 3245-3260)(Lishman et al. 2006, 544-558). Clara et al (2003) showed moderate removals for diclofenac and gemfibrozil of between 53 percent and 74r percent (Lishman et al. 2006, 544-558). 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 2.13. 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, 544-558); *--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 12 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 2.14. 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, 1721-1726); *****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. 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, Petrovic, and Barceló 2007, 1365-1377). 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 m³/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 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 2.15. Comparison of Membrane Bio Reactor and Conventional Activated Sludge**

Compound	Elimination percentage	
	MBR	CAS
Analgesic/Anti-inflammatory drugs		
<i>Naproxen</i>	99.3(1.52)	85.1(11.4)
<i>Ibuprofen</i>	99.8(0.386)	82.5(15.8)
<i>Diclofenac</i>	87.4(14.1)	50.1(20.1)
Anti-epileptic drugs		
<i>Carbamazepine</i>	No elimination	No elimination
Antibiotic		

<i>Sulfamethoxazole</i>	60.5(33.9)	55.6(35.4)
Lipid Regulator/Cholesterol lowering statin drug		
<i>Gemfibrozil</i>	89.6(23.3)	38.8(16.9)

** (Radjenovic, Petrovic, and Barceló 2007, 1365-1377)

This dissertation 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. 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, 4021-4026). $Fe(II)Cl_2$ 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 2.16. 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, 4021-4026)

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, 3245-3260). The average daily flow rates ranged from 58,100 to 89,900 m³/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 m³/day to 89,900 m³/day. The removals of bezafibrate, diclofenac, naproxen and clofibrac acid were

significantly reduced on the rainfall day and only bezafibrin (<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, 3245-3260). 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 et al. 2005, 3139-3152).

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, 107-124; Anderson et al. 2003, 4021-4026). 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.

2.3 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.

Combined sewers are single drainage systems that 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, 4451-4462) 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, 539-549). 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, 45-57). 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.

PAHs in Combined Sewer Overflows (CSOs)

One objective of this project is to determine if PAHs are entering the treatment plant at different concentrations during wet and dry weather and how each unit treatment process provides treatment. PAHs are divided into two categories: low molecular weight (LMW) PAHs and high molecular weight (HMW) PAHs. There does appear to be a correlation between the reductions of PAHs and their molecular weights (Manoli and Samara 1999, 176-186).

Table 2.17. 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)fluoranthene
Anthracene	Fluoranthene

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 m³/d (58.1 MGD) for the Se`vres 1-Ache`res Rueil;(2) 360,000 m³/d (95.1 MGD) for the Saint Denis-Ache`res (3); 900,000 m³/d (237 MGD) for the

Clichy-Ache`res junction of Argenteuil; (4) 600,000 m³/d (159 MGD) for the Clichy-Ache`res junction of Bezons and (5) 600,000 m³/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. Atmospheric fallout was also monitored for this study.

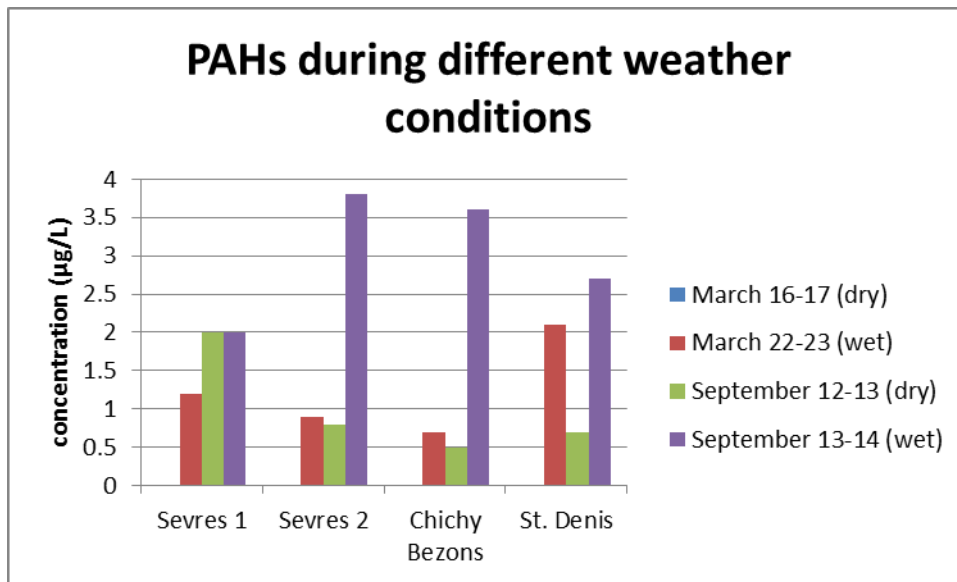


Figure 2.1. *Comparison of dry and wet weather concentrations for total PAHs* (Blanchard et al. 2001, 3679-3687)

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.

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 Proulx 1997, 1887-

1896). 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 Proulx 1997, 1887-1896). 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 m³/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 m³/d (740 MGD).

Pham (1997) investigated several PAHs and their removals. 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 2.18. 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	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 Proulx 1997, 1887-1896)

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 m³/d, consisting mainly of the residential discharges from the city of Thessaloniki (Manoli and Samara 1999, 176-186). 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 2.19. 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, 176-186)

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 the 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 part of the facility.

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 plant of the city of Thessaloniki, Greece, serves about 1 million residents by treating 120.000–150.000 tons/d of wastewater (Katsoyiannis and Samara 2004, 2685-2698). 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 Cl₂. During the Katsoyiannis (2004) study, much of the pesticide concentrations were reduced during both the primary and secondary treatment processes. This is consistent with their physicochemical properties, albeit 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.

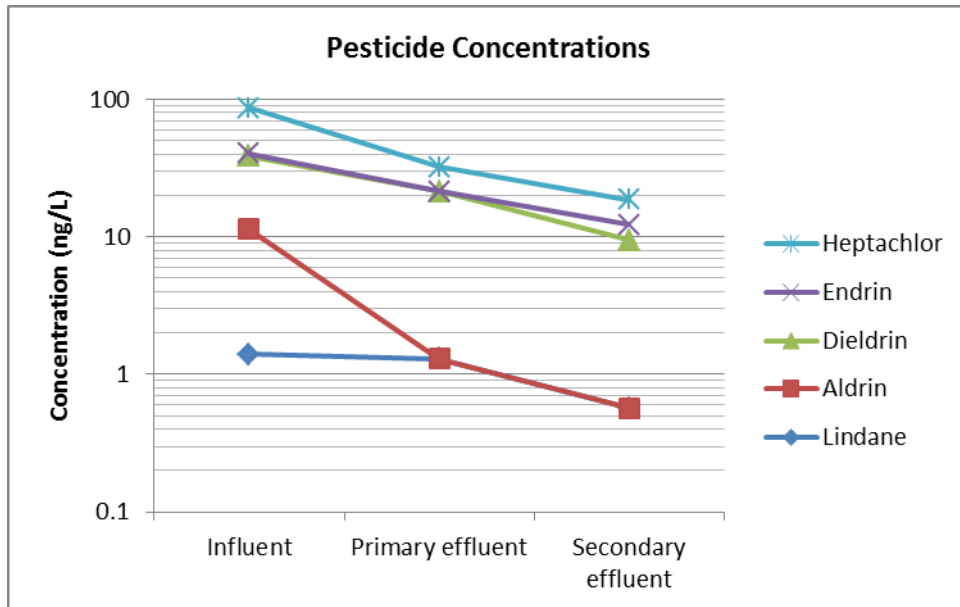


Figure 2.2 Concentrations of pesticides;
(Katsoyiannis and Samara 2004, 2685-2698)

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 m³/d or 58.1 MGD), (2) the Saint Denis-Ache`res (360,000 m³/d or 95.1 MGD); (3) the Clichy-Ache`res junction of Argenteuil (900,000 m³/d or 237 MGD), for the Clichy-Ache`res junction of Bezons (600,000 m³/d or 158 MGD), and the Se`vres 2-Ache`res junction of Saint-Cloud Nanterre (600,000 m³/d or 158 MGD). Arochlor, which is a polychlorinated biphenyl, were observed by Blanchard (2004) to be significantly reduced during the primary treatment process.

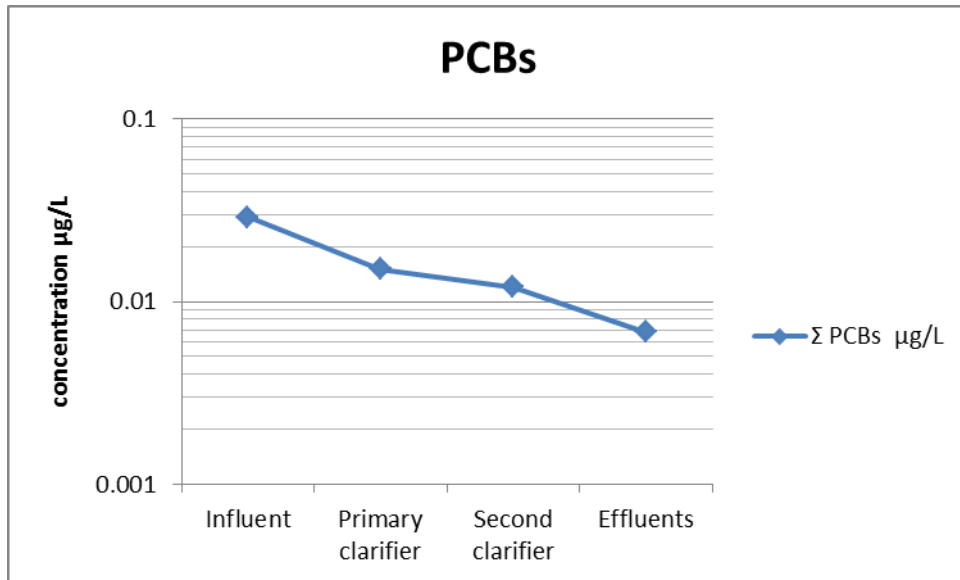


Figure 2.3. Concentration of Σ PCBs

(Blanchard et al. 2004, 184-197)

2.4 FINDINGS FROM THE LITERATURE AND NEED FOR RESEARCH

The literature show that combined sewers during wet weather conditions have increased influent pollutant concentrations for many ECs and increased concentrations in the treated effluent. Municipal wastewater treatment systems, affected by large amounts of stormwater I&I, could have a similar effect. An important part of this dissertation research is therefore to directly monitor changes in treatment plant conditions and performance during wet weather.

Emerging contaminants are a growing concern and understanding their behavior at wastewater treatment facilities during both wet and dry weather is important. Almost all available literature pertains to dry weather performance. To better understand treatability of the ECs, chemical behavior needs to be known and treatability needs to be related to their physical and chemical properties if modeling of removal is to be improved. Solubility and $\log K_{ow}$ values

are important when studying these compounds in aqueous solutions. However, literature reports indicate a high level of variability in treatment performance even for compounds with similar solubilities and log K_{ow} values. Although there is significant variability, each study presents an illustration of how effective treatment plants are in eliminating these compounds. Gemfibrozil and fluoxetine have high log K_{ow} values, hence are predicted to have a large portion sorbed onto particles (and therefore likely removed by sedimentation processes). Carbamazepine and sulfamethoxazole have low log K_{ow} values so they are expected to remain in aqueous solutions under neutral conditions. Reported carbamazepine removals range from zero to 45 percent, indicating resistance to biodegradation in conventional activated sludge systems. Triclosan and ibuprofen showed removals between 60 and 90 percent, coinciding with the chemical characteristics of these compounds. Gemfibrozil has a high octanol-water coefficient, and data indicate removal rates ranging between 35 percent and 76 percent.

Phillip (2009) and Benotti (2007) reported that during heavy rainfalls, reductions occurred in the concentrations of the examined pharmaceuticals compared to the concentrations under dry weather conditions. For Benotti (2007), seven ECs exhibited lower concentrations under wet conditions than during dry conditions: caffeine, carbamazepine, codeine, cotinine, paxanthine, sulfamethoxazole, and trimethoprim. Blanchard (2001) conducted a study that showed an increase in concentrations of PAHs and PCBs entering the treatment plant during large rain events. The concentration ranges for each of the studied compounds were large; however the data indicated which compounds typically were not effectively treated in standard conventional wastewater treatment systems.

During a rain event with a large volume of stormwater infiltrating the wastewater system, changes could affect how each unit process affects the pollutants. From the studies reported, it is

apparent that stormwater infiltration itself can be a major contributor of some of the ECs, even pharmaceuticals and personal care products. Dilution can occur and reduce the concentrations of other pollutants, resulting inadequately treated conditions due to reductions in residence times in the unit processes.

2.5 SUMMARY OF LITERATURE REVIEW

Table 19 summarizes the chemical characteristics and their treatability as reported in the preceding literature review for constituents being examined. This table shows the most likely means of removal, the ranges of influent and effluent concentrations and the ranges of the percentage removals for each constituent.

The pharmaceuticals gemfibrozil, ibuprofen, triclosan and fluoxetine were 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 $\mu\text{g/L}$, and the effluent concentrations ranged from 0.11 to 0.23 $\mu\text{g/L}$. 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. Naphthalene had the lowest reduction rates ranging from 31 to 40 percent. Naphthalene has a Henry's Law constant of $0.019 \text{ atm}\cdot\text{m}^3/\text{mol}$, making it more volatile than the other PAHs and more likely to volatilize 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. Volatilization 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 $\mu\text{g/L}$. Effluent concentrations for LMW PAHs had a range from 0.002 to 0.7 $\mu\text{g/L}$. Influent concentrations for the HMW PAHs ranged from 0.044 to 0.47 $\mu\text{g/L}$. Effluent concentrations for HMW PAHs ranged from 0.013 to 0.06 $\mu\text{g/L}$.

Table 2.20a. 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
Polycyclic Aromatic Hydrocarbons					
Constituent	Log kow	Solubility	Volatility	Biodegradation rate	Toxicity
Napthalene	3.37	31.7	4.6×10^{-4}	0.8-43 days	LC 50 Pimephales promelas 7.76 mg/L
Acenaphthene	4.02	1.93	7.91×10^{-5}	1-25 days	LC 50 Salmo gairdneri 1570 µg/L
Fluorene	4.12	1.68-1.98	1.0×10^{-4}	2-64 days	EC 50 V. fischeri 4.10 µg/mL
Fluoranthene	5.14	0.20-0.26	6.5×10^{-6}	880 days	EC 50 S. capricornutum 54,400 µg/L
Acenaphthylene	3.89	3.93	1.5×10^{-3}	21-121 days	Did not find
Phenanthrene	4.48	1.20	2.56×10^{-5}	19 days ; 35-37 days;	Did not find
Anthracene	4.53	0.0076	1.77×10^{-5}	108-139 days	EC 50 D.magna 211 µg/L;
Pyrene	5.12	0.0077 (Dabestani and Ivanov 1999, 10-34)	4.3×10^{-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)			n/a	n/a	n/a

fluoranthene, Benzo(k) fluoranthene, Benzo(a) pyrene, and indeno(1,2,3,cd) pyrene					
Benzo(a,h) anthracene and Benzo(g,h,i) perlene			n/a	n/a	n/a
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 2.20b. Summary of Characteristics and Treatability of Targeted Pollutants (continued)

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	Range of influent	Range effluent concentration	Range of removal at conventional

	method	concentration (µg/L)	(µg/L)	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) pyrene	Adsorption	0.42	0.076	82%
Benzo(a,h) anthracene and Benzo(g,h,i) perlene	Adsorption	0.044	0.013	71%
	Reported most important treatment method	Range of influent concentration (µg/L)	Range effluent concentration (µg/L)	Range of removal at conventional wastewater treatment facility
Methoxychlor	n/a	n/a	n/a	n/a
Aldrin	n/a	n/a	n/a	n/a
Dieldrin	n/a	n/a	n/a	n/a
Chlordane	n/a	n/a	n/a	n/a
Arochlor Σ	n/a	n/a	n/a	n/a
Lindane	n/a	n/a	n/a	n/a
Heptachlor	n/a	n/a	n/a	n/a
Heptachlor-epoxide	n/a	n/a	n/a	n/a

3.0 METHODOLOGY

The literature review discusses the study of common emerging contaminants such as PAHs, pesticides, over-the-counter drugs, prescription medications (particularly pet pharmaceuticals), antibiotics, hormones and steroids, suntan lotion and fragrances. Literature information has been observed for EC treatability; but little information is available for separate stormwater treatability. The literature did review some research regarding combined sewer municipal wastewater systems.

The purpose of this research 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 questions investigated are as follows:

1. Does infiltration occur at significant levels in the treatment system (increased flows during wet weather)?
2. Is treatability of ECs at the wastewater facility reduced during wet weather during the different unit process (compared to dry weather conditions)?
3. What is the discharge of ECs to the treatment plant from the stormwater contributions during wet weather?

3.1 HYPOTHESES

HYPOTHESIS 1: Treatability of emerging contaminants depends on their solubility and adsorption potential as important physical-chemical characteristics, including concentrations, and the operation of the treatment plant.

Prediction 1: Stormwater I&I entering wastewater treatment facilities during wet weather changes the concentrations of the ECs and the treatment flow rates which influences how the different unit processes affect their removal.

HYPOTHESIS 2: There will be a statistically significant difference in treatability of wastewater during wet weather compared to dry weather.

Prediction 1: There will be a higher variability for the influent concentrations and for primary treatment during wet weather, but the final effluent quality will be more consistent. Treatability is expected to be reduced due to increase in mass during rain events or by dilution due to increase in volume of influent.

3.2 SITE LOCATION

3.2.1 General characteristics

The Hilliard N. Fletcher Wastewater Treatment Plant is located in Tuscaloosa, AL, one of the largest cities in Alabama with a population of 90,483 according to the 2010 U.S. Census (U.S. Census 2010 2010). The total area of Tuscaloosa is 66.7 mi² and 10.5 mi² of it is water from Lake Tuscaloosa and the Black Warrior River. The population density for Tuscaloosa is about 1,610 people/mi², 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 of 5.1 inches. Summer temperature range from 60°F to 90°F and can reach 100°F; average monthly rainfall depths are approximately 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 dollar expansion was designed in 1995, increasing the capacity of the treatment plant to 24 million dollars per day (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. Assuming a population density of about 1480 people/mi², the service area is estimated to be about 74 mi². It is a separate sanitary treatment system and is not designed for stormwater treatment. There are also industrial discharges entering the Tuscaloosa treatment facility.

3.2.2 Description of the Unit Processes

The Hilliard N. Fletcher Wastewater facility uses pre-treatment, primary sedimentation, biological treatment and disinfection for treatment of wastewater. 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 UV disinfection. After disinfection, it is discharged to two outlets through a HCR or a Hydrologically Controlled Release Structure, which is aerated.

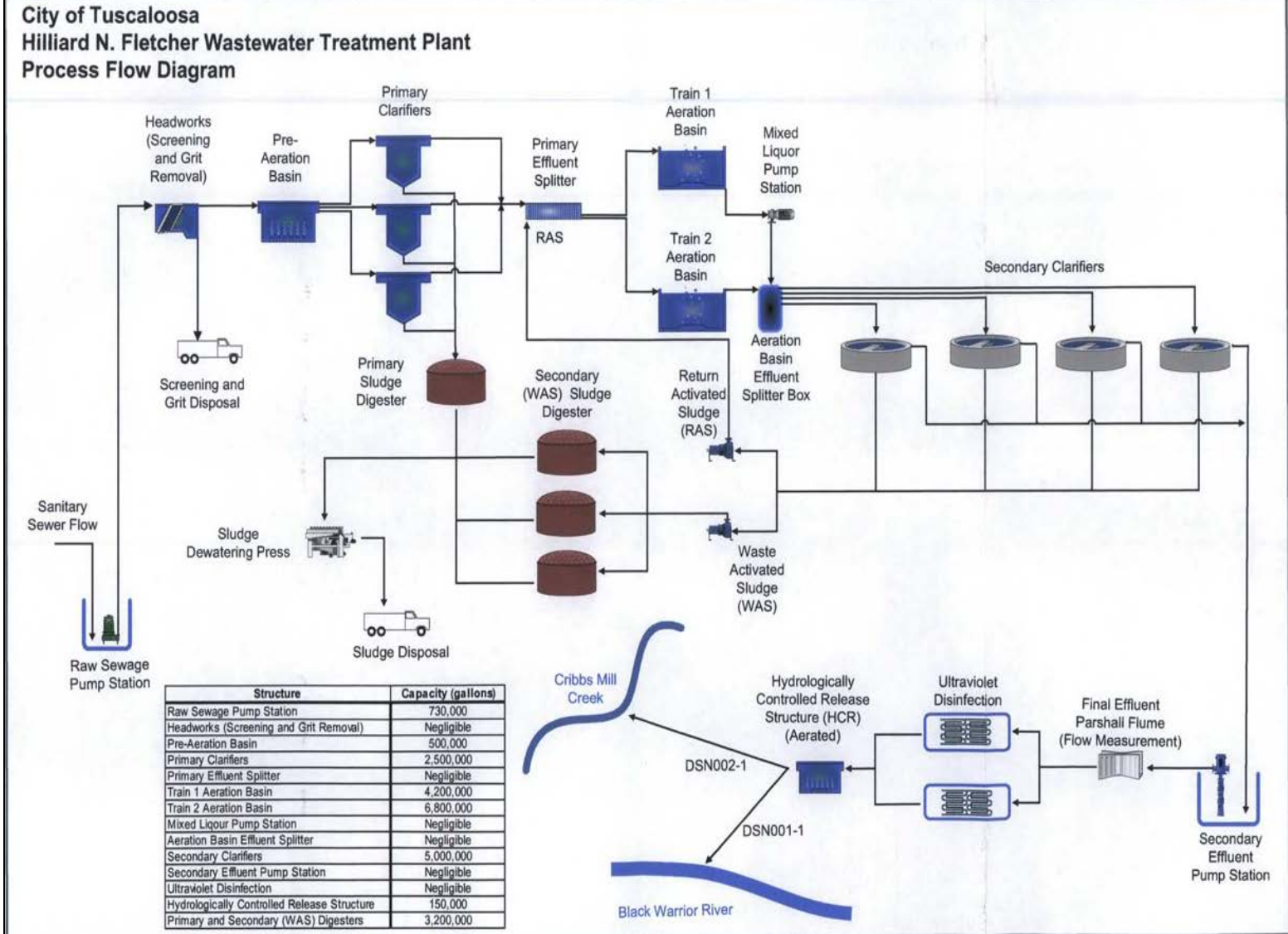


Figure 3.1. Schematic of Hilliard N. Fletcher WWTP

The Hilliard N. Fletcher wastewater treatment plant services a population of approximately 110,000. 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 3.1. 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 researcher; (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.

3.2.3 Drainage around the treatment plant

The Hilliard N. Fletcher WWTP is located on Kauloosa Avenue and is surrounded by many industrial facilities. The treatment plant itself is surrounded by land covered with trees. It 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.

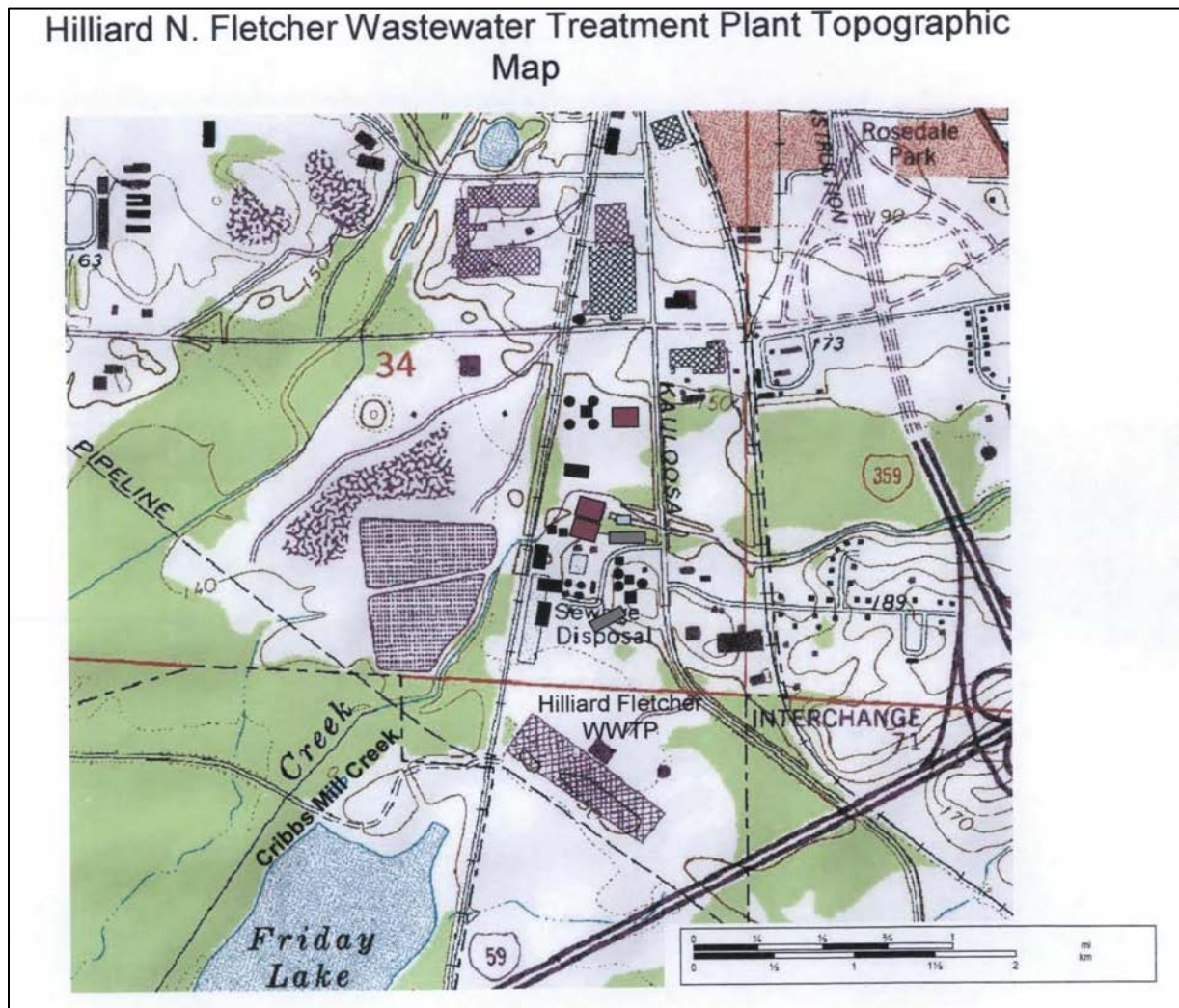


Figure 3.2. Topographic map from NPDES permit

3.2.4 Industrial Influent

The Hilliard N. Fletcher wastewater treatment plant receives raw sewage from the surrounding municipal sanitary sewer system, along with some pre-treated industrial wastewaters. 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 (0.99 MGD). 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. Cintas' 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 the chicken production.

Table 3.2. 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

3.2.5 Performance Parameters at Tuscaloosa WWTP

As previously noted, the Hilliard N. Fletcher wastewater treatment plant system 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. Routinely monitored wastewater parameters to ensure treatment compliance at the wastewater treatment plant include CBOD₅, BOD₅, 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. . These data from 2005 to 2008 were compared to reported rainfall information to identify any effects of increased flows on treatment efficiency. Figures 6a and 6b are influent and effluent probability plots for CBOD₅ and TSS indicating the high level of removal from the treatment plant. Figures 7 and 8 show

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.

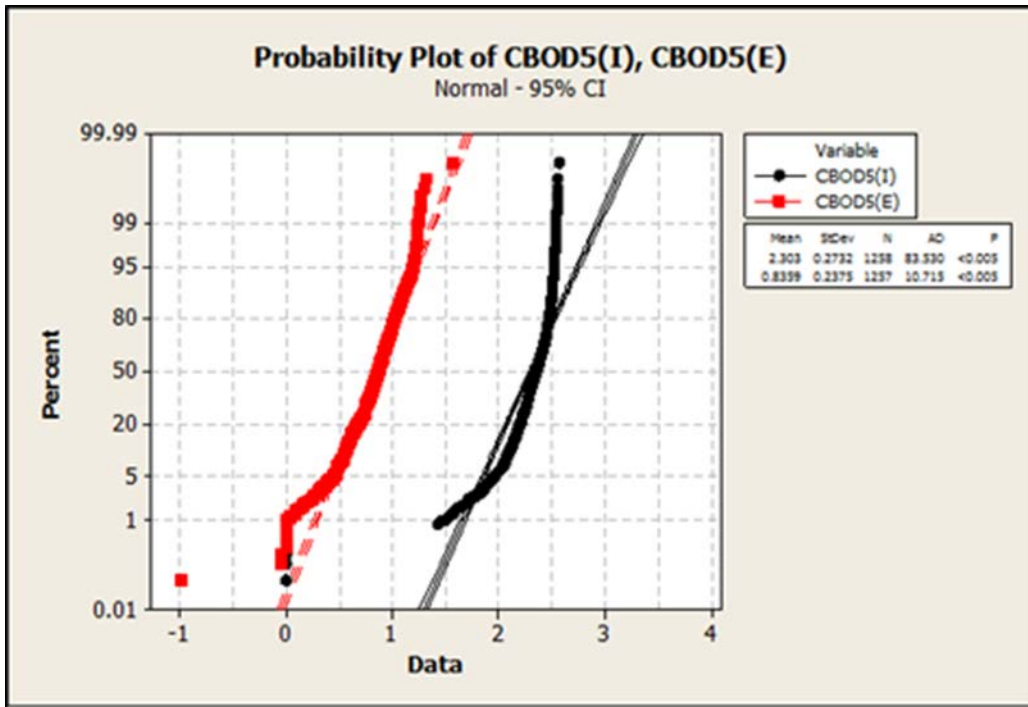


Figure 3.3a. Tuscaloosa Treatment plant CBOD influent and effluent data from 2005-2008

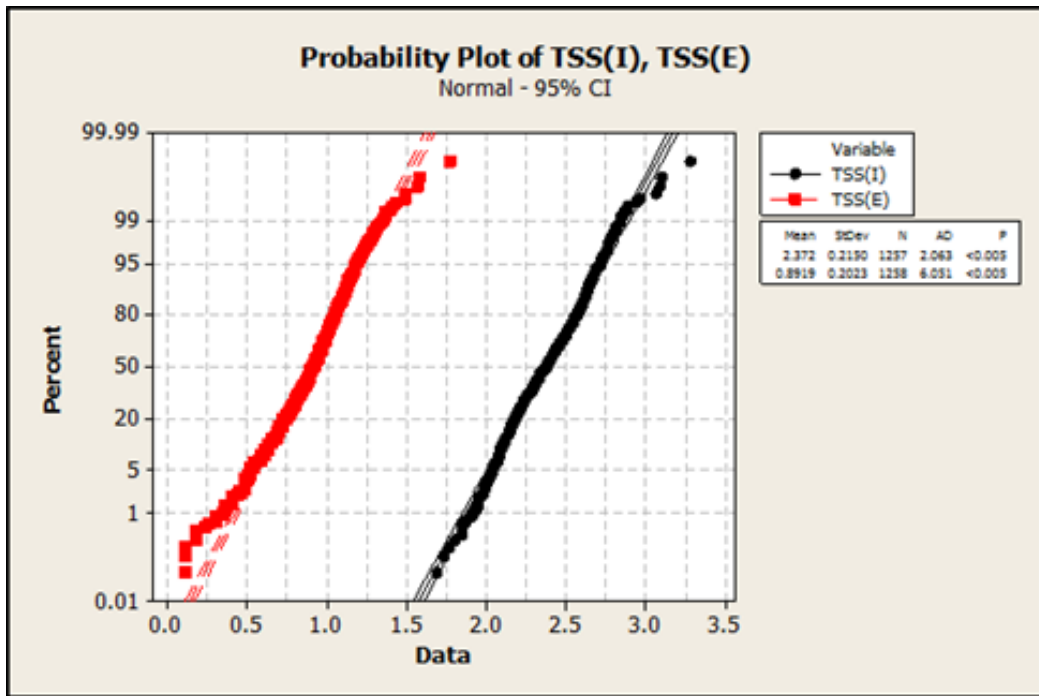
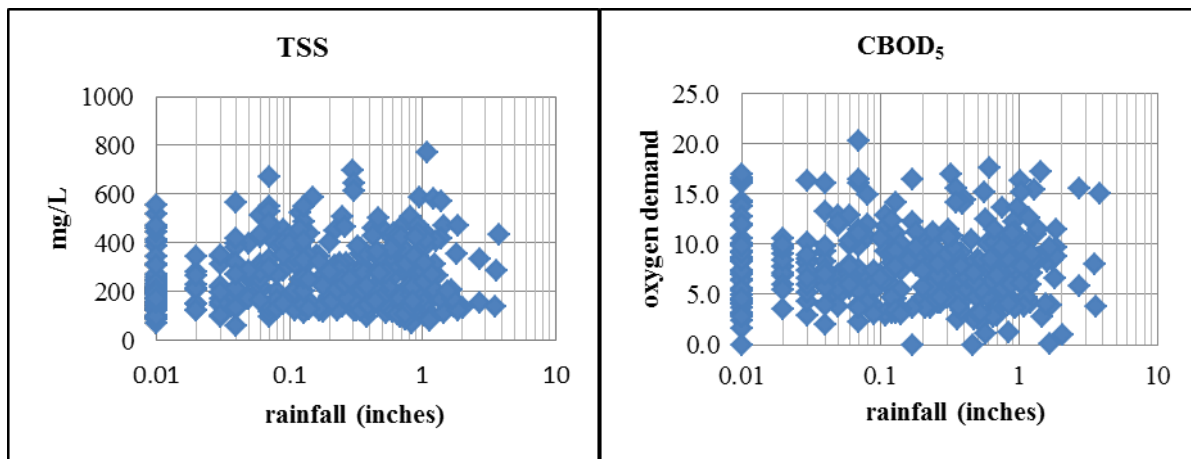


Figure 3.3b. Tuscaloosa Treatment plant TSS influent and effluent data from 2005-2008



Figures 3.4 and 3.5. Scatterplots of TSS and CBOD concentrations vs. daily rain depths.

Figure 3.6 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 rate with increasing rainfall as the daily rainfall increases above about 1 inch (also associated with increased flow scatter).

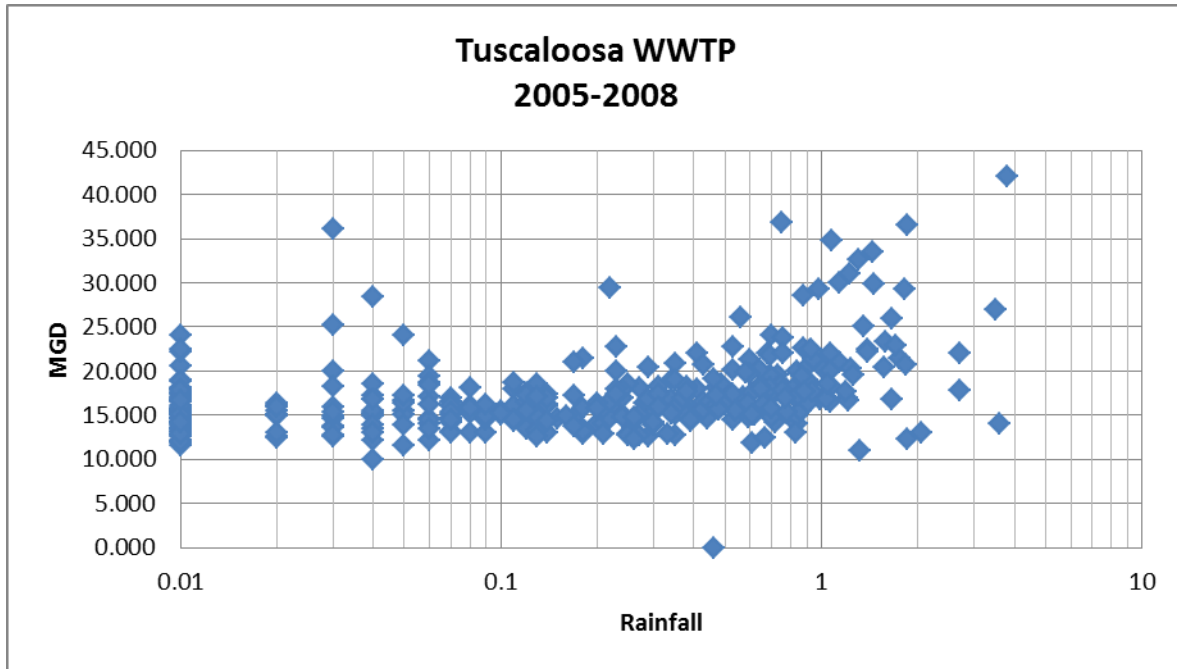


Figure 3.6. Comparison of rainfall and flow rates

Figure 3.7 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.

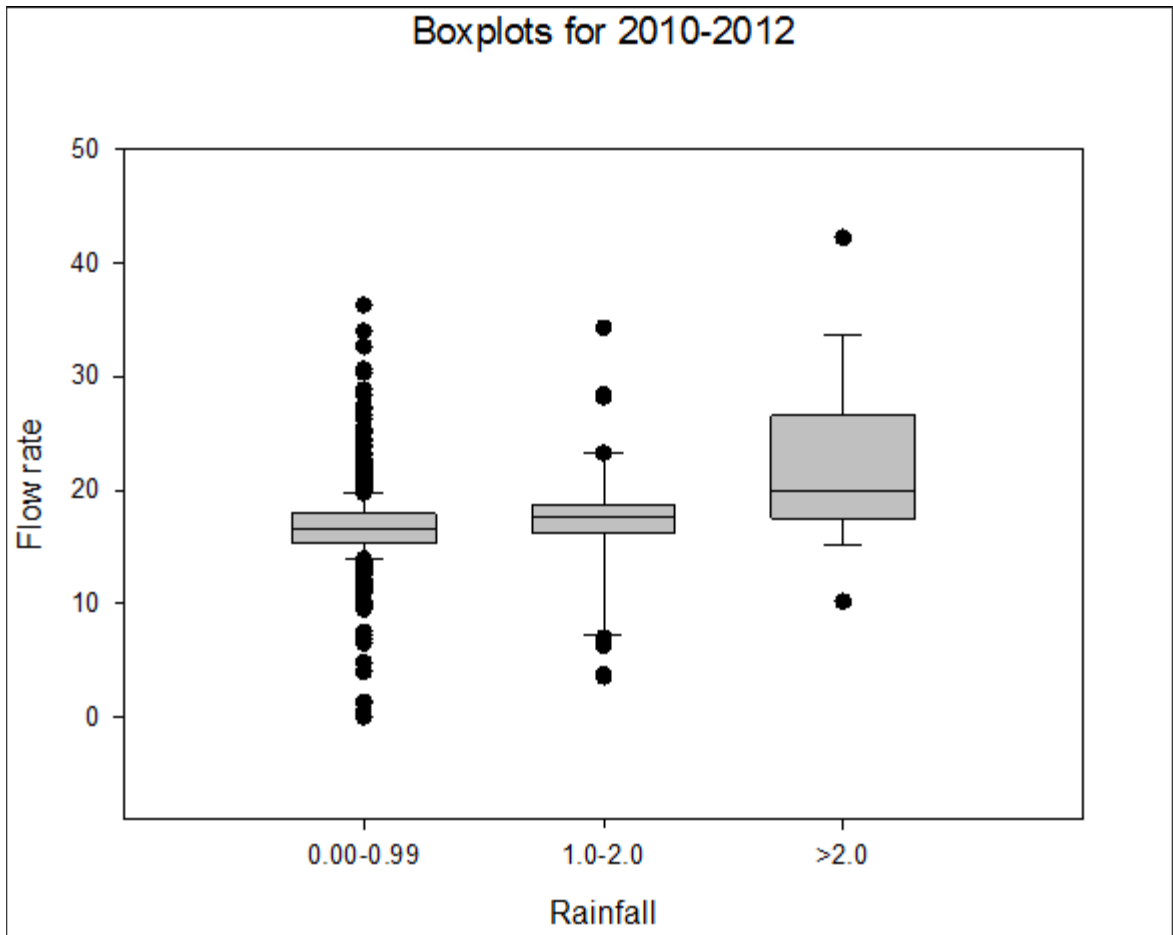


Figure 3.7: Boxplots showing rainfall vs. flows for 2010-2012

Figure 3.8 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 3.3 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.

Table 3.3. 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

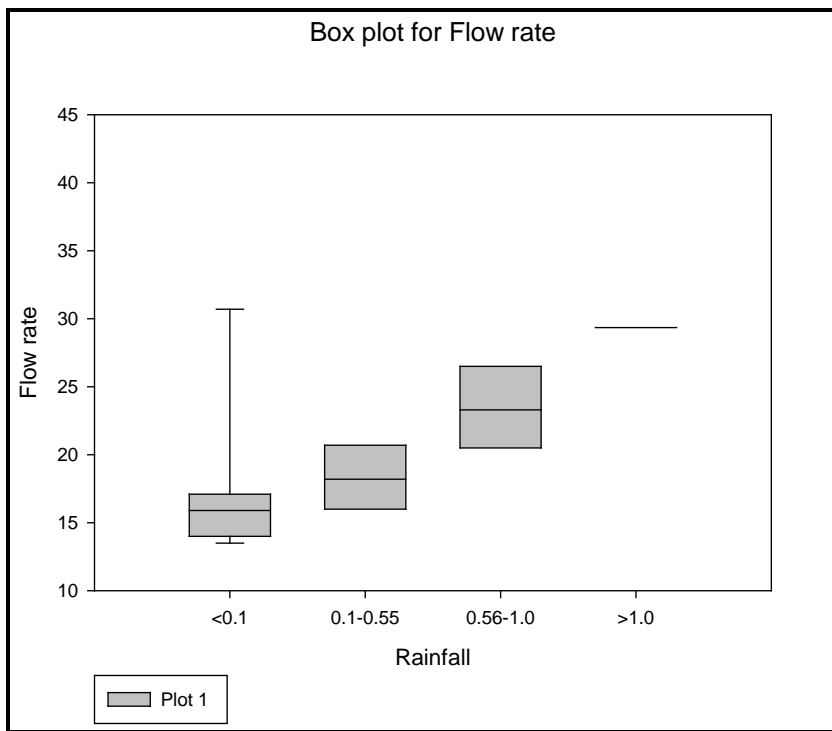


Figure 3.8. Box and Whisker plot for sampling events

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 3.9, 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.

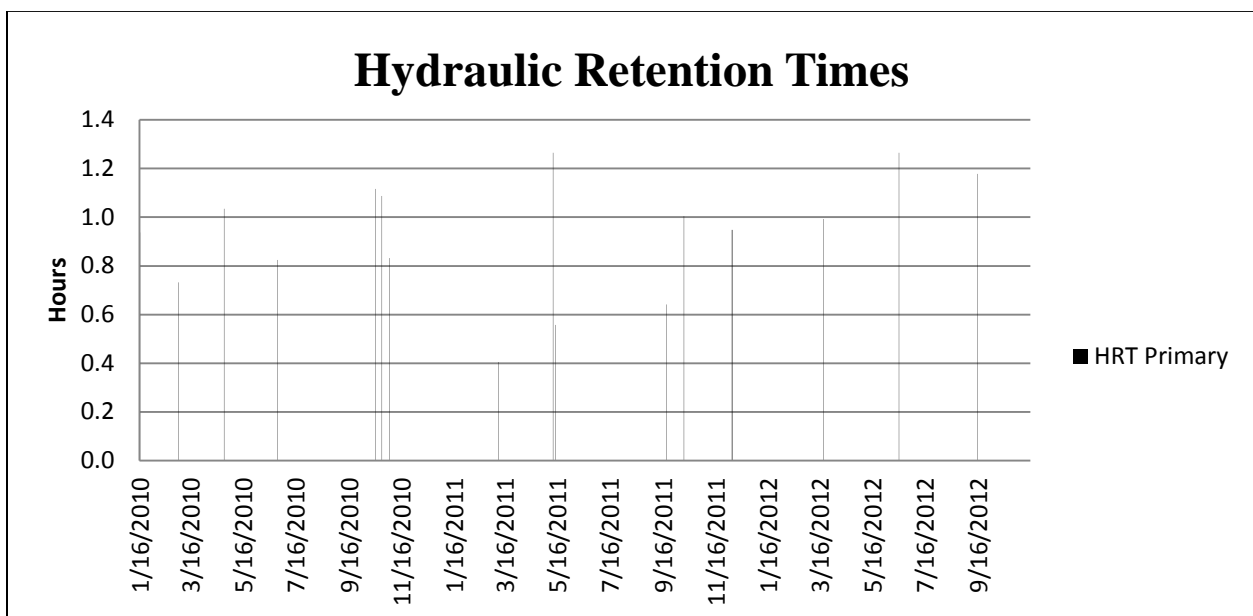


Figure 3.9. Primary clarifier hydraulic resident time (HRT) during days of sampling for the Hilliard N. Fletcher WWTP.

The sewage is treated biologically by activated sludge in the aeration basins. As shown in Figure 3.10, the aeration basins biologically treat the wastewater for approximately one to three hours on the days of sampling.

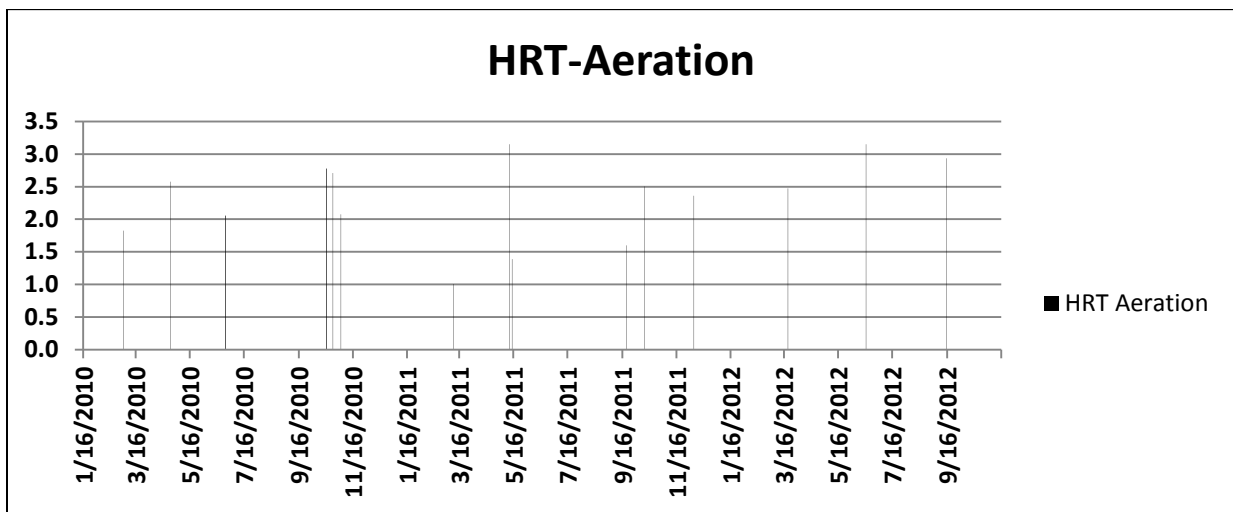


Figure 3.10. Graph of HRT for aeration basin during days of sampling for the Hilliard N. Fletcher WWTP.

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 3.11 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.

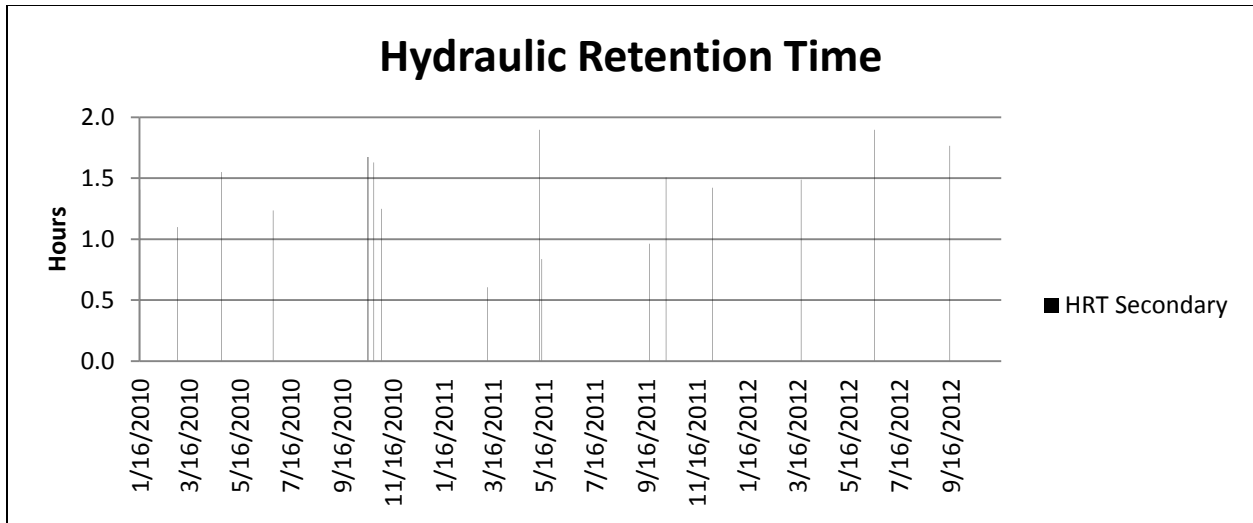


Figure 3.11. Graph of HRT for secondary clarifiers during days of sampling for the Hilliard N. Fletcher WWTP.

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.

3.3 EXPERIMENTAL DESIGN

The primary objectives of this research were 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. 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 samples were obtained at the wastewater plant during wet weather and nine sets of 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 samples. Twenty-eight samples were collected for PAHs, pharmaceuticals and pesticides during dry weather conditions. The wet and dry conditions are the causal or independent variables. This study is designed to measure the effects of wet weather on wastewater treatment of these ECs. 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. 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.

The EPA determined standard analytical processing (storage, extraction, and analysis) procedures for each category of compound. 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.

For PAHs, the method was EPA method 8310. 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.

3.4 DATA ANALYSES

The data analyses were conducted in several steps. Descriptive statistics were used to illustrate patterns in the concentrations through the treatment plant, and to present basic statistical differences. The statistical tests were used to quantify any relationships and differences. The same sets of plots and statistical tests were repeated for each analyte and are presented in Appendix A, with summaries in the results and conclusions sections.

3.4.1. Descriptive Statistics

The influent and effluent concentrations for each sample date are graphed as a line graph to observe concentration changes throughout the treatment plant. Box and whisker plots for each treatment process also show the variability of concentrations. Probability plots for influent and effluent sample dates were created to establish normality and to visualize effects of concentration on treatability. Data series plots also were prepared to compare the influent concentrations vs. flow to illustrate any trends with weather conditions. Appendix A shows all statistical analyses for the tested ECs.

3.4.1.1. Statistical tests

Basic statistical tests were conducted to determine if there were significant differences between influent and effluent for each unit process and overall influent and effluent concentrations, based on the number of samples obtained and the data variability. In addition, relationships between influent characteristics and rain conditions were also examined. Basic statistical summaries of the concentrations and loads are shown in Appendix A (from SigmaPlot

ver. 11). Nonparametric Kurskal-Wallis one way ANOVA on ranks (using SigmaPlot ver. 11) was used to identify if any of the four sampling location groups significantly differed from the others. SigmaPlot was also used for nonparametric Mann-Whitney rank sum tests comparing influent vs. primary effluent; primary effluent vs. secondary effluent; secondary effluent vs. final effluent; and influent vs. effluent. Scatterplots and associated linear regression equations, with ANOVA analyses of the regressions, were prepared in Excel. The regressions were initially developed with both an intercept and slope term. The ANOVA calculations identified if the intercept was significant. If not, the regressions (and ANOVAs) were repeated with the intercept set to zero, forcing the regression line through the origin. The calculated influent mass values were evaluated as a function of reported rain depth using the same scatterplot, regression, and ANOVA procedure.

3.4.1.2 Critical Tests

The Kurskal-Wallis ANOVA tests reveal if there are any differences in the four treatment processes of the treatment plant. Upon determining if there was a statistically significant difference, the Mann-Whitney rank sum tests, in conjunction with the plots, were used to identify which ones were significant. During this dissertation research, comparisons of the concentrations in each unit process were made between wet weather and dry weather to identify if stormwater I&I affected the EC treatment, the influent concentrations and the mass loads.

Comparisons of dry and wet weather sample results were conducted using non-parametric Mann-Whitney rank sum tests. Additional investigations also used combinations of Pearson correlation, Spearman correlation, and/or covariance tests. The performance of the treatment plant was examined by investigating the performance for conventional constituents by

rain and flow characteristics. Hydraulic residence times in the clarifiers and aeration/activated sludge tanks determined for the days the samples were collected. This information was previously noted in the section describing the treatment plant.

4.0 RESULTS

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 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.

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.

The dissertation hypotheses are:

- 1. Treatability of emerging contaminants depends on their physical-chemical characteristics, including concentrations, and the operation of the treatment plant.*

It is predicted for the first hypothesis that stormwater I&I will increase the concentration of ECs entering wastewater treatment facilities during wet weather changes due to the exposure to pollutants from stormwater. Depending on the concentrations and mixtures of ECs in the influent, treatability may be affected by multiple unit processes.

2. There will be a statistically significant difference in treatability of wastewater during wet weather compared to dry weather.

Due to stormwater I&I's contributions to the increases of EC discharges at the treatment plant, the concentrations during dry weather and wet weather will be significantly different. Therefore the concentrations will be compared in the wet and the dry weather samples. The variability of the influent EC concentrations and the primary effluents during wet weather are expected to be higher than the secondary effluents and the final effluents. However the treatability may not significantly affect the final effluent quality.

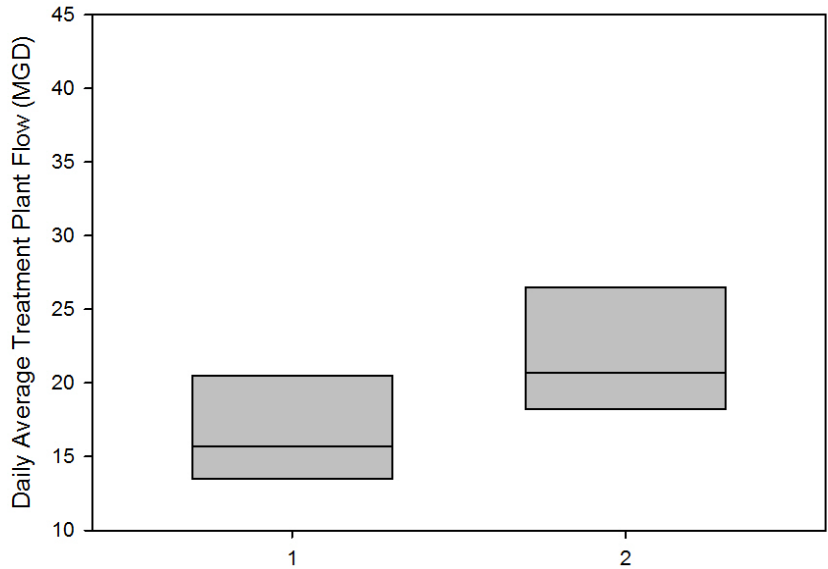
To test the hypothesis, eight dry weather samples were taken in addition to nine wet weather samples at four locations at the treatment facility. Some of the constituents did not have values for some of the sample dates and in a few instances, insufficient sample volumes were available to complete the full suite of analyses. Therefore, the final number of data observations varied. Each sample set was tested for selected PAHs, pharmaceuticals 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.

Table 4.1. 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 15 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 is 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 area 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.

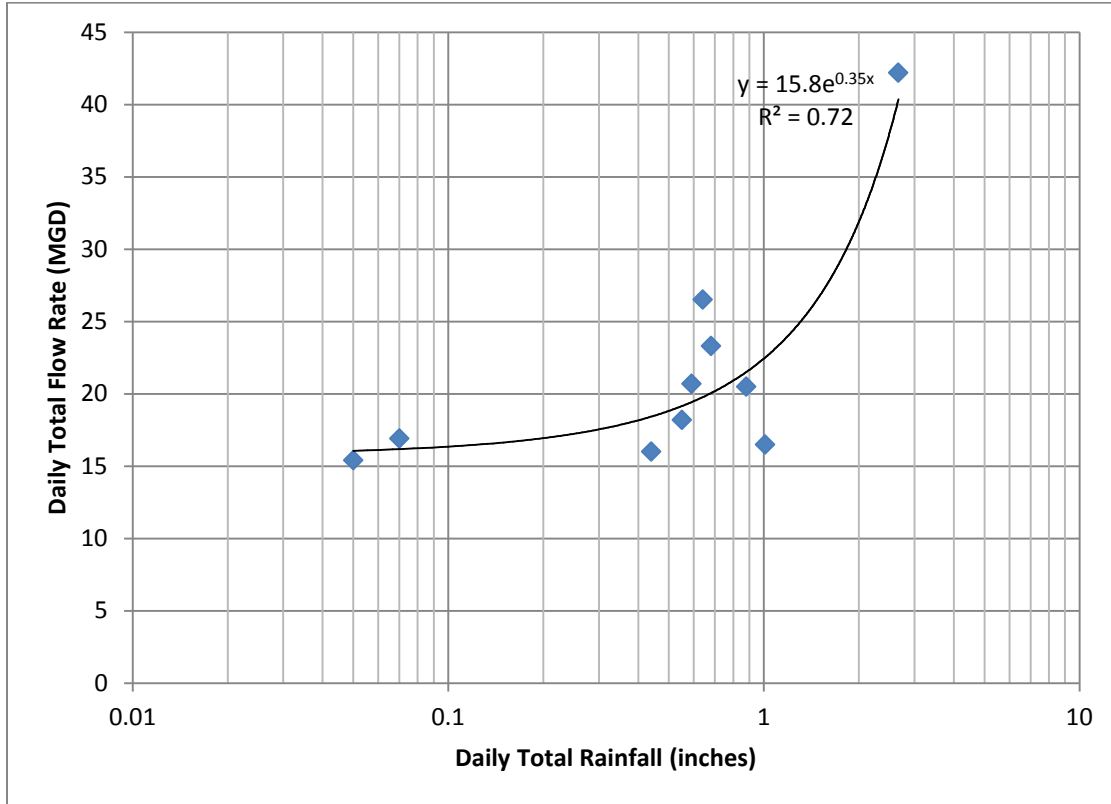


Figure 4.2. Treatment plant flow compared to rain total.

Table 25 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 substantial uncertainty associated with these calculations, but they indicate the amount of rainfall entering the sanitary sewer system and causing increased flows is very small (<2% even for the largest rains). However, 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 4.2. 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 mi²; the population served: 110,000; the total length of sewers: 600 miles

The mass loads of PAHs and pharmaceuticals during wet weather are compared to the mass loads during wet weather to determine if there are consistently higher mass loads under wet weather conditions. Tables 4.3 and 4.4 list calculated influent mass loads for three example pharmaceuticals during dry and wet weather.

Table 4.3. Influent Mass Load Data for Pharmaceuticals during Dry Weather

Date	Rainfall (inches)	Flow rate (MGD)	Ibuprofen (g/day)	Gemfibrozil (g/day)	Triclosan (g/day)
5/11/2011	0.00	13.5	n/a	n/a	n/a
5/14/2011	0.00	30.7	21,817	37,367	16,130
3/20/2012	0.00	17.1	0	4,266	2,392
6/16/2012	0.00	13.5	0	714	0
9/15/2012	0.00	14.5	0	1,480	0
11/1/2012	0.00	17.1	3,297	5,106	970
11/4/2012	0.05	15.4	0	1,572	0
Average Dry Weather Conditions	0.01	17.4	4,186	8,418	3,249

Table 4.4. Influent Mass Load Data for Pharmaceuticals during Wet Weather

Date	Rainfall (inches)	Flow rate (MGD)	Ibuprofen (g/day)	Gemfibrozil (g/day)	Triclosan (g/day)
1/16/2010	0.55	18.2	1,582	688	69
3/2/2010	0.68	23.3	352	1,761	352
4/24/2010	1.01	16.5	1,684	2,807	3,306

6/25/2010	0.59	20.7	2,973	2,034	626
11/2/2010	0.88	20.5	2,325	4,649	n/a
3/9/2011	2.67	42.2	<dl	2,712	n/a
9/20/2011	0.64	26.5	<dl	5,409	10,217
Average Wet Weather Conditions	1.00	24.0	1,274	2,866	2,081

There is substantial variability in the mass discharges and the average loads are not greater during wet weather, as expected. However, regression analyses of influent concentrations vs. treatment plant flow rate indicated significant slope terms for all three of these pharmaceutical compounds, as shown in the following figures for triclosan (complete statistical analyses are presented in Appendix A).

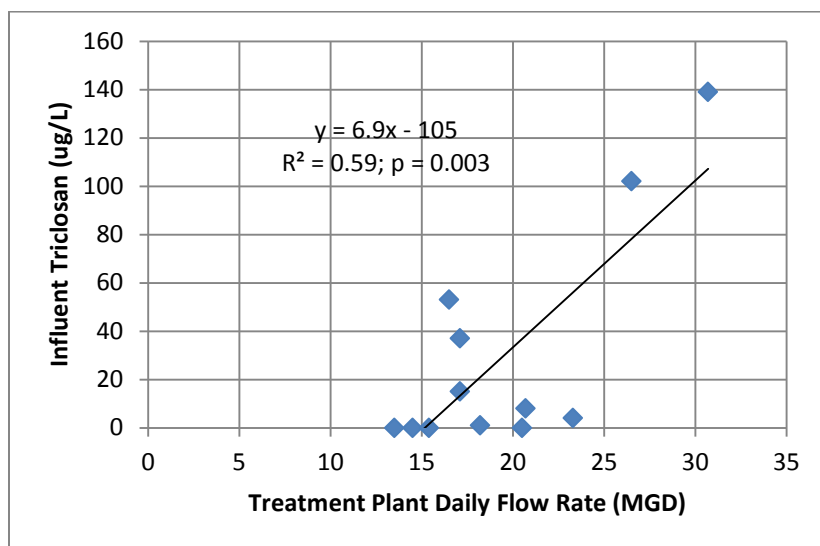


Figure 4.3. Triclosan influent concentrations vs. treatment plant flow rates.

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 4.5 summarizes the average concentrations obtained at each of the four sampling locations and an indication of the apparently 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.

Table 4.5. Performance Data for Earl Hilliard WWTP

Constituent	Avg Influent concentration (µg/L)	Avg Primary effluent concentration (µg/L)	Avg Secondary effluent concentration (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	44.8	Secondary
Gemfibrozil (d)	80.29	23.38	22.30	18.63	70.9	Primary
Ibuprofen (w)	21.63	21.00	17.57	9.57	57.8	UV
Ibuprofen (d)	44.71	35.25	20.75	15.25	67	Secondary
Triclosan (w)	33.9	16.9	15.0	12.3	62.8	Primary
Triclosan (d)	16.72	3.29	12.86	0.43	98	UV
Carbamazepine (w)	2.38	5.00	5.00	2.57	-8	UV
Carbamazepine (d)	15.9	10.5	2.50	1.38	94	Primary
Fluoxetine (w)	14.1	41.7	3.29	1.86	86	Secondary
Fluoxetine (d)	61.7	36.8	11.6	9.63	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)	3.13	3.14	3.86	2.00	33	UV
Trimethoprim (d)	16.3	28.3	21.1	21.0	-31	None
Polycyclic Aromatic Hydrocarbons						
Naphthalene (w)	15.3	4.74	25	22.7	-47	None
Naphthalene (d)	7.1	11.1	3.8	1.3	82	Secondary
Acenaphthene (w)	16.9	5.07	0.39	0.64	96	Primary
Acenaphthene (d)	7.70	0.82	0.10	0.02	99	Primary
Fluorene (w)	10.3	1.03	0.56	0.57	91	Primary
Fluorene (d)	0.67	1.19	0.04	0.05	93	Secondary
Fluoranthene (w)	10.3	4.23	0.54	0.53	95	Primary
Fluoranthene (d)	0.31	0.53	0.02	0.04	87	Secondary
Acenaphthylene (w)	10.5	0.60	0.61	0.67	92	Primary
Acenaphthylene (d)						

	0.08	0.58	0.01	0.02	75	Secondary
Phenanthrene (w)	6.14	4.36	0.05	0.15	98	Secondary
Phenanthrene (d)	1.56	0.77	0.16	0.12	90	Primary and secondary
Anthracene (w)	198	2.27	9.70	0.81	100	Primary
Anthracene (d)	60.07	0.18	0.24	0.15	100	Primary
Pyrene (w)	10.24	4.04	0.72	0.51	95	Primary and secondary
Pyrene (d)	0.66	0.95	0.13	0.13	80	Secondary

Figure 4.4 is a line-treatability plot for naphthalene for the dry weather events. Each sample event varies in treatability. Naphthalene appears to have significant removal during secondary treatment, but with limited removal during both primary sedimentation and the final disinfection stages.

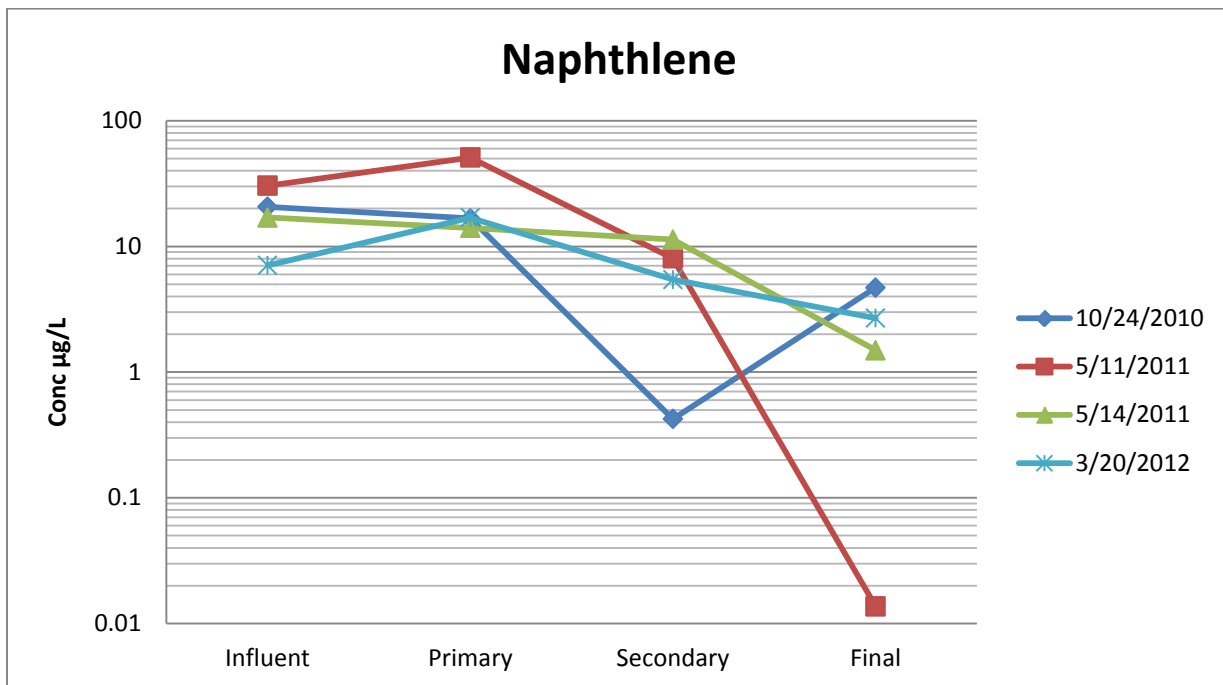


Figure 4.4. Treatability line plot for naphthalene during dry weather.

Table 4.6 is a summary of the preliminary analyses for semivolatile compounds (phthalates and pesticides) detected. Although no statistical analysis was conducted on this data, it is seen that all secondary and final effluent concentrations were below the concentration

detection limits, indicating that all of the analytes were removed during secondary treatment. No pesticides were detected at the 0.5 to 1 µg/L detection limit.

Table 4.6. Preliminary semivolatile analyses results (phthalate esters and pesticides)

Sample date	Influent	Primary	Secondary/Final
1/16/2010	Butylbenzylphthalate 11.1 Di-n-Butylphthalate 3.9 Diethylphthalate 12.3 bis(2-Ethylhexyl)phthalate 53.9 Naphthalene 2.0	Butylbenzylphthalate 3.5 Di-n-Butylphthalate 2.7 Diethylphthalate 6.3 bis(2-ethylhexyl)phthalate 17.8 Naphthalene 1.0	all ND
3/2/2010	bis(2-Ethylhexyl)phthalate 6.9 2-Methylnaphthalene 2.2 Naphthalene 1.1	bis(2-Ethylhexyl)phthalate 8.6 Fluorene 0.52 2-Methylnaphthalene 2.0 Metribuzin 1.9 Naphthalene 1.1	all ND
4/24/2010	bis(2-Ethylhexyl)phthalate 8.8	bis(2-Ethylhexyl)phthalate 7.1	all ND
6/25/2010	Benzo(a)anthracene 0.63 Butylbenzylphthalate 13.3 Chrysene 0.77 bis(2-Ethylhexyl)phthalate 26.2 Phenanthrene 0.77 Pyrene 0.52	Butylbenzylphthalate 9.0 Di-n-Butylphthalate 2.6 bis(2-Ethylhexyl)phthalate 15.8	all ND all ND (duplicate)
11/2/2010	Butylbenzylphthalate 4.6 Di-n-Butylphthalate 4.5 Diethylphthalate 7.8 bis(2-Ethylhexyl)phthalate 9.6 2-Methylnaphthalene 4.6 Naphthalene 2.5	Butylbenzylphthalate 3.3 Di-n-Butylphthalate 3.2 Diethylphthalate 6.7 bis(2-Ethylhexyl)phthalate 10.4 2-Methylnaphthalene 6.0 Naphthalene 3.7	all ND
3/9/2011	Anthracene 0.54 Fluoranthene 0.57 2-Methylnaphthalene	2-Methylnaphthalene 3.8 Naphthalene 1.9	all ND

	3.9 Naphthalene 2.0 Phenanthrene 0.87 Pyrene 0.55	Phenanthrene 0.86	
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5.0 CONCLUSIONS

The purpose of this research was to investigate 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. These preliminary findings are based on results for three pharmaceuticals for which data are currently available: triclosan, gemfibrozil and ibuprofen.

The dissertation's hypotheses are below:

1. Treatability of emerging contaminants depends on their physical-chemical characteristics, including concentrations and the operation of the treatment plant.

Ibuprofen has a pKa value of 4.9. In wastewater consistently having pH values above 6 (and generally close to neutral), ibuprofen is therefore ionized. 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. The gemfibrozil in the treated effluent ranged from 19.1 to 89.2 µg/L during dry weather and from 17.5 to 33.1 µg/L during wet weather, which was 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.

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 4.8-5.4 indicating a high adsorption potential. 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. Primary 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 $\mu\text{g/L}$ during dry weather and 2.2 to 28 $\mu\text{g/L}$ during wet weather, also larger than reported in the literature. The primary removal unit process during dry weather was secondary treatment (incorporating biodegradation through oxidation) and primary treatment (sedimentation) during wet weather conditions.

Carbamazepine has a log K_{ow} value of 2.45 and a pKa of 13.9. It is 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 (ToxNET). 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 (Zhang 2008). 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 9.6 and 12%, respectively. Our findings are similar to findings from the literature. The one way ANOVA and rank sum tests show that there were no statistically significant differences in the treatment of carbamazepine.

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 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 (Brooks et al. 2003, 169-183). 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. 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 wet weather removal of fluoxetine was 64%, with secondary treatment being the major removal process. Under dry weather conditions, there were no reductions noted.

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 (Yang et al. 2009, 1201-1208).

Sulfamethoxazole has a half-life of 10 hours (Hazardous Substance Database 2012). 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 9.12 and 0.50%, respectively.

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 affect biological treatability due to

toxicity (Yang et al. 2009, 1201-1208). 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 was no statistically significant difference between each of the treatment processes during this research. Trimethoprim had reported 11% reductions during wet weather and 6% reductions during dry weather. The average influent concentrations were 16 µg/L for dry weather and 3.1 µg/L. 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 $4.6 \times 10^{-4} \text{ atm}\cdot\text{m}^3/\text{mol}$, 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 showed there was not a significant difference when all four sampling locations were compared, but the Mann-Whitney rank sum test showed that there was a significant difference in the primary and secondary treatment processes. 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 $7.91 \times 10^{-5} \text{ atm}\cdot\text{m}^3/\text{mol}$, so it is not very volatile. From the literature, influent concentrations ranged from 0.02 to 0.7 $\mu\text{g/L}$ and the effluent concentrations ranged from 0.005 to 0.11 $\mu\text{g/L}$. Reported removal rates ranged from 67 to 85% from the literature. The one way ANOVA tests indicated there were no significant differences between the four treatment locations, and the Mann-Whitney rank sum tests also indicated there were no statistically significant differences for any comparison of the treatment plant locations for the number of samples available. The experimental results show an average 69% percent removal during dry weather and an average 48% removal during wet weather. These reduction rates are similar to literature findings.

Flourene 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 locations. Experimental data indicated average 42% removals for dry weather conditions and a negative removal rate of -3 % for wet weather conditions.

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 experimental wet weather samples showed an overall 49 % percent removal and the experimental dry weather showed an average removal rate of 28%. The higher reductions during wet weather occurred for the primary unit process. During dry weather conditions, the most important reductions were for secondary treatment.

For pyrene, the statistical analyses indicated statistically significant reductions in the primary and secondary treatment unit processes. The experimental results showed an average 50% removal rate during wet weather and a 27% removal rate during dry weather.

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. Literature indicated the large amount of variability in the treatment of these constituents that indicate that there are other factors other than physical and chemical properties that affect these compounds.

2. There will be a statistically significant difference in treatability of wastewater during wet weather compared to dry weather.

Previous data from 2005 through 2008 showed poor correlations between rainfall depths and flow rates. The flow rates had an apparent increase when rainfall exceeded two inches, but the variation was large. When the flow and rainfall data were compared for the sampling days, a somewhat clearer relationship was shown. Box and whisker plots compared the flow rates for rainfall depths for <0.1 inch, 0.1 to 0.55 inch, 0.56 to 1.0 inch and >1.0 inches. Although there were obvious flow rate increases as the rain depths increased, especially for the larger rains, a Kurskal-Wallis 1-way ANOVA on ranks did not identify any significant differences between any of the rain range groups. Again, the range of flow observations, along with the relatively few observations, hindered this statistical comparison.

Influent concentrations and mass loads for the three pharmaceutical compounds having complete data sets at this time were also compared. Regressions indicated significant relationships between concentrations and flow rates, but not for the mass loads versus rain depths, as shown in Figure 4.4. Mann-Whitney rank sum tests were conducted for each constituent comparing influent and effluent concentrations for each unit process and for the overall influent and effluent concentrations. For the ECs, only gemfibrozil and fluoxetine showed significant differences between the influent and the final effluent, and no unit process alone indicated significant concentration differences. In addition, Kurskal-Wallis one way ANOVAs showed no statistical differences between any of the unit processes for these three analytes. For the PAHs, acenaphthene, phenanthrene, fluorene, fluoranthene, and pyrene showed significant differences in the influent and the final concentrations, and also in the secondary and final treatment locations. Secondary treatment is an important treatment mechanism for PAHs according to our findings.

Table 5.1 summarizes the statistical test results and the concentrations observed at the sampling locations.

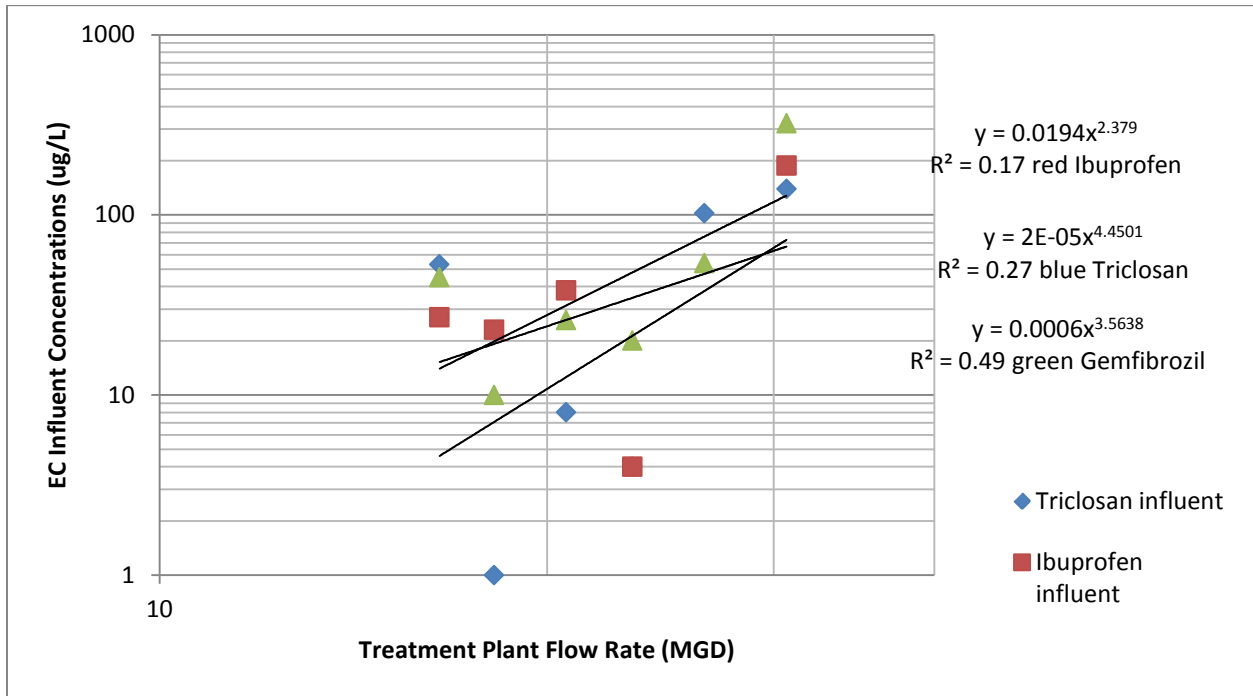


Figure 5.1. EC concentrations vs. treatment plant flow rate

For these three pharmaceutical compounds, there were no statistically significance differences between samples taken during dry weather conditions and samples taken under wet weather conditions. However, several of the PAHs indicated differences in performance.

6.0 LIMITATIONS

The observed concentrations were all very low and very close to the analytical detection limits and had high variabilities. The effluent pharmaceutical concentrations at the treatment plant were all much greater than effluent values reported in the literature. Budget restrictions for this research limited the analytical methods to those having moderate detection

limits, not the ultra-low detection limits sometimes used in reported literature sources. This resulted in many non-detected observations that were not quantified at the effluent.

The box and whisker plots for the flow rates from 2010 to 2012 indicated statistically significant differences for three different rainfall categories. However, as to be expected, monitoring during large rains was not common, with most of the samples collected during the more likely smaller events that did not produce significant stormwater I&I. The numbers of samples collected were also limited by the continued dry weather during most of the sampling period.

The wastewater treatment plant also receives industrial influent from eight different companies, as described previously (including a commercial laundry and petrochemical service company, amongst others, that may contribute personal care products and PAHs, respectively, to the wastewater). Some of these companies discharge large volumes of effluent and can make up a large portion of the total flow entering the Tuscaloosa treatment plant. These industrial flows (pre-treated) also likely add to the variability of the treatment plant flows and characteristics.

Table 5.1. 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., %)	Dry weather influent mass (avg. g/day)	Wet weather influent mass (avg. g/day)	p that dry weather influent mass ≠ wet weather influent mass	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	69%	8,418	2,866	0.67	2.8 (p = 0.01)
Ibuprofen	28	15	0.51	0.48	0.40	0.64	46%	4,186	1,274	0.90	6.7 (p = 0.02)
Triclosan	28	6.8	0.57	0.92	0.79	0.27	76%	3,249	2,428	0.66	6.9 (p = 0.003)
Carbamazepine	8.6	1.9	0.32	0.98	0.74	0.44	11%	953	160	Not calculated	Not calculated
Fluoxetine	36	6	0.77	0.013	0.42	0.004	27%	4,941	4,046	Not calculated	Not calculated
Sulfamethoxazole	38	19	0.17	0.90	0.63	0.15	4.8 %	6,096	927	Not calculated	Not calculated
Trimethoprim	9.3	12.1	0.58	0.96	0.80	0.70	8.4 %	998	275	Not calculated	Not calculated
										Not calculated	Not calculated
Polycyclic Aromatic Hydrocarbons										Not calculated	Not calculated
Naphthalene	11	11	0.90	0.04	0.74	0.08	none	491	1,077	Not calculated	Not calculated
Acenaphthene	11	0.30	0.11	0.003	1.00	<0.001	75%	483	957	Not calculated	Not calculated
Fluorene	4.7	0.2	0.65	0.04	0.70	0.04	19%	39	463	Not calculated	Not calculated
Fluoranthene	4.6	0.27	0.83	0.011	0.75	0.04	38%	19	460	Not calculated	Not calculated
Acenaphthylene	4.9	0.32	0.61	0.13	0.72	0.06	28%	3.7	484	Not calculated	Not calculated
Phenanthrene	3.4	0.1	0.70	0.008	0.90	0.011	50%	75	63	Not calculated	Not calculated
Anthracene	119	0.4	0.17	0.86	0.47	0.069	none	3,235	8,865	Not calculated	Not calculated
Pyrene	4.8	0.3	0.89	0.021	1.00	0.045	38%	32	458	Not calculated	Not calculated

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APPENDIX A: DETAILED OBSERVATIONS

A.1 Pharmaceuticals

A.1.1. Summary Data for 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

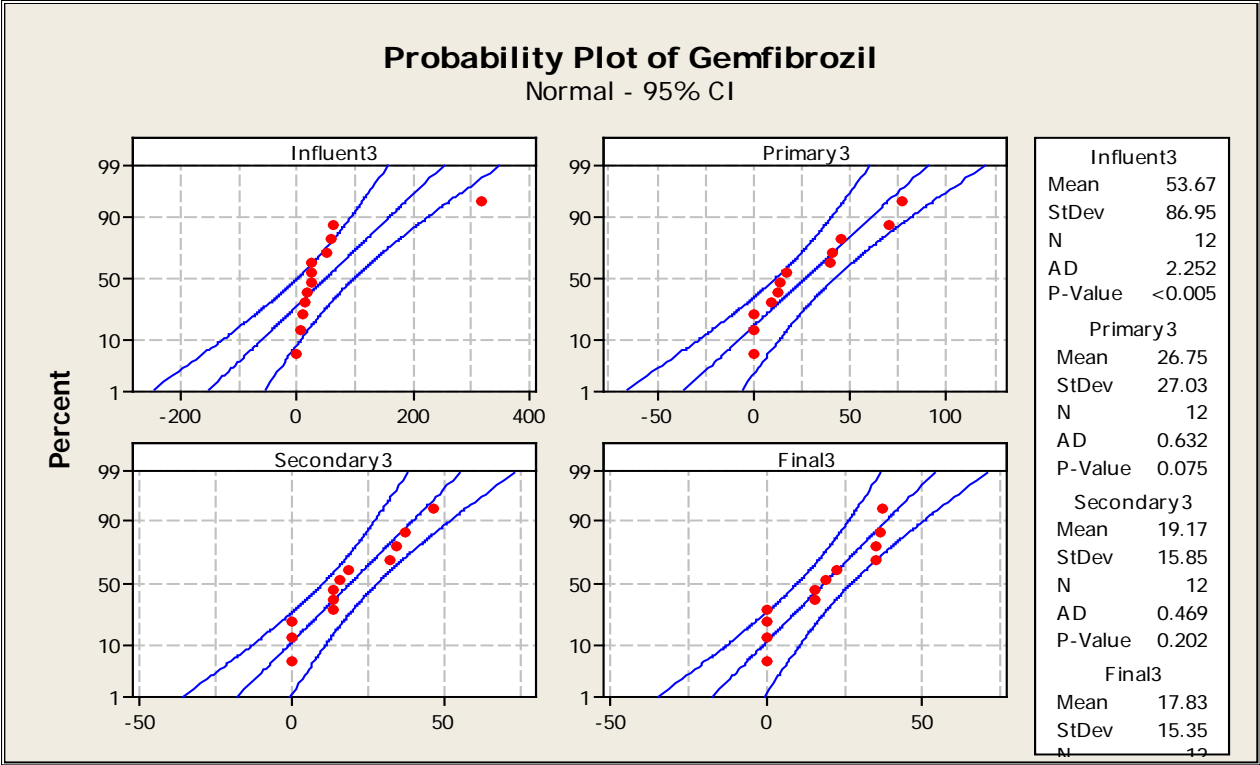


Figure A.1.1.1 Probability plot for Gemfibrozil

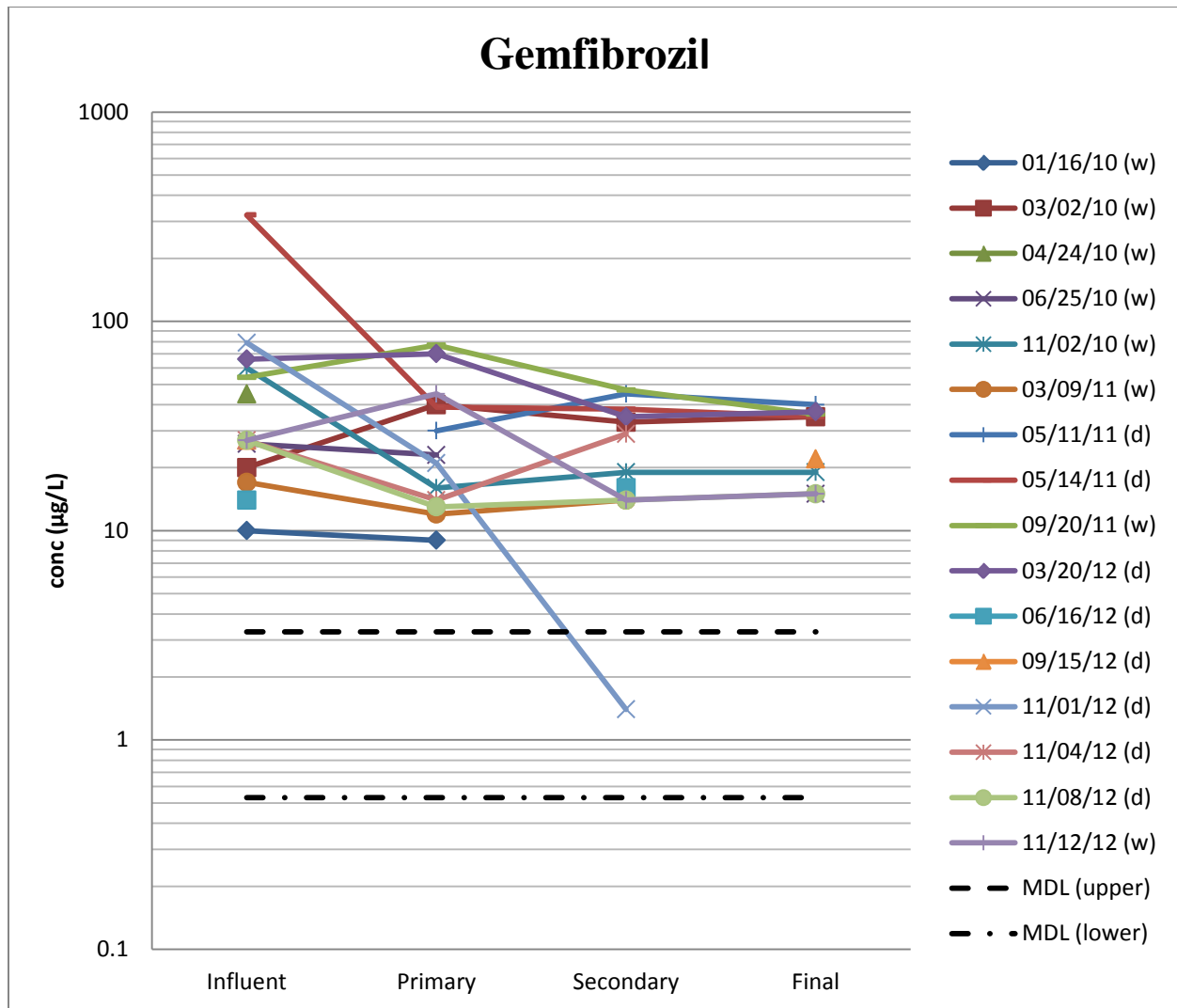


Figure A.1.1.2 Line graph of Gemfibrozil at four sampling locations

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

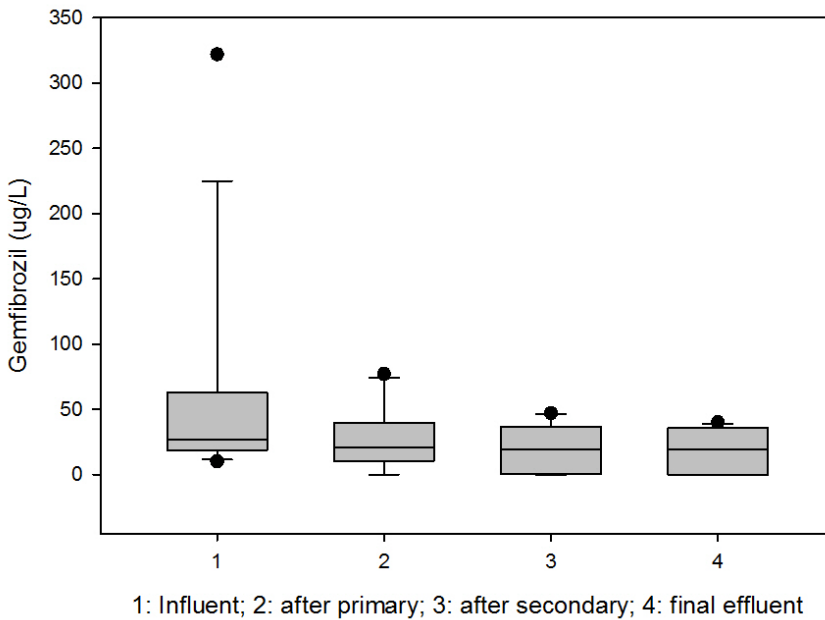


Figure A.1.1.3 Box and Whisker plots for Gemfibrozil

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 secondary	15	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 secondary	15	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

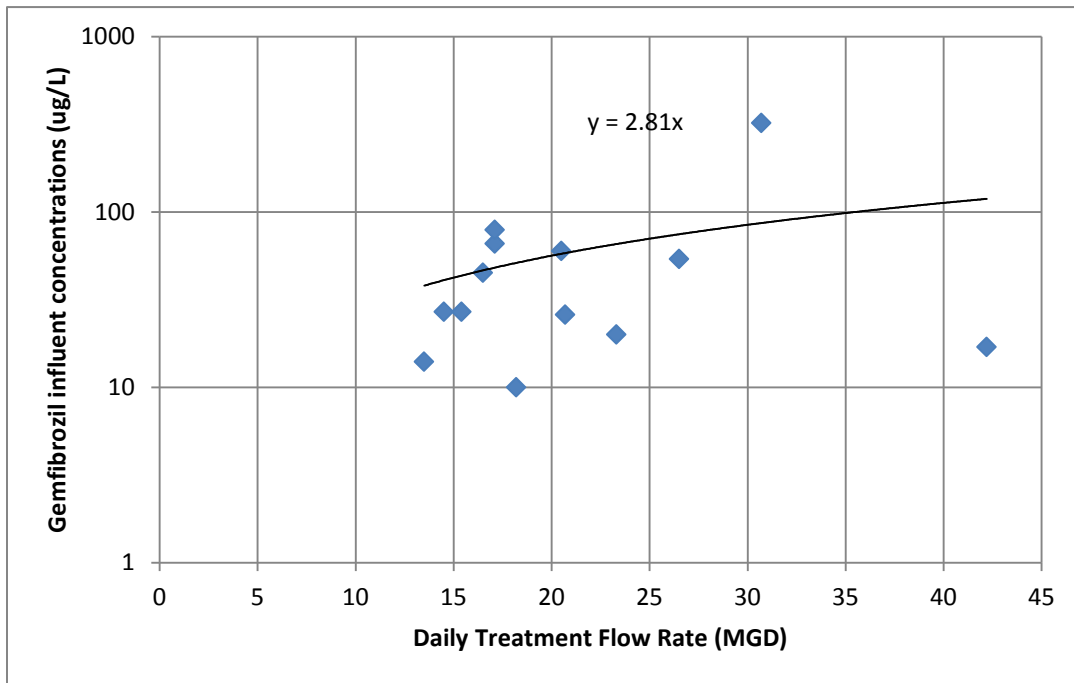
Normality Test (Shapiro-Wilk) Failed (P < 0.050)

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)

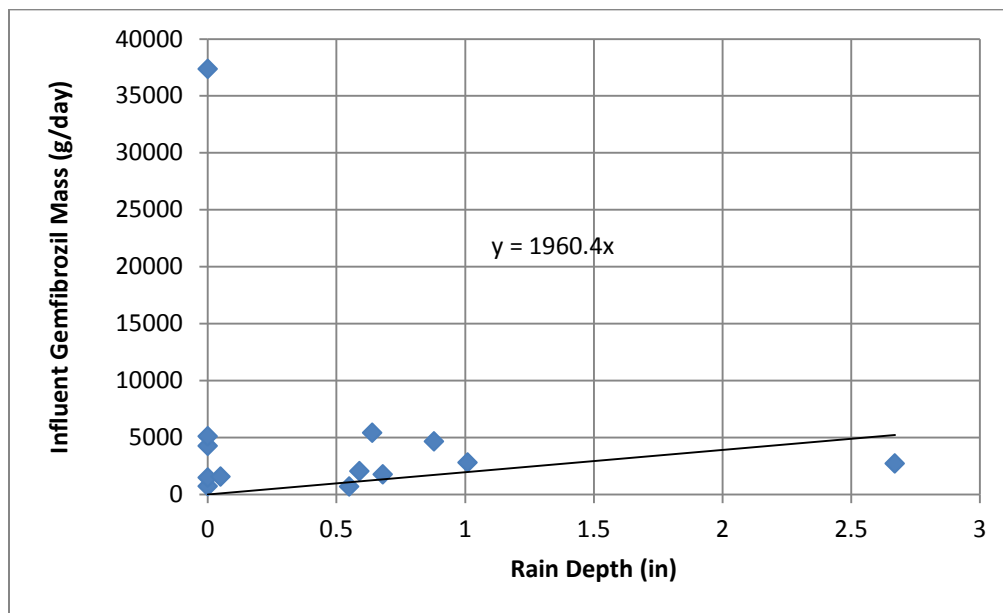
The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.039)



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

A.1.2. Summary Data for Ibuprofen

	Influent ($\mu\text{g/L}$)	After Primary ($\mu\text{g/L}$)	After Secondary ($\mu\text{g/L}$)	Final Effluent ($\mu\text{g/L}$)	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	0.5	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

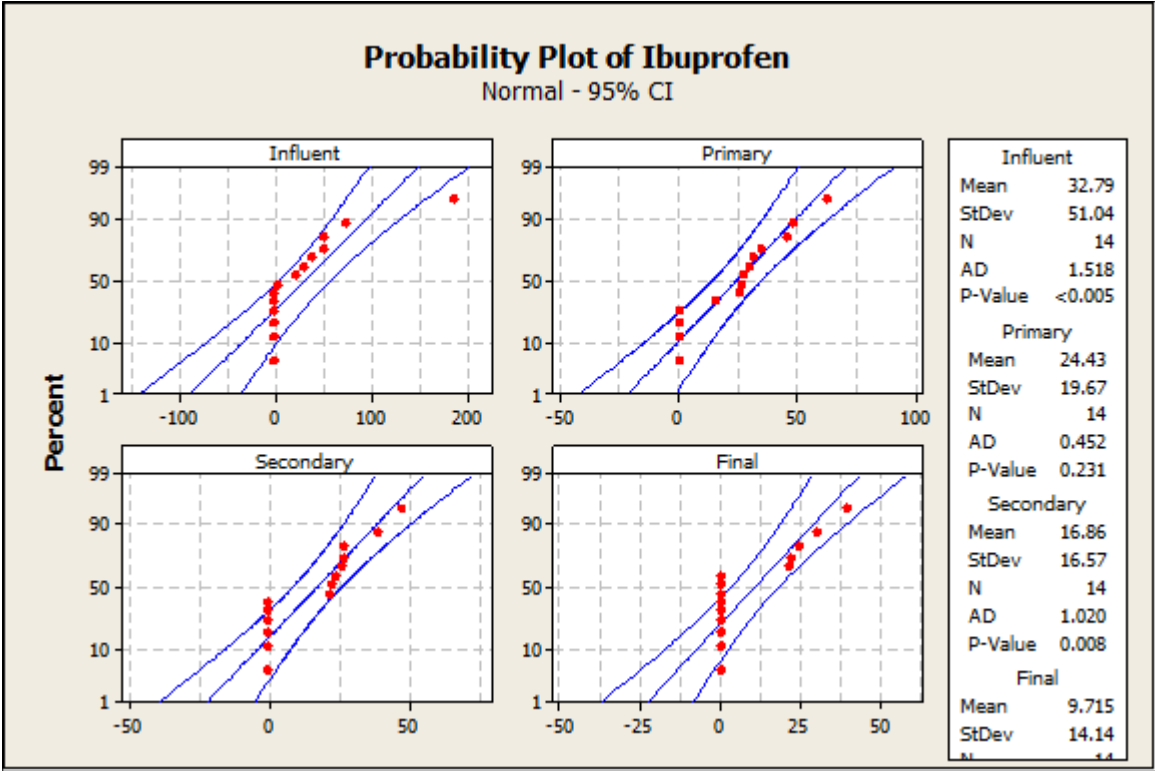


Figure A.1.2.1. Probability plots for Ibuprofen

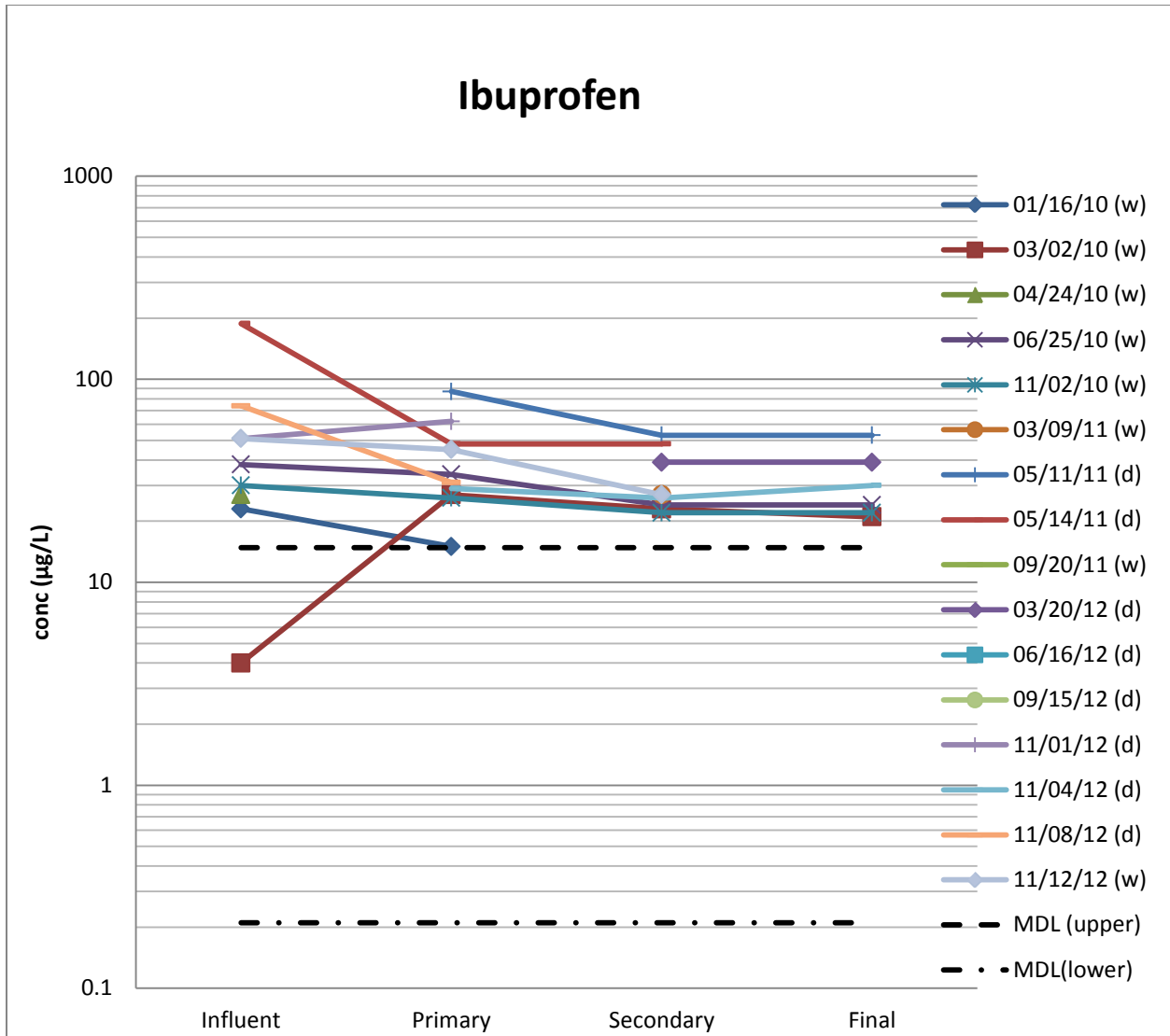


Figure A.1.2.2. Line graphs for Ibuprofen at four sampling locations

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

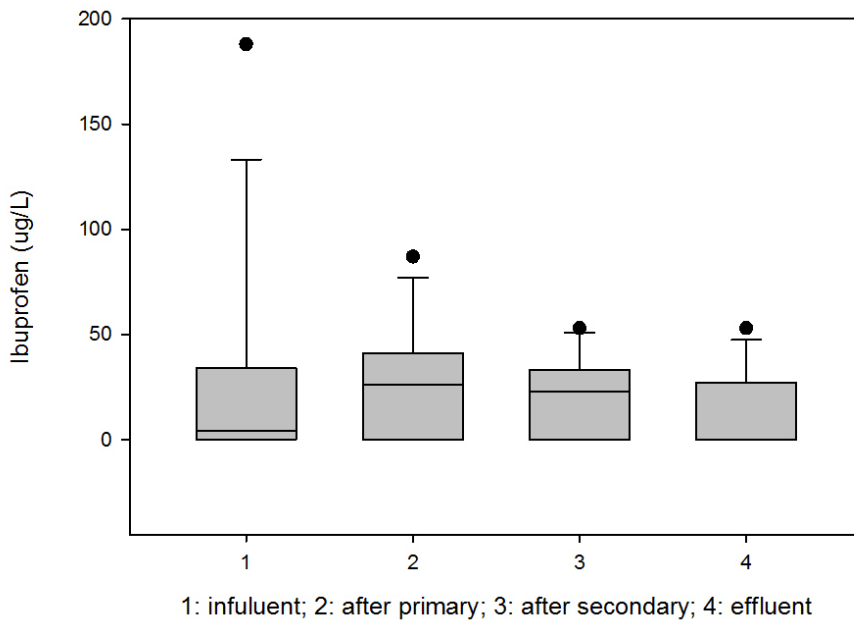


Figure A.1.2.3 Box and Whisker plots for Ibuprofen

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

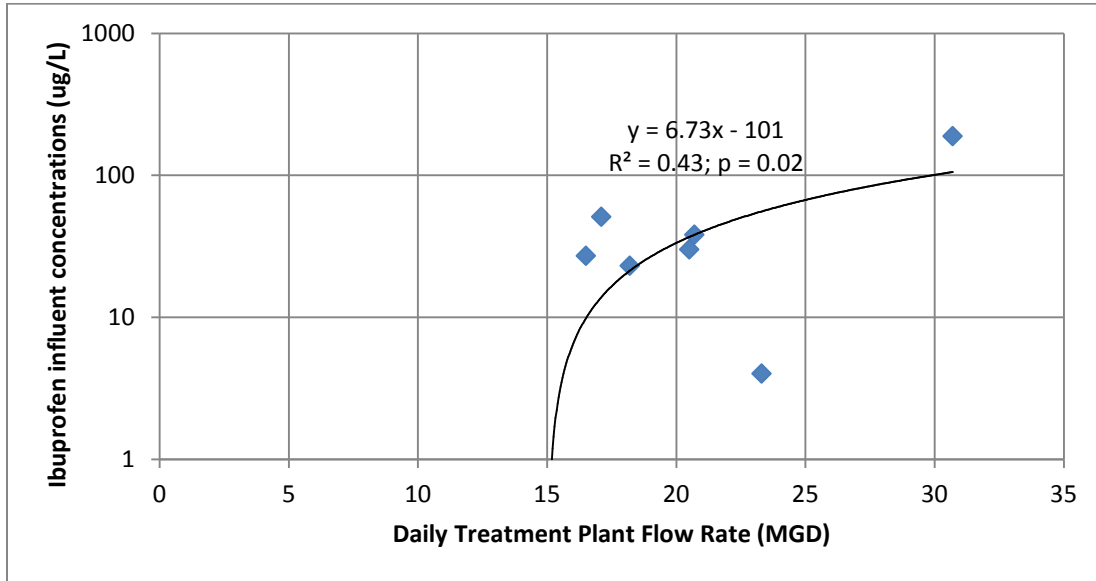
Normality Test (Shapiro-Wilk) Failed (P < 0.050)

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

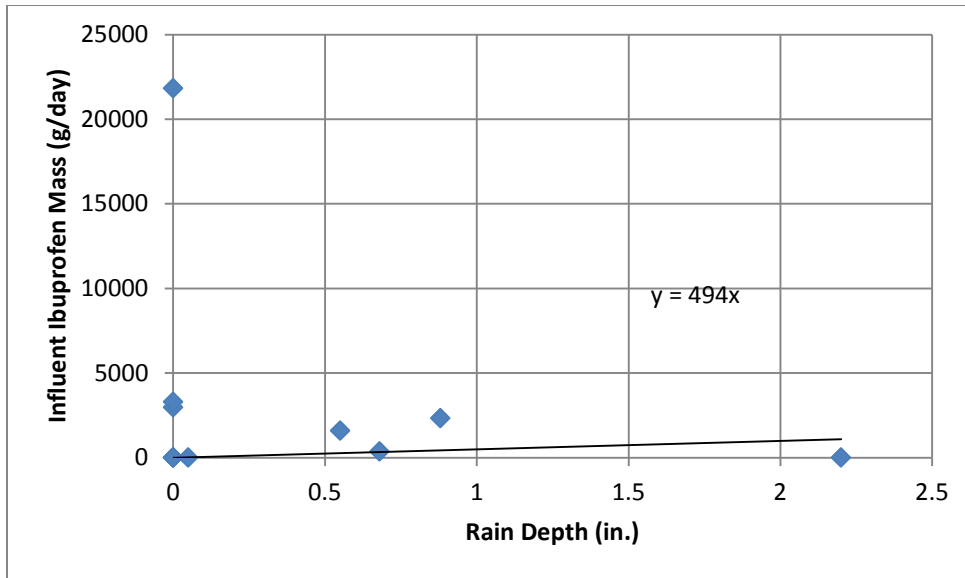
T = 184.500 n(small)= 13 n(big)= 13 (P = 0.641)

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						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-101	49.3	-2.06	0.067*	-211	8.44
Slope term	6.74	2.45	2.75	0.020*	1.28	12.2

*overall regression, intercept (marginal), 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

A.1.3. Summary Data for 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)

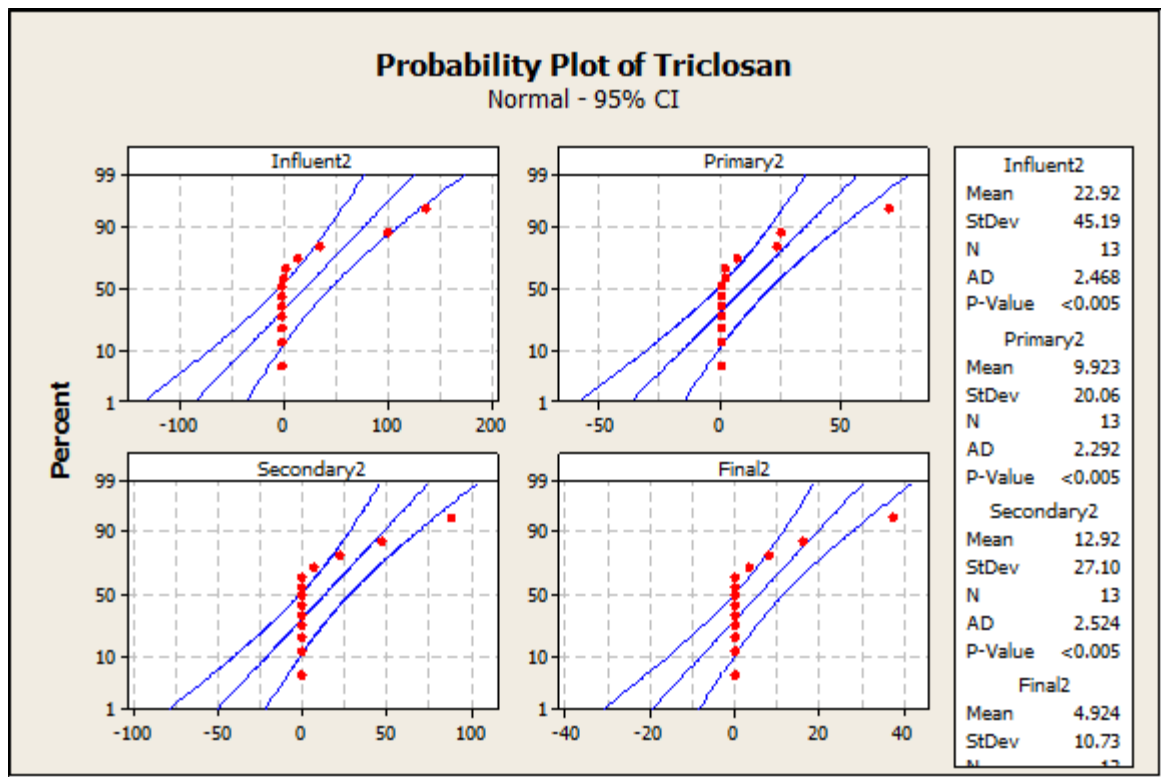


Figure A.1.3.1 Probability plots of Triclosan

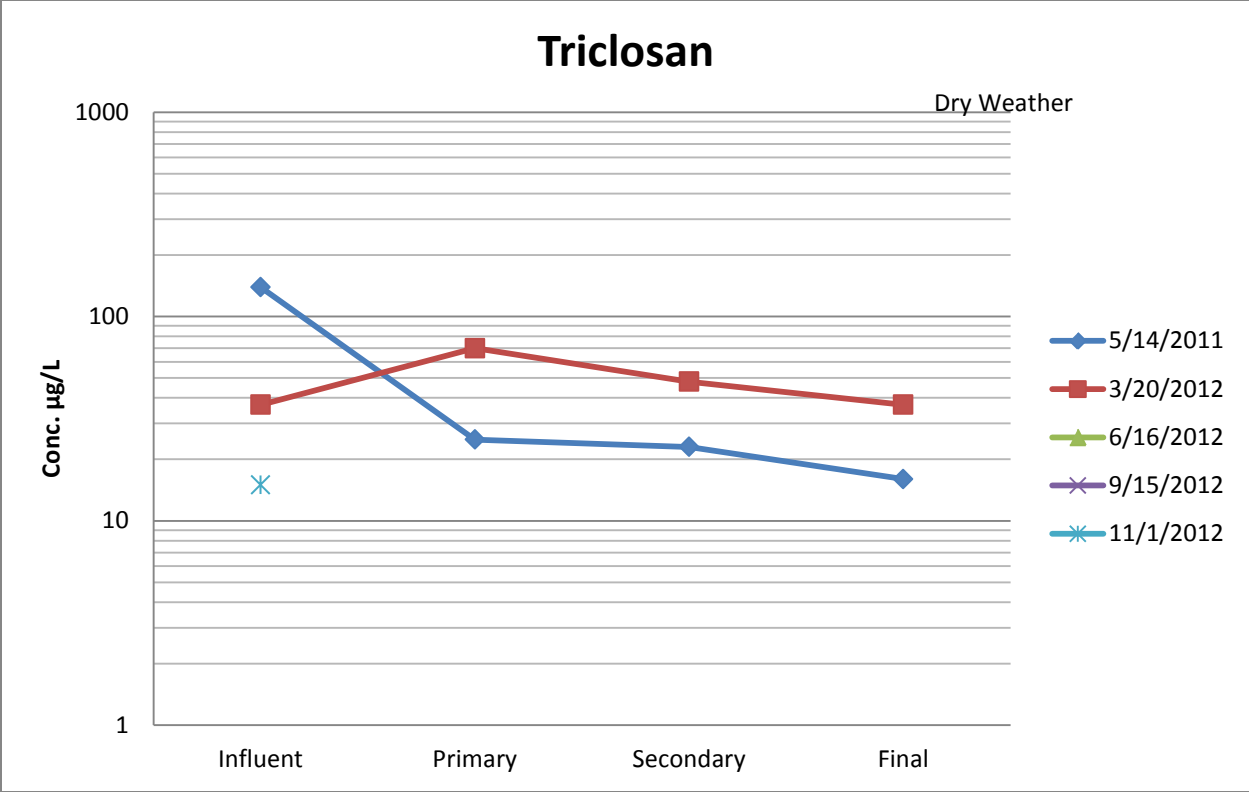


Figure A.1.3.2 .Graph of Triclosan during Dry Weather

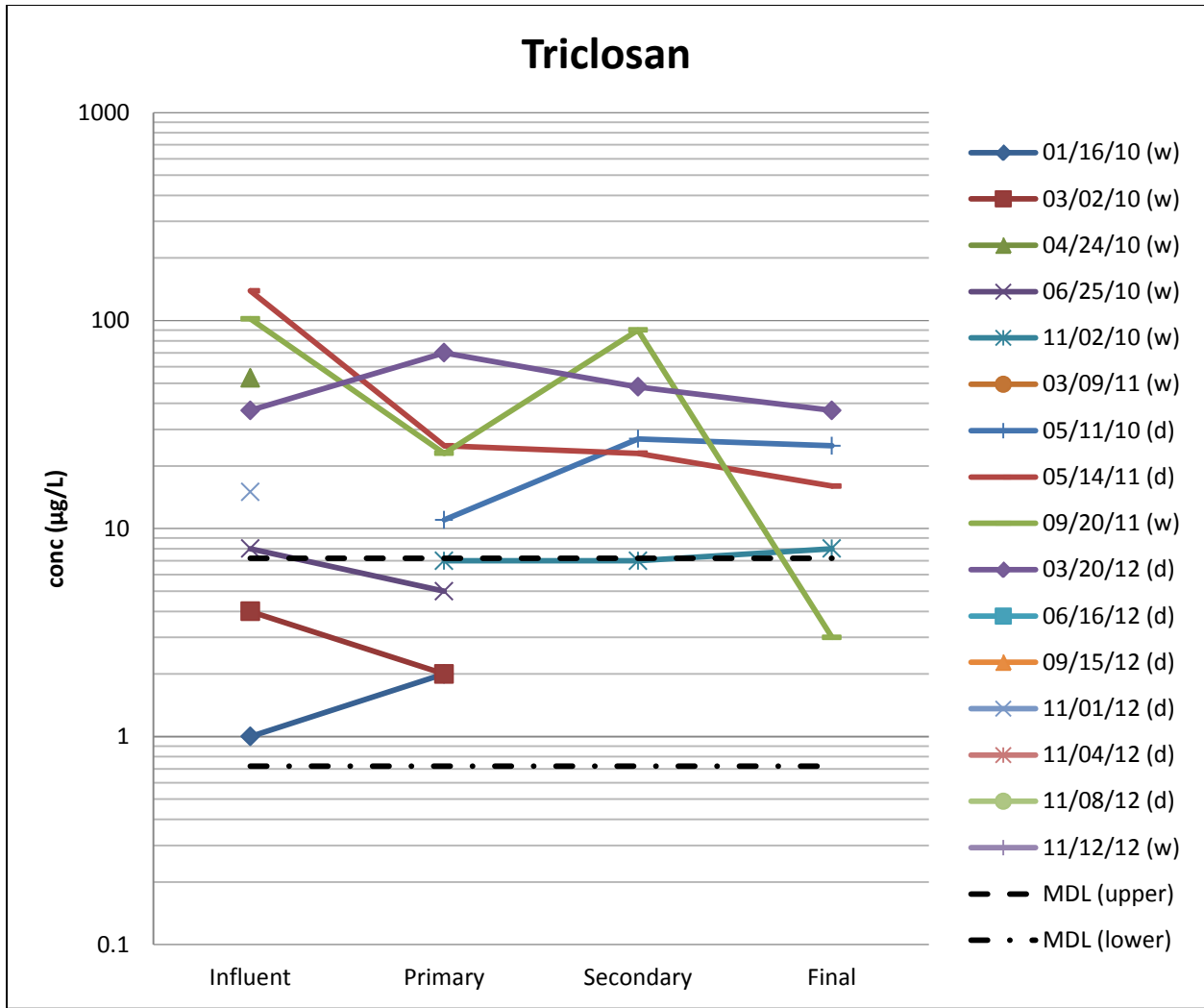


Figure A.1.3.3 Line plots of Triclosan at four sampling locations

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

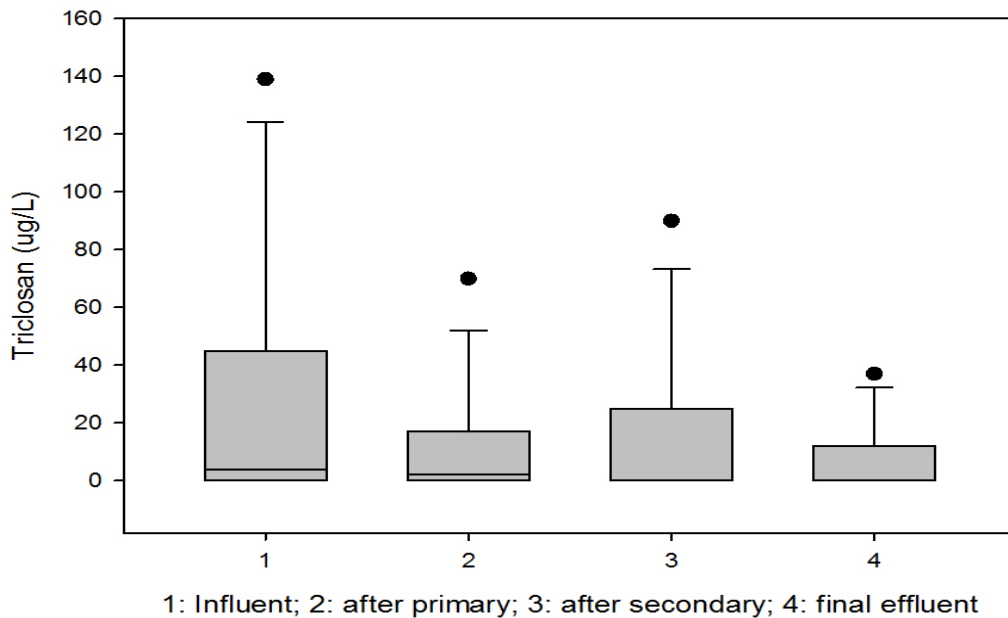


Figure A.1.3.4 Box and Whisker plot of Triclosan

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 secondary	14	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 secondary	14	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

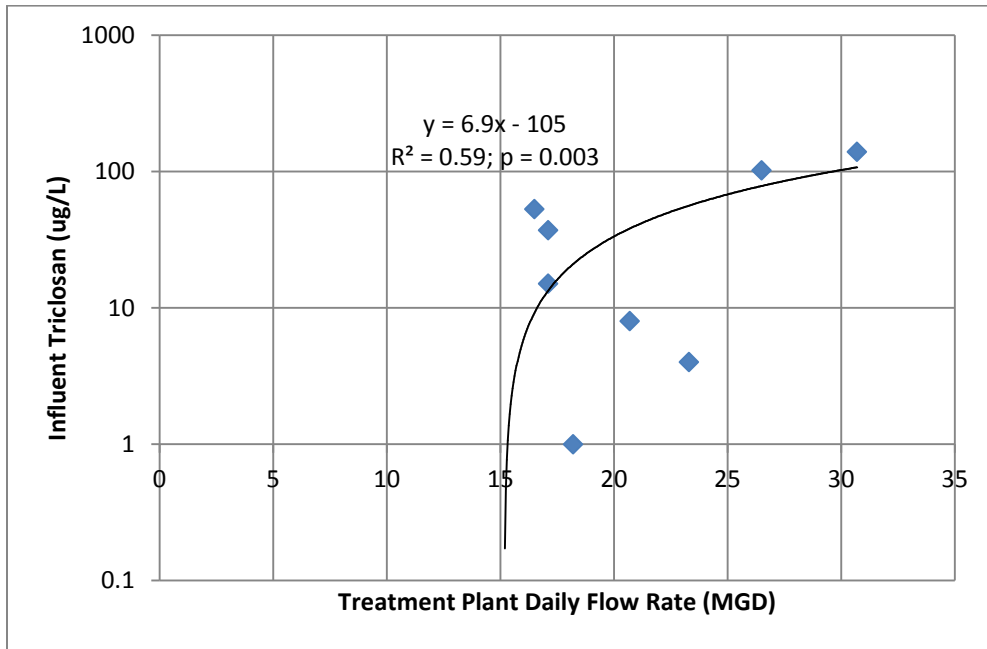
Normality Test (Shapiro-Wilk) Failed (P < 0.050)

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

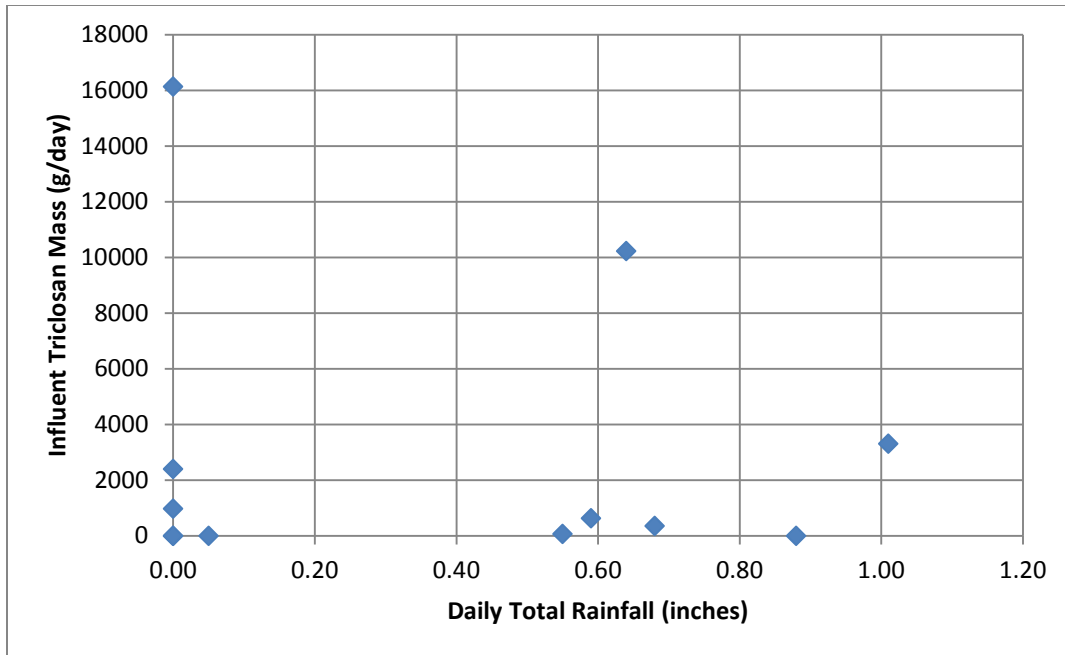
T = 197.000 n(small)= 13 n(big)= 13 (P = 0.274)

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						
	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

A.1.4. Summary Data for 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)

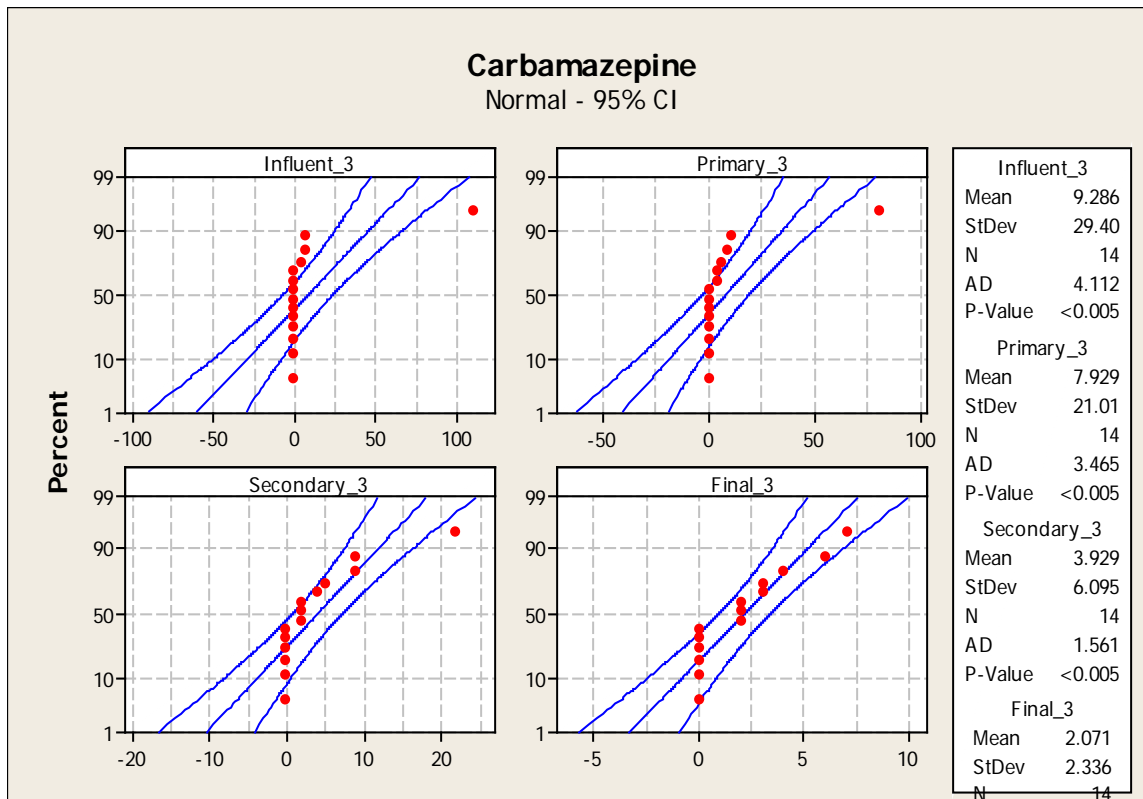


Figure A.1.4.1. Probability Plot for Carbamazepine

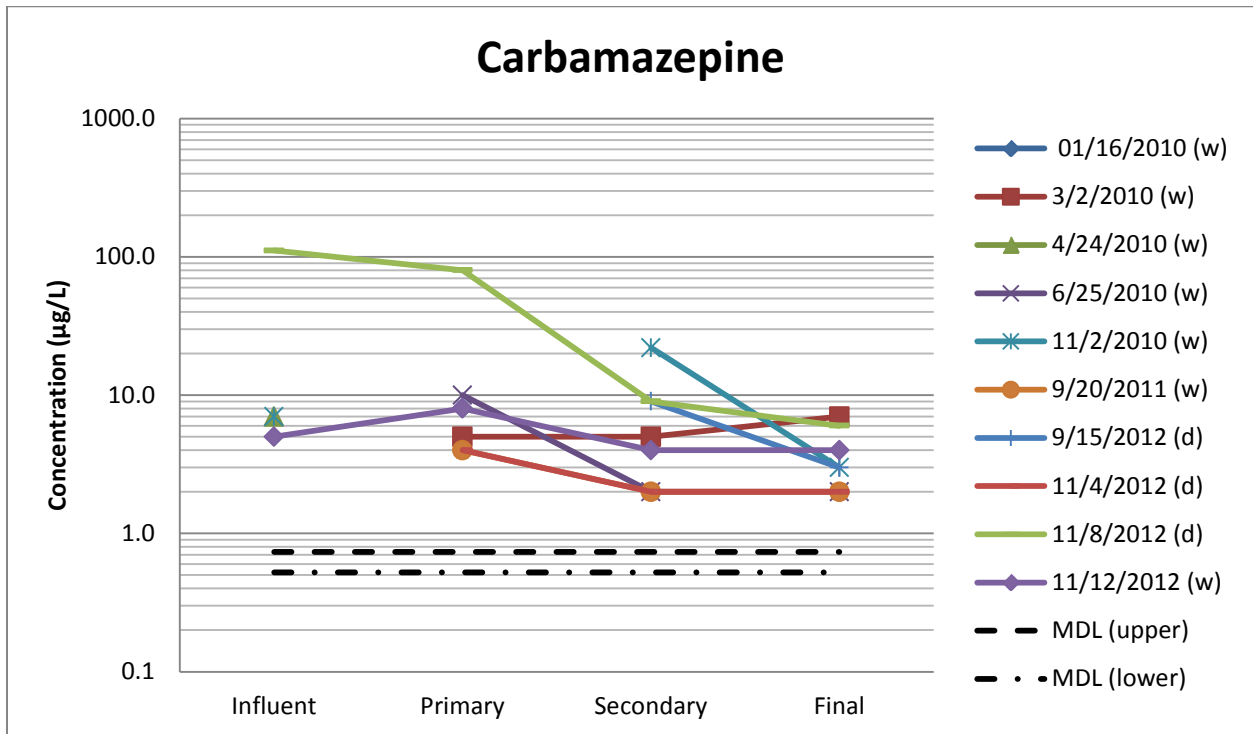


Figure A.1.4.2 Line plot for Carbamazepine at four sampling locations

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

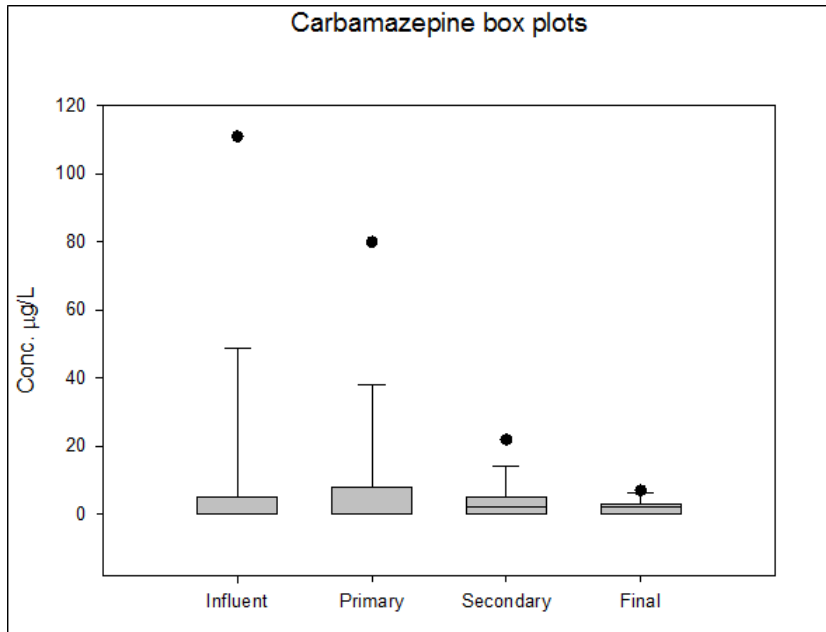


Figure A.1.4.3. Box and Whisker Plots for Carbamazepine

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**)

A.1.5. Summary Data for 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)

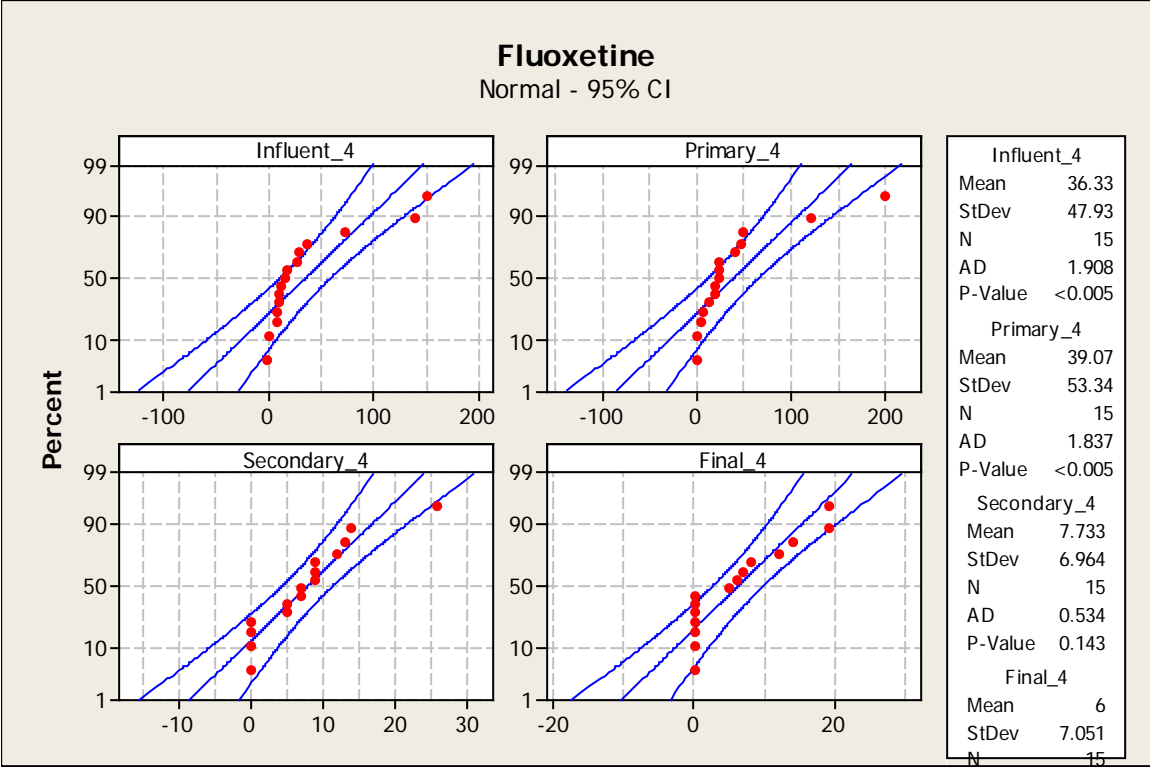


Figure A.1.5.1. Probability plot for Fluoxetine

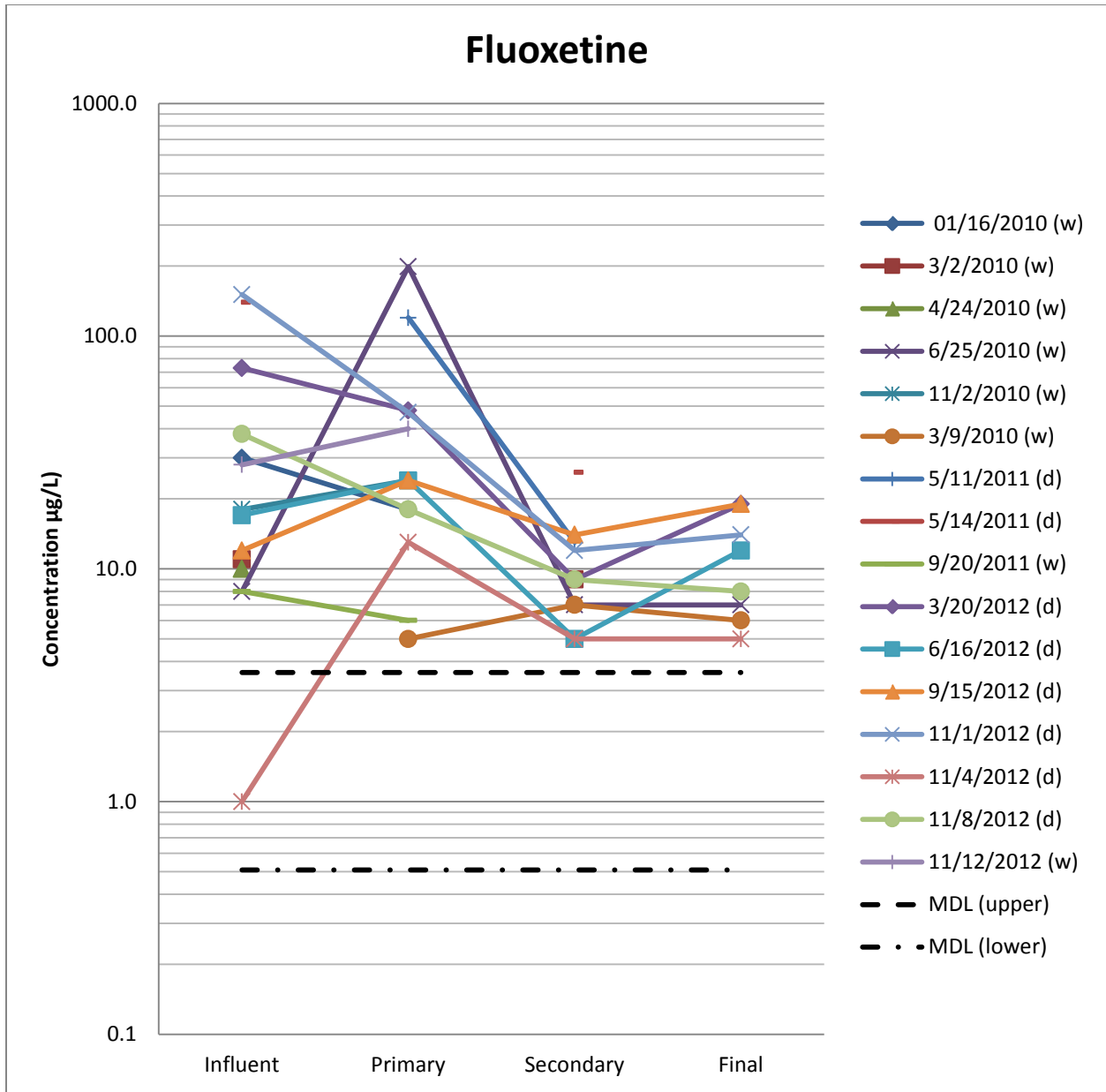


Figure A.1.5.2 Line graph of Fluoxetine at different sampling locations

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

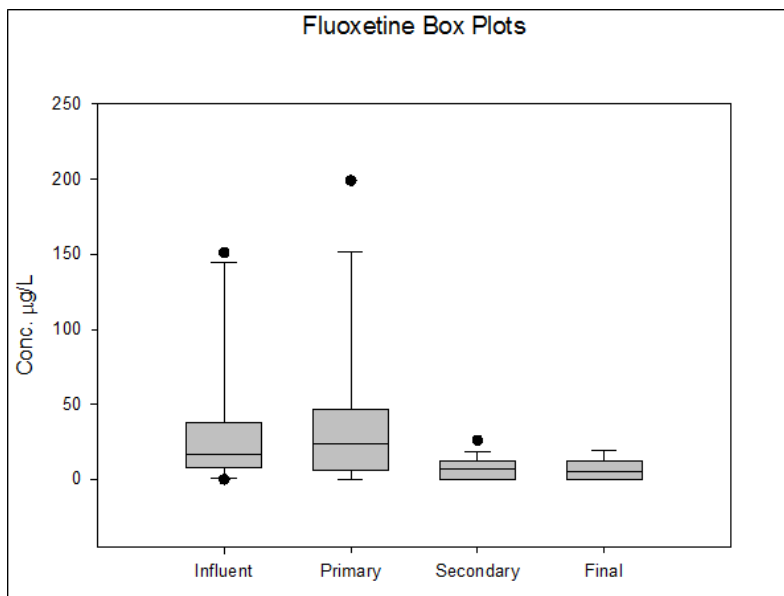


Figure A.1.5.3 Box and Whisker Plots for Fluoxetine

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	0.207	Do Not Test
Col 6 vs Col 9	278.500	4.117	Yes
Col 6 vs Col 8	223.500	3.304	Do 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**)

A.1.6. Summary Data for 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)

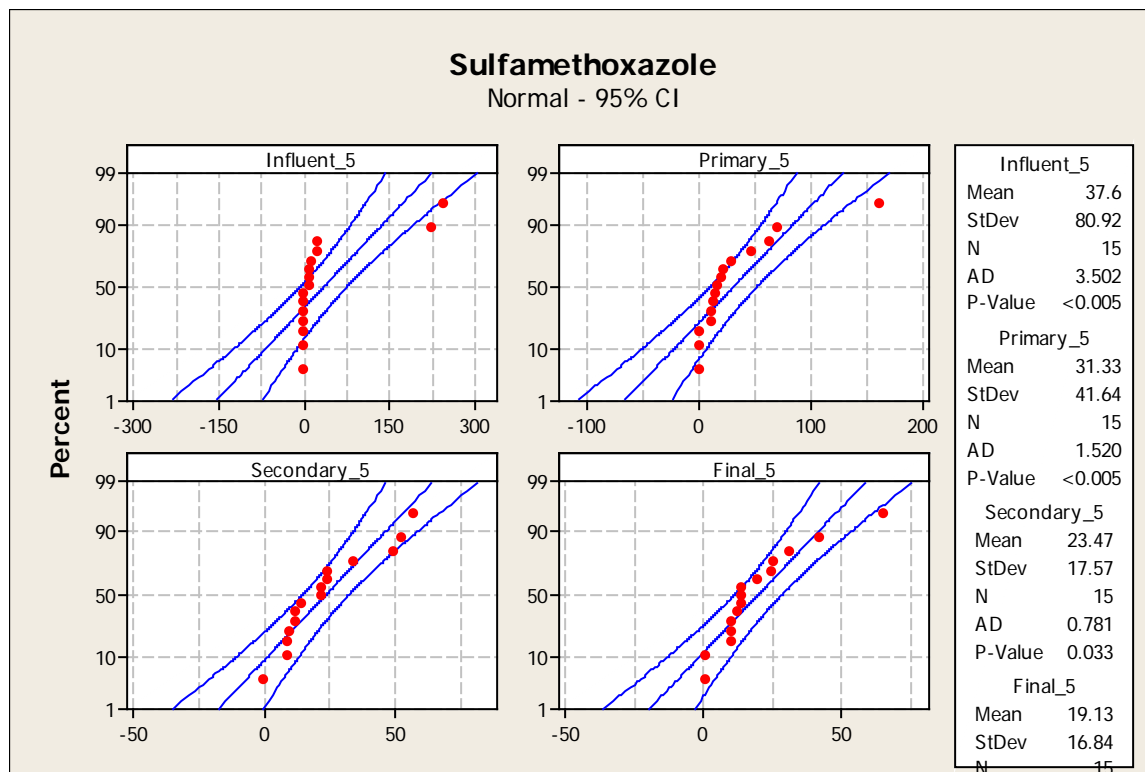


Figure A.1.6.1 Probability Plot for Sulfamethoxazole

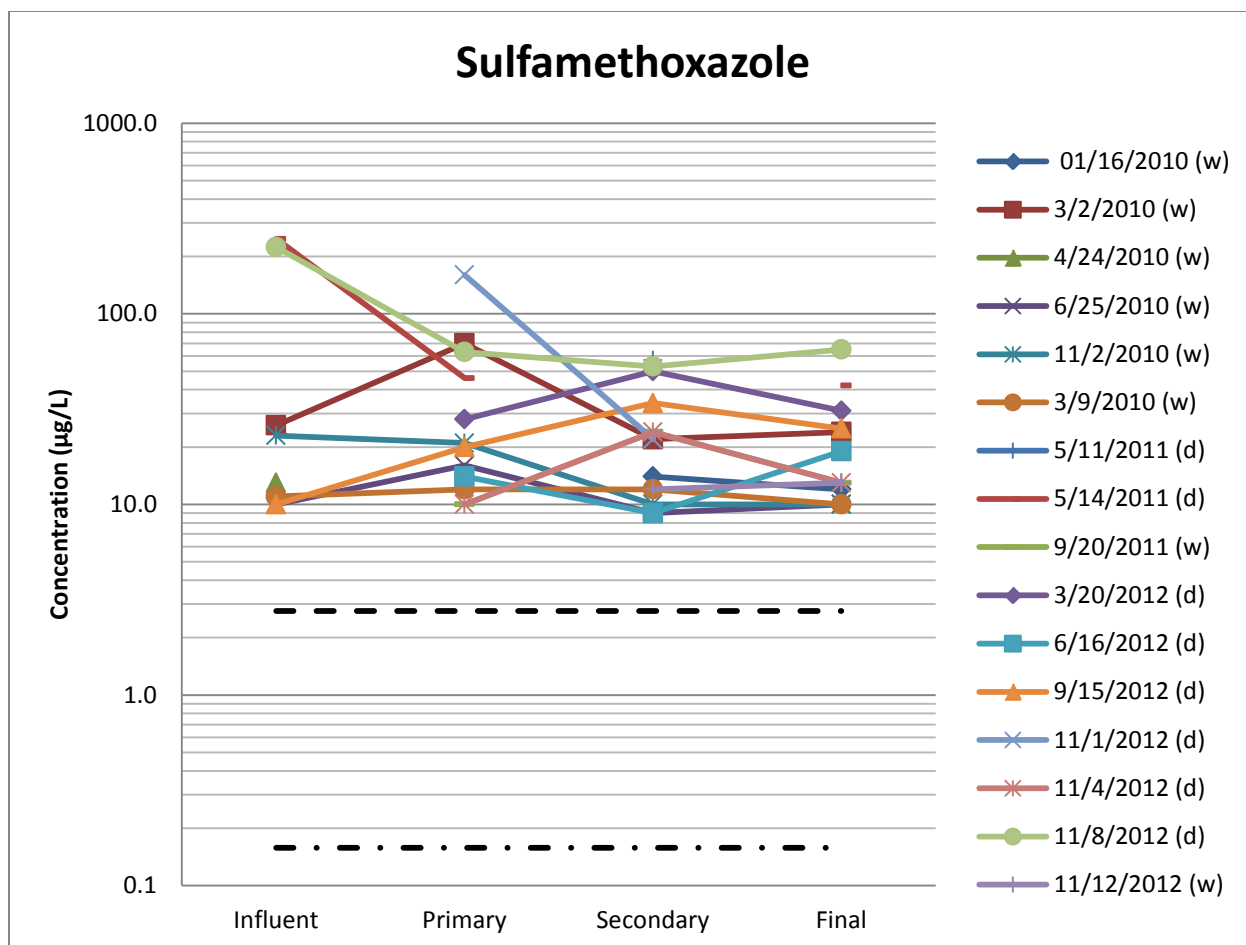


Figure A.1.6.2 Line graph for Sulfamethoxazole at different sampling locations

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

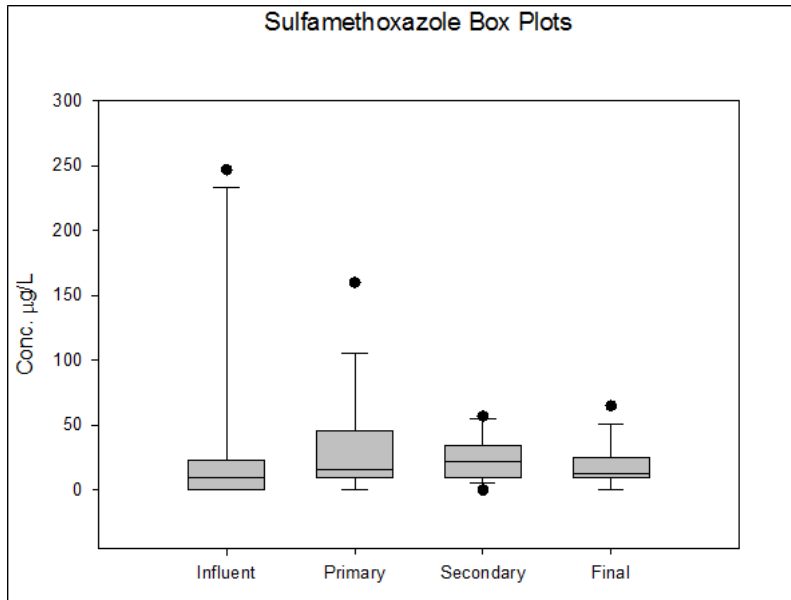


Figure A.1.6.3. Box and Whisker Plots for Sulfamethoxazole

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**)

A.1.7. Summary Data for 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)

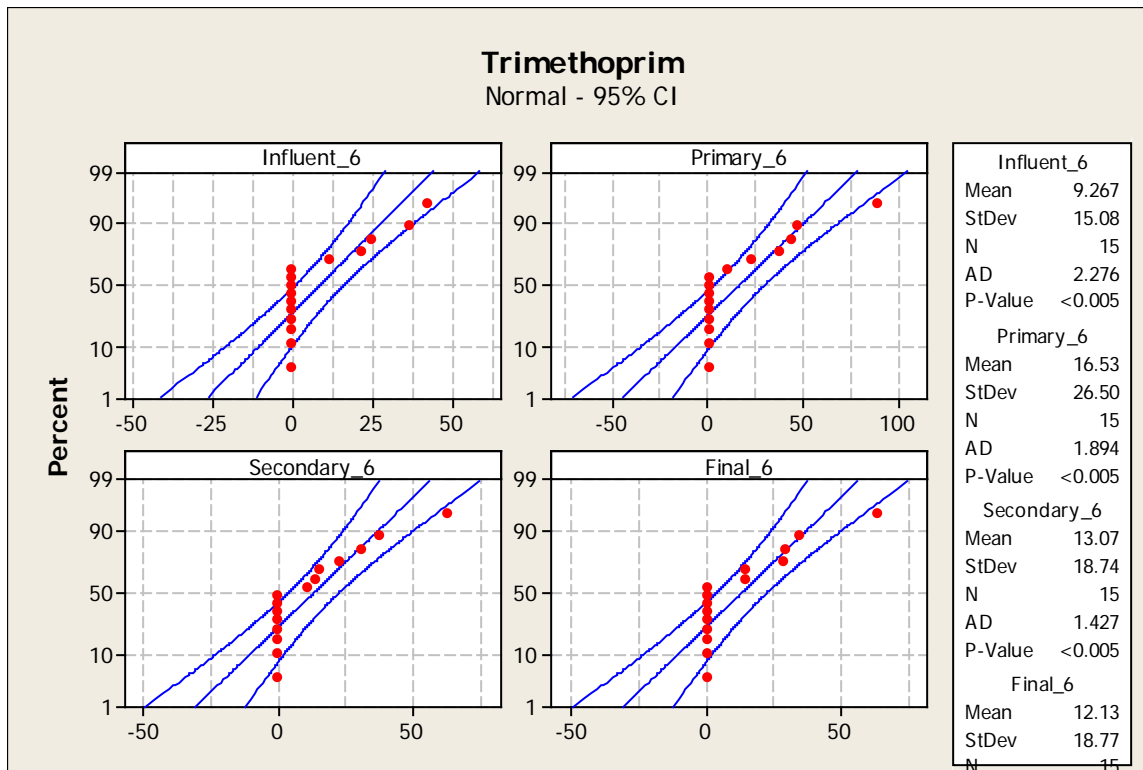


Figure A.1.7.1 Probability Plot for Trimethoprim

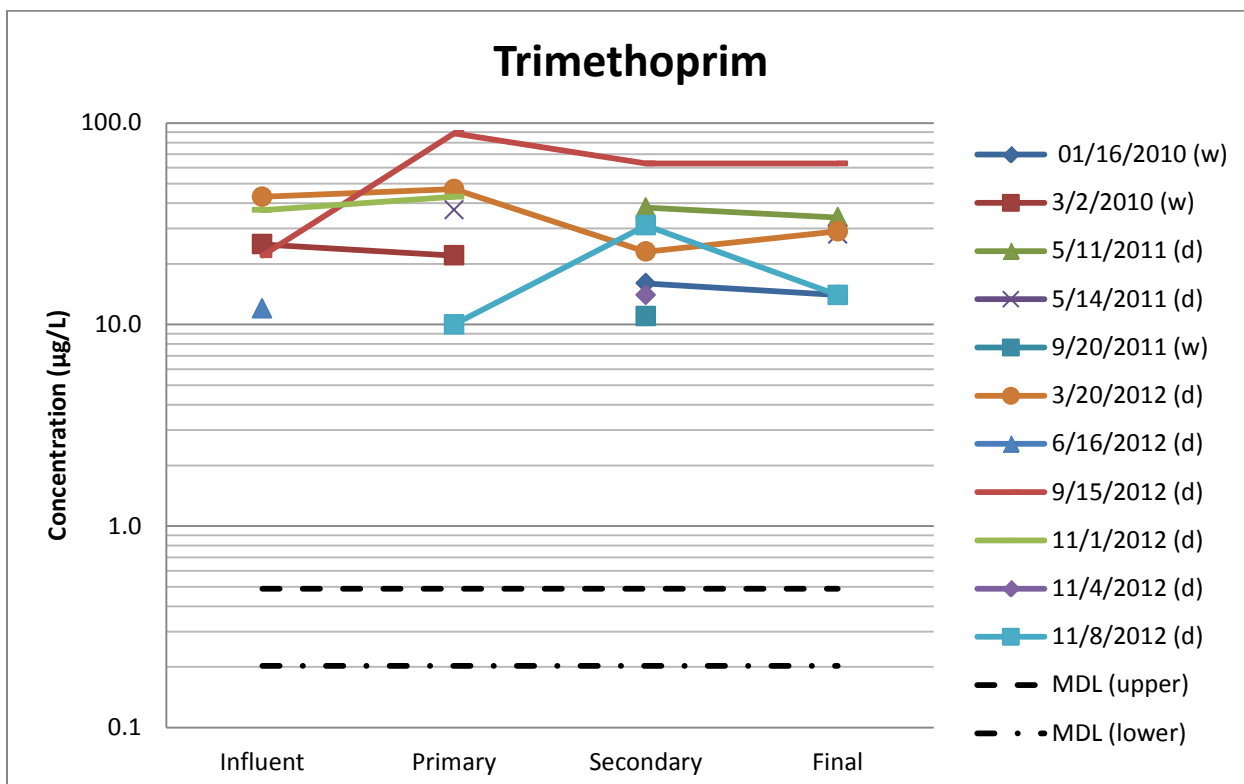


Figure A.1.7.2 Line graph for Trimethoprim at different sampling locations

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

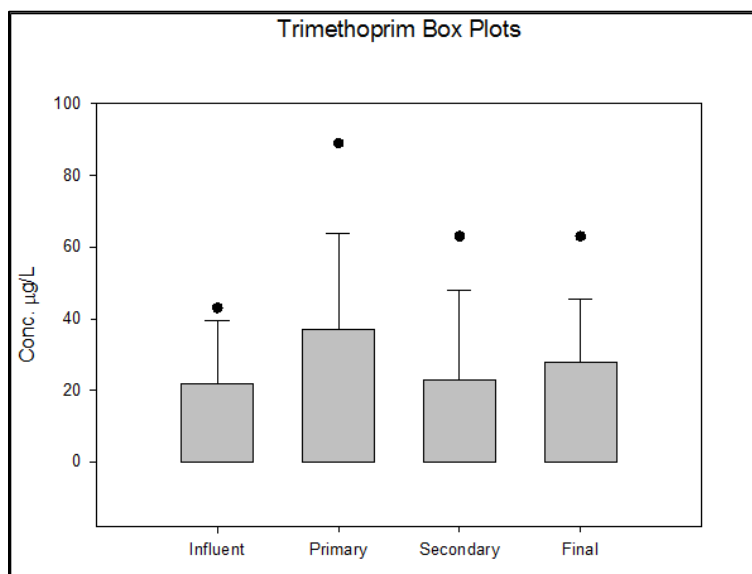


Figure A.1.7.2 Box and Whisker Plots for Trimethoprim

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**)

A.2. Polycyclic Aromatic Hydrocarbons (PAHs)

A.2.1. Summary Data for 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)

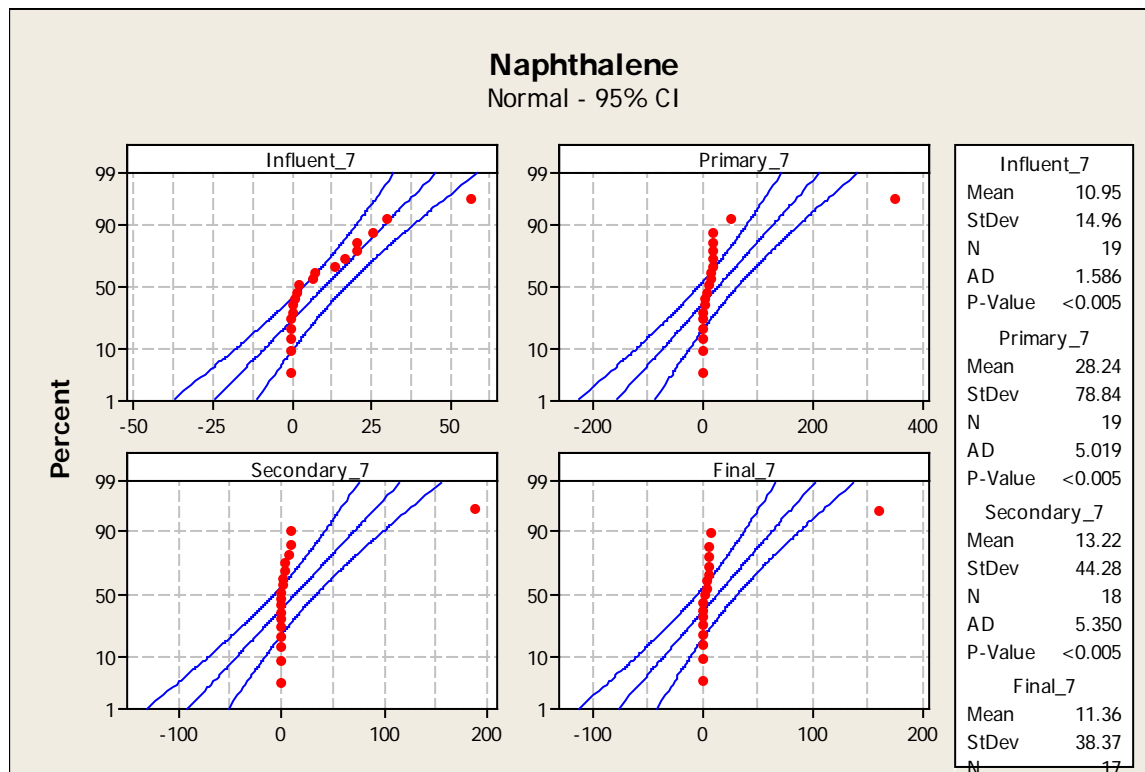


Figure A.2.1.1. Probability plots for Naphthalene

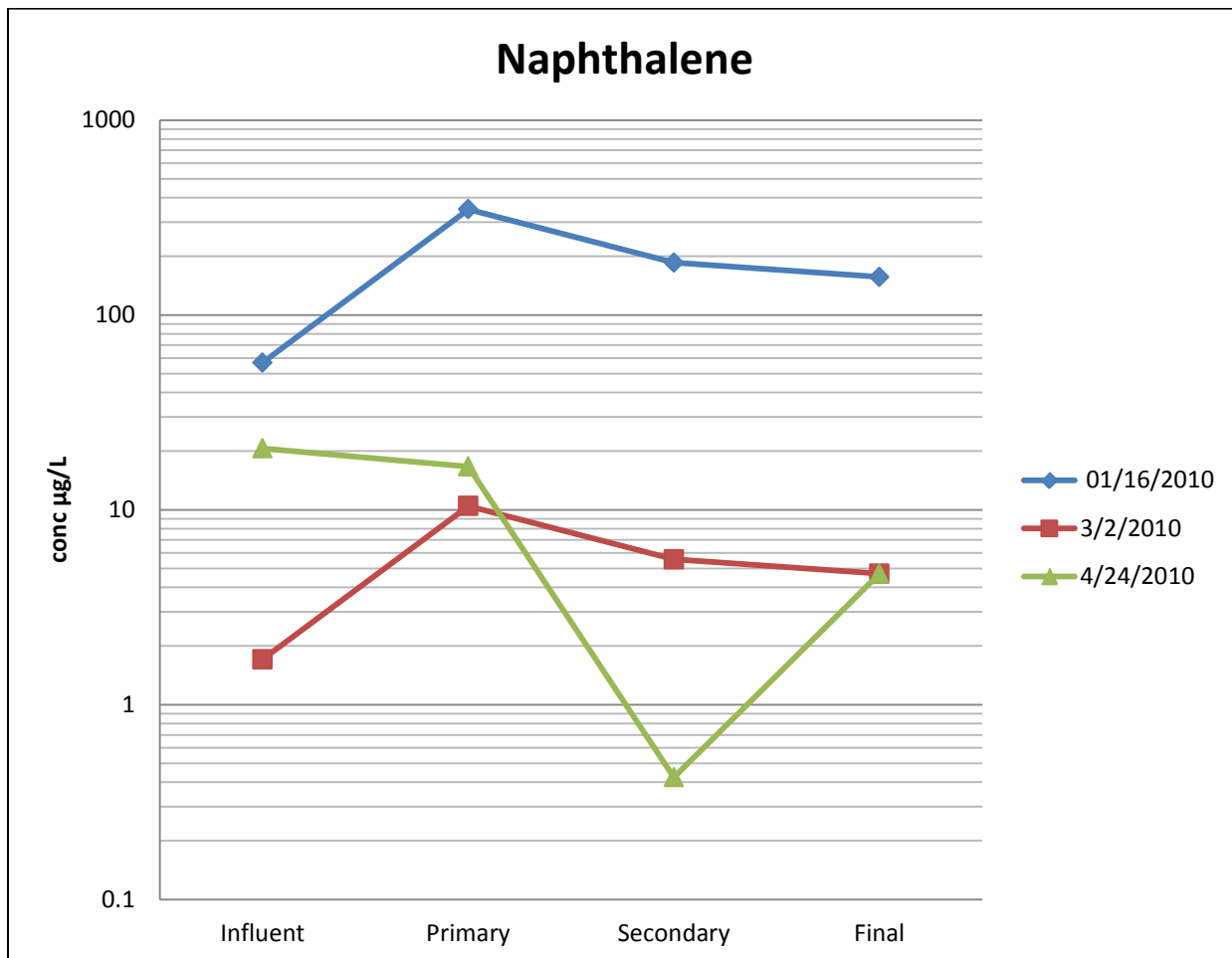


Figure A.2.1.2. Graph of Naphthalene during Wet Weather

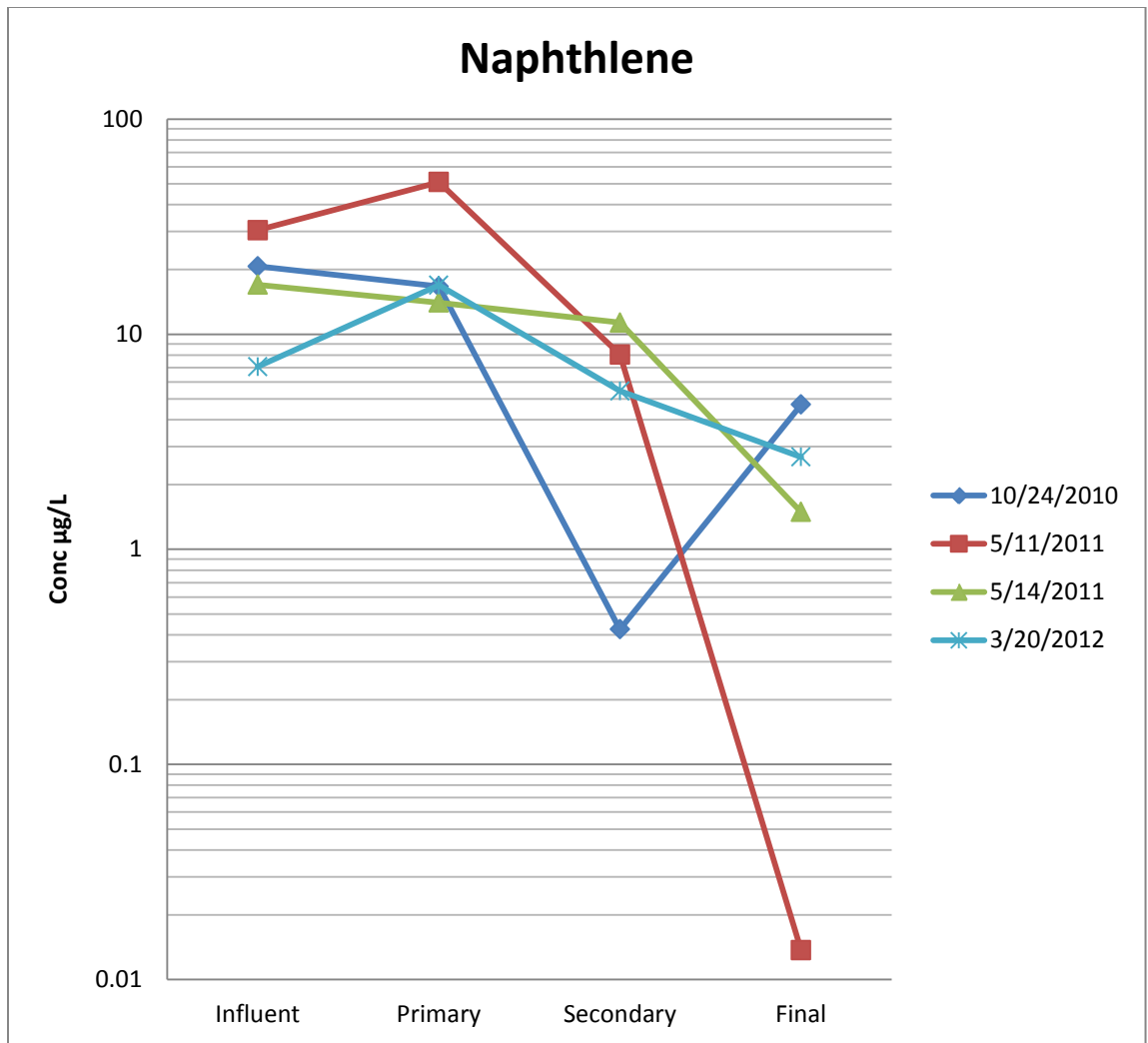


Figure A.2.1.3. Graph of Naphthalene during Dry Weather

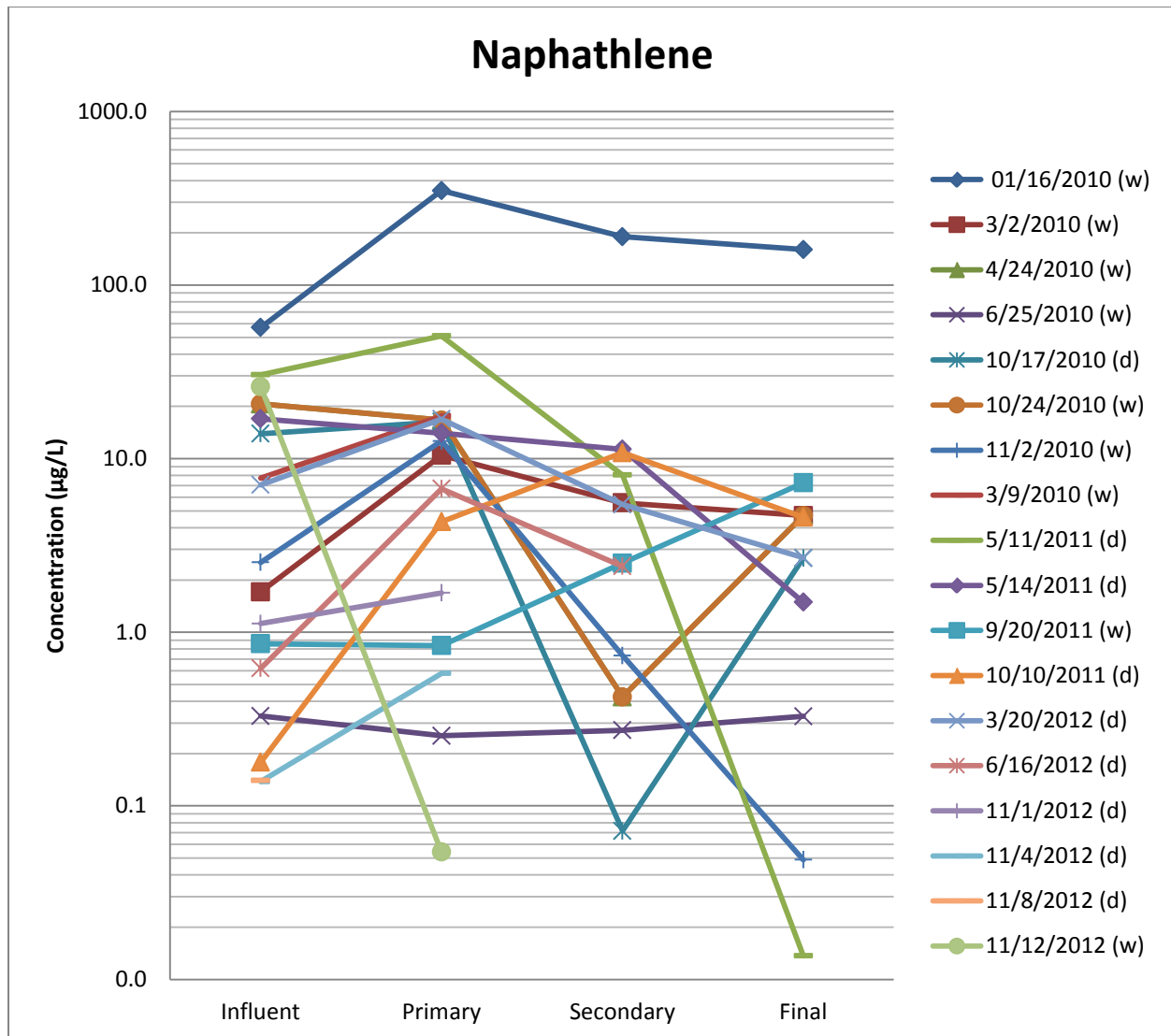


Figure A.2.1.4. Line graph for Naphthalene (total) at four sampling locations

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-P	19	0	28.241	78.841	18.087	38.000
Naphthalene-S	19	1	13.224	44.283	10.437	22.021
Naphthalene-F	19	2	11.365	38.374	9.307	19.730

Column	Range	Max	Min	Median	25%	75%
Naphthalene-I	56.996	56.996	0.000	2.528	0.402	19.751
Naphthalene-P	350.000	350.000	0.000	10.458	0.644	16.666
Naphthalene-S	190.000	190.000	0.000	0.579	0.000	5.567
Naphthalene-F	160.000	160.000	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-I	208.053	6307.469
Naphthalene-P	536.588	127040.994
Naphthalene-S	238.032	36483.767
Naphthalene-F	193.205	25756.844

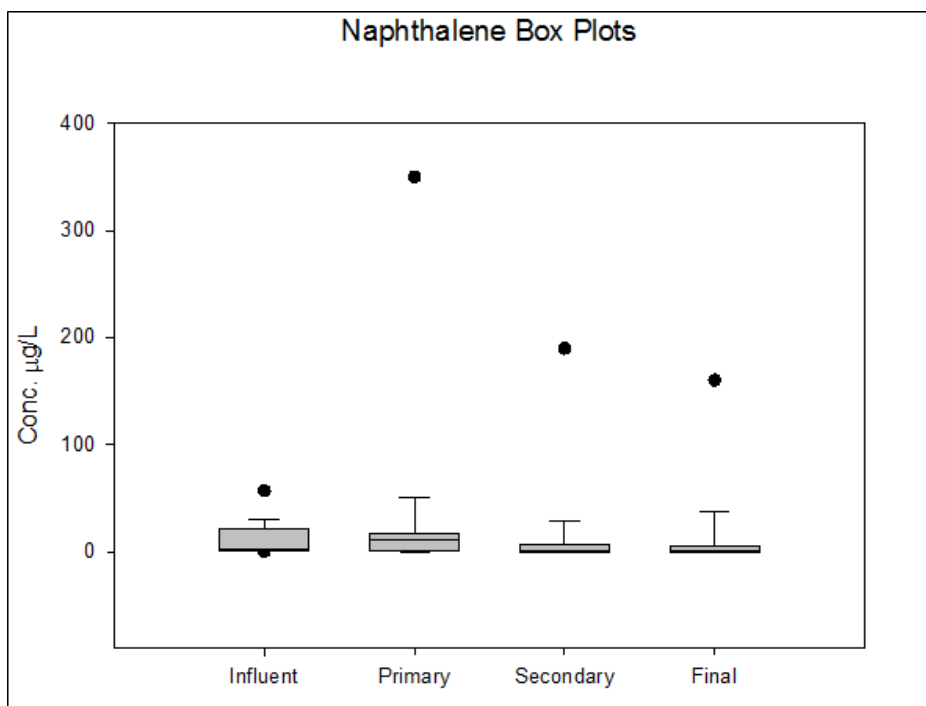


Figure A.2.1.5. Box and Whisker plot for Naphthalene

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**)

A.2.2. Summary Data for 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)

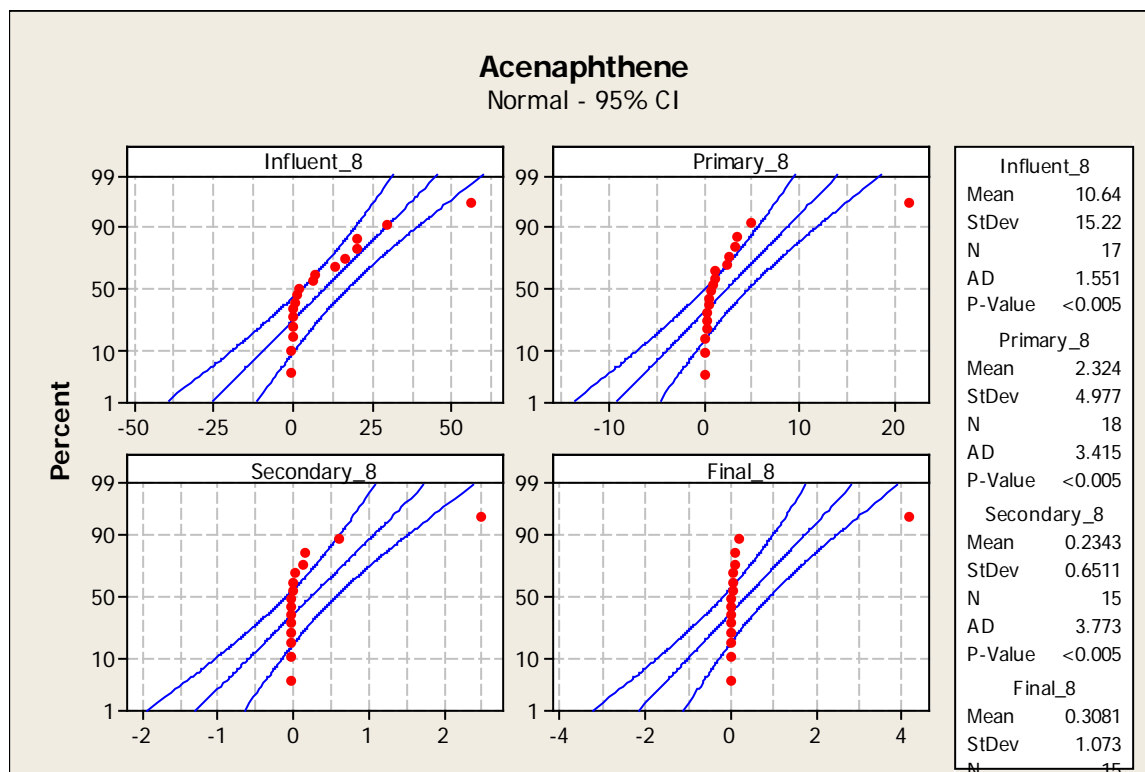


Figure A.2.2.1. Probability Plot for Acenaphthene

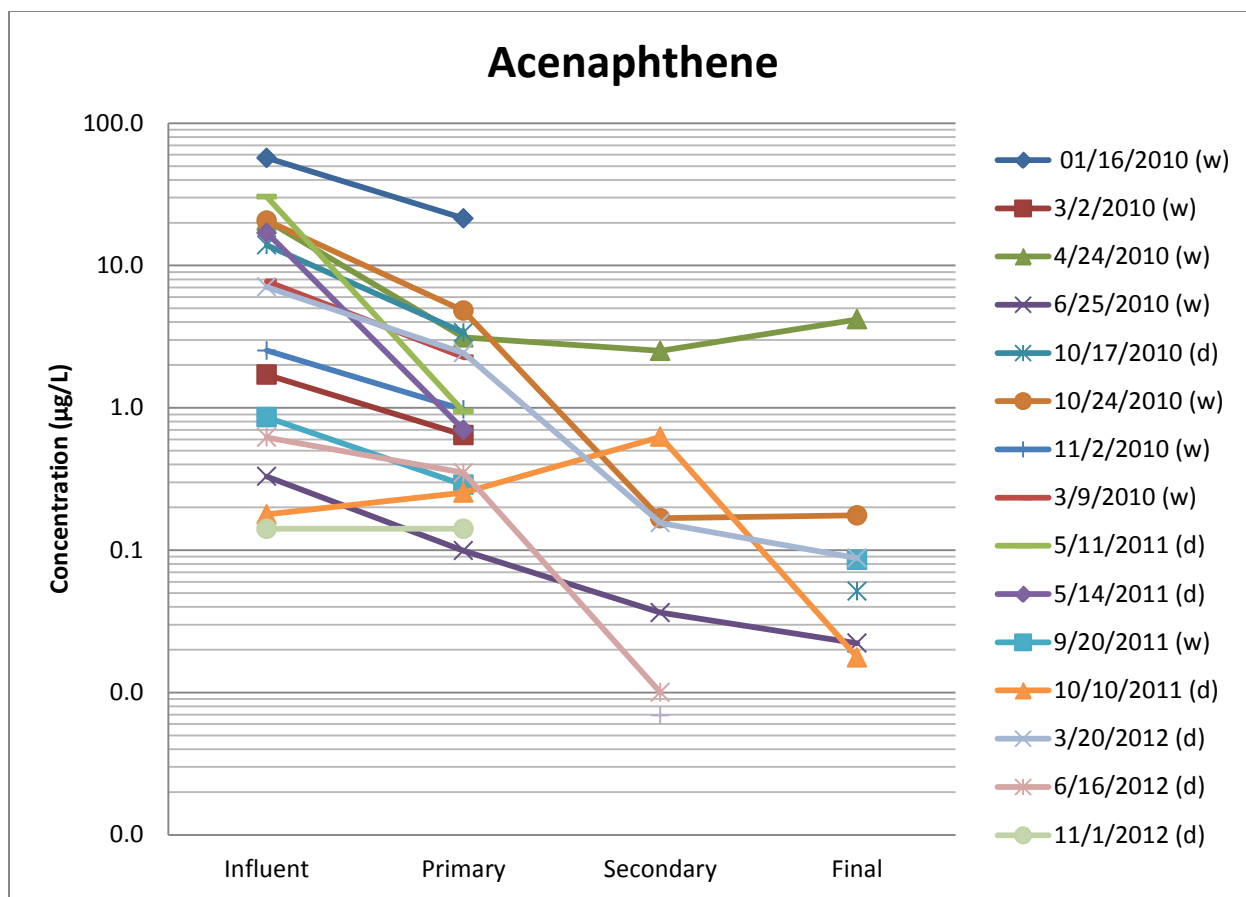


Figure A.2.2.2 Line graph for Acenaphthene at four different sampling locations

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

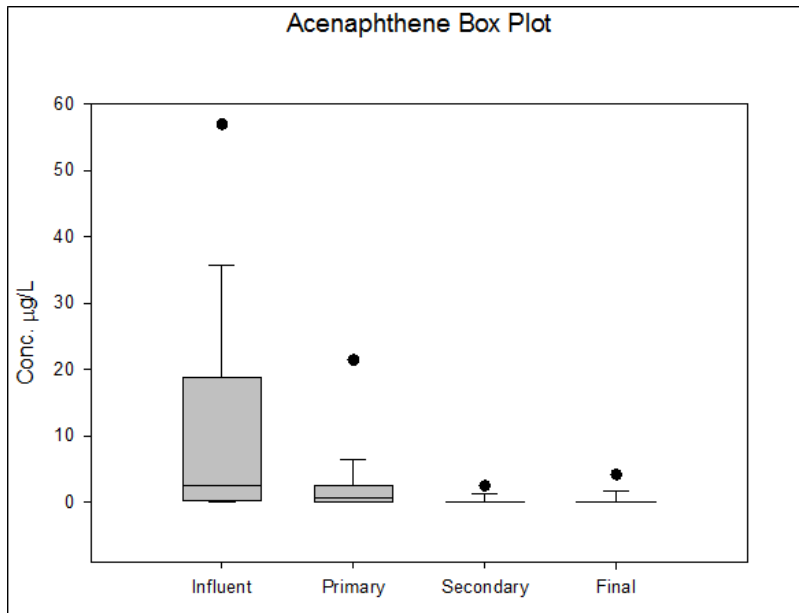


Figure A.2.2.3 Box and Whisker Plot for Acenaphthene

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-I	19	2	2.528	0.254	18.830
Acenaphthene-P	19	1	0.672	0.131	2.602
Acenaphthene-S	19	4	0.000	0.000	0.156
Acenaphthene-F	19	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-I	19	2	2.528	0.254	18.830
Acenaphthene-P	19	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-P	19	1	0.672	0.131	2.602
Acenaphthene-S	19	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-S	19	4	0.000	0.000	0.156
Acenaphthene-F	19	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-I	19	2	2.528	0.254	18.830
Acenaphthene-F	19	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**)

A.2.3. Summary Data for 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)								42.3 (calc from avg)
	0.67	1.19	0.04	0.05	17.95	38.89	0.01	
Average wet								-3.63 (calc from avg)
	10.26	1.03	0.56	0.57	22.18	462.98	0.84	

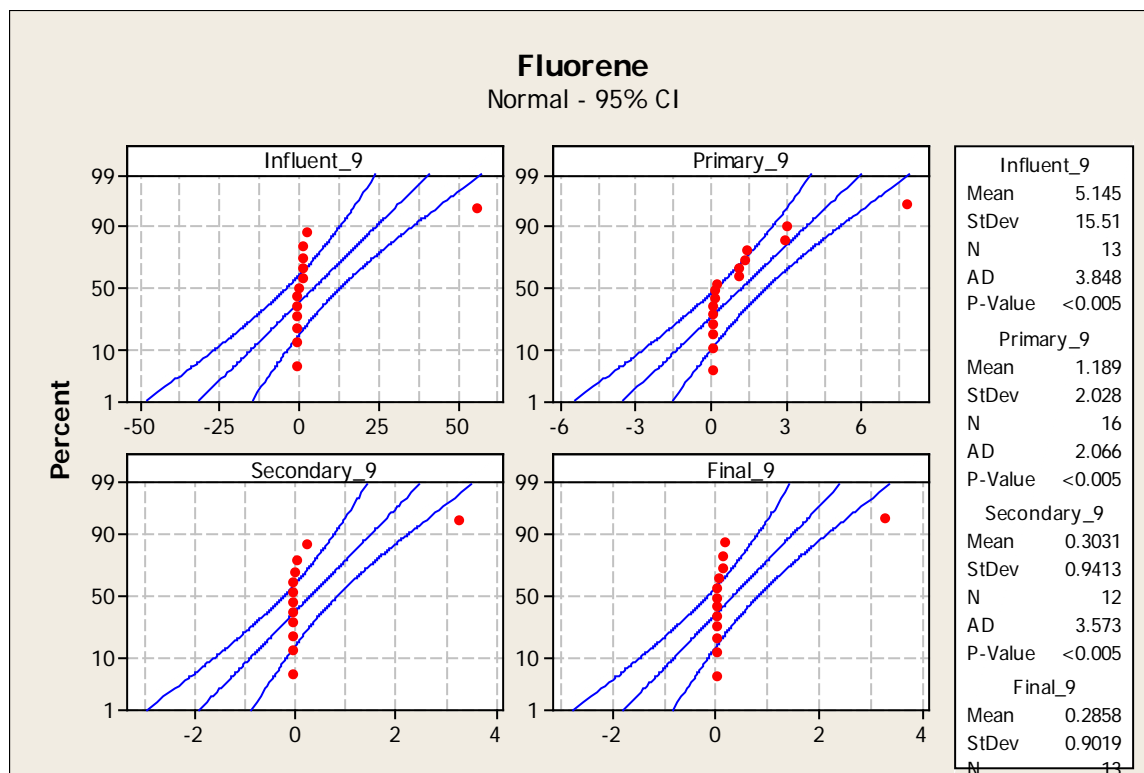


Figure A.2.3.1 Probability plot for fluorene

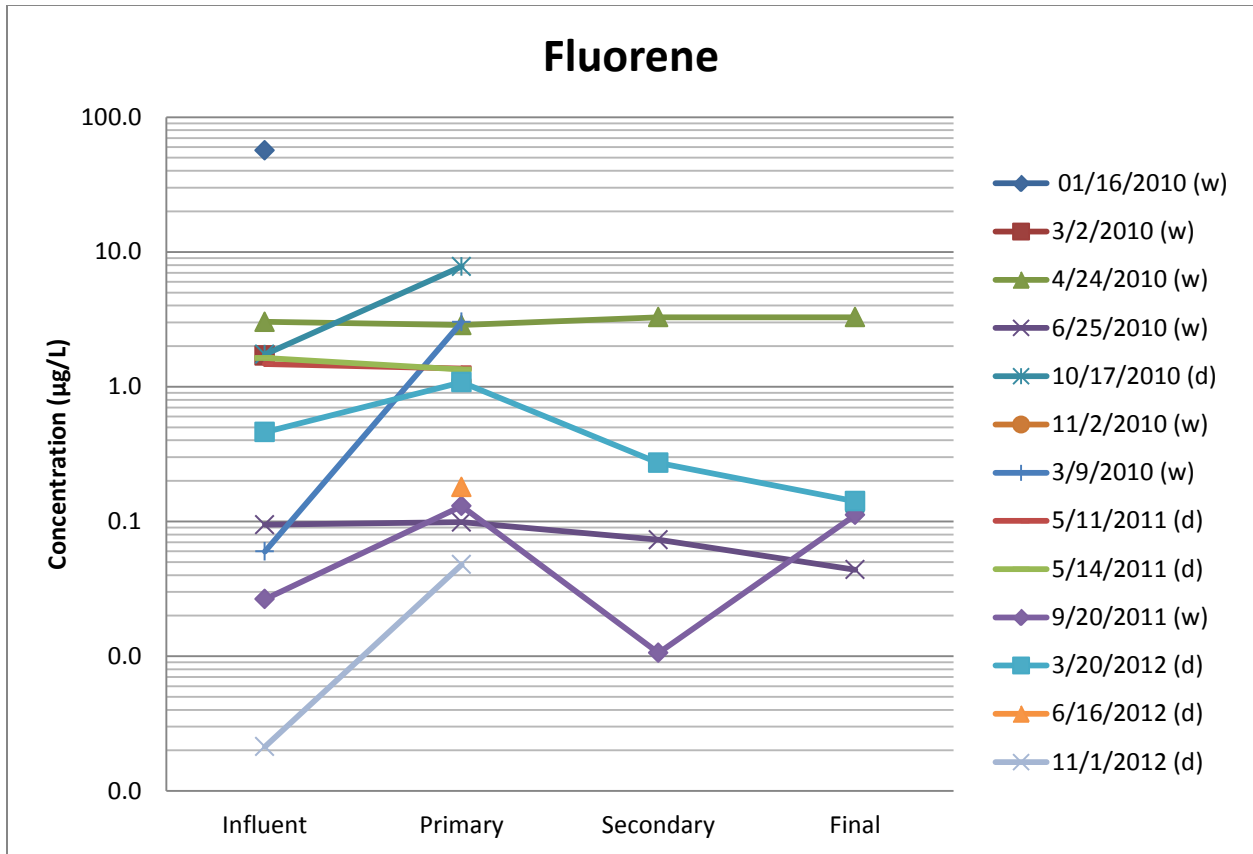


Figure A.2.3.2. Line plot for fluorene at four different sampling locations

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

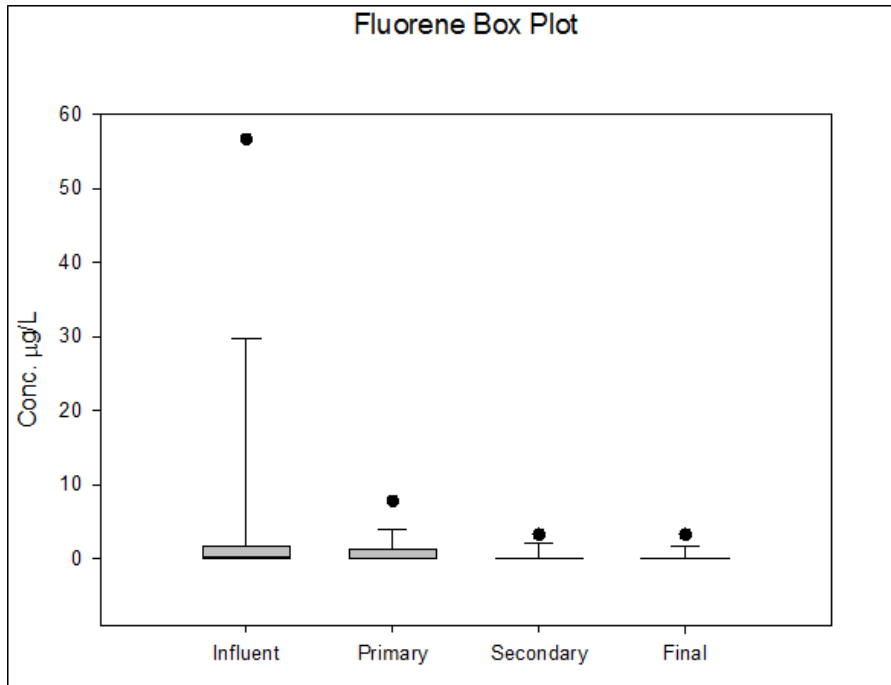


Figure A.2.3.3. Box and Whisker Plots for Fluorene

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**)

A.2.4. Summary Data for 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)

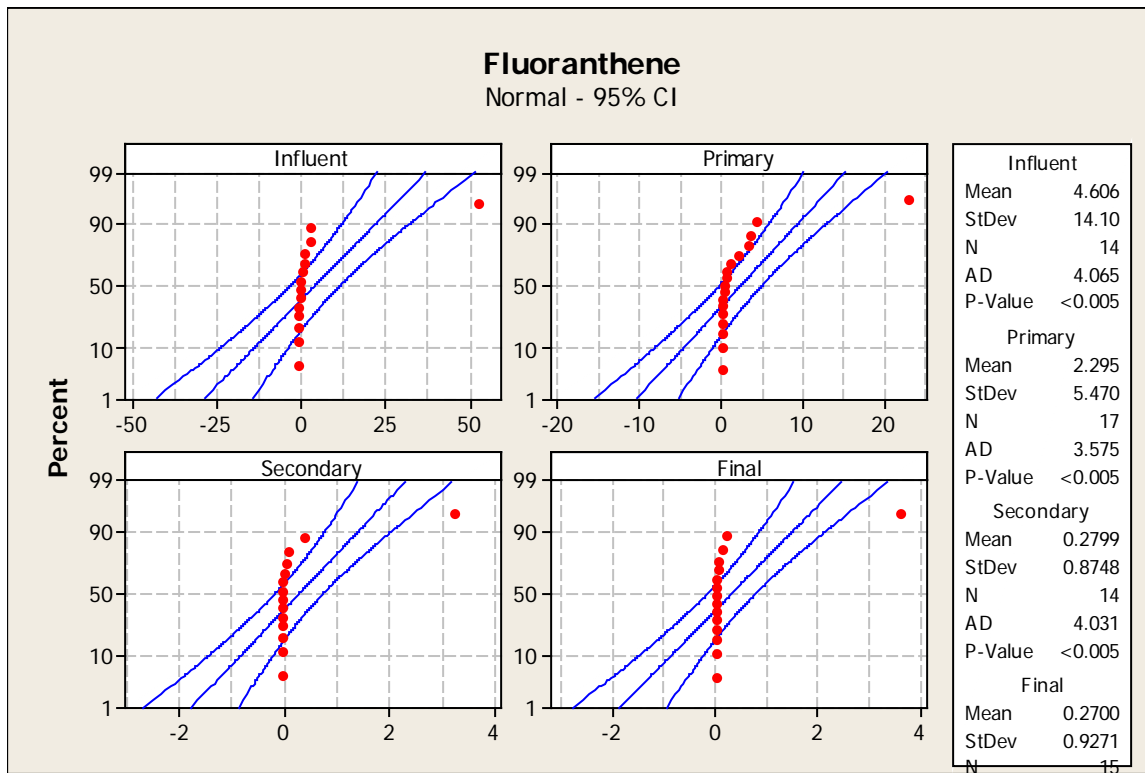


Figure A.2.4.1 Probability plots for Fluoranthene

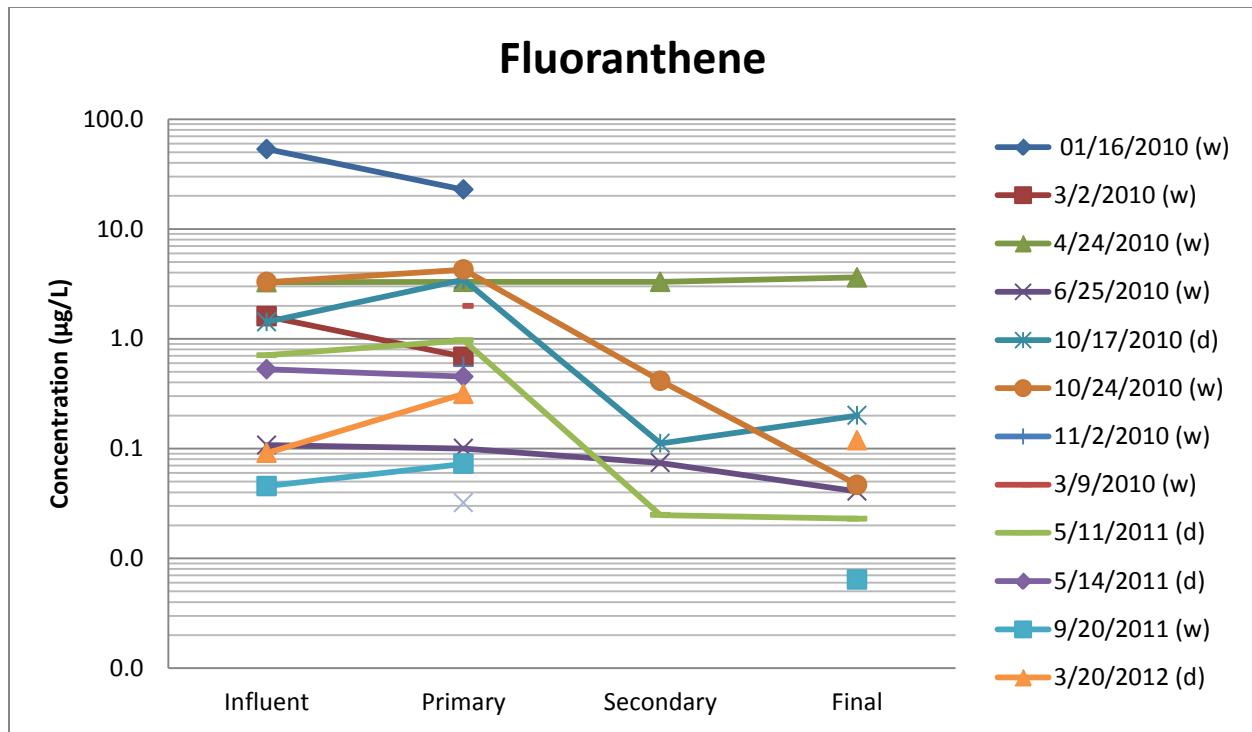


Figure A.2.4.2 Line graph for Fluoranthene at four different sampling locations

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

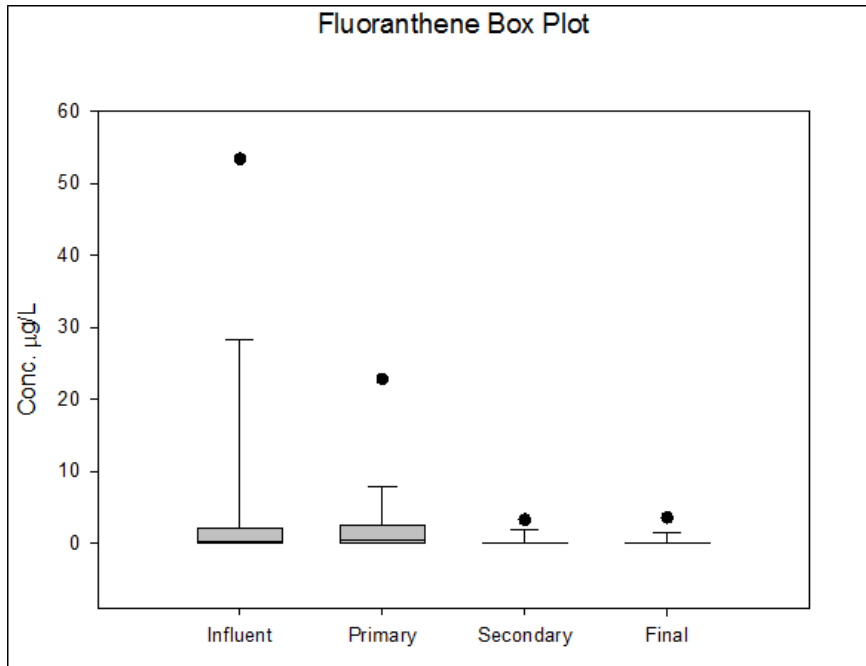


Figure A.2.3.3 Box and Whisker Plots for Fluoranthene

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-I	19	5	0.317	0.000	2.020
Fluoranthene-P	19	2	0.452	0.0160	2.638
Fluoranthene-S	19	5	0.000	0.000	0.0834
Fluoranthene-F	19	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-I	19	5	0.317	0.000	2.020
Fluoranthene-P	19	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-P	19	2	0.452	0.0160	2.638
Fluoranthene-S	19	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-S	19	5	0.000	0.000	0.0834
Fluoranthene-F	19	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**)

A.2.5. Summary Data for 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	0.08	0.58	0.01	0.02	17.95	3.74	0.01	8.98 (calc

rain)								from avg)
Average wet	10.55	0.60	0.61	0.67	22.18	484.49	0.84	47.54 (calc from avg)

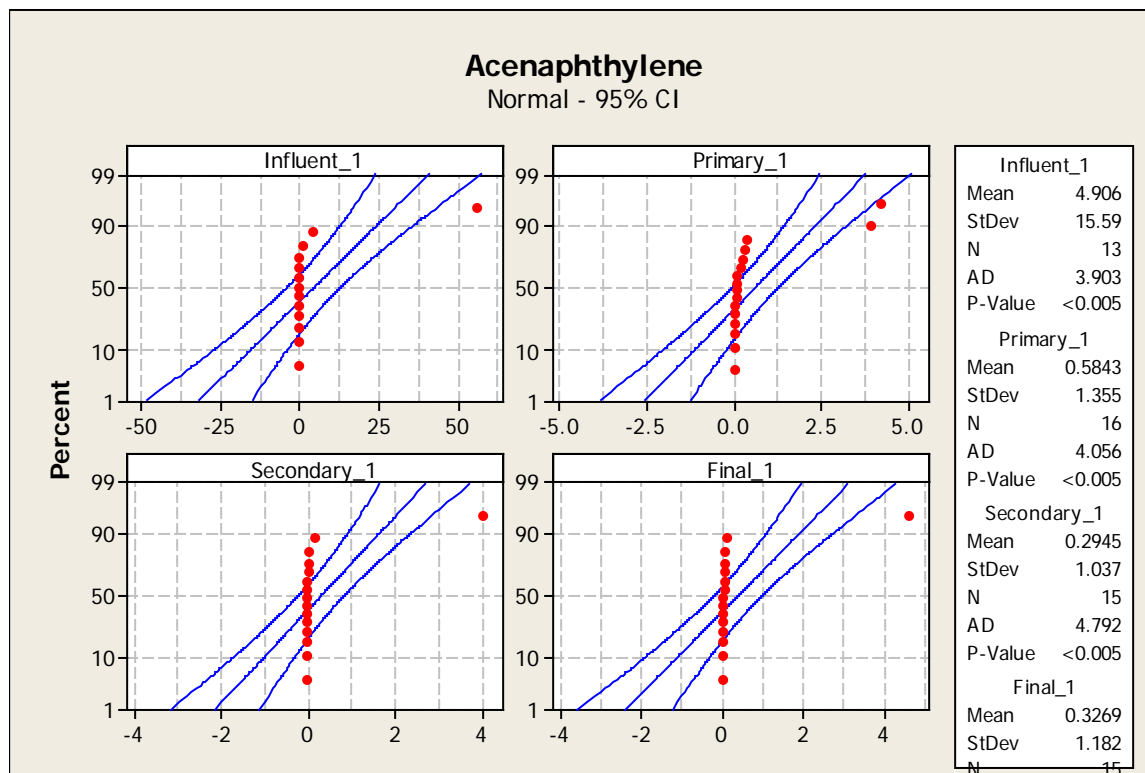


Figure A.2.5.1. Probability plot for Acenaphthylene

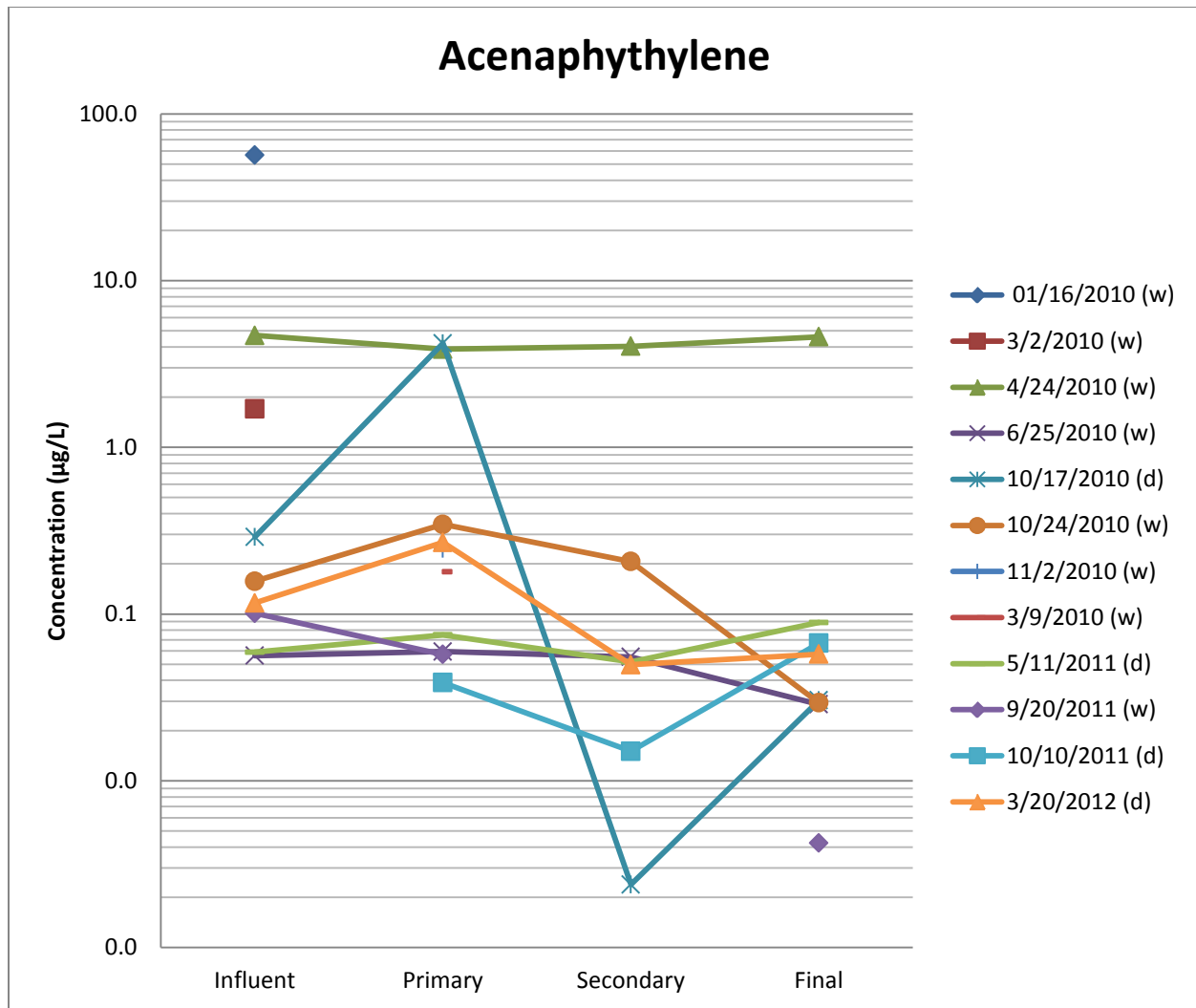


Figure A.2.5.2. Line graph for Acenaphthylene at four different sampling locations

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

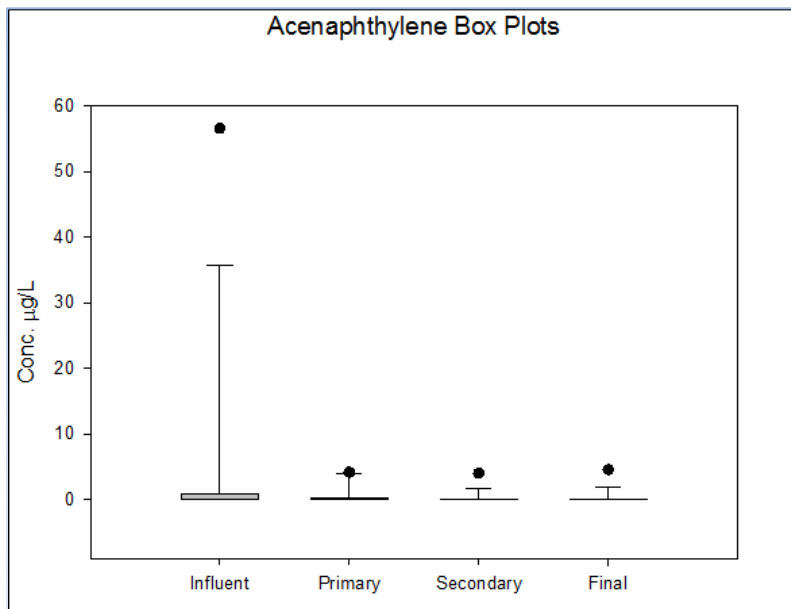


Figure A.2.5.1. Box and Whisker Plots for Acenaphthylene

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-I	19	6	0.101	0.000	0.994
Acenaphthylene-P	19	3	0.0584	0.000	0.263
Acenaphthylene-S	19	4	0.000	0.000	0.0516
Acenaphthylene-F	19	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-I	19	6	0.101	0.000	0.994
Acenaphthylene-P	19	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-P	19	3	0.0584	0.000	0.263
Acenaphthylene-S	19	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-S	19	4	0.000	0.000	0.0516
Acenaphthylene-F	19	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)

A.2.6. Summary Data for 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								47.60 (calc from avg)
	6.14	4.36	0.05	0.15	20.10	62.77	0.84	

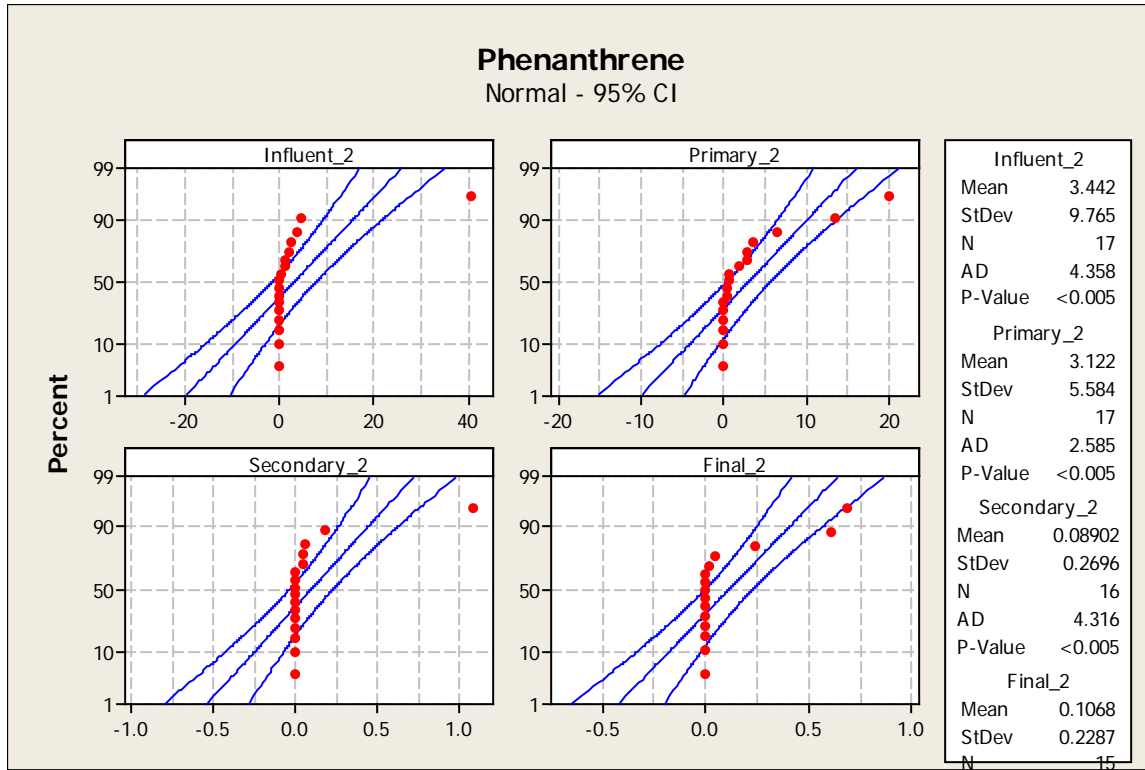


Figure A.2.6. 1. Probability plot for Phenanthrene

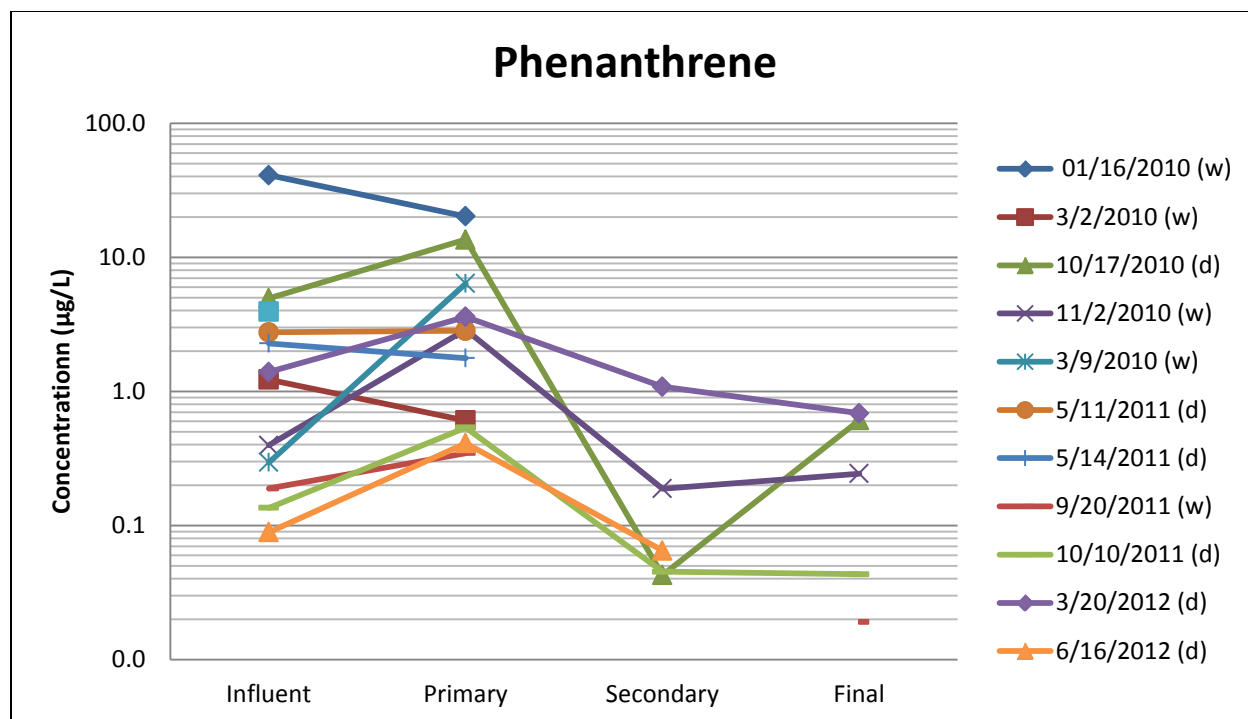


Figure A.2.6.2 Line graph for Phenanthrene at four different sampling locations

Column	Size	Missing	Mean	Std Dev	Std. Error	C.I. of Mean
Phenanthrene-I	19	2	3.442	9.765	2.368	5.021
Phenanthrene-P	19	2	3.122	5.584	1.354	2.871
Phenanthrene-S	19	3	0.0890	0.270	0.0674	0.144
Phenanthrene-F	19	4	0.107	0.229	0.0591	0.127

Column	Range	Max	Min	Median	25%	75%
Phenanthrene-I	40.873	40.873	0.000	0.295	0.000	2.396
Phenanthrene-P	20.179	20.179	0.000	0.538	0.000	3.064
Phenanthrene-S	1.083	1.083	0.000	0.000	0.000	0.0439
Phenanthrene-F	0.686	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-I	58.507	1727.075
Phenanthrene-P	53.075	664.664
Phenanthrene-S	1.424	1.217
Phenanthrene-F	1.601	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-I	19	2	0.295	0.000	2.515
Phenanthrene-P	19	2	0.538	0.000	3.241
Phenanthrene-S	19	3	0.000	0.000	0.0446
Phenanthrene-F	19	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

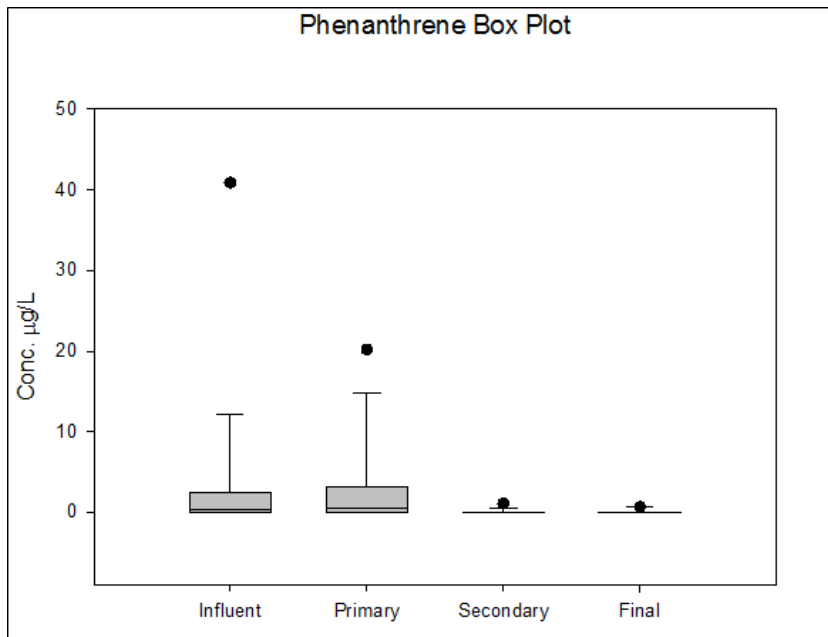


Figure A.2.6.3. Box and Whisker Plots for Phenanthrene

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-P	19	2	0.538	0.000	3.241
Phenanthrene-S	19	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-S	19	3	0.000	0.000	0.0446
Phenanthrene-F	19	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**)

A.2.7. Summary Data for 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)

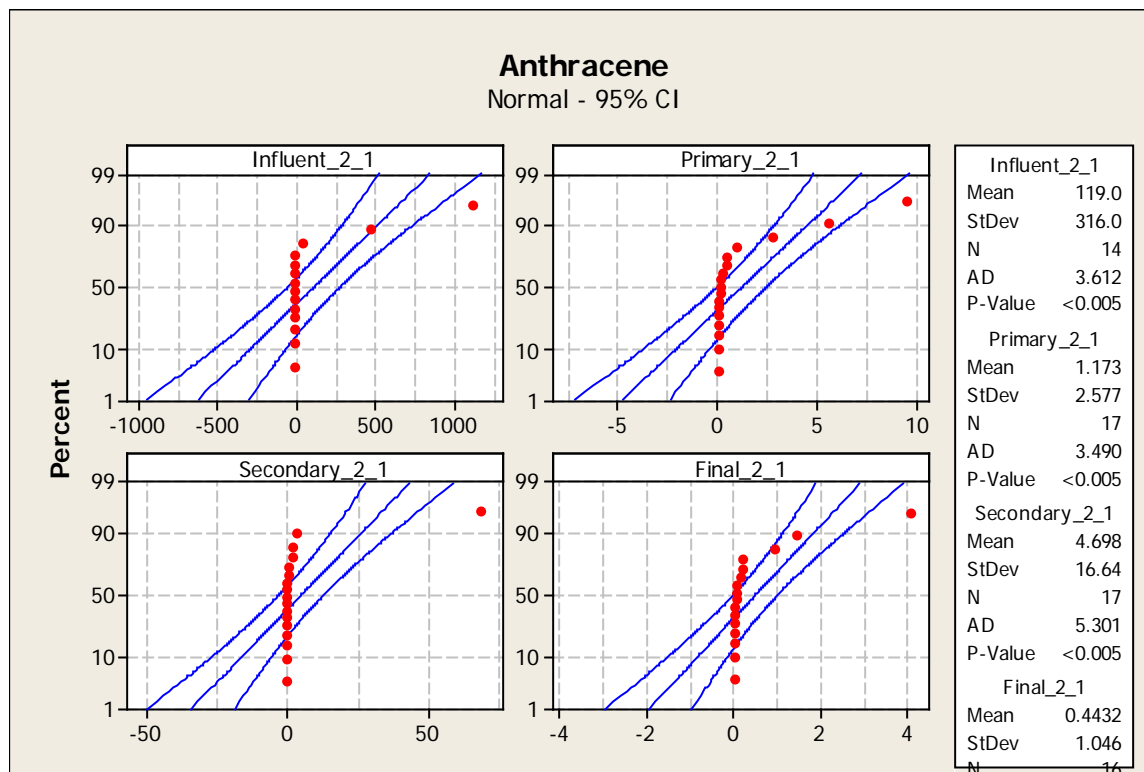


Figure A.2.7.1 Probability Plot for Anthracene

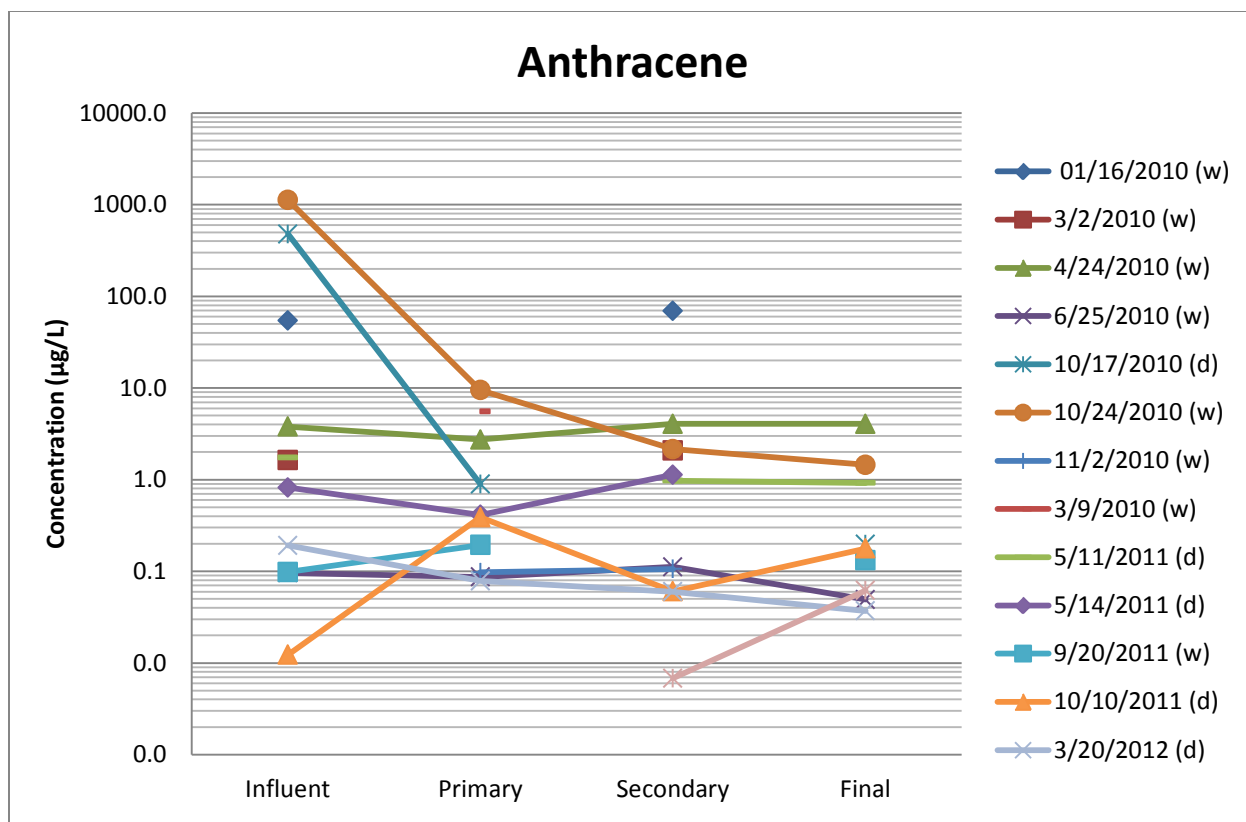


Figure A.2.7.2. Line graph for Anthracene at four different sampling locations

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

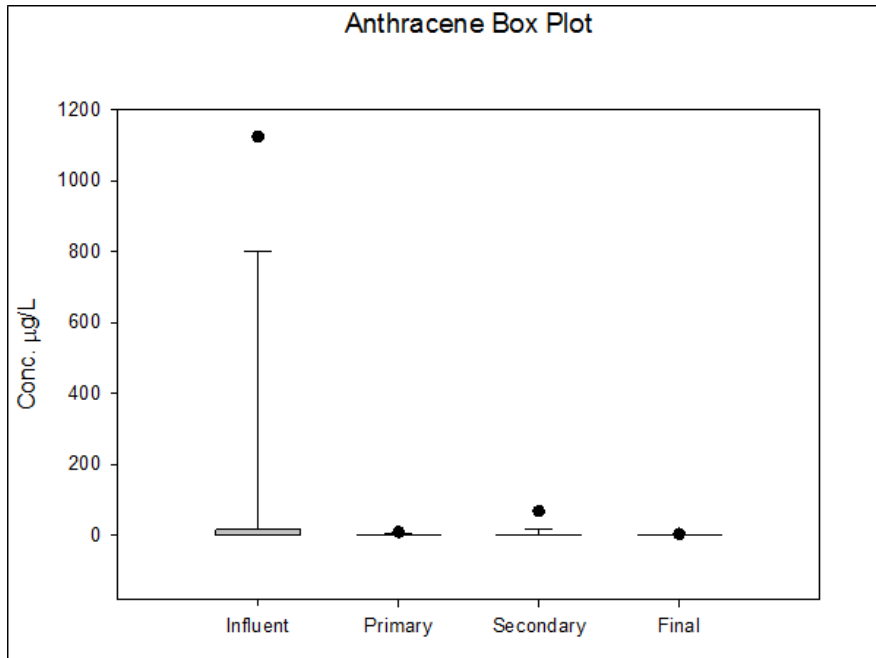


Figure A.2.7.3 Box and Whisker Plots for Anthracene

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-I	19	5	0.507	0.00922	16.465
Anthracene-P	19	2	0.0867	0.000	0.655
Anthracene-S	19	2	0.0605	0.000	1.603
Anthracene-F	19	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-I	19	5	0.507	0.00922	16.465
Anthracene-P	19	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-P	19	2	0.0867	0.000	0.655
Anthracene-S	19	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-S	19	2	0.0605	0.000	1.603
Anthracene-F	19	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**)

A.2.8. Summary Data for 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)

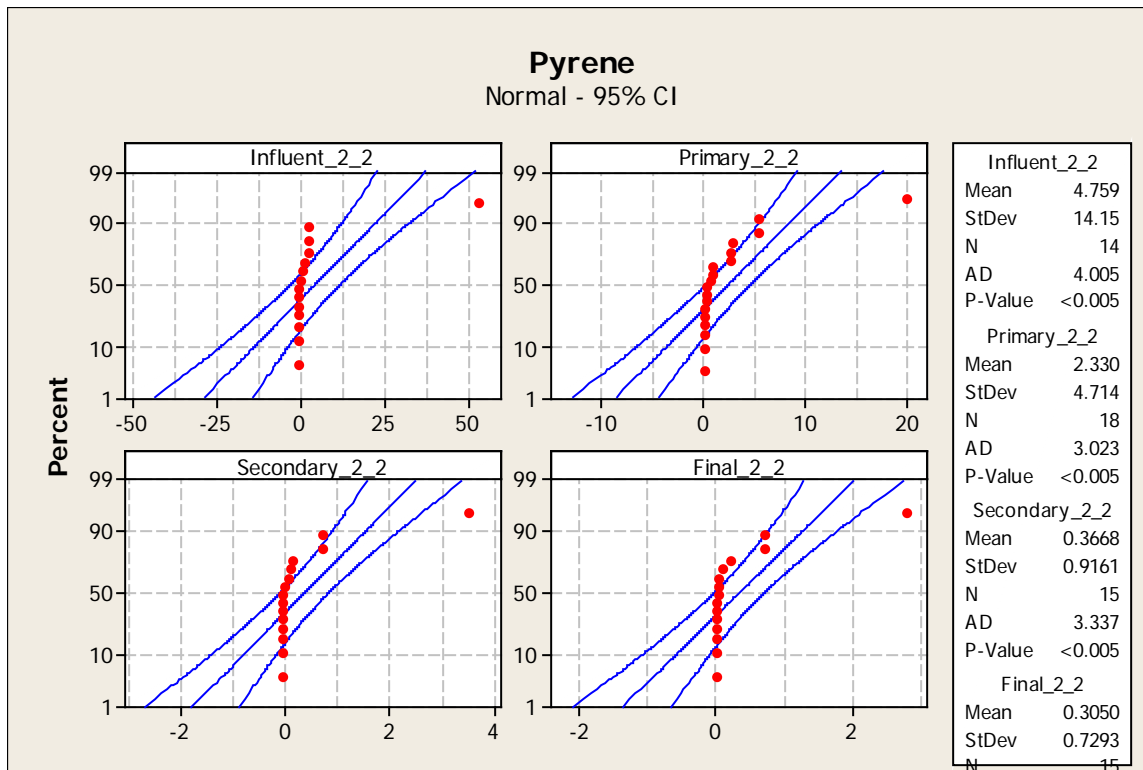


Figure A.2.8.1. Probability plots for Pyrene

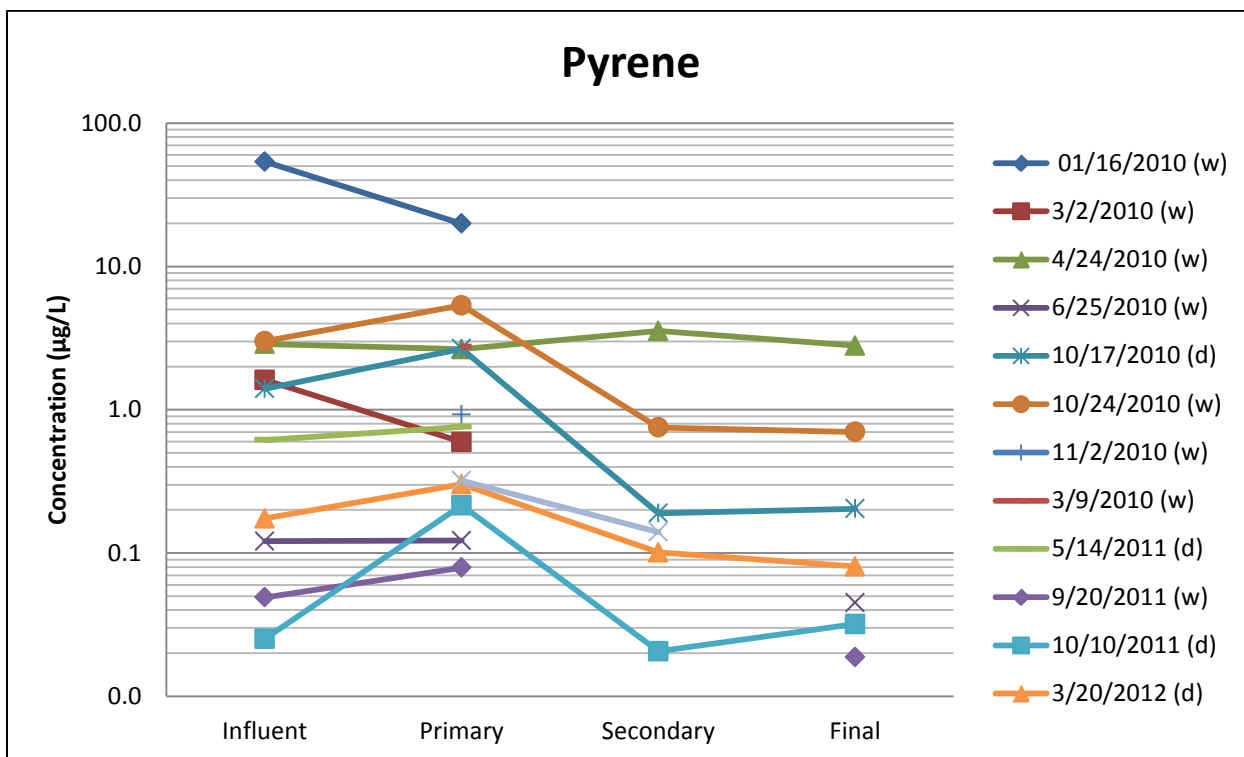


Figure A.2.8.2 Line graphs for Pyrene at four different sampling locations

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

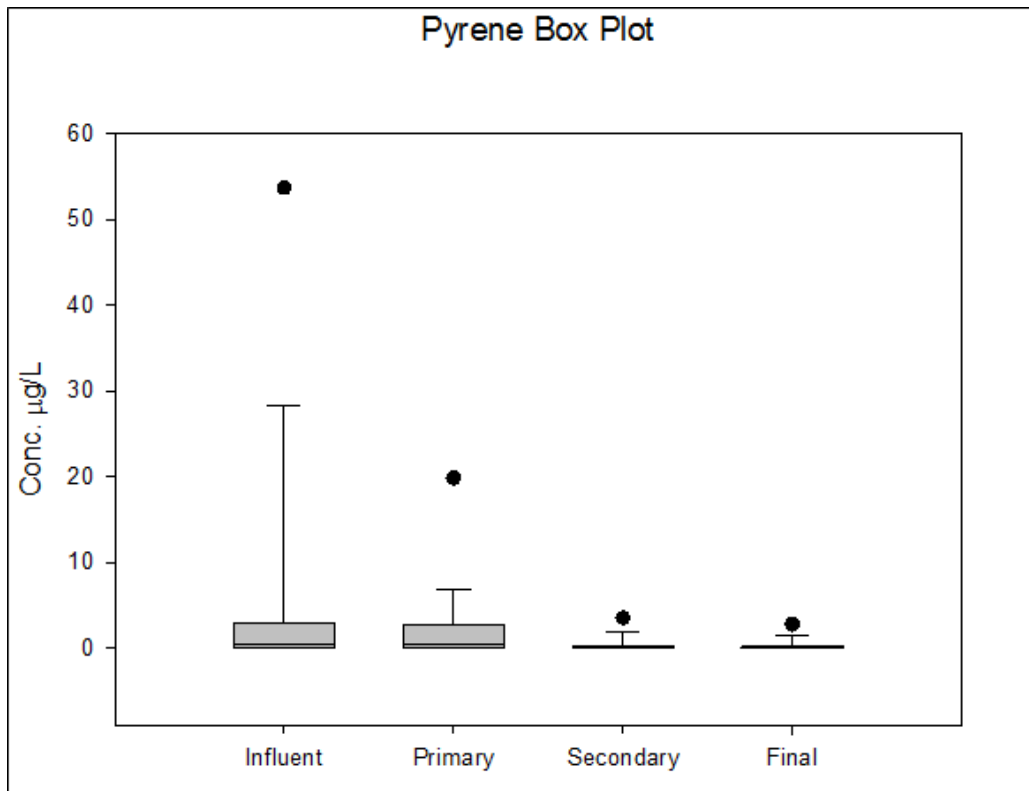


Figure A.2.8.3. Box and Whisker Plots for Pyrene

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)

A.2.9. Benzo(a)anthracene plus chrysene

A.2.10. Benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, and indeno(1,2,3,cd)pyrene

A.2.11. Benzo(a,h)anthracene plus benzo(g,h,i) perylene

A.3. Pesticides

APPENDIX B: CHROMATOGRAPHS FOR SAMPLE ANALYSES

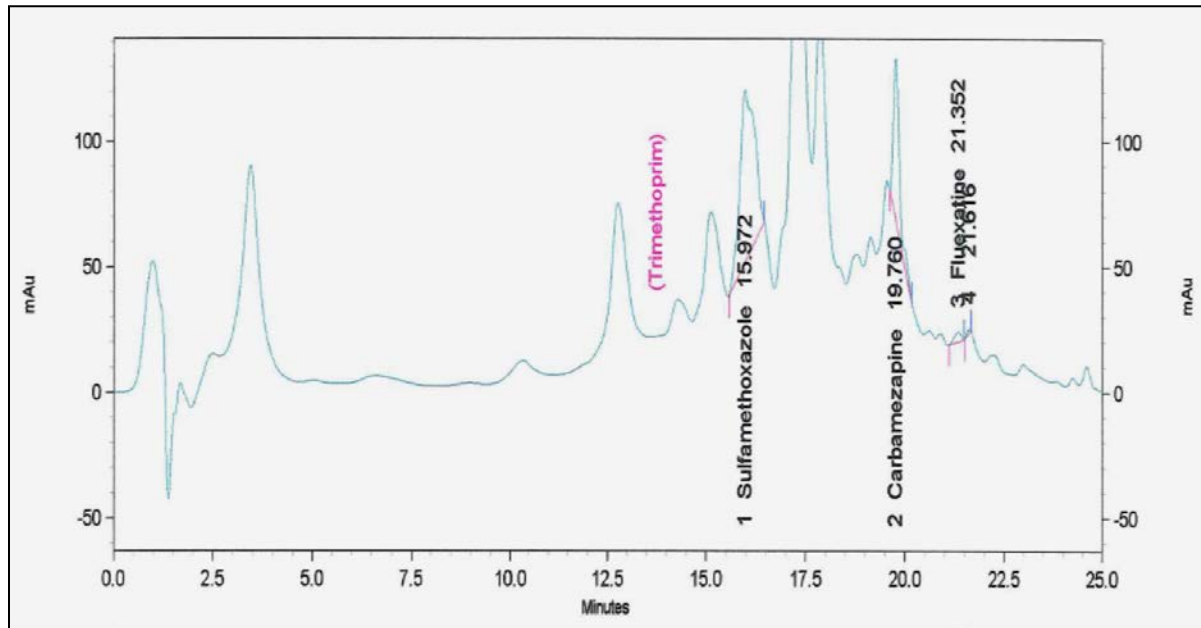


Figure B.1. Influent Sample for 11/08/12: Acid Group I

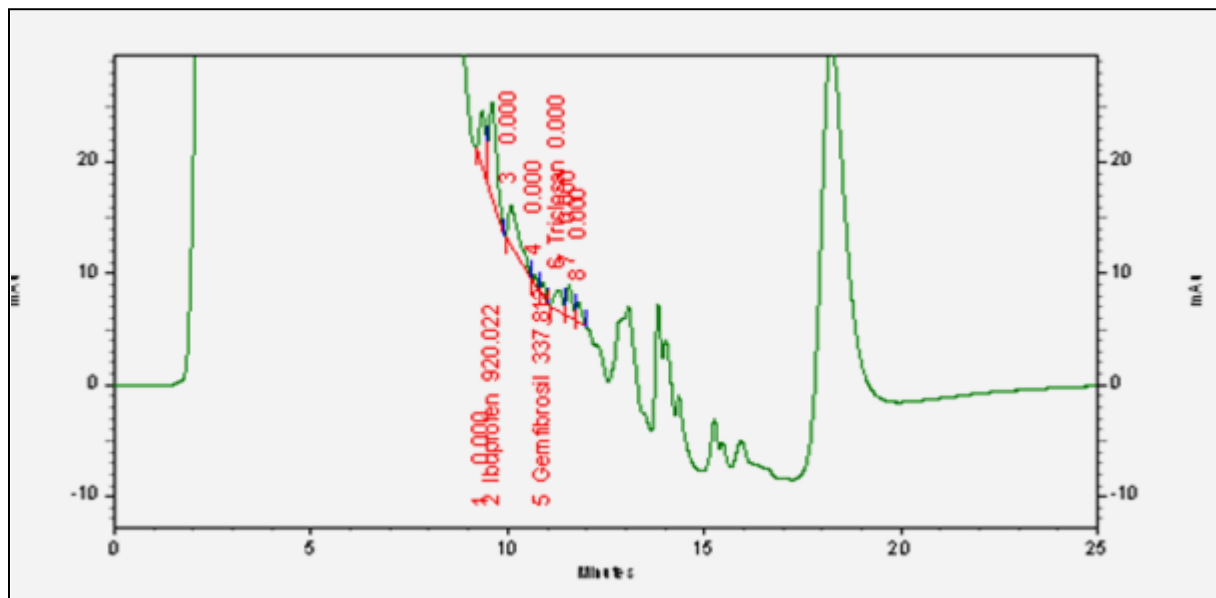


Figure B.2. Influent Sample for 11/08/12: Acid Group II

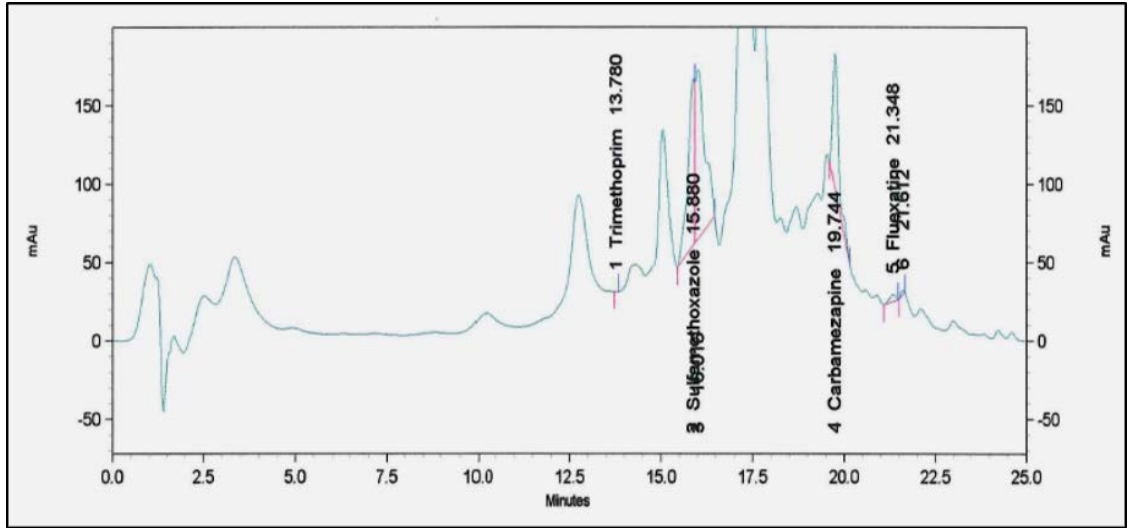


Figure B.3. Primary Effluent Sample for 11/08/12: Acid Group I

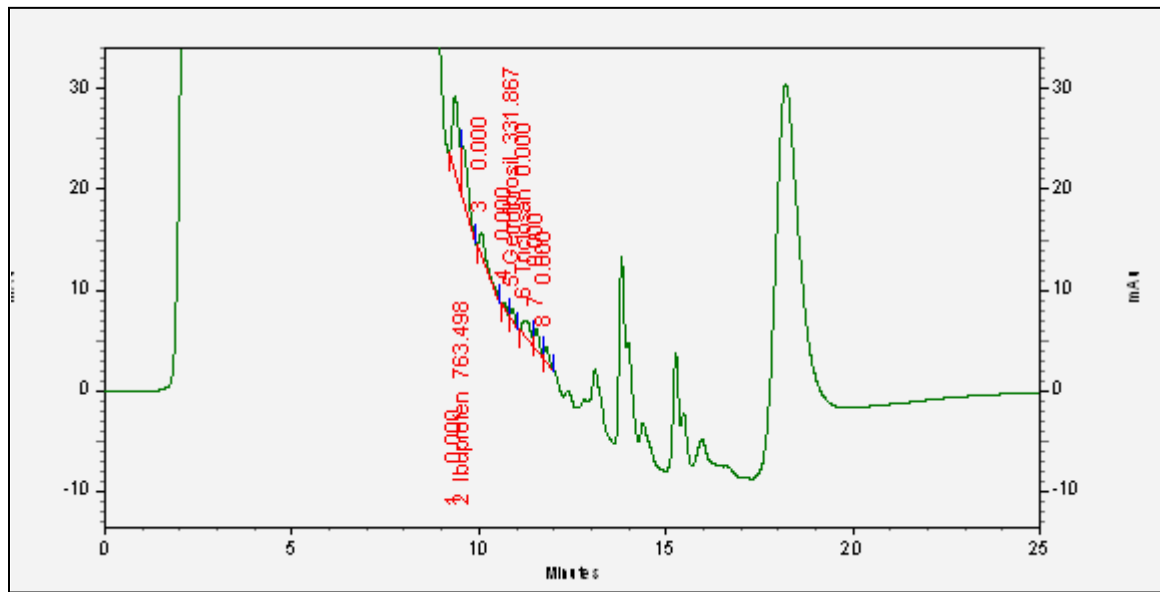


Figure B.4. Primary Effluent Sample for 11/08/12: Acid Group II

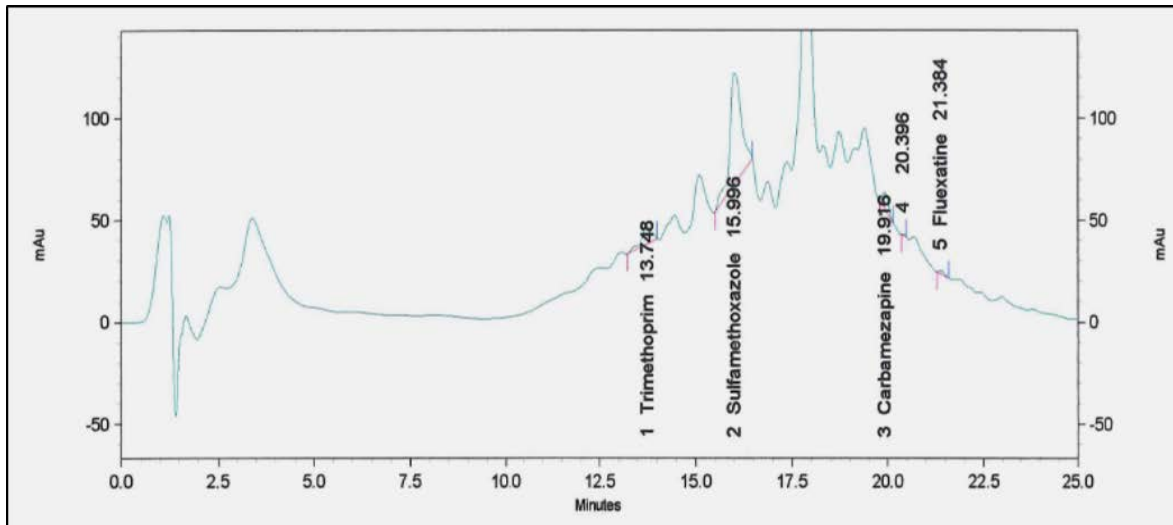


Figure B.5. Secondary Effluent Sample for 11/08/12: Acid Group I

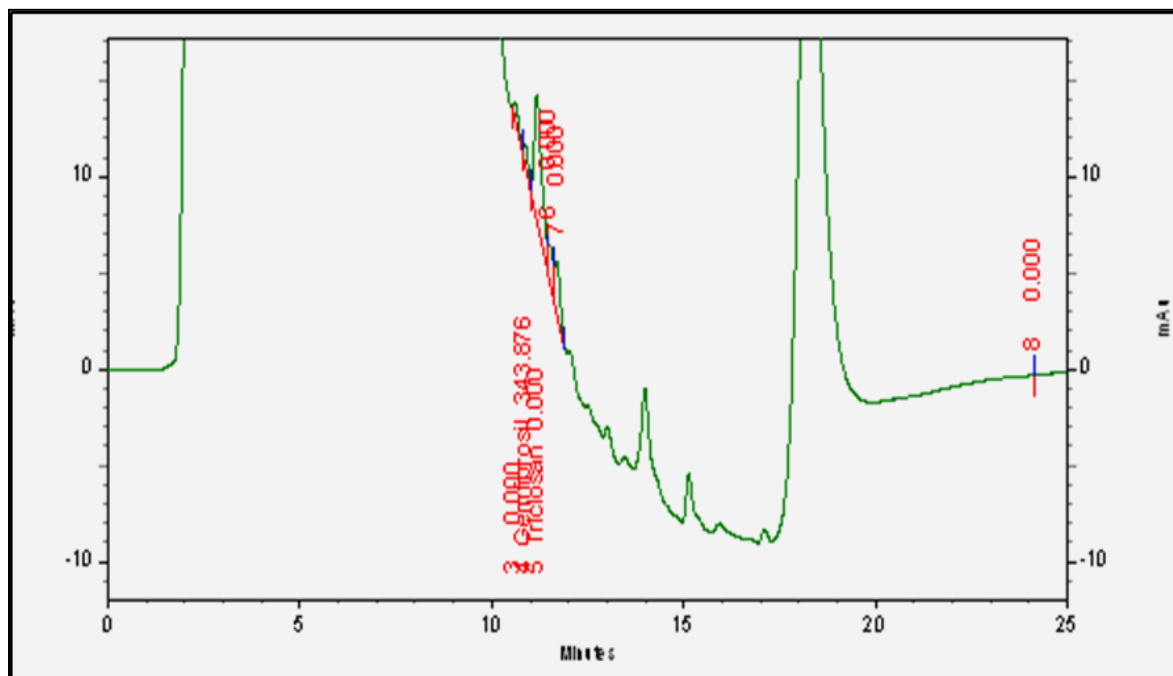


Figure B.6. Secondary Effluent Sample for 11/08/12: Acid Group II

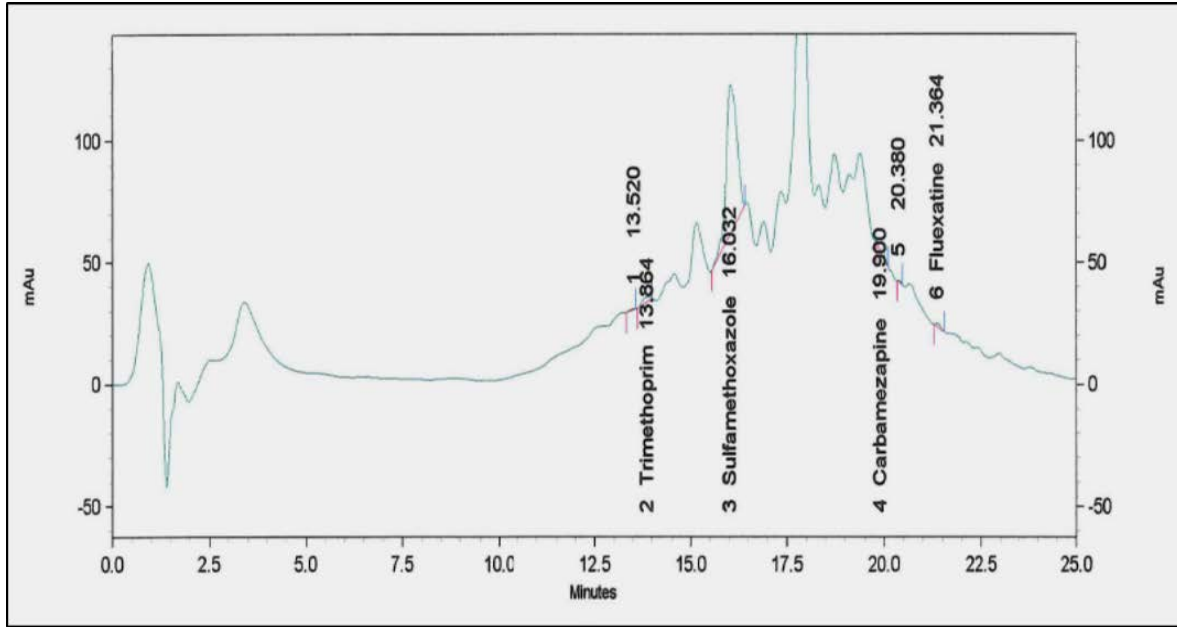


Figure B.7. Final Effluent Sample for 11/08/12: Acid Group I

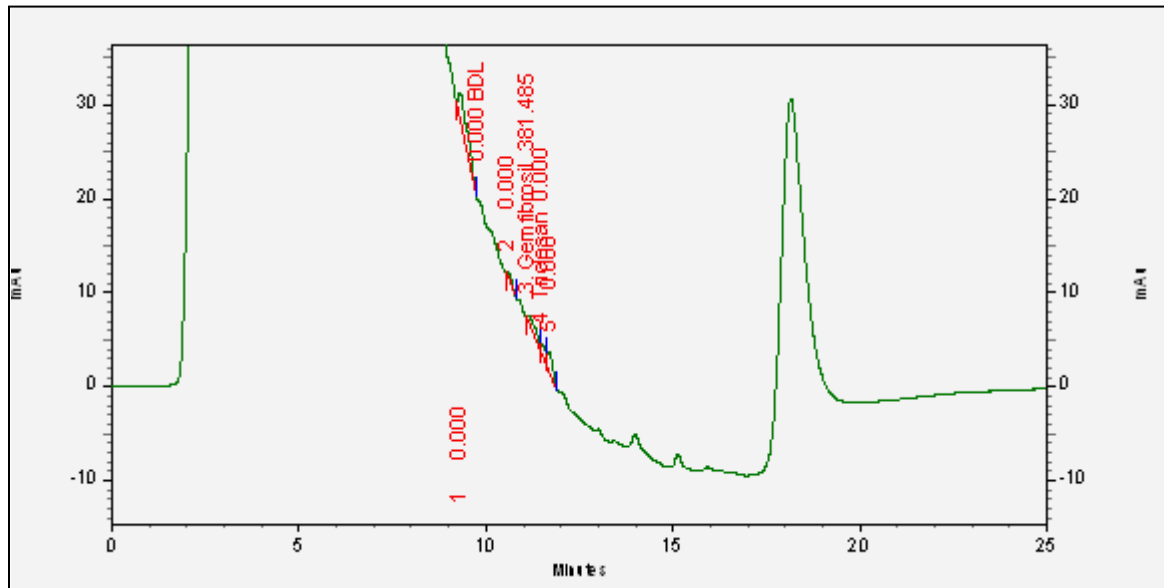


Figure B.8. Final Effluent Sample for 11/08/12: Acid Group II

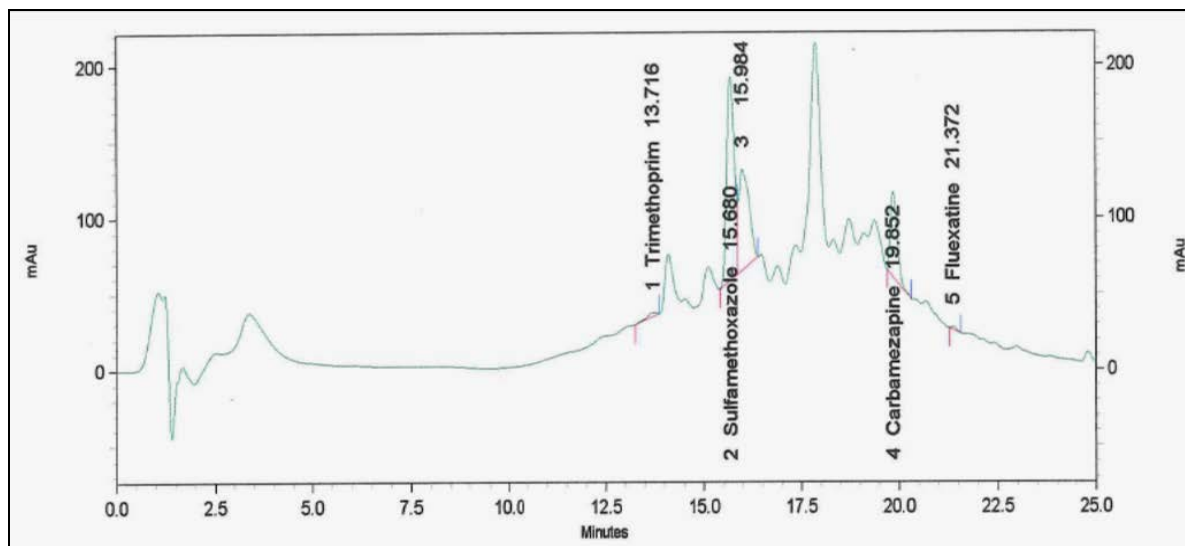


Figure B.9. Final Spiked Effluent Sample for 11/08/12: Acid Group I

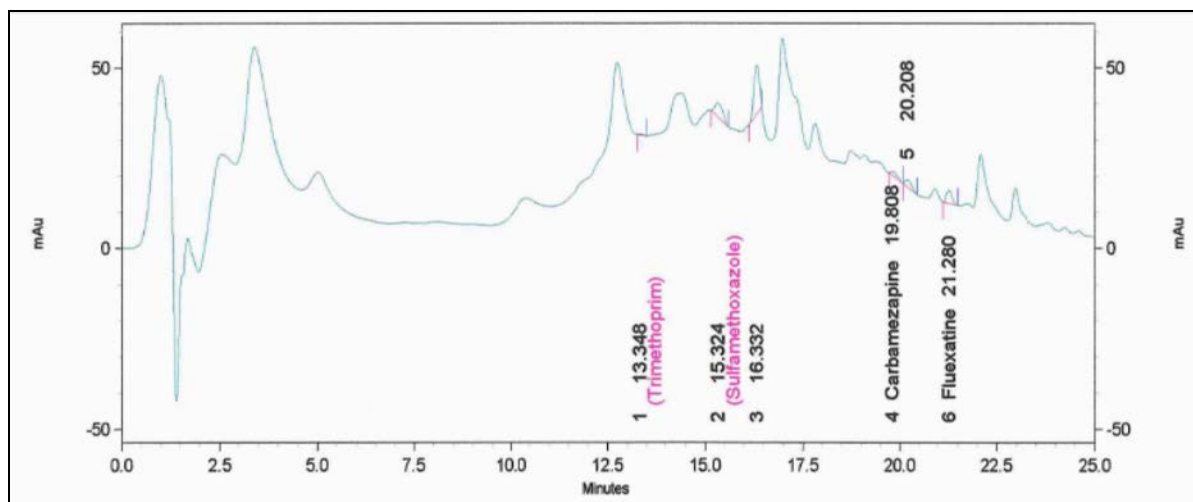


Figure B.10. Influent Sample for 11/12/12: Acid Group I

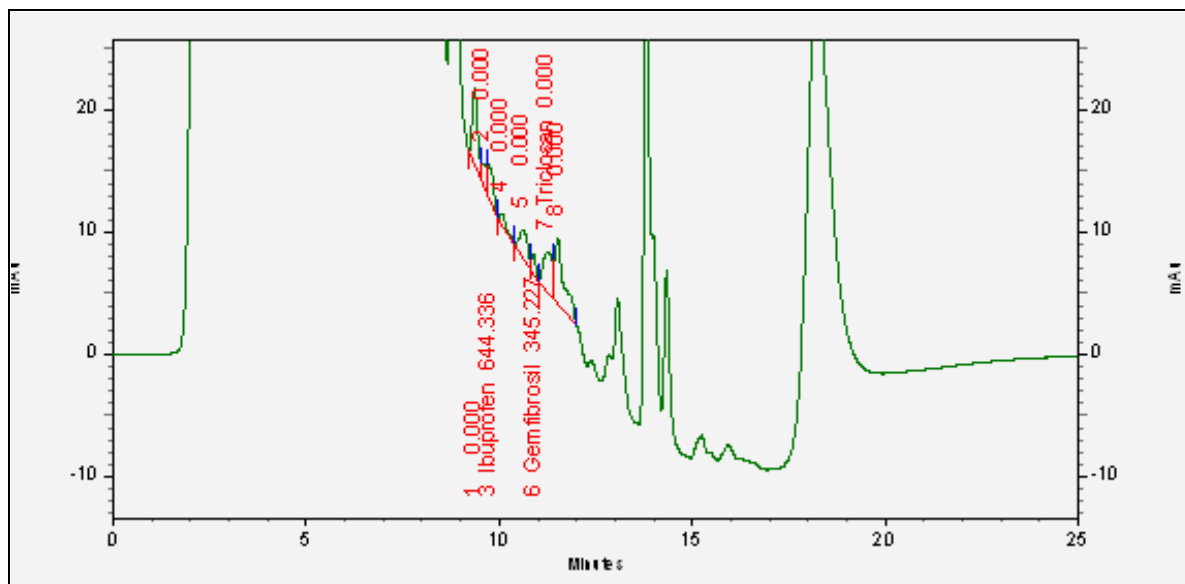


Figure B.11. Influent for 11/12/12: Acid Group II

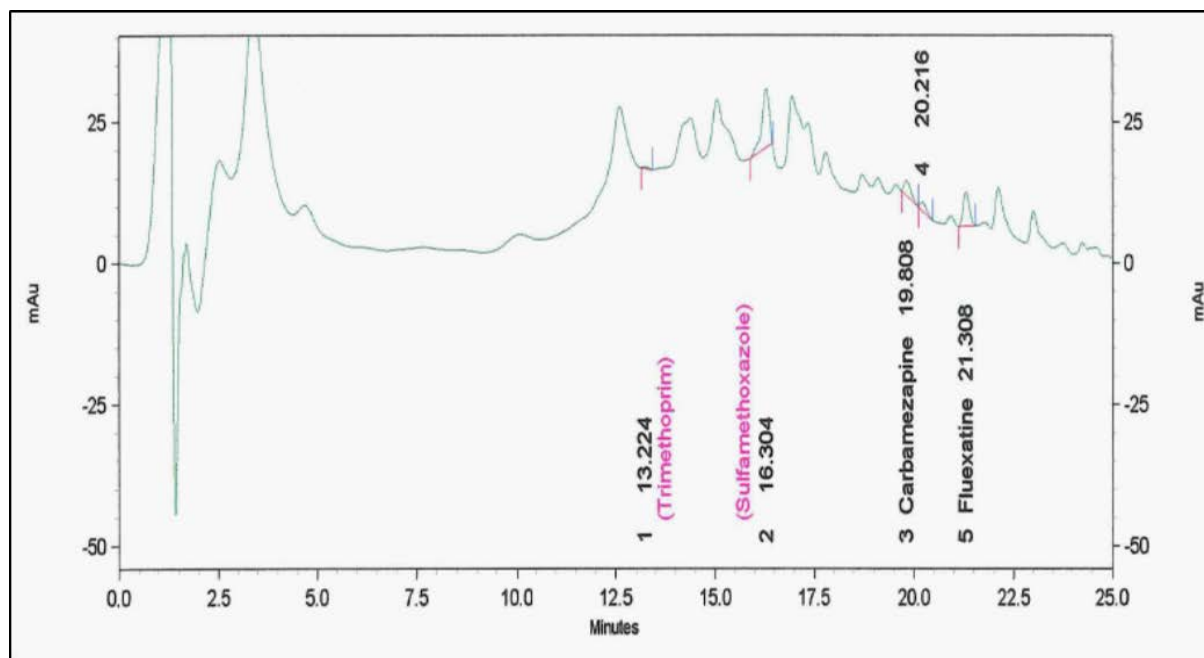


Figure B.12. Primary Effluent for 11/12/12: Acid Group I

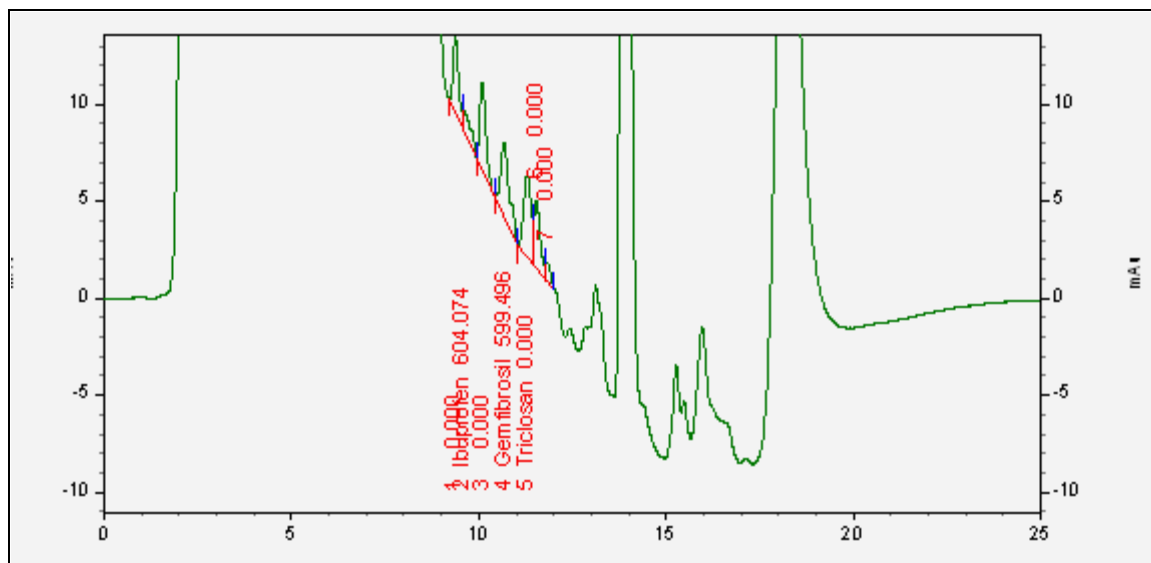


Figure B.13. Primary Effluent for 11/12/12: Acid Group II

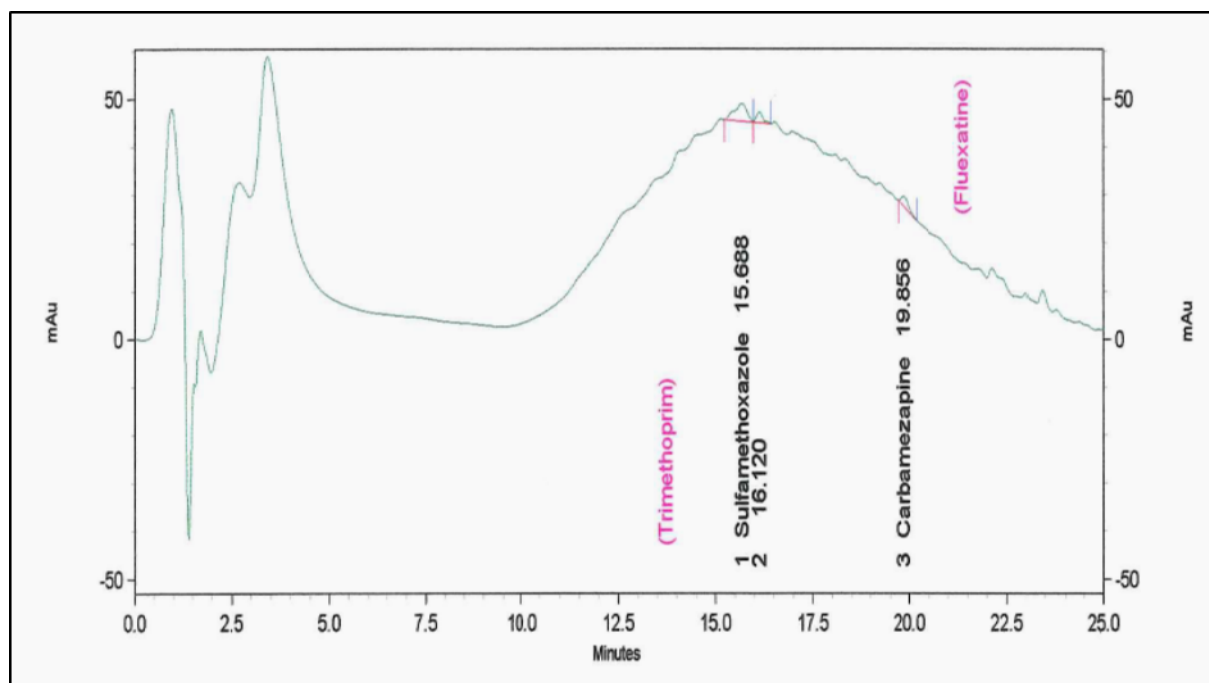


Figure B.14. Secondary Effluent for 11/12/12: Acid Group I

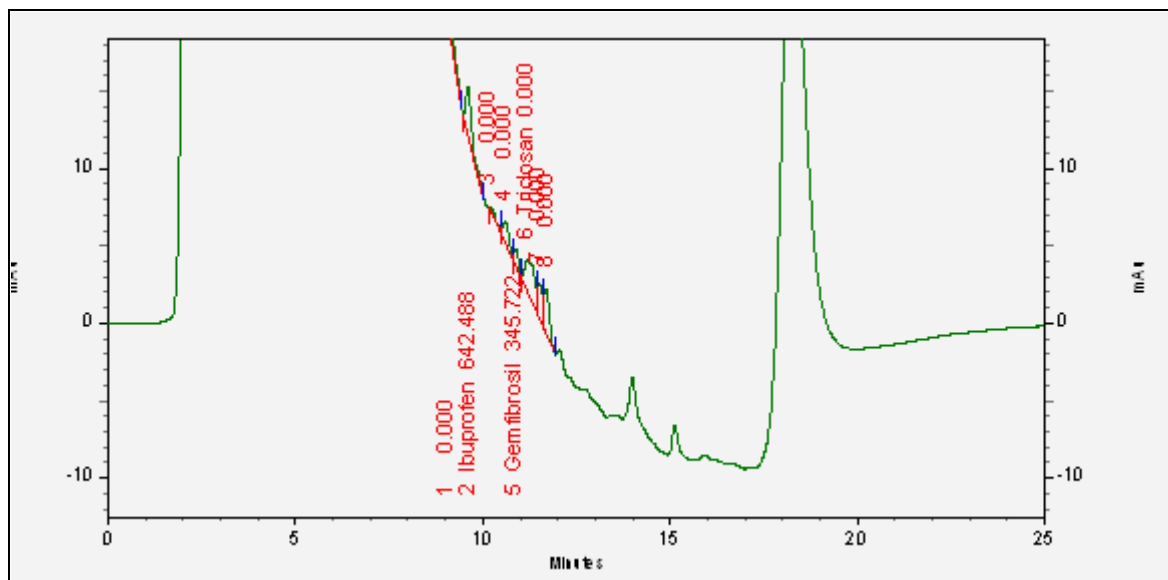


Figure B.15. Secondary Effluent from 11/12/12: Acid Group II

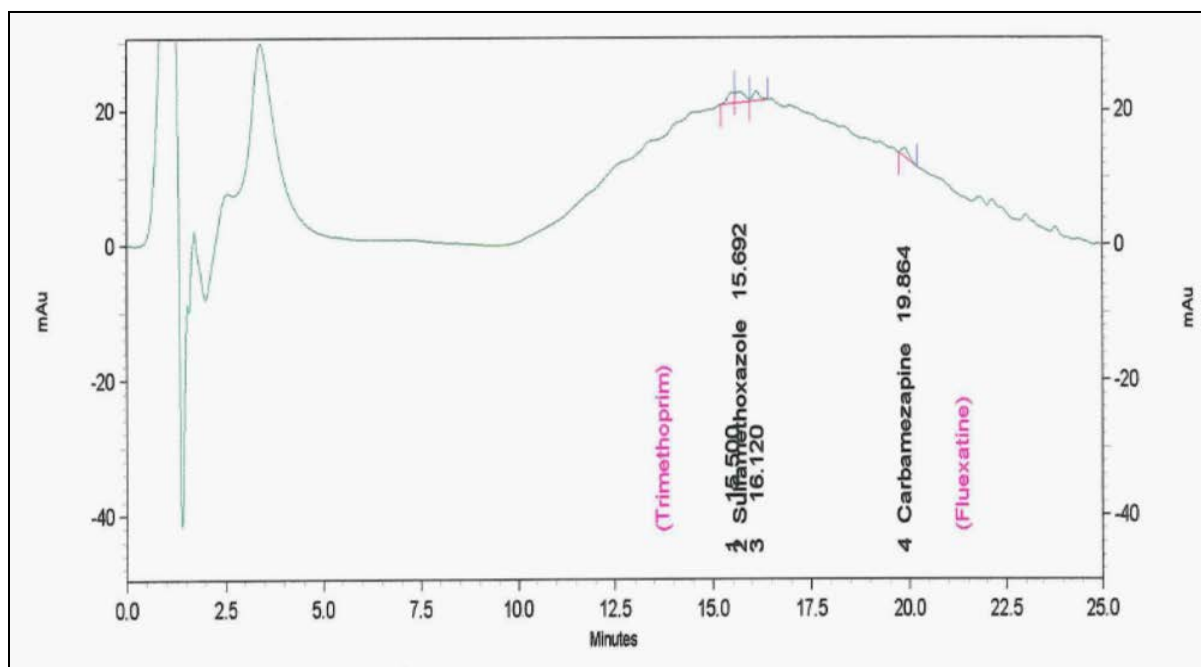


Figure B.16. Final Effluent for 11/12/12: Acid Group I

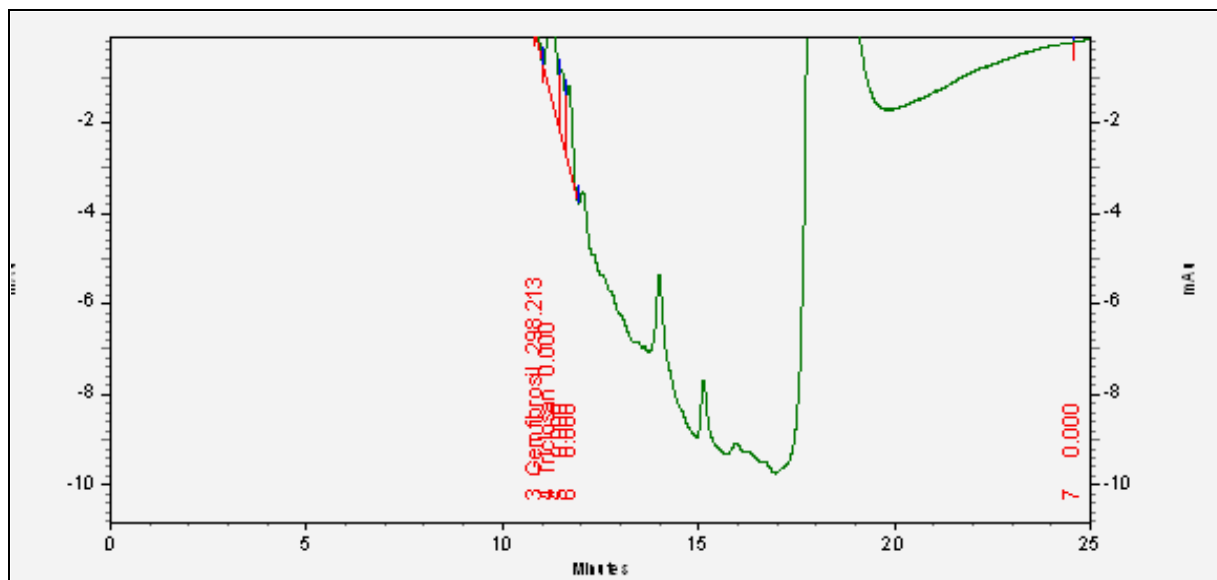


Figure B.17. Final Effluent from 11/12/12: Acid Group II

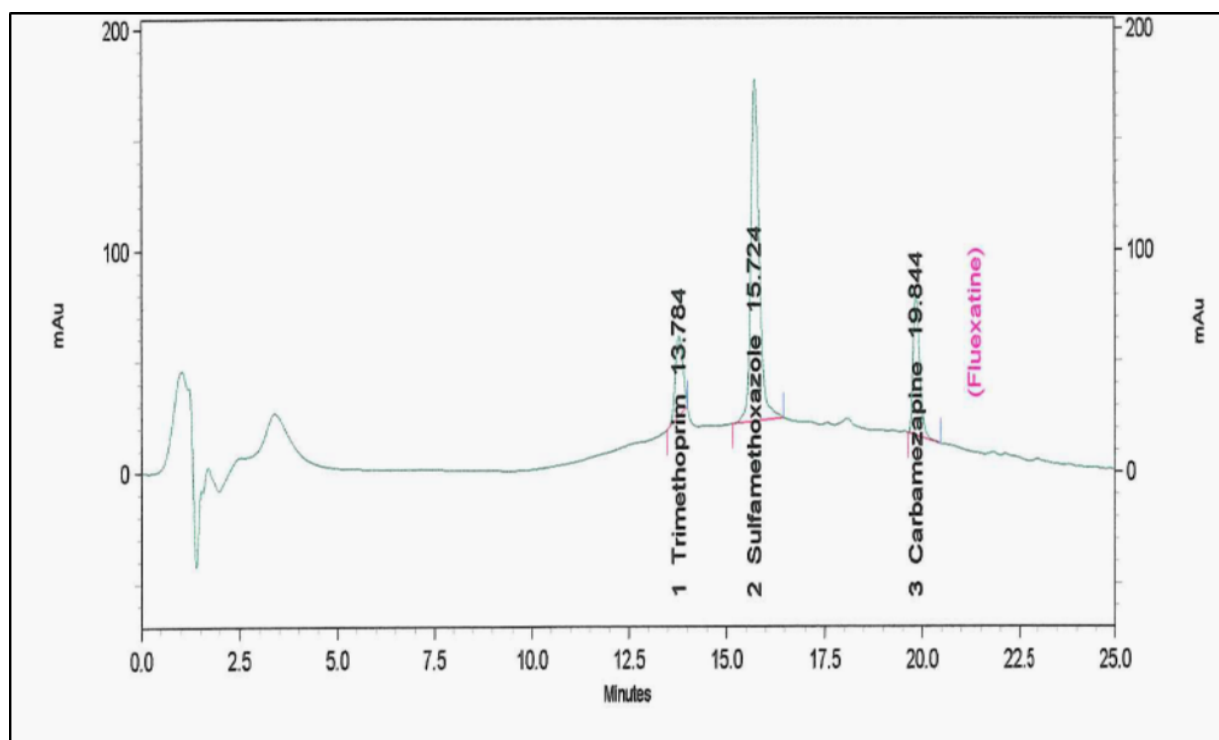


Figure B.18. Final Effluent (Spiked) for 11/12/12: Acid Group I

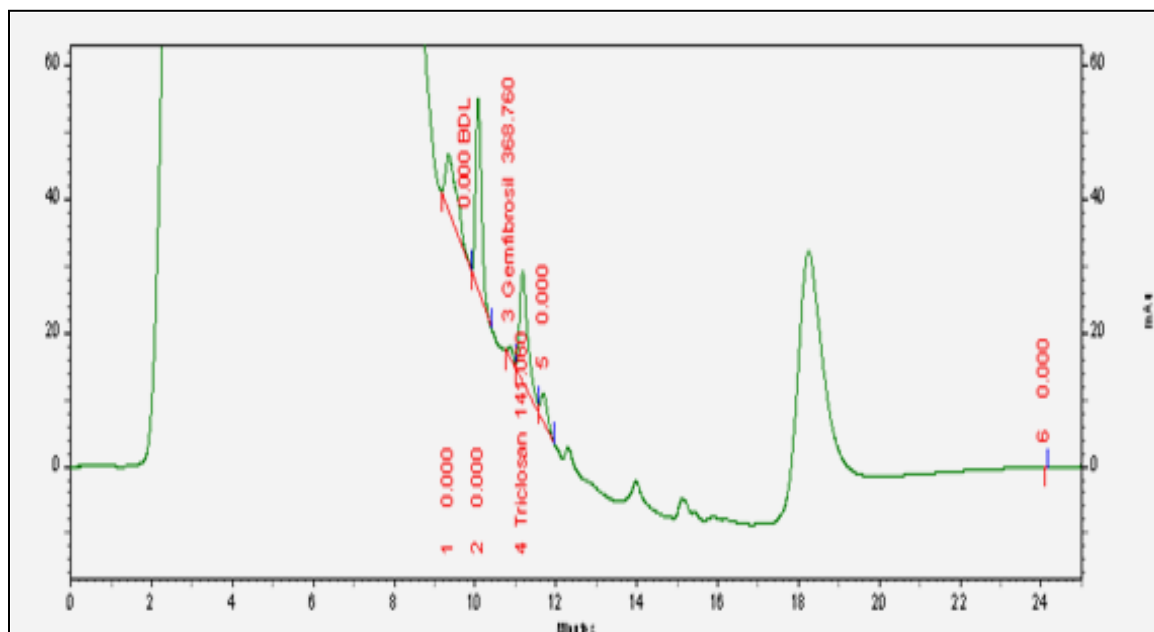


Figure B.19. Primary Effluent from 05/11/11: Acid Group II

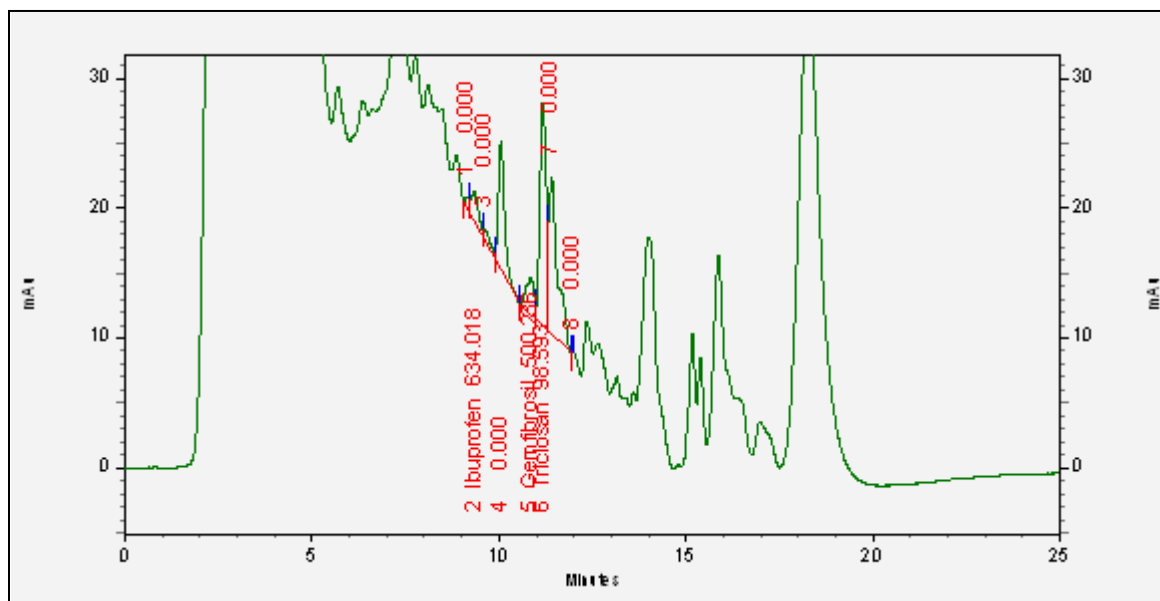


Figure B.20. Influent from 03/02/10: Acid Group II

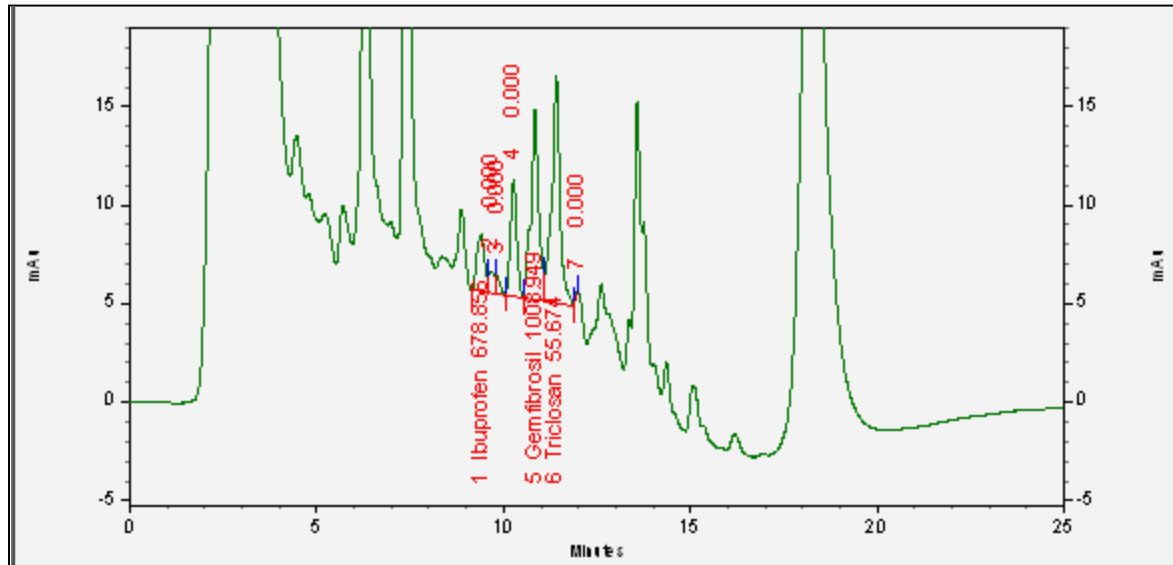


Figure B.21. Primary Effluent from 03/02/10: Acidic Group II

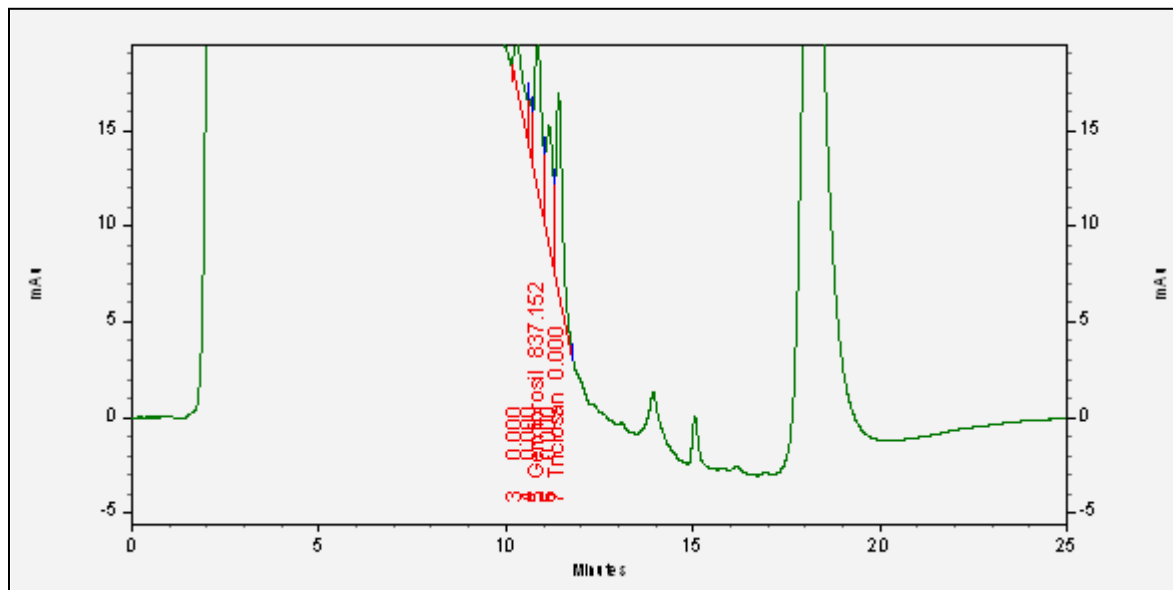


Figure B.22. Secondary Effluent from 03/02/10: Acid Group II

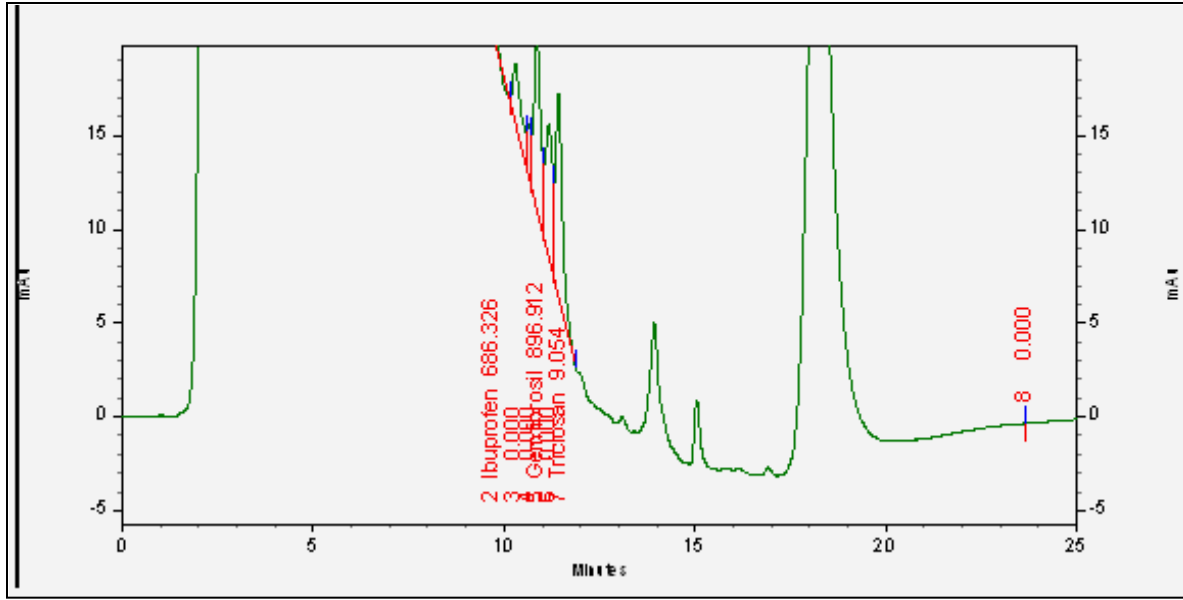


Figure B.23. Final Effluent from 03/02/10: Acid Group II

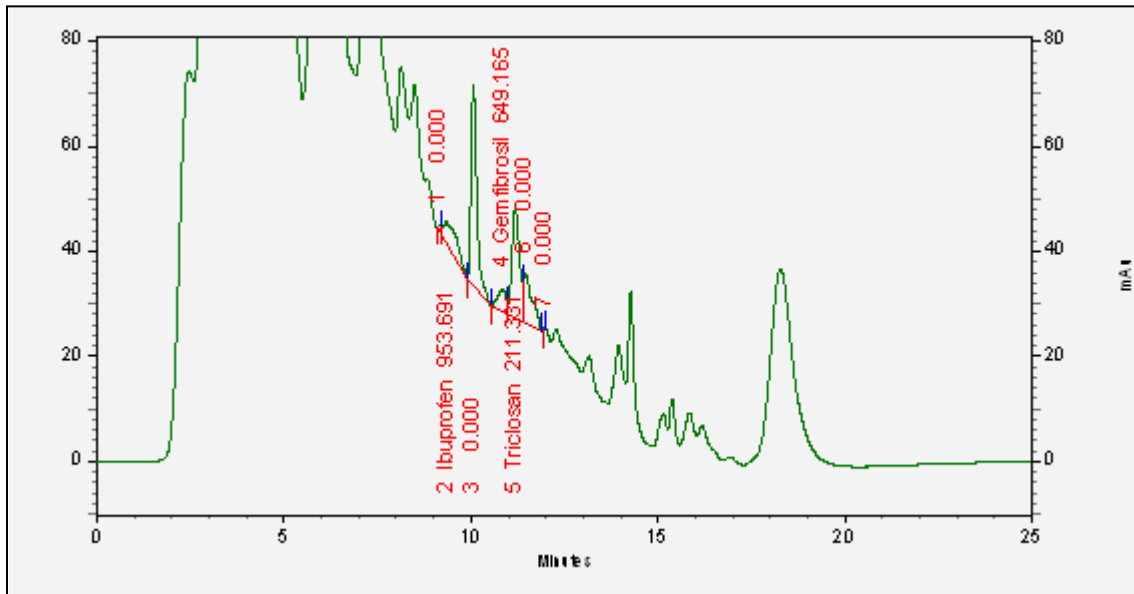


Figure B.24. Influent from 06/25/10: Acid Group II

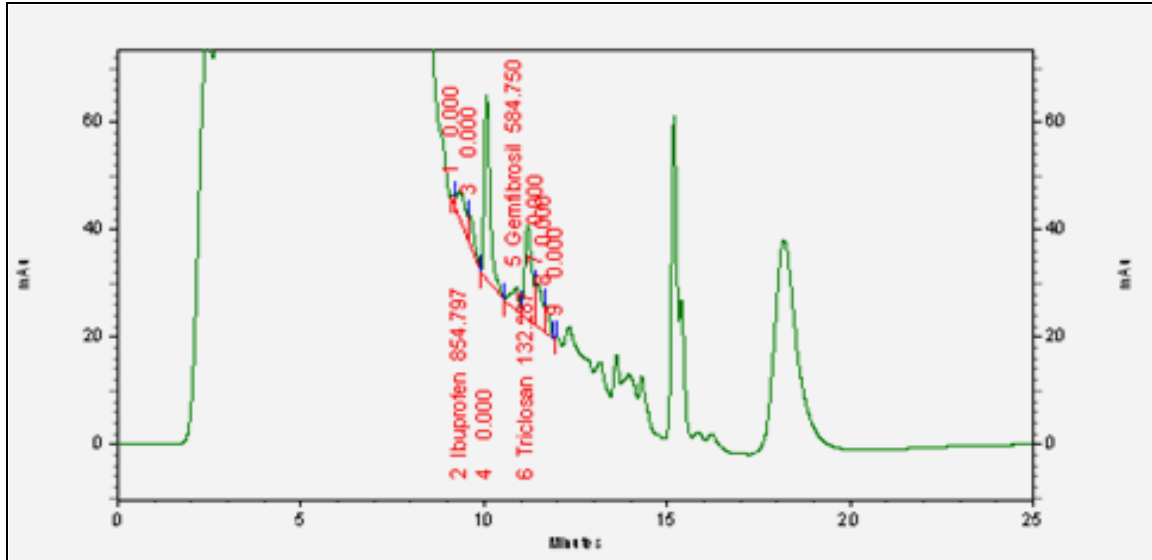


Figure B.25. Primary Effluent from 06/25/10: Acid Group II

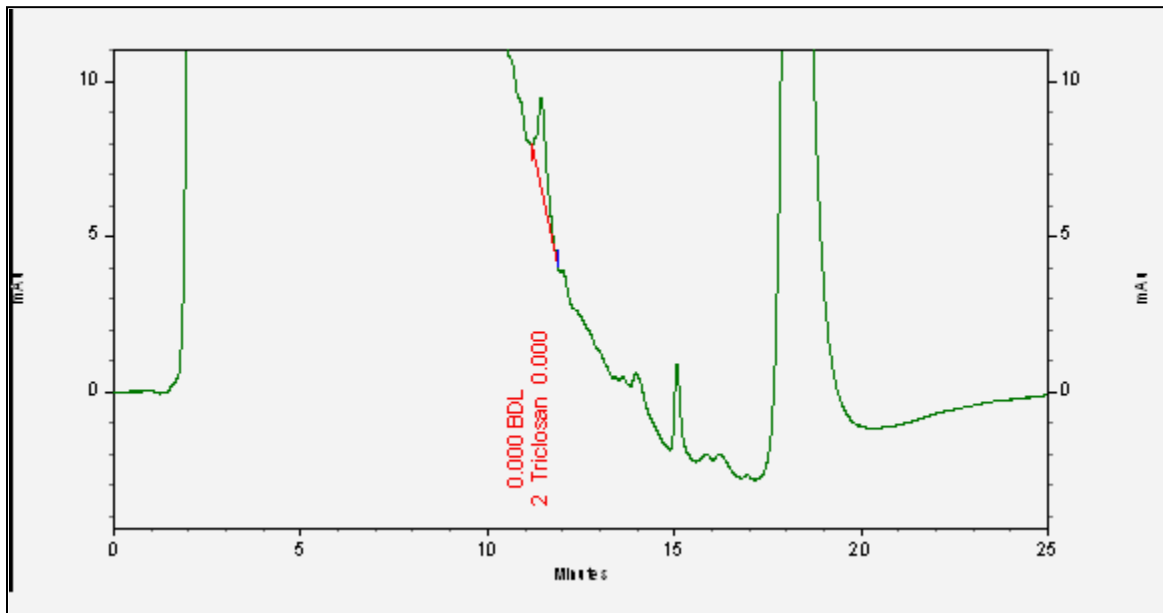


Figure B.26. Secondary Effluent from 06/25/10: Acid Group II

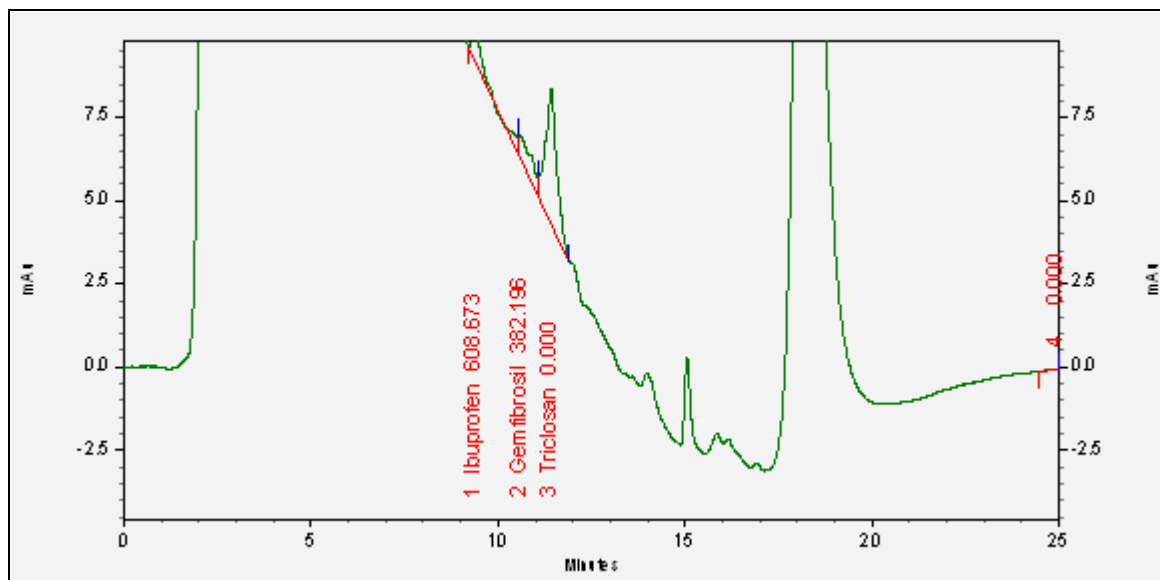


Figure B.27. Final Effluent from 06/25/10: Acid Group II

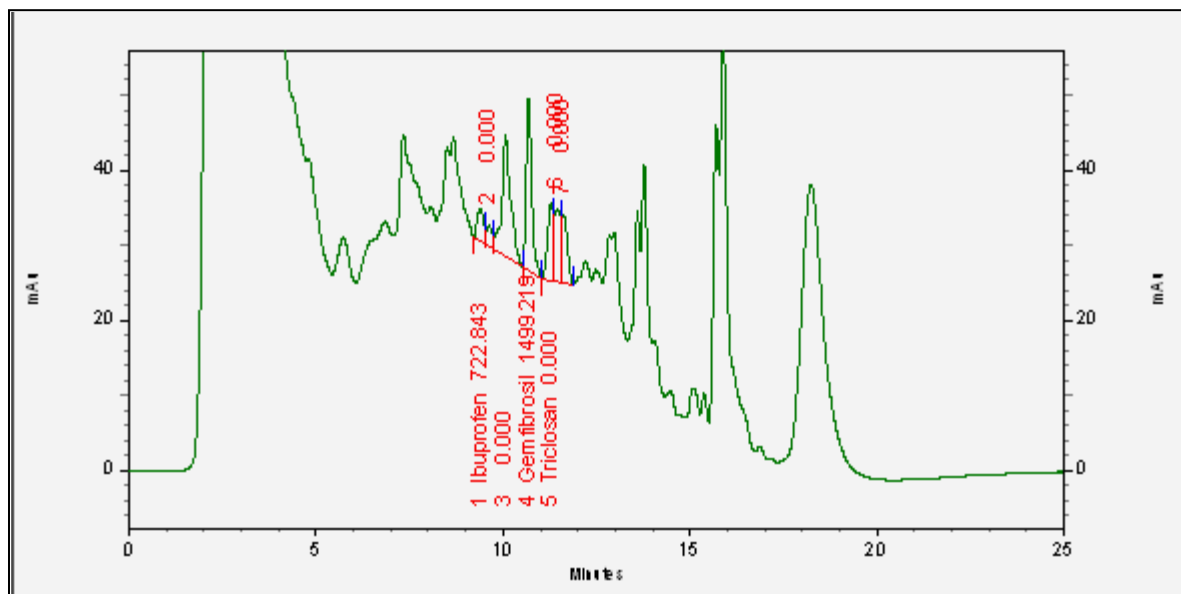


Figure B.28. Influent from 11/02/10: Acid Group II

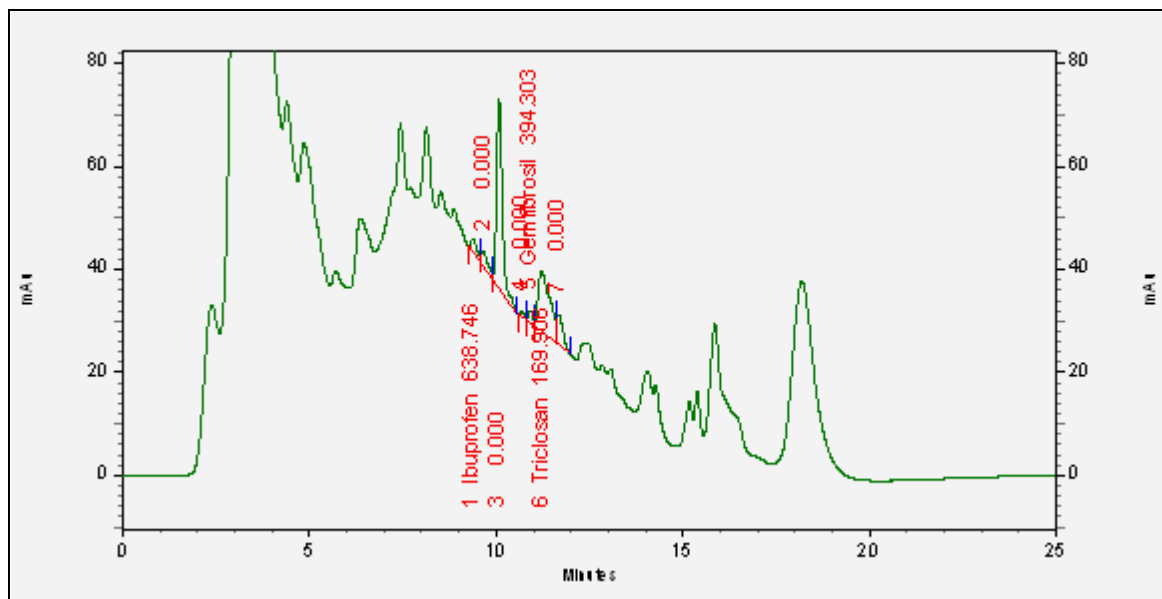


Figure B.29. Primary Effluent from 11/02/10: Acid Group II

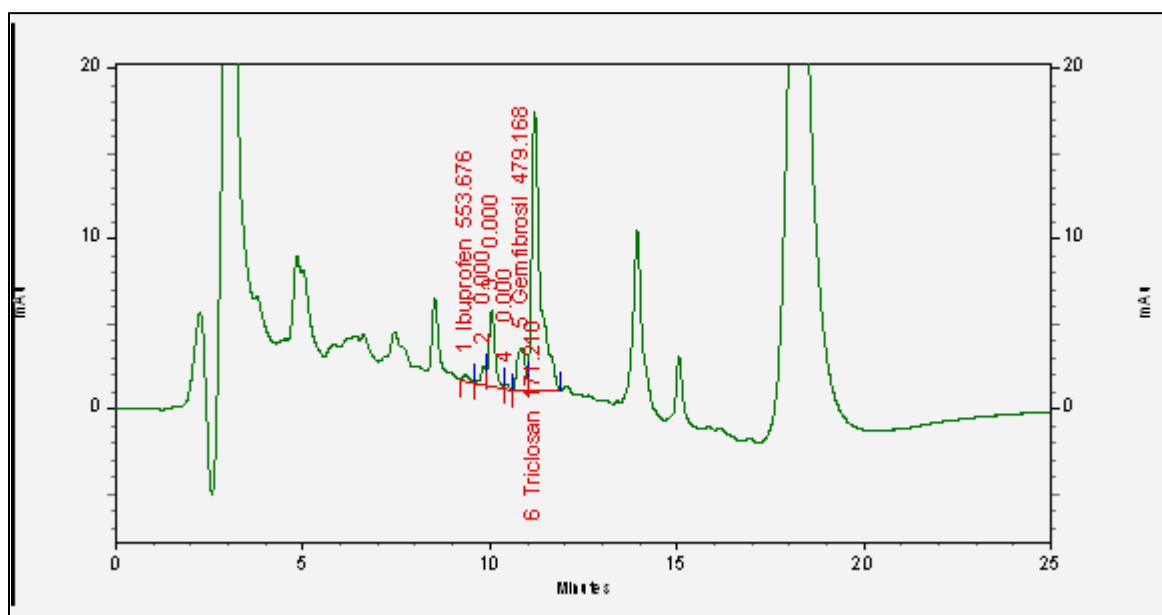


Figure B.30. Secondary Effluent from 11/02/10: Acid Group II

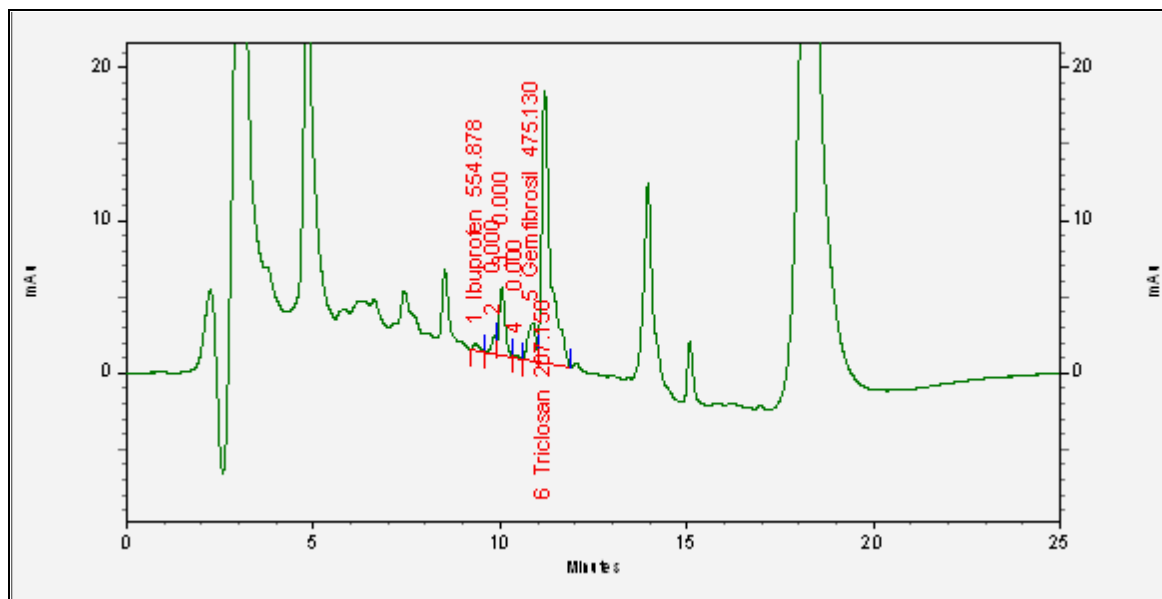


Figure B.31. Final Effluent from 11/02/10: Acid Group II

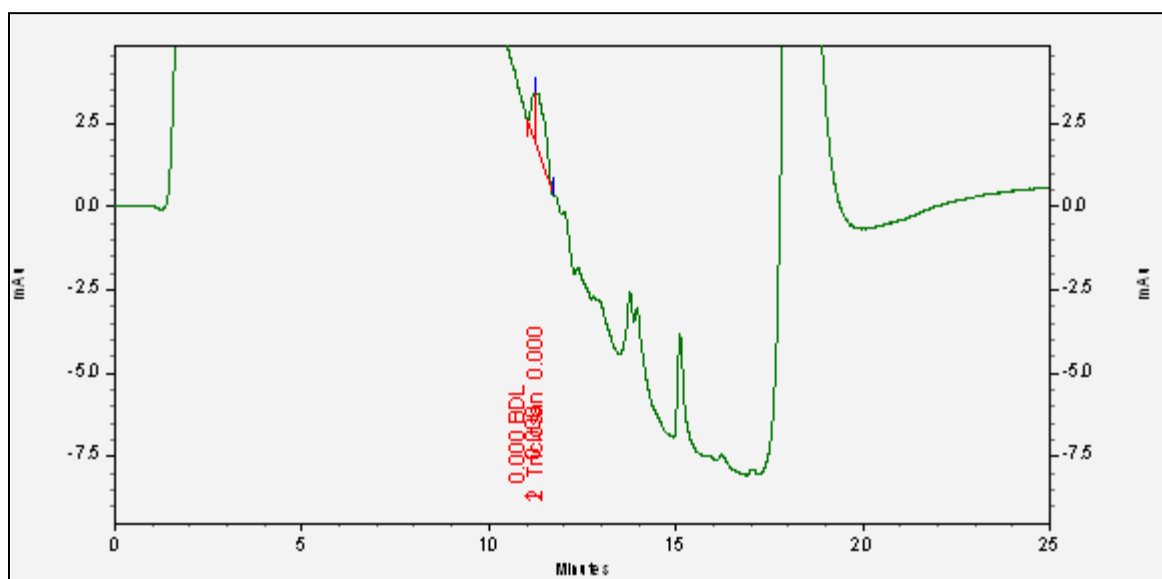


Figure B.32. Influent from 03/09/11: Acid Group II

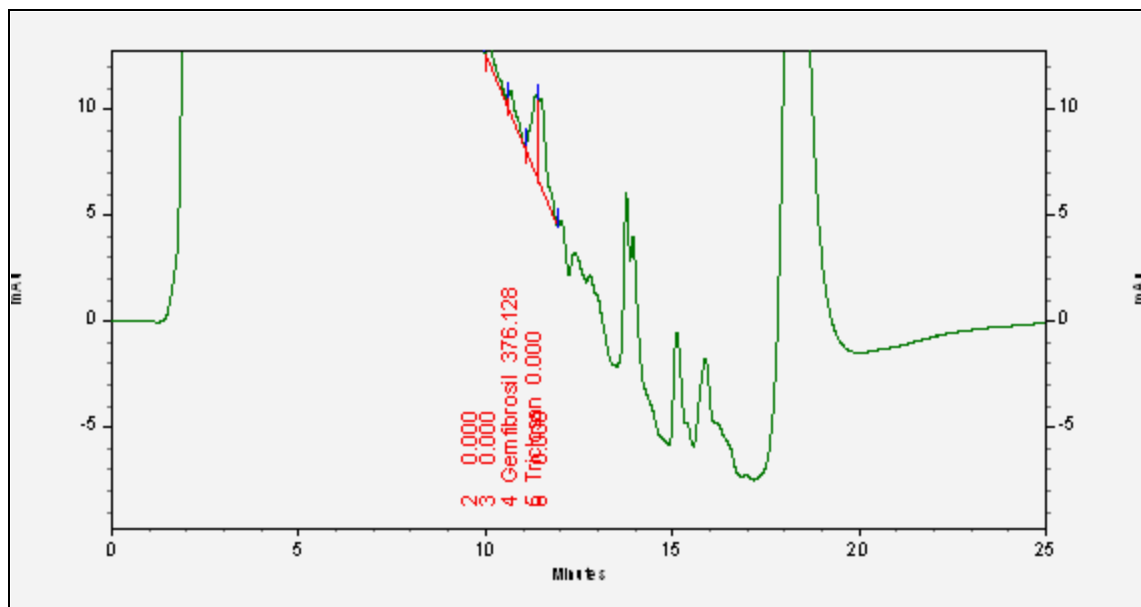


Figure B.33. Primary Effluent from 03/09/11: Acid Group II

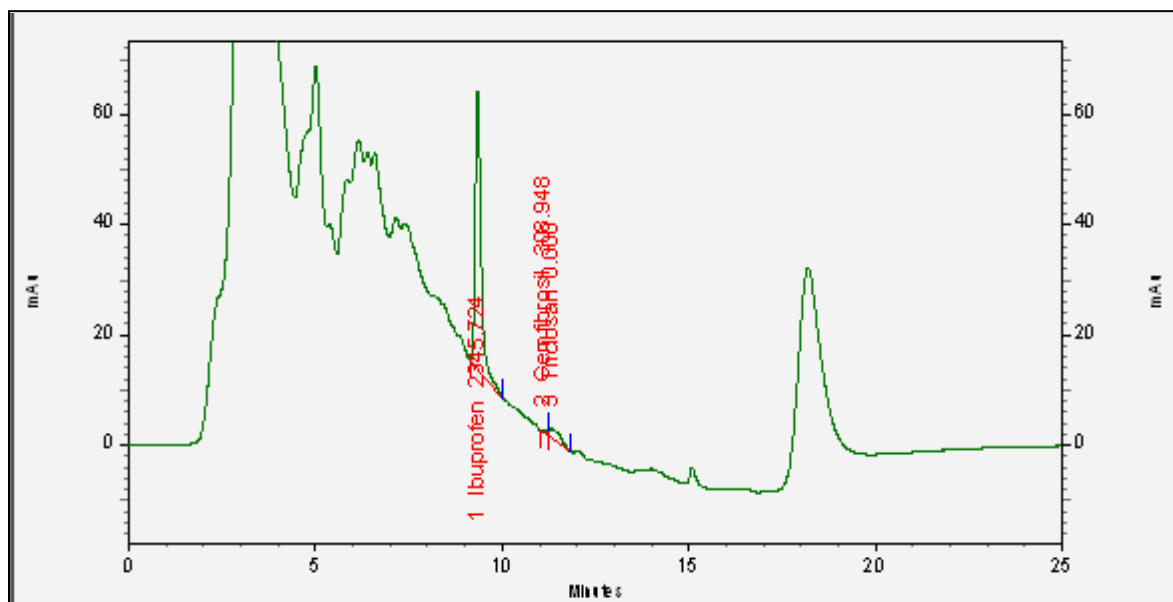


Figure B.34. Secondary Effluent from 03/09/11: Acid Group II

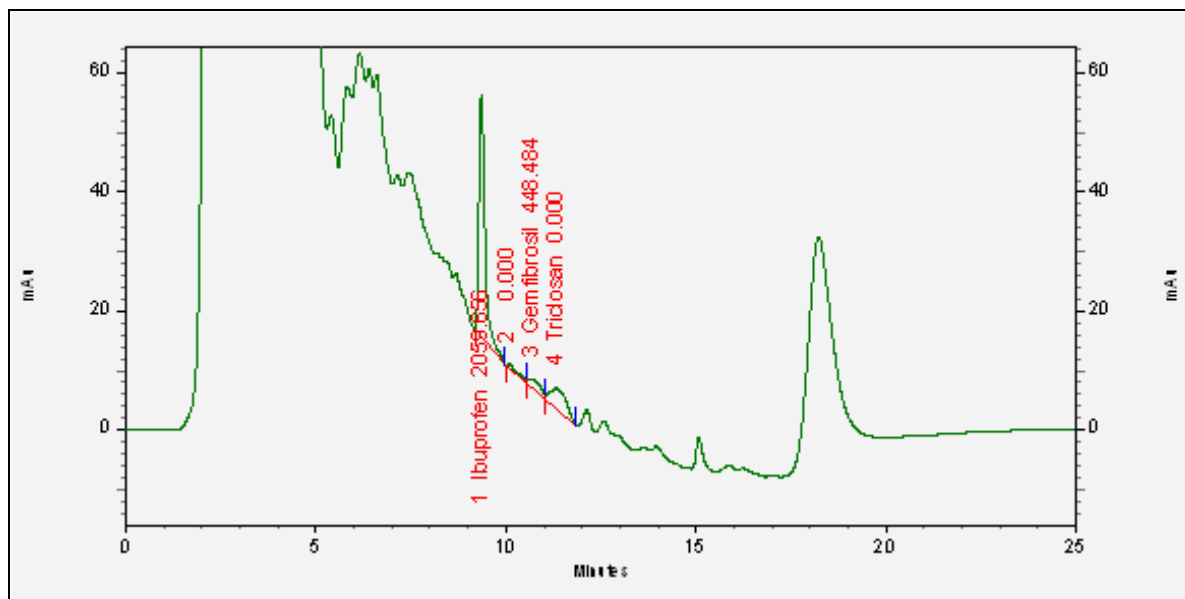


Figure B.35. Final Effluent from 03/09/11: Acid Group II

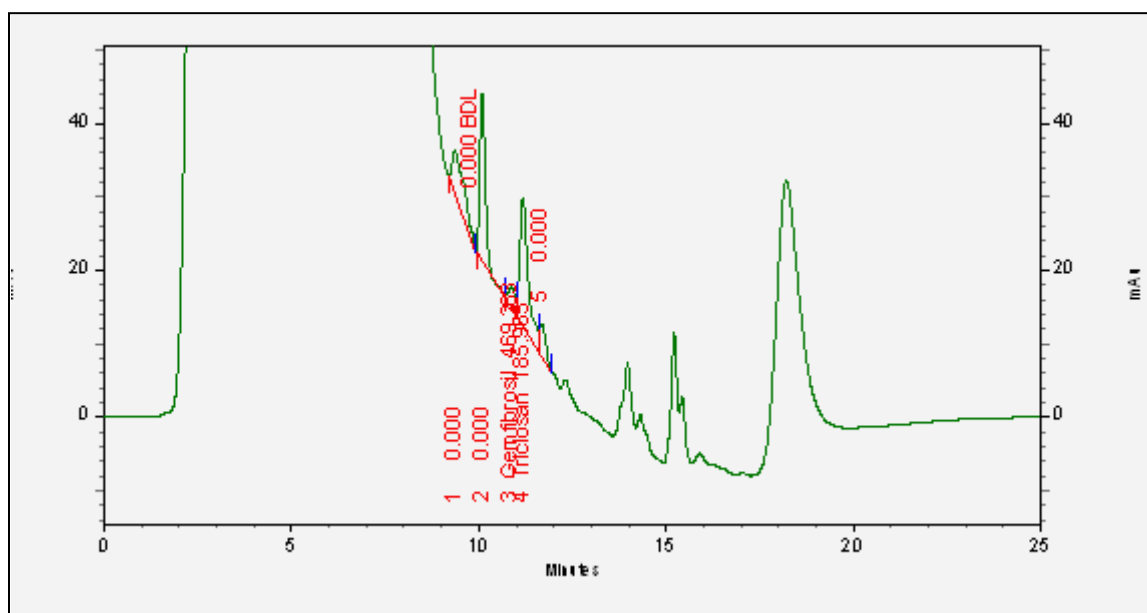


Figure B.36. Influent from 05/14/11: Acid Group II

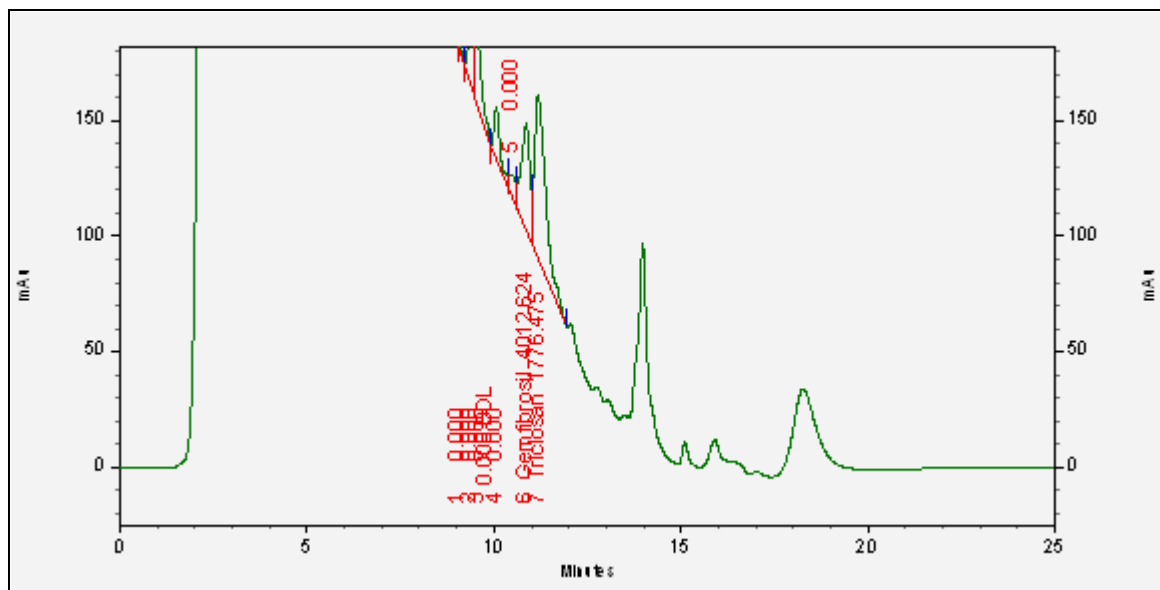


Figure B.37. Primary Effluent from 05/14/11: Acid Group II

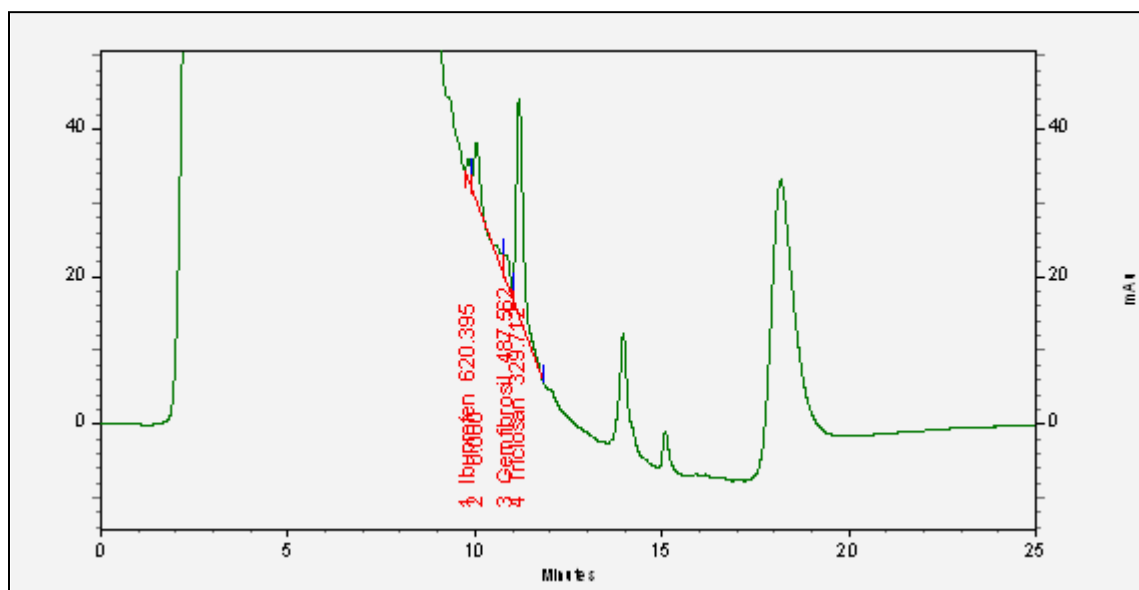


Figure B.38. Secondary Effluent from 05/14/11: Acid Group II

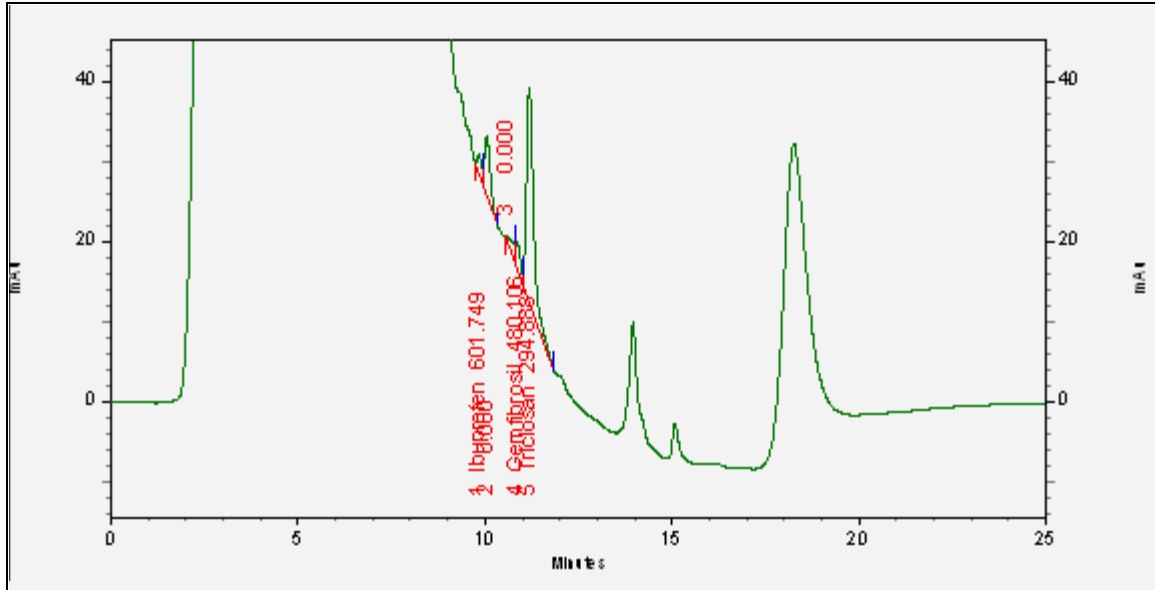


Figure B.39. Final Effluent from 05/14/11: Acid Group II

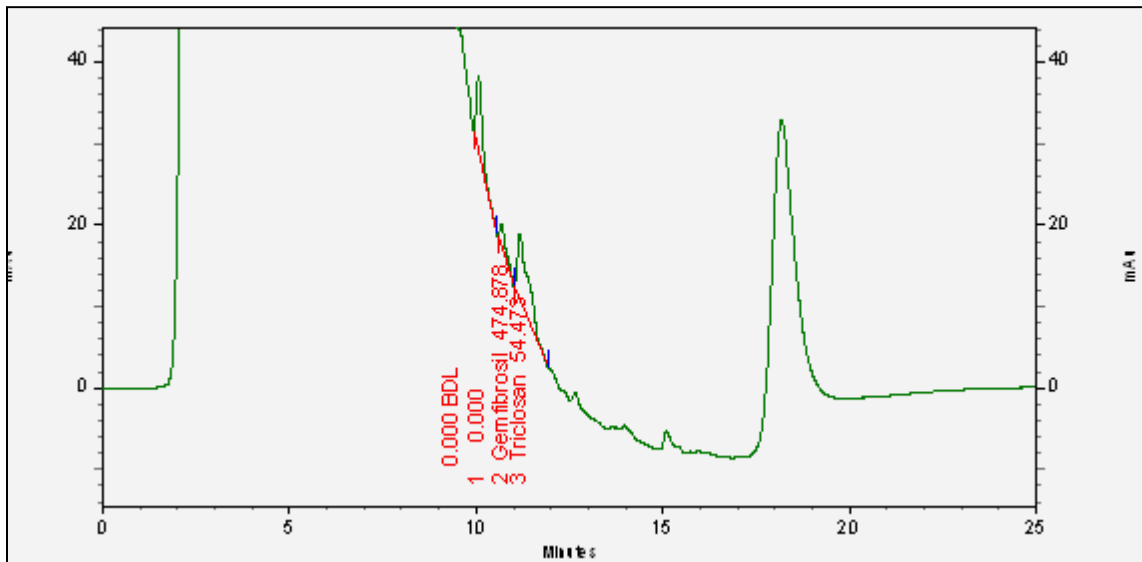


Figure B.40. Influent from 09/20/11: Acid Group II

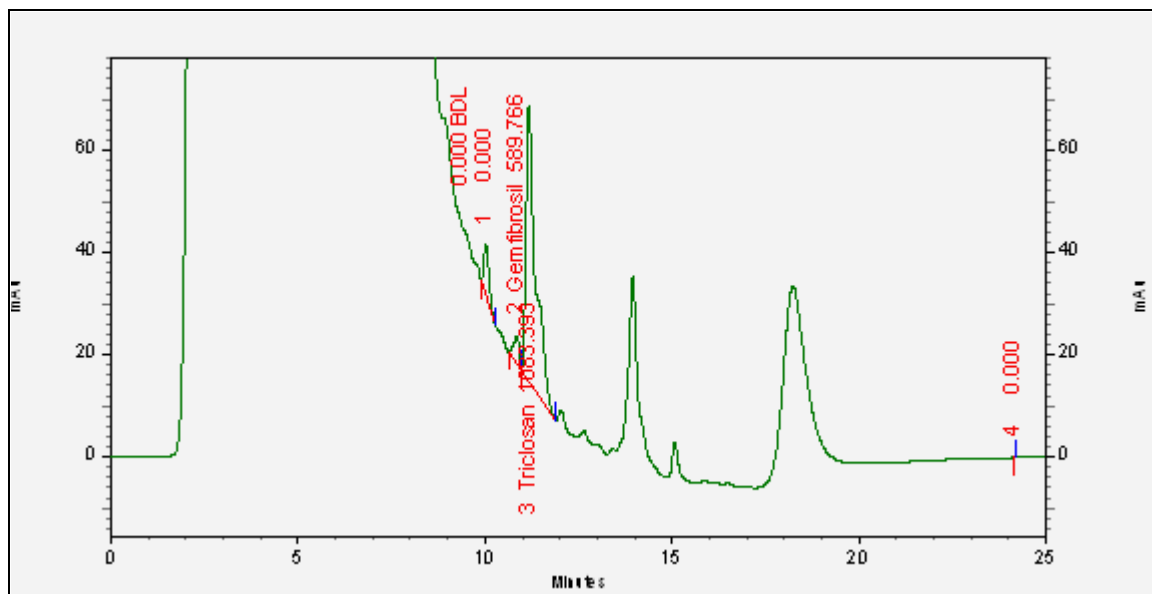


Figure B.41. Primary Effluent from 09/20/11: Acid Group II

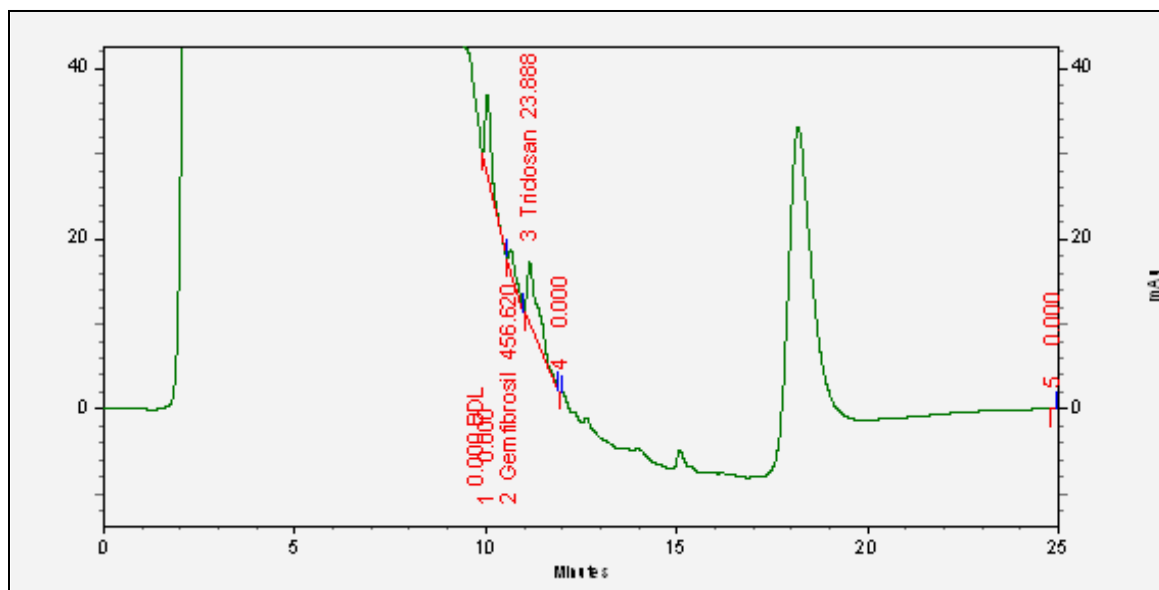


Figure B.42. Secondary Effluent from 09/20/11: Acid Group II

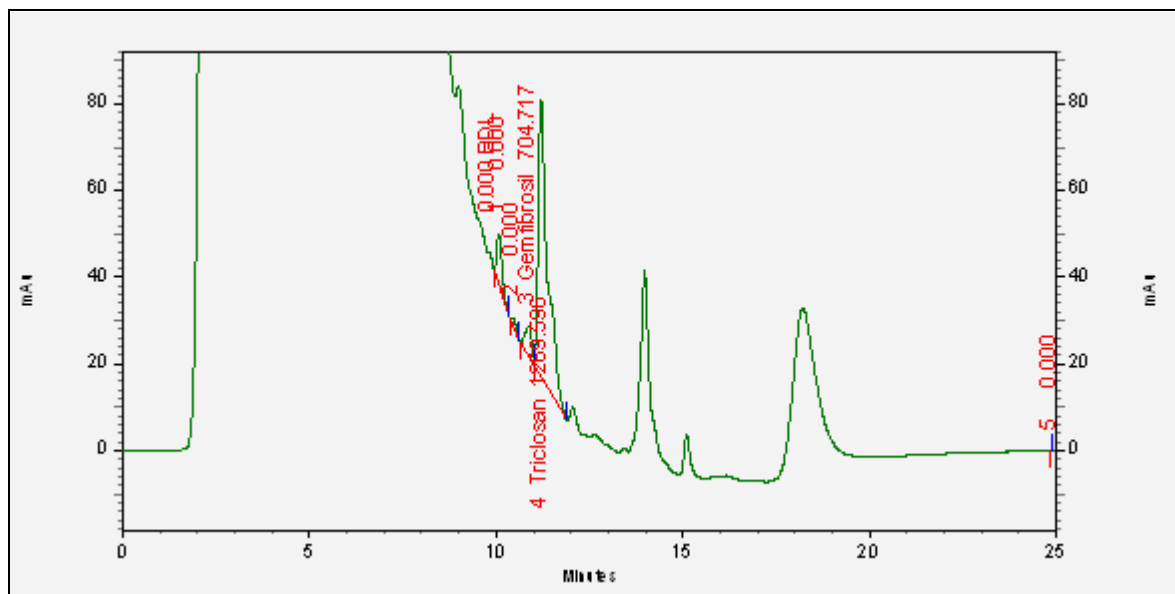


Figure B.43. Final Effluent from 09/20/11: Acid Group II

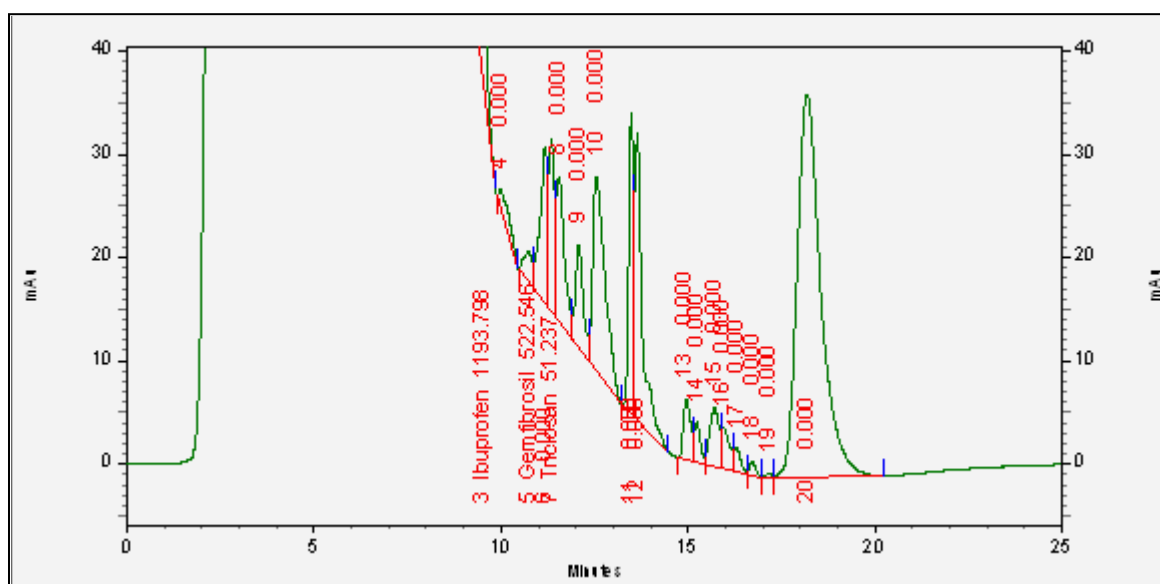


Figure B.44. Influent from 01/16/10: Acid Group II

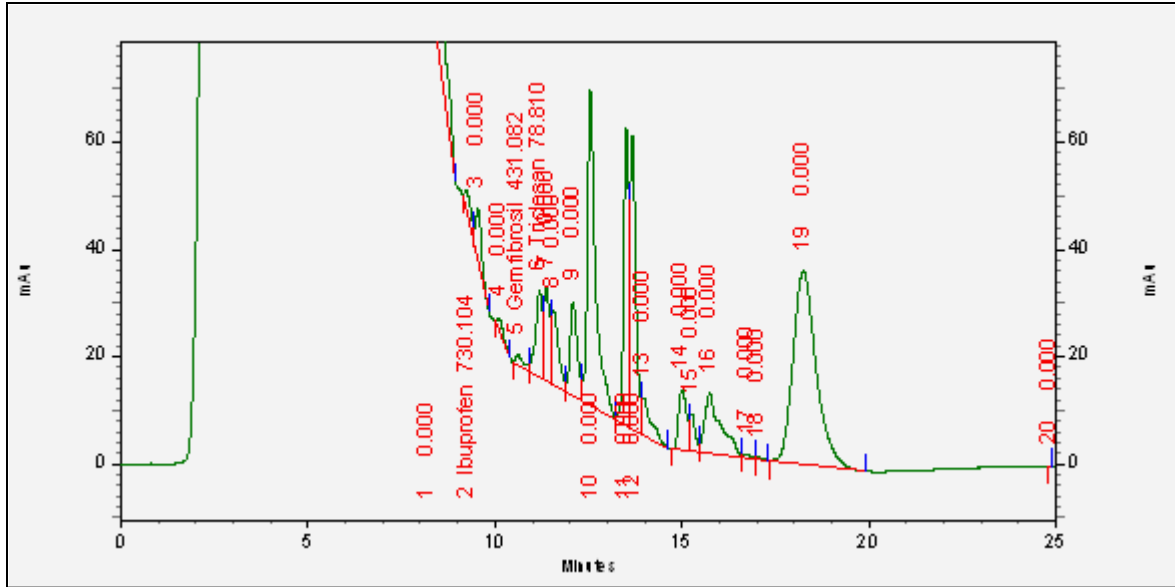


Figure B.45. Primary Effluent for 01/16/10: Acid Group II

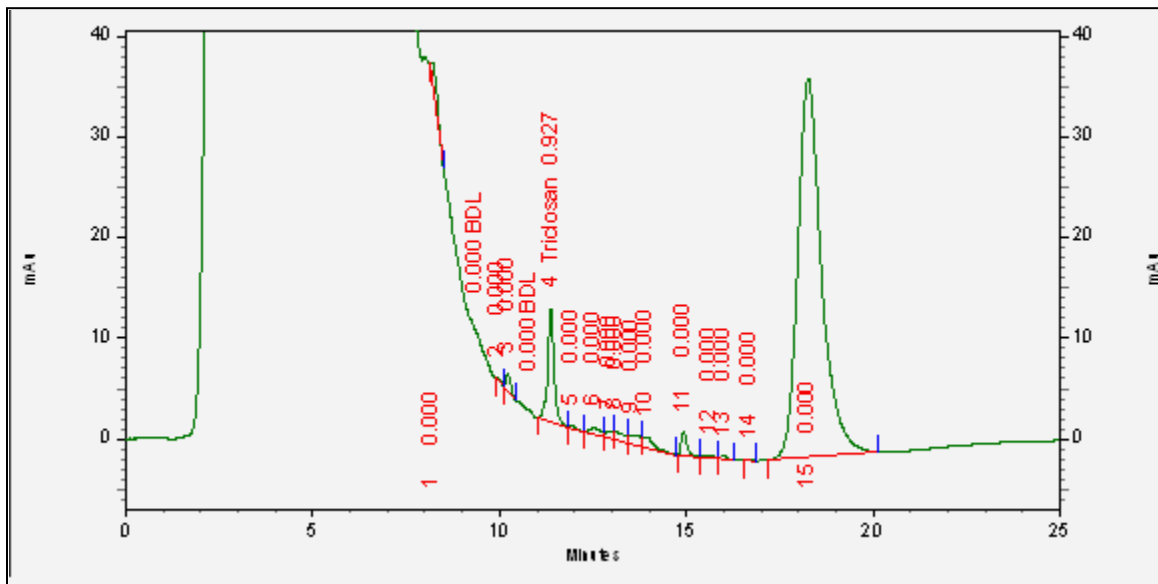


Figure B.46. Secondary Effluent for 01/16/10: Acid Group II

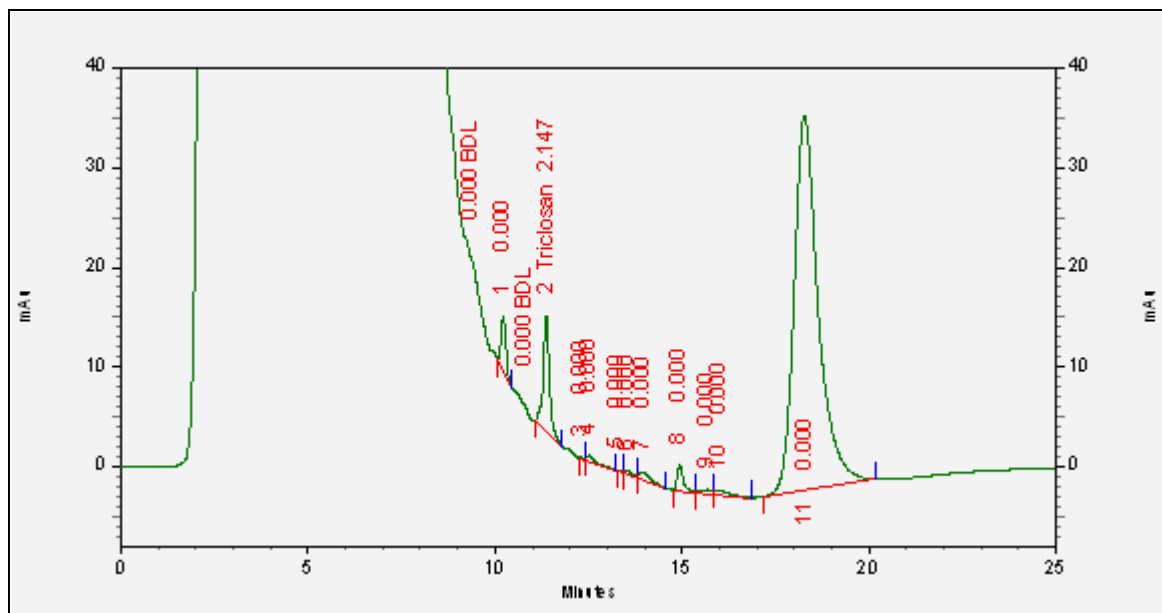


Figure B.47. Final Effluent for 01/16/10: Acid Group II

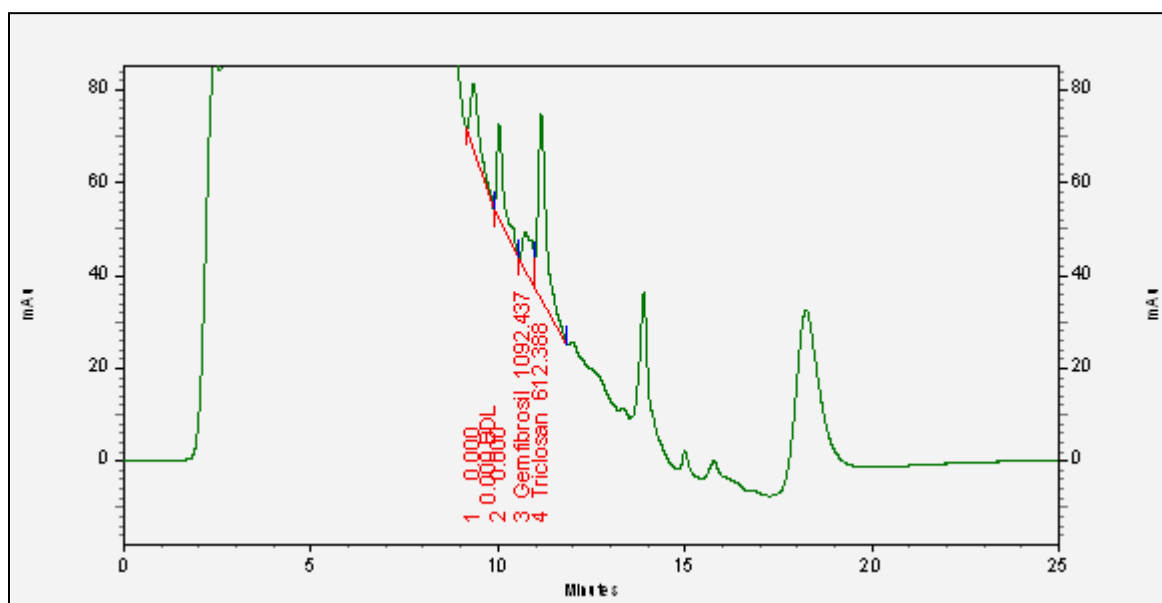


Figure B.48. Influent from 03/20/11: Acid Group II

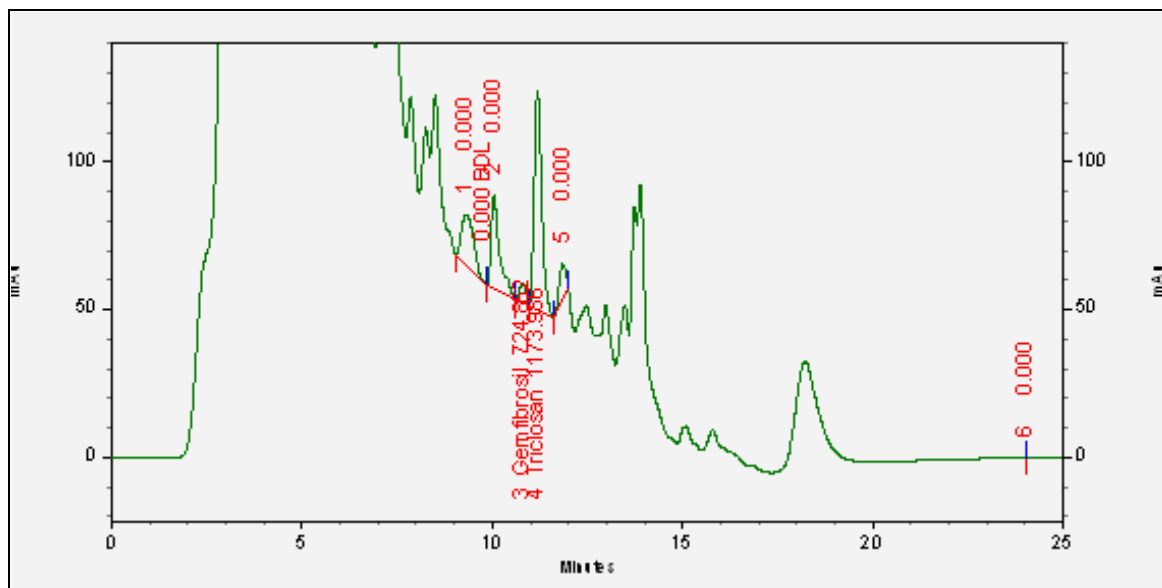


Figure B.49. Primary Effluent from 03/20/11: Acid Group II

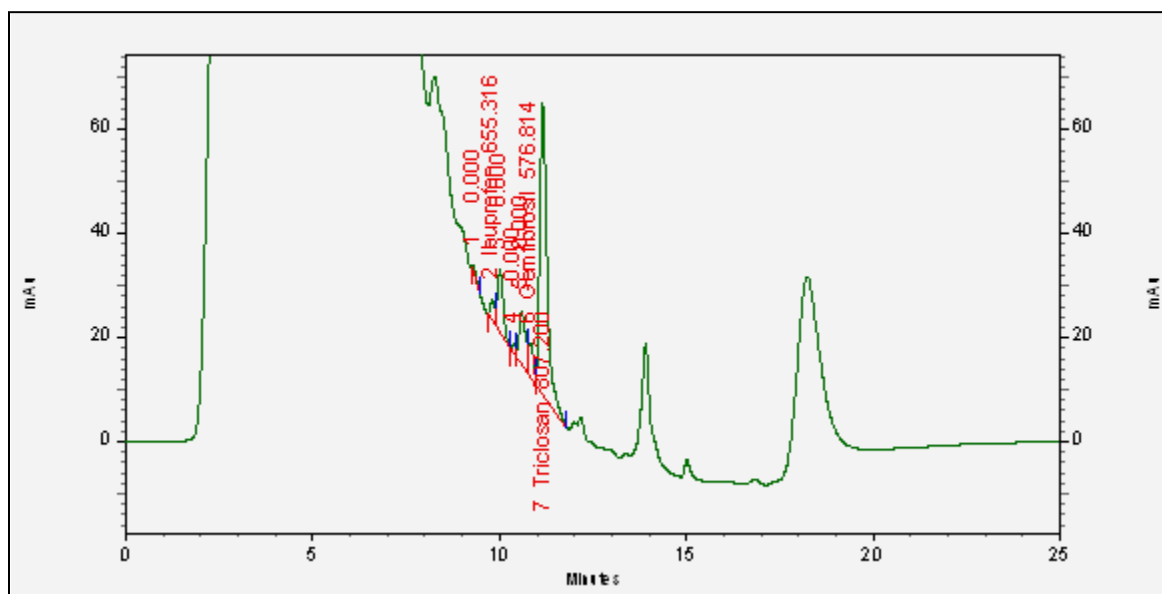


Figure B.50. Secondary Effluent for 03/20/12: Acid Group II

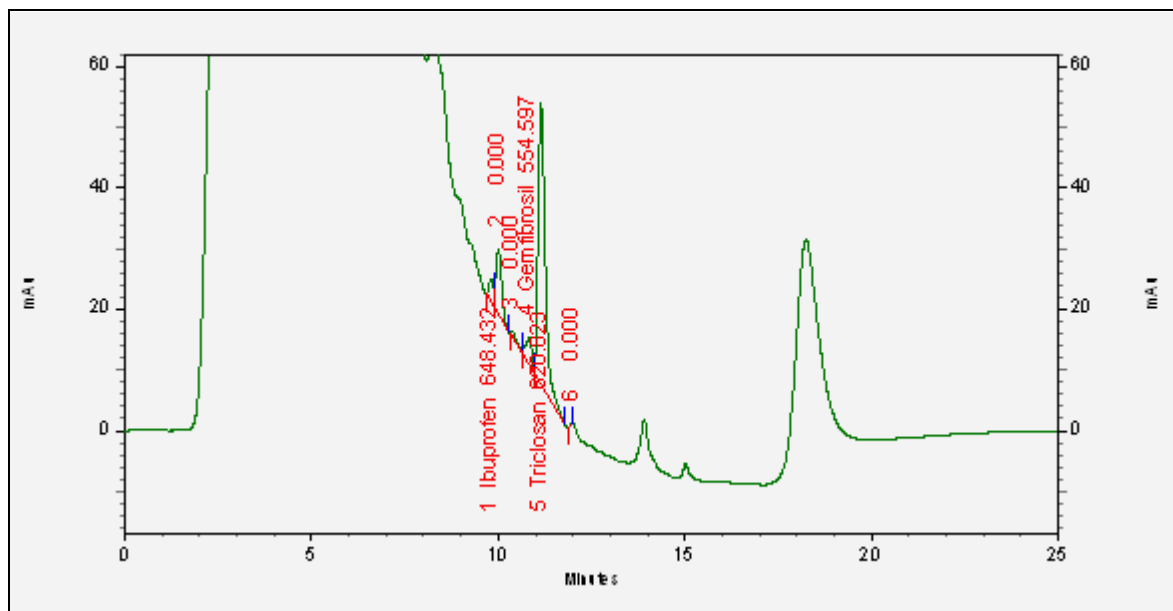


Figure B.51. Final Effluent for 03/20/12: Acid Group II

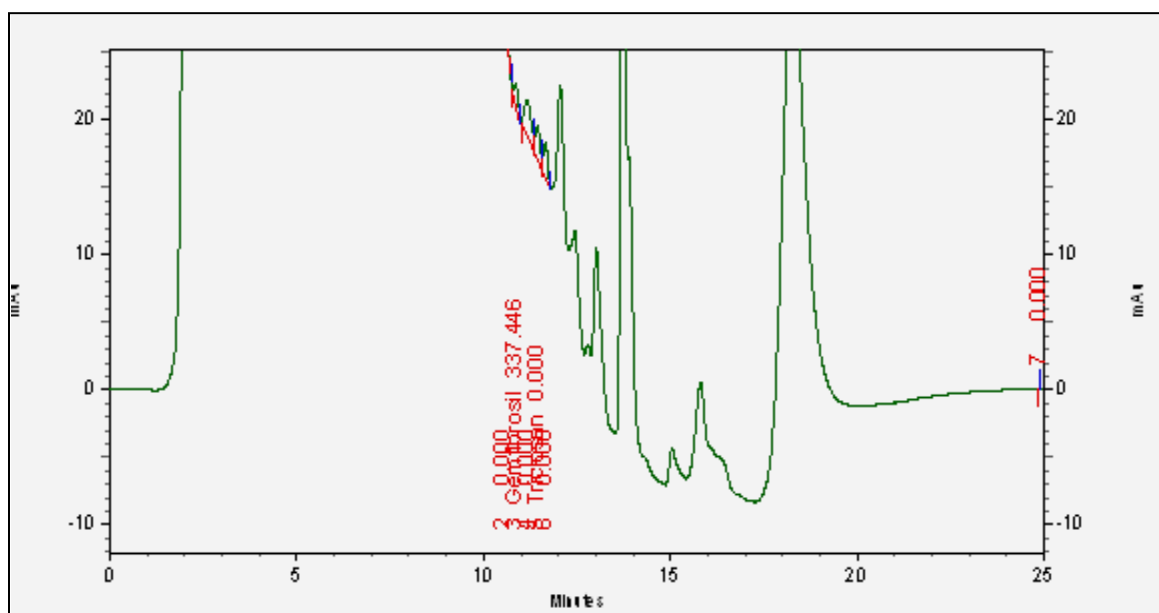


Figure B.52. Influent from 06/16/12: Acid Group II

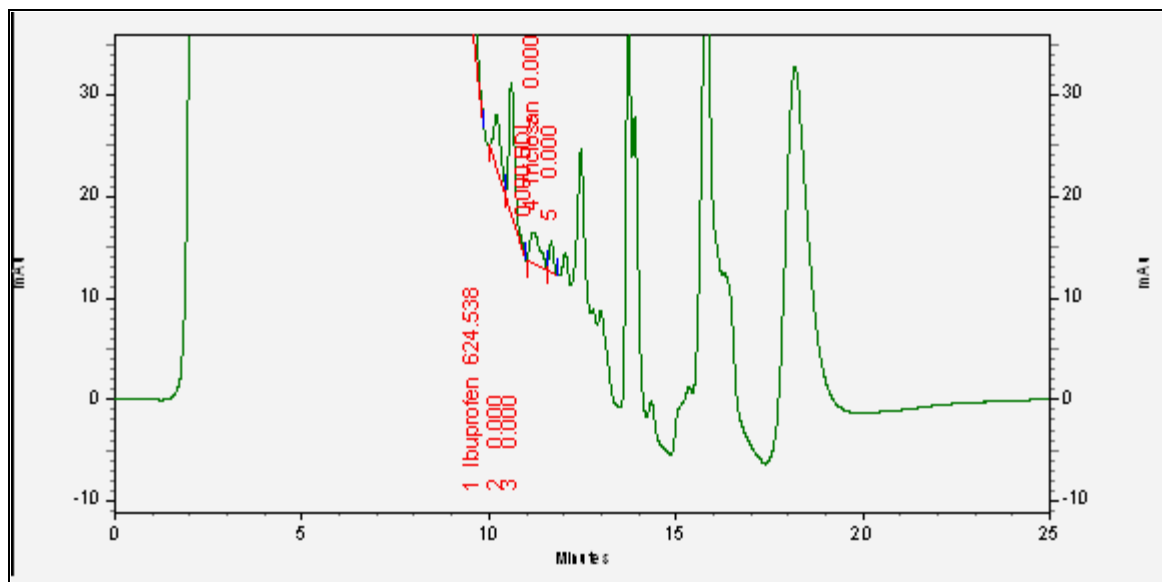


Figure B.53. Primary Effluent from 06/16/12: Acid Group II

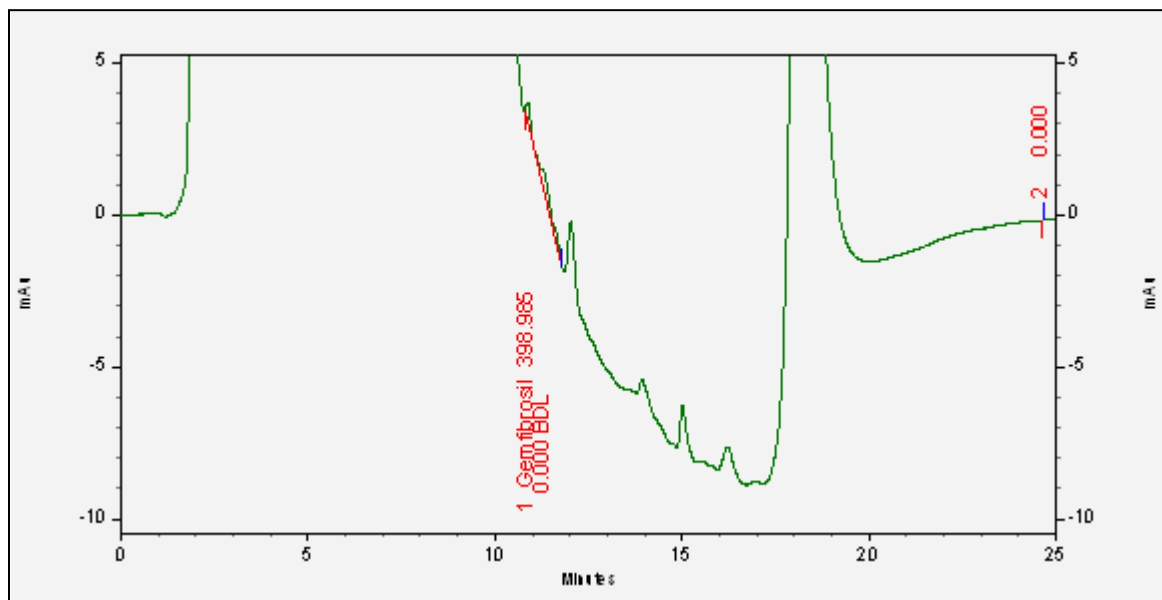


Figure B.54. Secondary Effluent from 06/16/12: Acid Group II

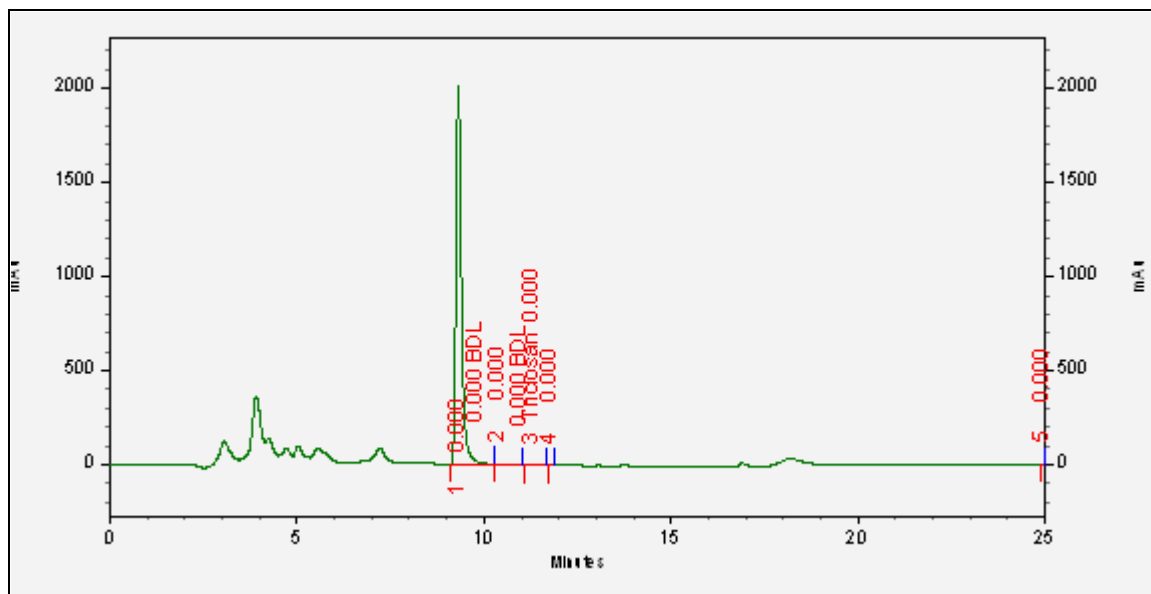


Figure B.55. Final Effluent for 06/16/12: Acid Group II

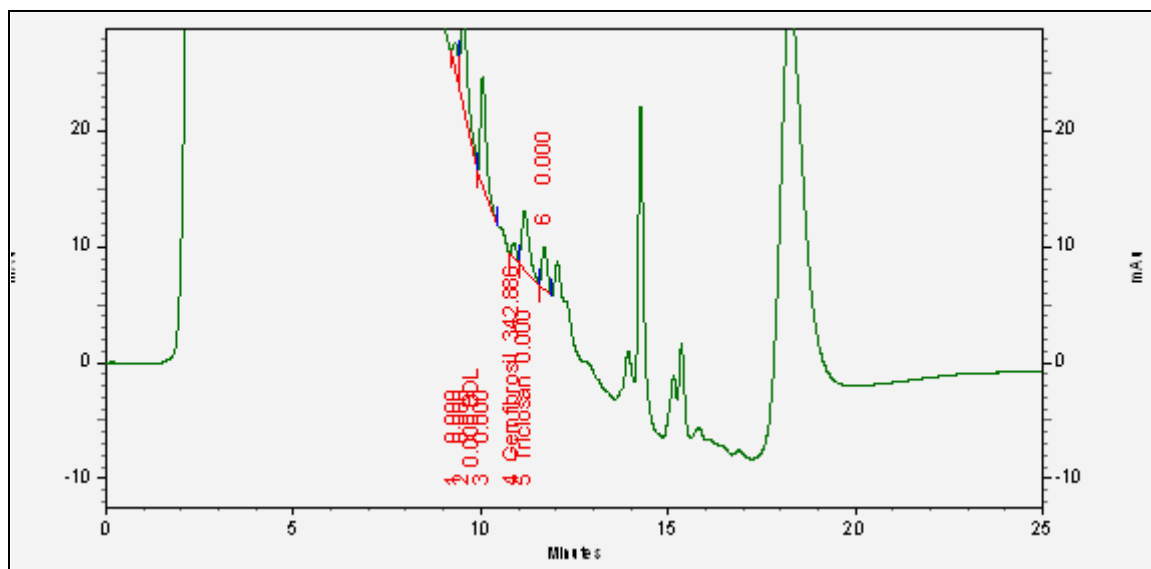


Figure B.56. Influent from 09/15/12: Acid Group II

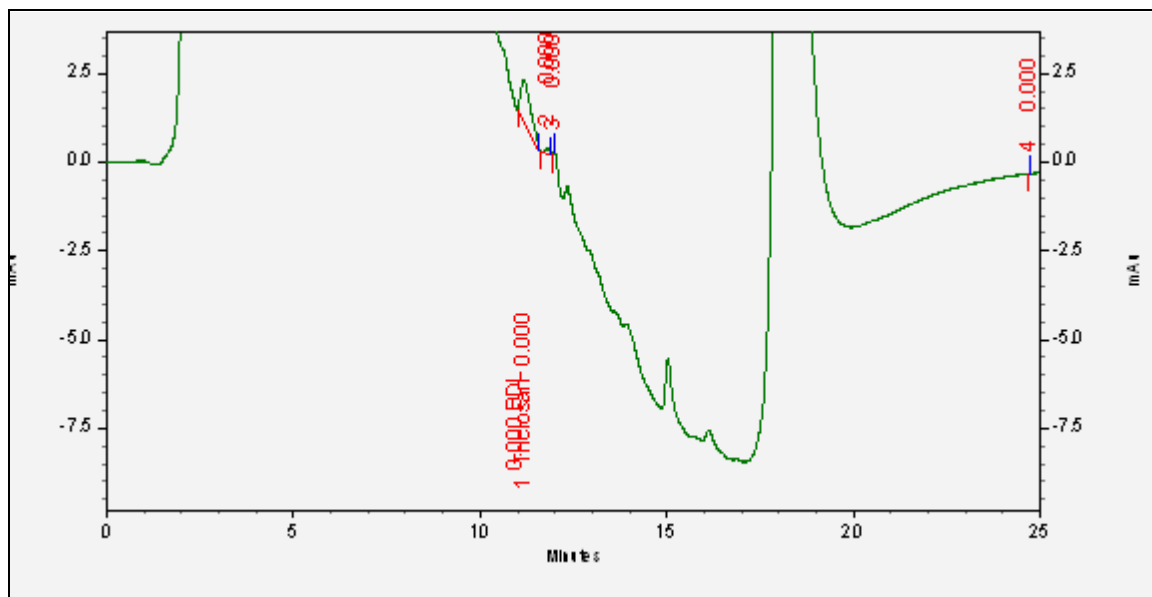


Figure B.57. Primary Effluent from 09/15/12: Acid Group II

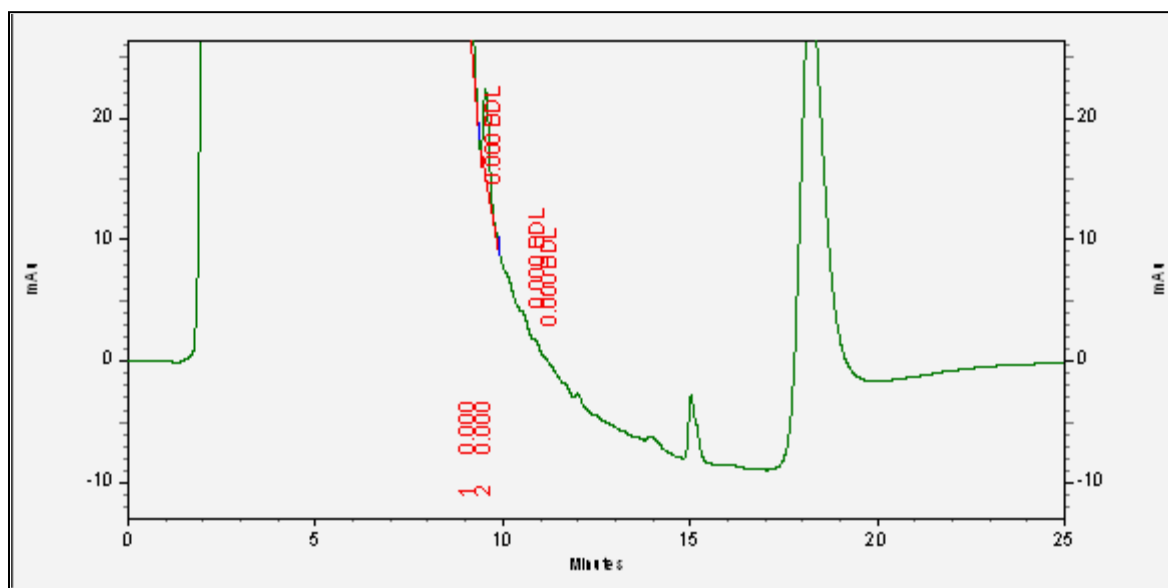


Figure B.58. Secondary Effluent from 09/15/12: Acid Group II

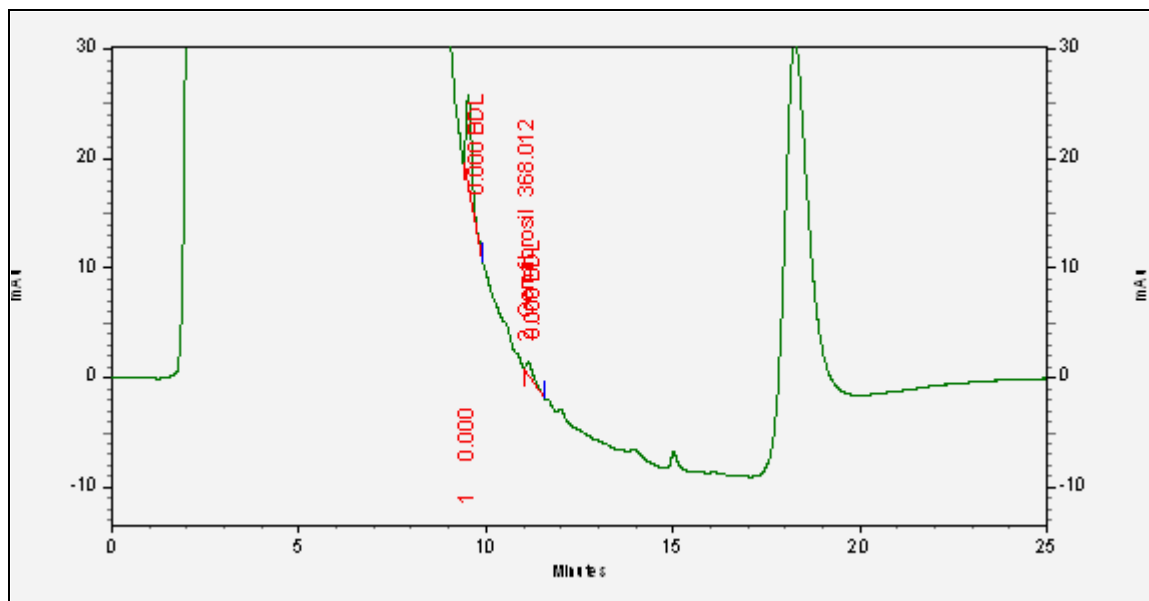


Figure B.59. Final Effluent from 09/15/12: Acid Group II

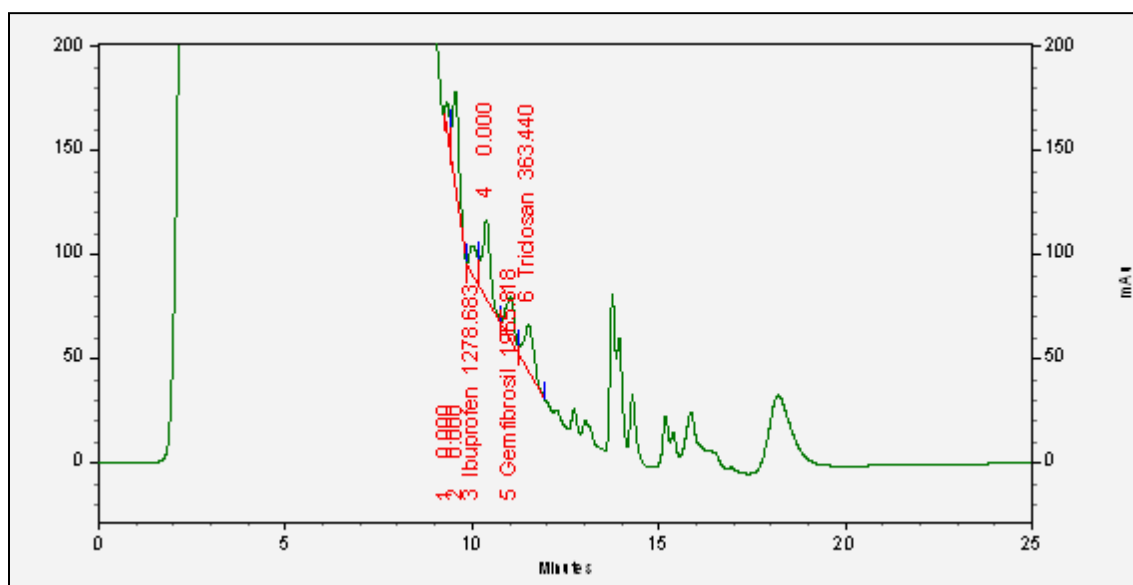


Figure B.60. Influent from 11/01/12: Acid Group II

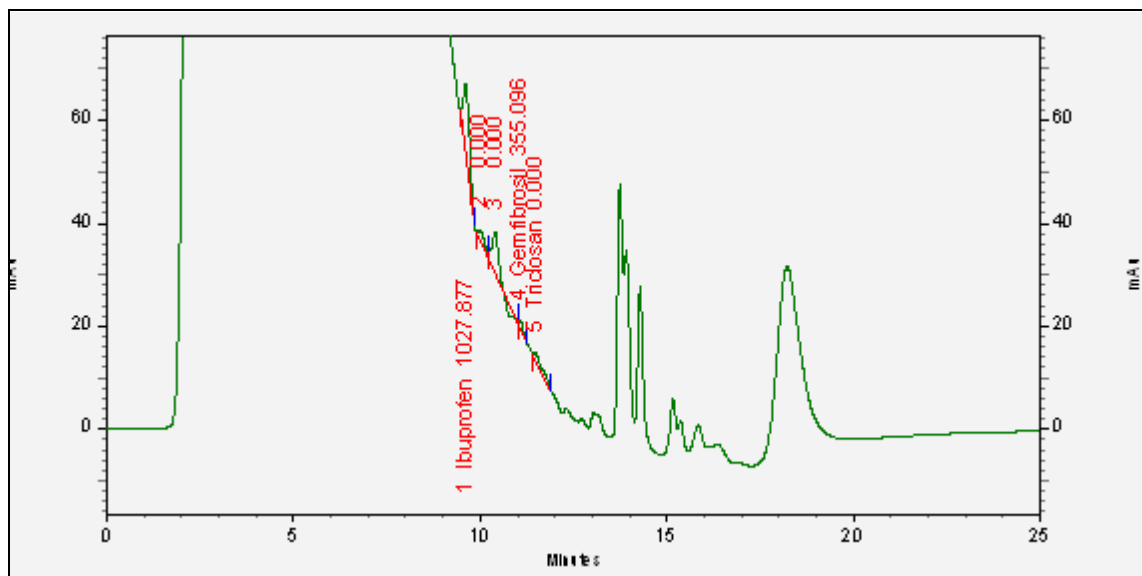


Figure B.61. Primary Effluent from 11/01/12: Acid Group II

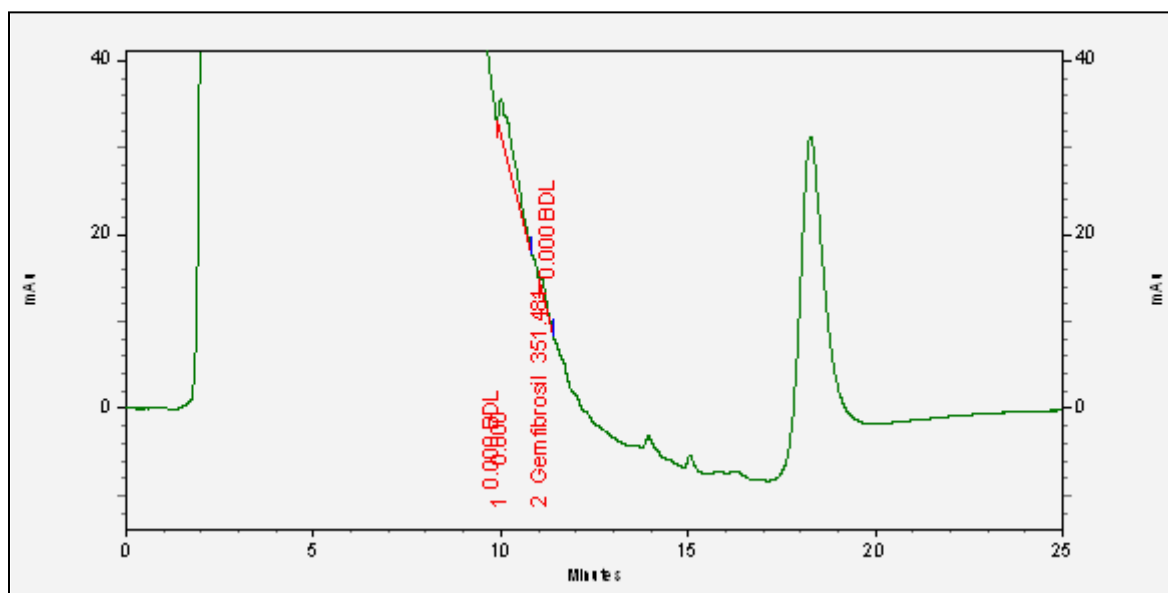


Figure B.62. Secondary Effluent from 11/01/12: Acid Group II

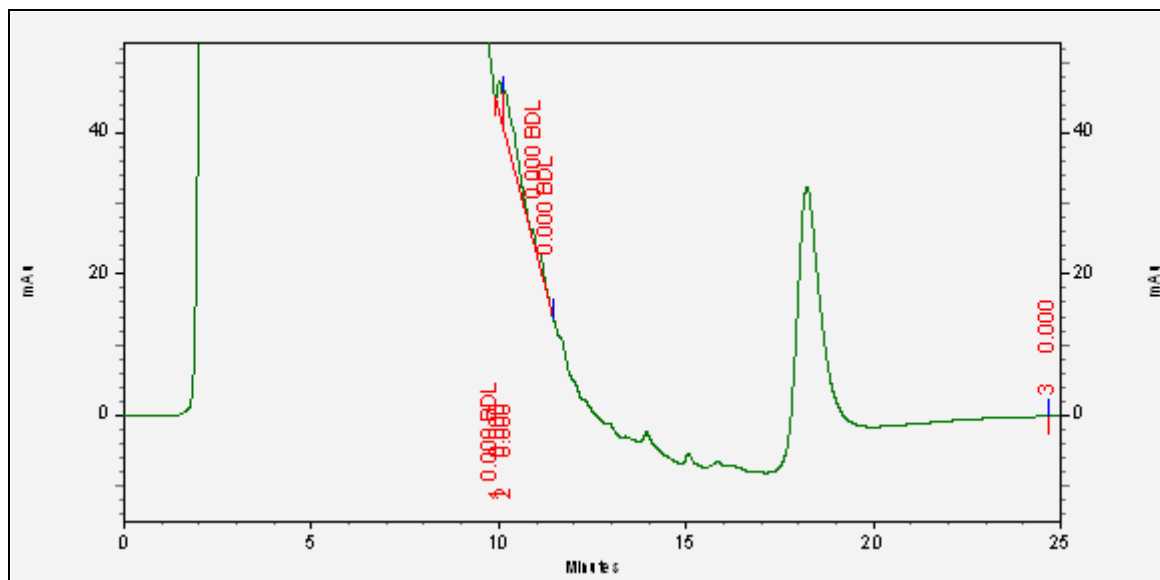


Figure B.63. Final Effluent from 11/01/12: Acid Group II

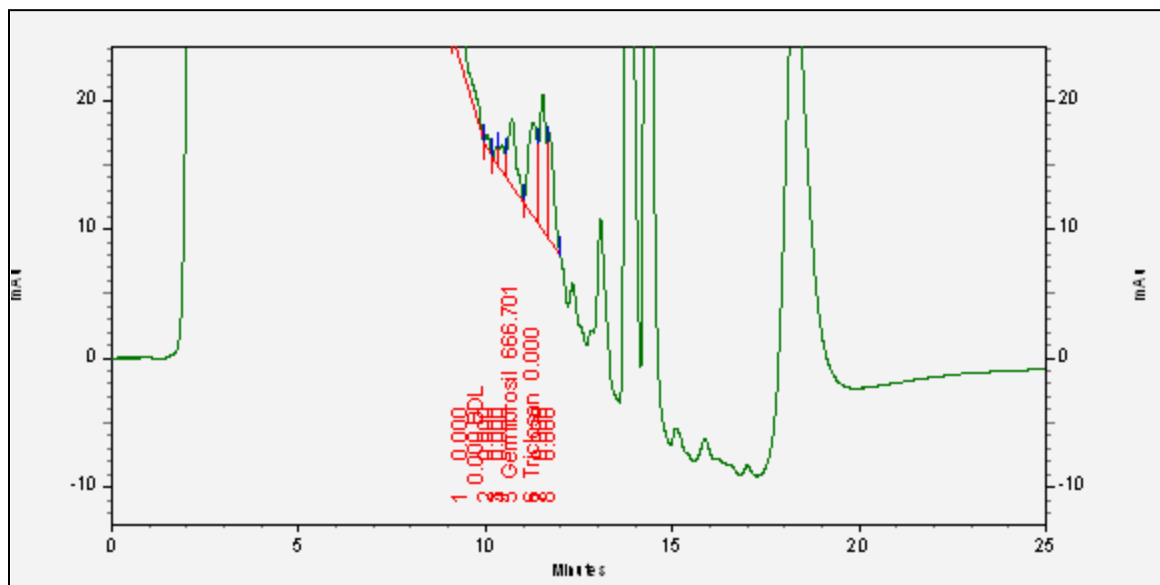


Figure B.64. Influent from 11/04/12: Acid Group II

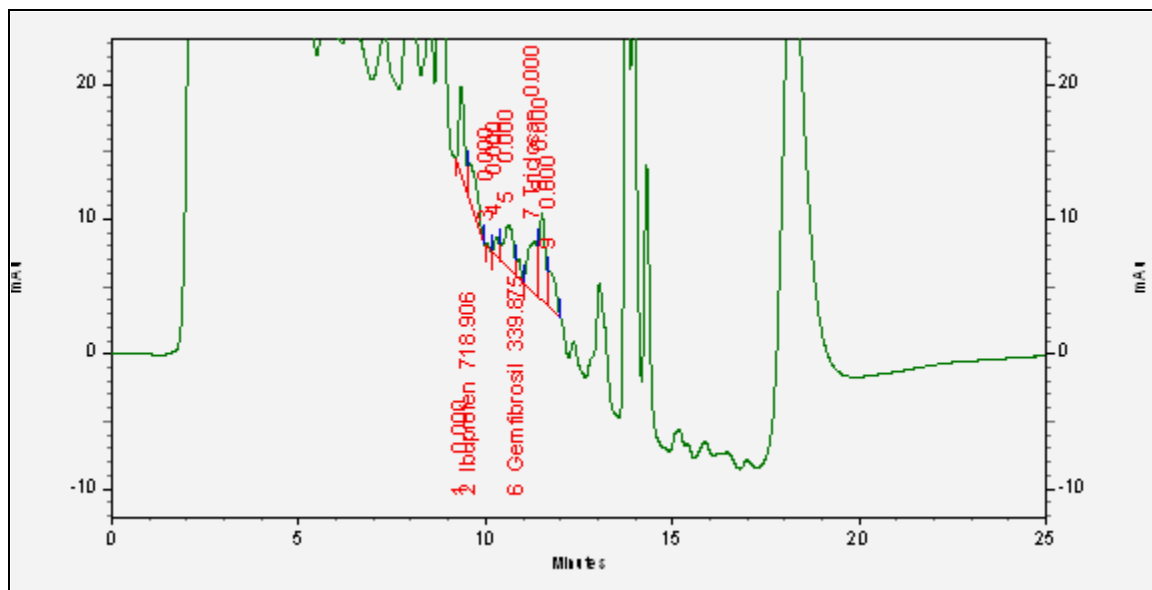


Figure B.65. Primary Effluent from 11/04/12: Acid Group II

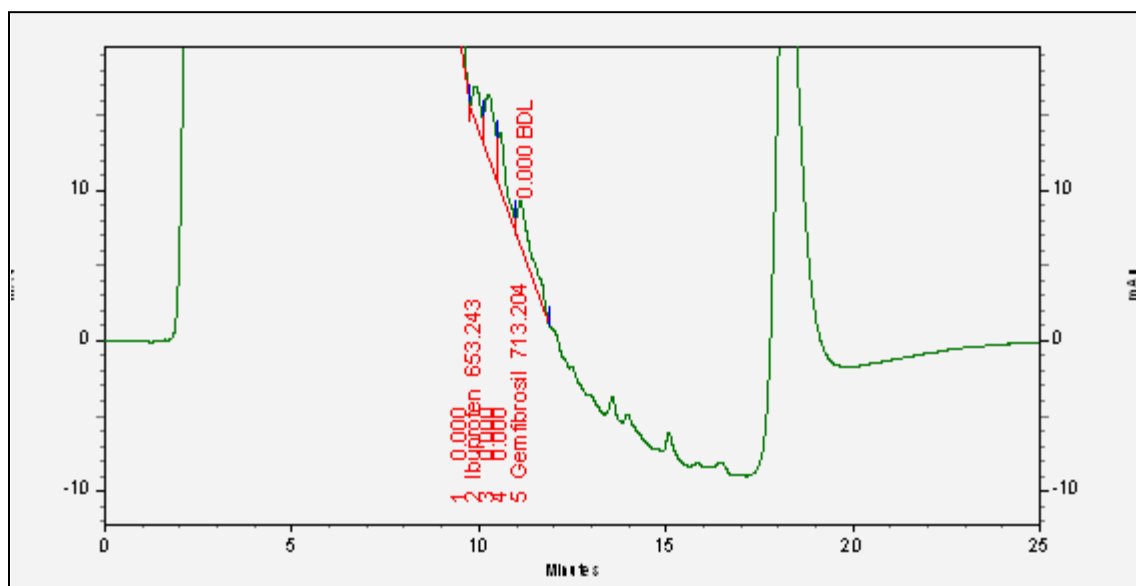


Figure B.66. Secondary Effluent from 11/04/12: Acid Group II

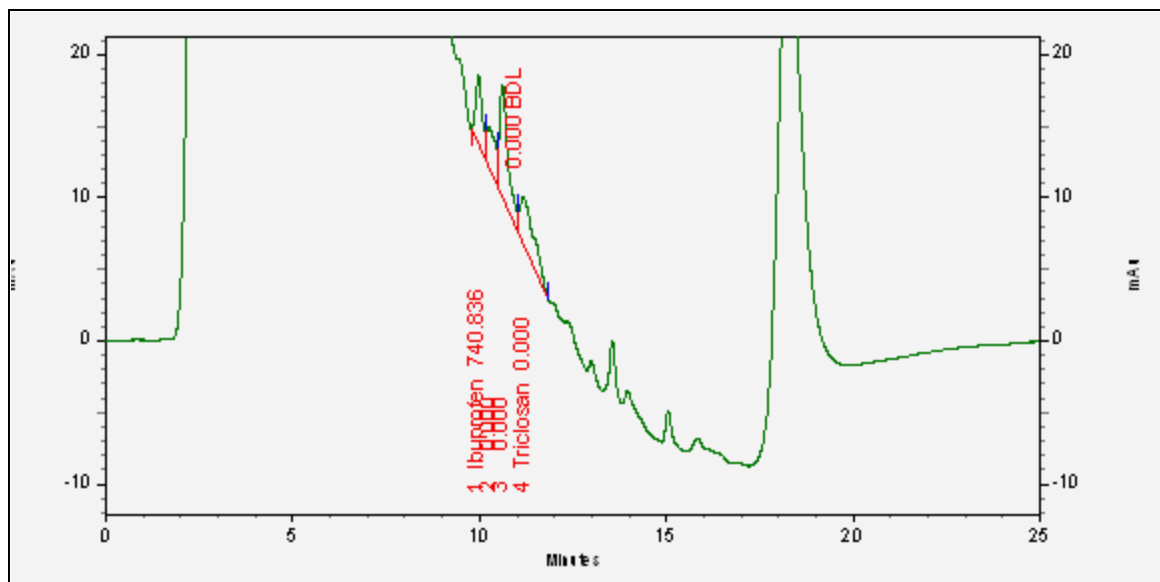


Figure B.67. Final Effluent from 11/04/12: Acid Group II

APPENDIX C: QUALITY ASSURANCE AND QUALITY CONTROL DATA

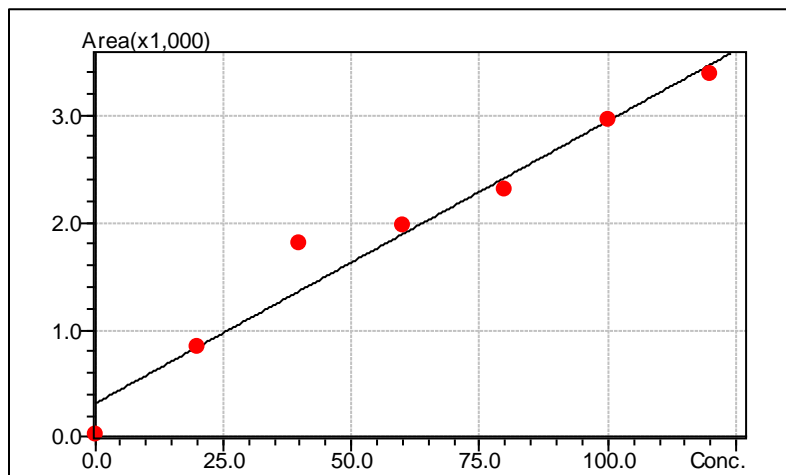


Figure C.1. Standard Curve for Naphthalene

$Y = 26.29821X + 318.6786$
$R^2 = 0.9637912$
$R = 0.9817287$
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

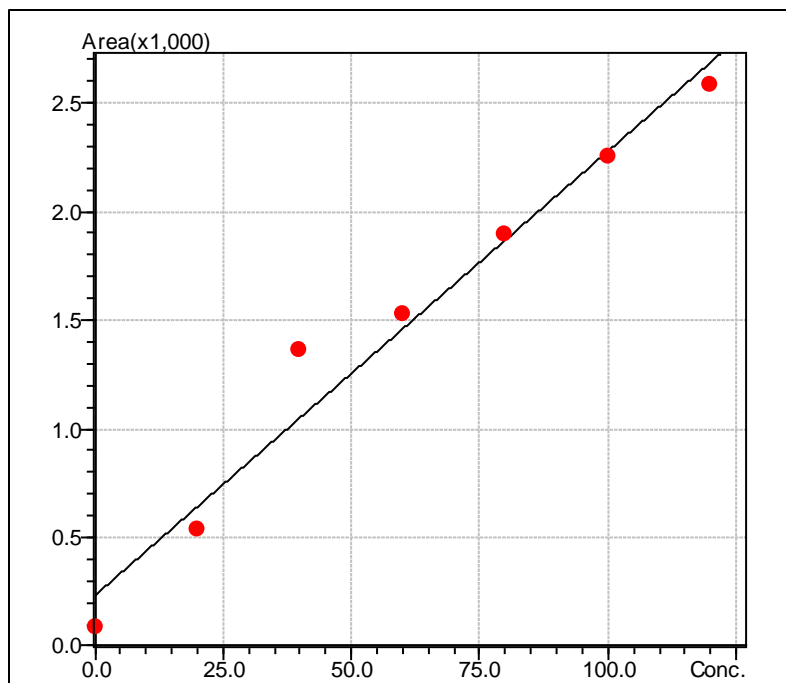


Figure C.2. Standard Curves for Acenaphthylene

$Y = 20.44643X + 236.6429$
$R^2 = 0.9691085$
$R = 0.9844331$
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

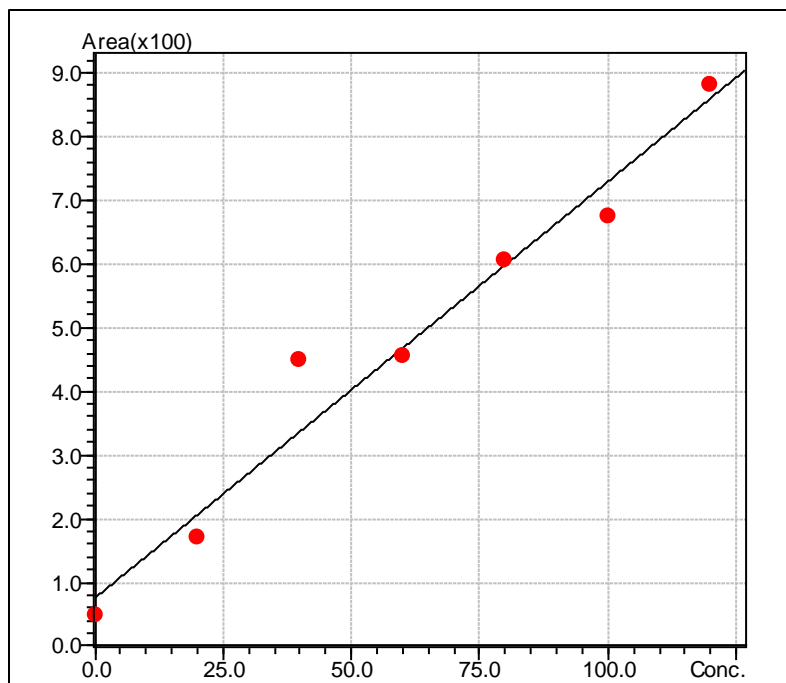


Figure C.3. Standard Curve for Acenaphthene

$Y = 6.539286X + 76.5$
$R^2 = 0.9635812$
$R = 0.9816217$
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

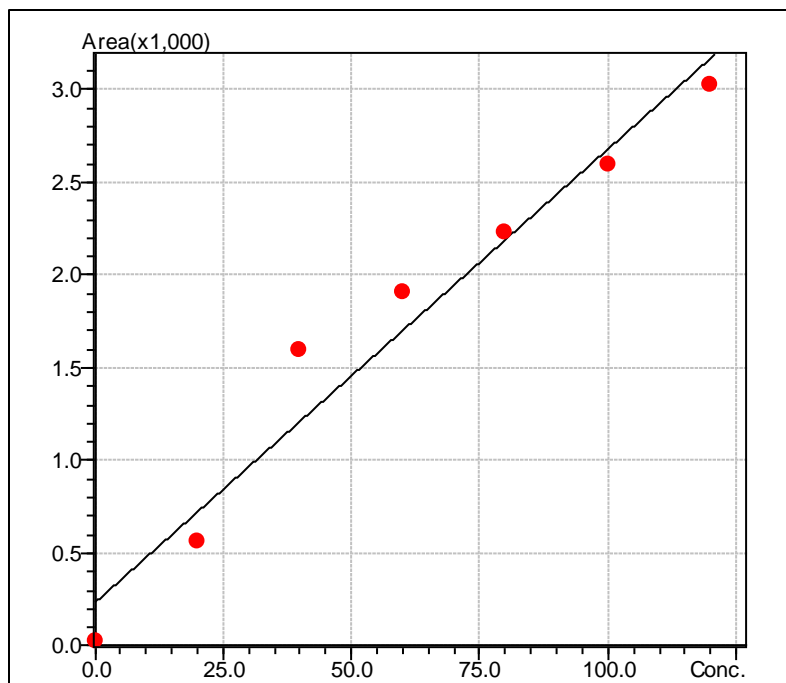


Figure C.4. Standard Curve for Fluorene

$Y = 24.46786X + 237.7857$
$R^2 = 0.9584859$
$R = 0.9790229$
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

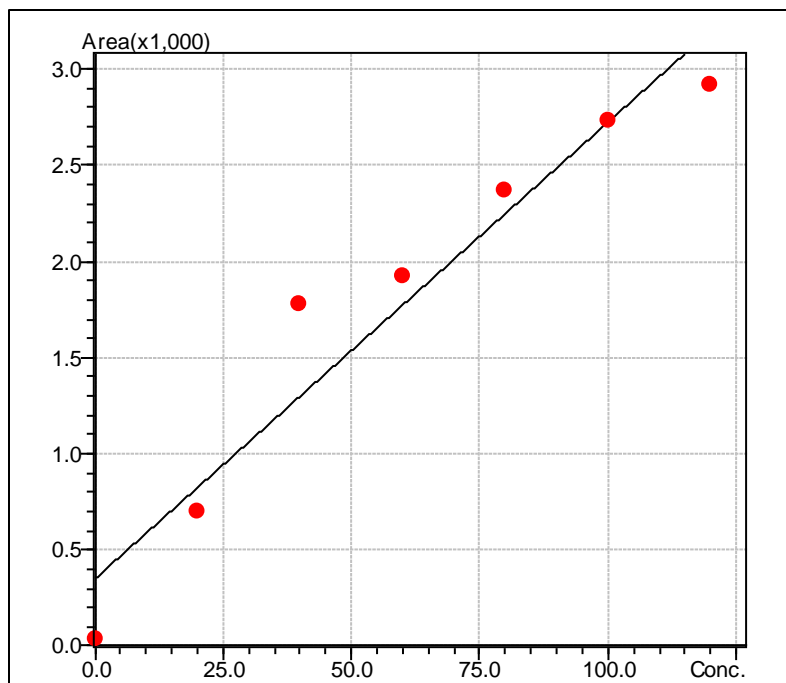


Figure C.5. Standard Curve for Phenanthrene

$Y = 23.75179X + 353.6071$
$R^2 = 0.9329065$
$R = 0.9658708$
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

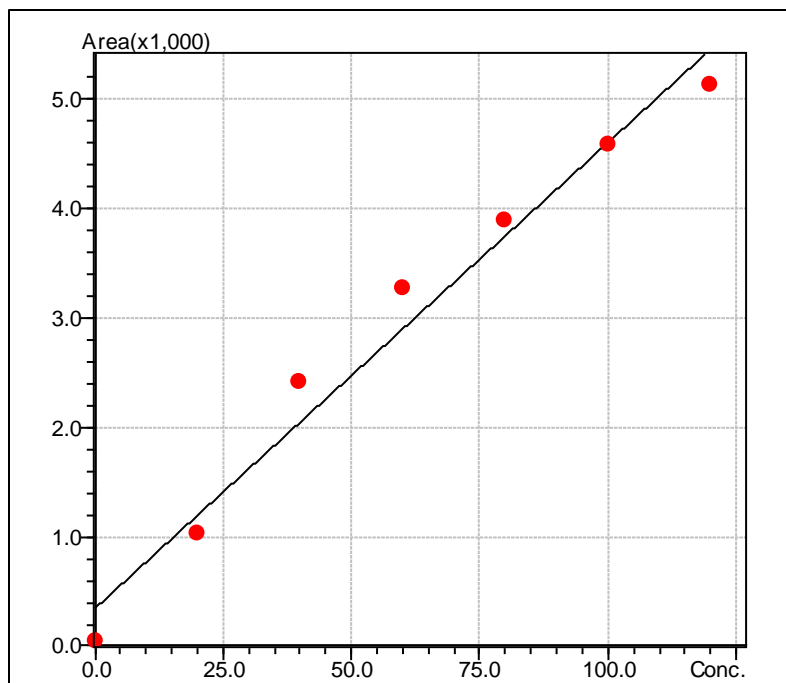


Figure C.6. Standard Curve for Anthracene

$Y = 42.61429X + 351.1429$
$R^2 = 0.9746687$
$R = 0.9872531$
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

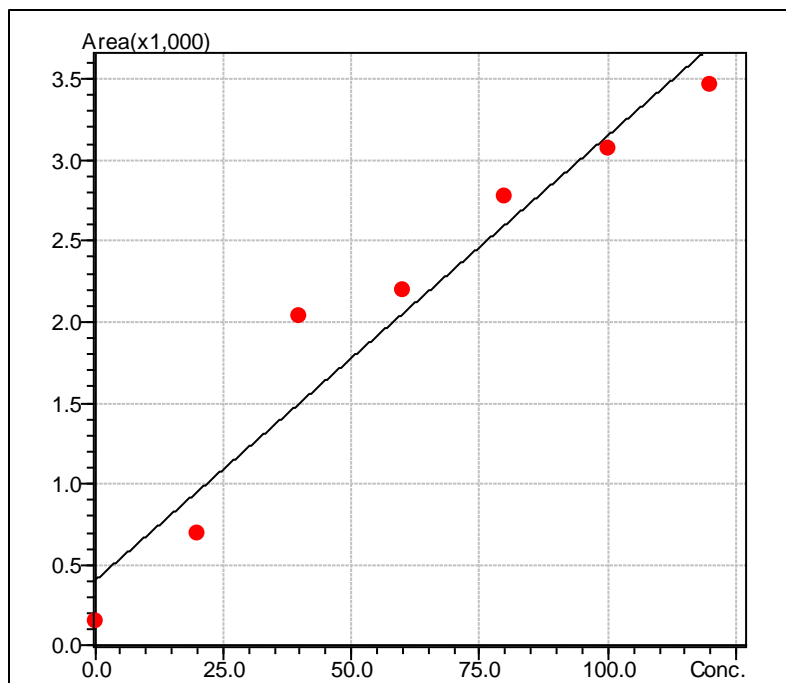


Figure C.7. Standard Curve for Fluoranthene

$Y = 27.46786X + 408.9286$
$R^2 = 0.9403727$
$R = 0.9697282$
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

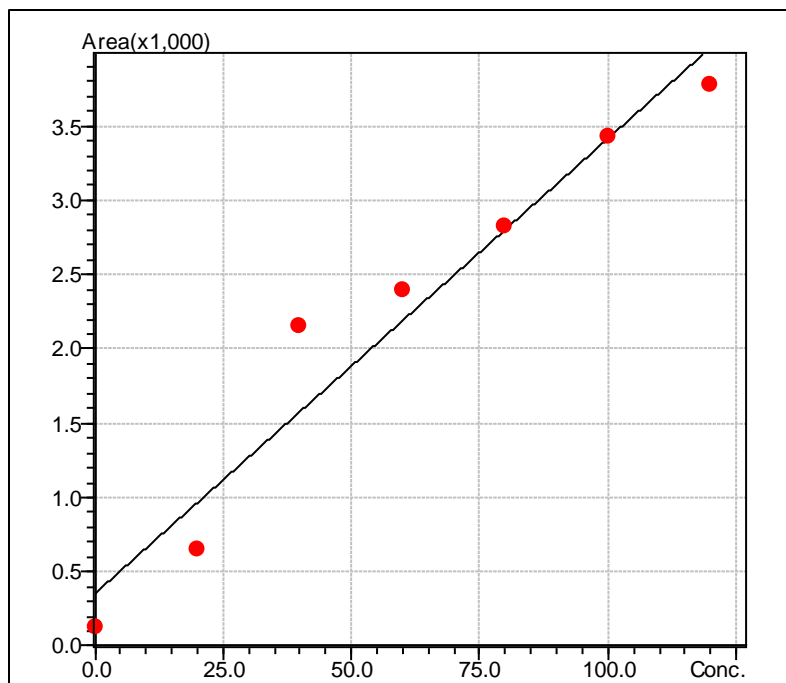


Figure C.8. Standard Curve for Pyrene

$Y = 30.62321X + 358.8929$
$R^2 = 0.9465796$
$R = 0.9729232$
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

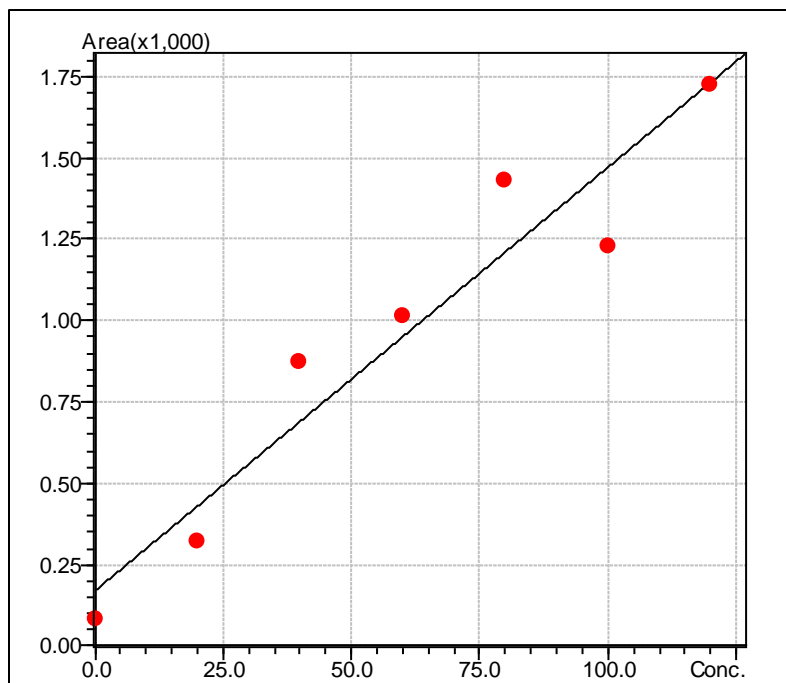
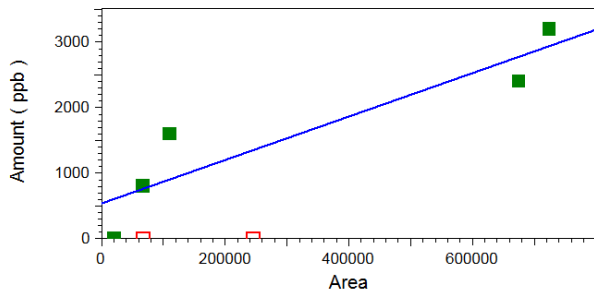


Figure C.9. Standard Curve for Chrysene

$Y = 13.02143X + 171.8571$
$R^2 = 0.9204694$
$R = 0.959411$
External Standard
Curve: Linear
Origin: Force
Through(Polyline)
Weighting Method: None
Mean RF : 32.51202
RF SD : 16.25551
RF %RSD : 49.99846

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 (r²): 0.834275

Peak: Ibuprofen -- ESTD -- 2: 240 nm, 4 nm



n/a

n/a

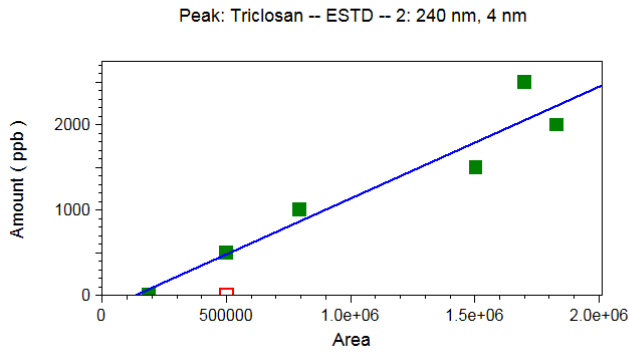
	Level 1	Level 2	Level 3
Amount	0	800	1600
Area	20780	67358	110875
RF	0	0.011876837198254	0.014430665163472
Last Area		1	4
Residual	-609.994	35.7731	691.676
Rep StDev			
Rep %RSD			
Rep 1 Area	20780	67358	110875
Rep 2 Area	67358*		

	Level 4	Level 5	Level 6
Amount	2400	3200	0
Area	675061	724728	245256*
RF	0.003555234267718	0.004415449658354	0
Last Area	03	58	
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 (r²): 0.917712



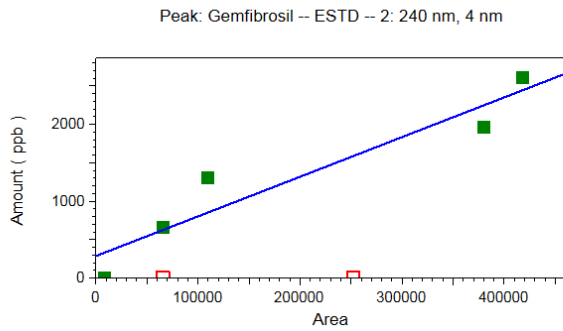
	Level 1	Level 2	Level 3
Amount	0	500	1000
Area	188001	500441	795420
RF	0	0.000999118777238	0.001257197455432
Last Area		476	35
Residual	-72.9466	17.6481	131.123
Rep StDev			
Rep %RSD			
Rep 1 Area	188001	500441	795420
Rep 2 Area	500441*		

	Level 4	Level 5	Level 6
Amount	1500	2000	2500
Area	1504396	1829194	1700205
RF	0.000997077897043	0.001093377739047	0.001470410921035
Last Area	066	91	99
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 (r²): 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 Gemfibrosil

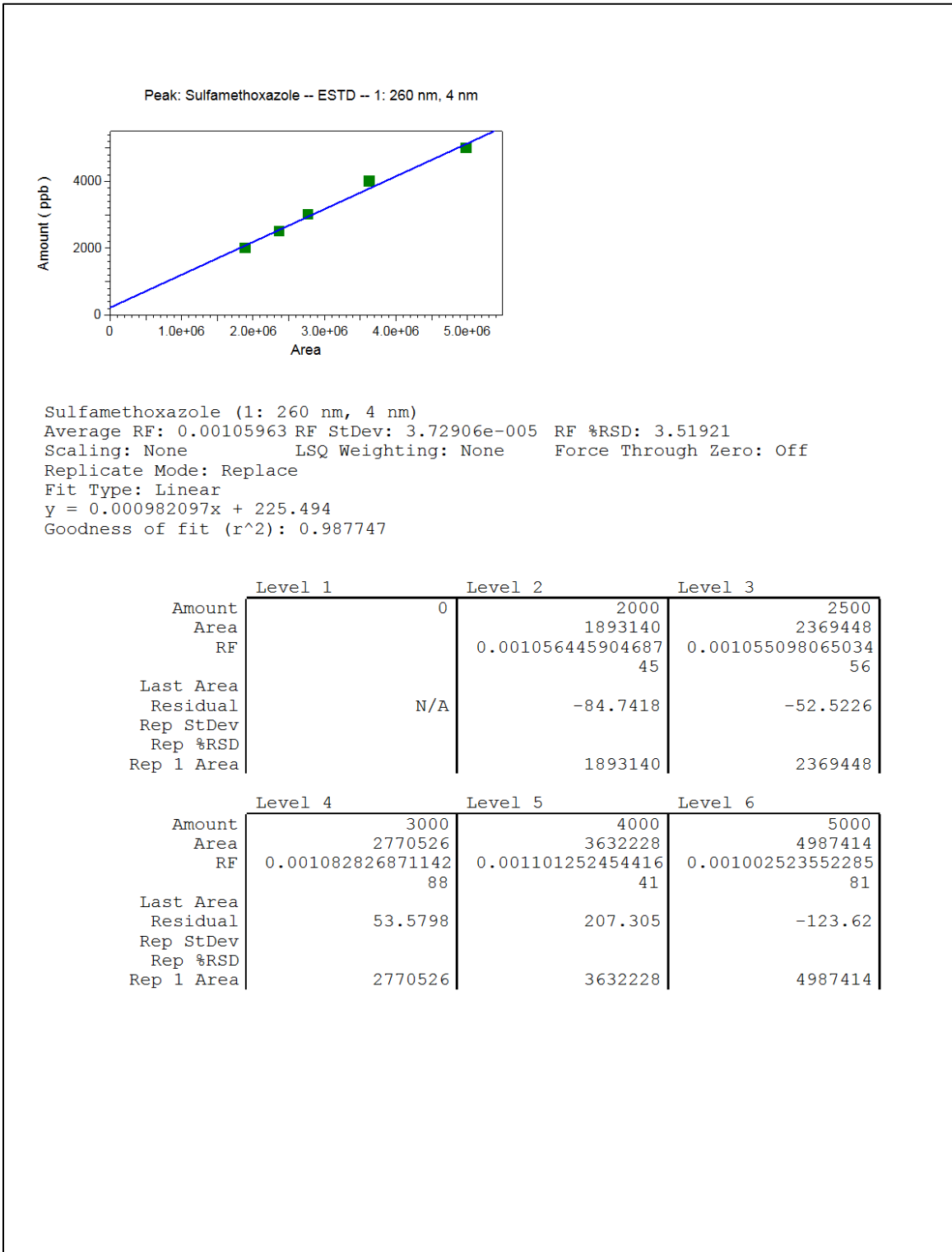
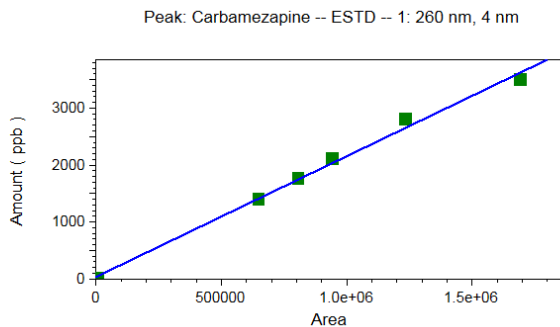


Figure C.13. Standard Curve for Sulfamethoxazole

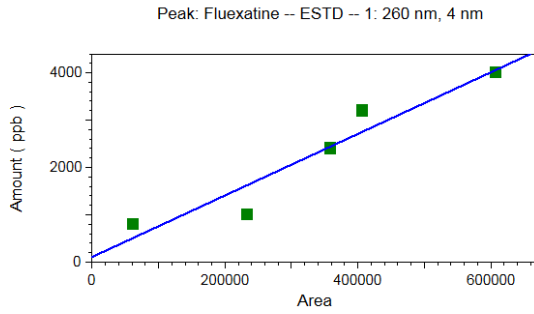


Carbamazepine (1: 260 nm, 4 nm)
 Average RF: 0.00181177 RF StDev: 0.000890131 RF %RSD: 49.1306
 Scaling: None LSQ Weighting: None Force Through Zero: Off
 Replicate Mode: Replace
 Fit Type: Linear
 $y = 0.00212261x + 33.9499$
 Goodness of fit (r^2): 0.993956

	Level 1	Level 2	Level 3
Amount	0	1400	1750
Area	10811	650029	807961
RF	0	0.002153750063458	0.002165946128587
Last Area		71	89
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
Last Area	39	88	62
Residual	59.4286	141.149	-131.041
Rep StDev			
Rep %RSD			
Rep 1 Area	945357	1236640	1694657

Figure C.14. Standard Curve for Carbamazepine



Fluoxetine (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		0.012823389863110	0.004282691928838
		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

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

Table C.1. Pesticide and PAH detection limits (from PSH Analysis)

Detection Limits (µg/L)
Acenaphthene 0.50
Acenaphthylene 0.50
Acetochlor 1.0
Alachlor 1.0
Aldrin 1.0
Anthracene 0.50
Atrazine 1.0
gamma-BHC 0.50
Benzo(a)anthracene 0.50
Benzo(a)pyrene 0.50
Benzo(b)fluoranthene 0.50
Benzo(g,h,i)perylene 0.50
Benzo(k)fluoranthene 0.50
Butachlor 1.0
Butylbenzylphthalate 2.5
Chrysene 0.50
4,4'-DDE 1.0
Di-n-Butylphthalate 2.5
Dibenzo(a,h)anthracene 0.50
Dibenzofuran 0.50
Dieldrin 1.0
Diethylphthalate 5.0
Dimethylphthalate 2.5
2,4-Dinitrotoluene 2.5
2,6-Dinitrotoluene 2.5
EPTC 1.0
Endrin 1.0
Di(2-Ethylhexyl)adipate 2.5
bis(2-Ethylhexyl)phthalate 5.0

Fluoranthene 0.50
Fluorene 0.50
Heptachlor 0.50
Heptachlor Epoxide 0.50
Hexachlorobenzene 0.50
Hexachlorocyclopentadiene 1.0
Indeno(1,2,3-cd)pyrene 0.50
Methoxychlor 1.0
2-Methylnaphthalene 1.0
Metolachlor 1.0
Metribuzin 1.0
Molinate 1.0
Naphthalene 1.0
Phenanthrene 0.50
Propachlor 1.0
Pyrene 0.50
Simazine 1.0
Terbacil 2.5
2,4,5-Trichlorobiphenyl 0.50