POLLUTANT ASSOCIATIONS
WITH PARTICULATES
IN STORMWATER

by

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A DISSERTATION

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LIST OF ABBREVIATIONS AND SYMBOLS

Zn	Zinc
Cu	Copper
Cd	Cadmium
Pb	Lead
Mg	Magnesium
Mn	Manganese
Fe	Iron
Al	Aluminum
Ca	Calcium
Na	Sodium
K	Potassium
N	Nitrogen
P	Phosphorus
Si	Silicon
Cr	Chromium
Co	Cobalt
Ni	Nickel
PO_4^{3-}	Phosphate ion
NO_3	Nitrate

H^+	Hydrogen ion
<	Less than
>	Greater than
µm	Micrometer
µg	Microgram
kg	Kilogram
cm	Centimeter
m	Meter
L	Liter
sec	Second
hr	Hour
%	Percent
IC_{50}	Approximate concentration required for 50% inhibition of bacterial fluorescence.
NTU	Nephlometric Turbidity Units
DOC	Dissolved Organic Carbon
EMC	Event Mean Concentration
PAH	Polyaromatic Hydrocarbon
SPLITT	Split-Flow Thin-Cell
STORET	STORage and RETrieval database.
NURP	National Urban Runoff Program
na	Not available, too few detectable observations for calculation
filt.	Filterable

part.	Particulate
NPDES	National Pollution Discharge Elimination System
MS4	Municipal Separate Storm Sewer System
CSO	Combined Sewer Overflow
USEPA	United States Environmental Protection Agency
ORP	Ortho-reactive phosphorous
BOD5	5-day Biological Oxygen Demand
d	particle diameter
ASV	Anodic Stripping Voltammetry
OAS	Osmotic Adjusting Solution

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ABSTRACT

Many studies have identified metals in urban runoff as a major contributor to the degradation of urban streams and rivers. Metals of most concern are copper, cadmium, chromium, lead, mercury, and zinc. Metals in urban runoff can occur as dissolved, colloidal and particulate-bound species. Therefore, it is important to measure all forms of heavy metals, especially the particulate and filterable fractions, when determining their fate and effects.

The objectives of these tests were to determine the associations of heavy metals and nutrients with different-sized particulates using cascade sieves and filters. Sequential extraction experiments were also conducted to examine the treatability and other characteristics of the filterable (<0.45 µm) portion of the heavy metals using Chelex-100 resin, UV-light exposure, and Anodic Stripping Voltammetry (ASV).

A decrease in concentration with sequential removal of particulates was obtained for total solids, turbidity, chemical oxygen demand and total phosphorus. Total solids, turbidity and total phosphorus were reduced by more than 50% with removal of particulates. Heavy metals were generally found more in the filterable fraction and not greatly removed by reduction in particulates. Less than 50% of Zn, Cu, Cd or Pb were associated with particulate fraction. New toxicity testing procedures were developed. Results showed that toxicity was not associated with the particulates in these samples. The use of ASV was also developed to measure the ionic forms of heavy metals in the filterable fractions. Good sensitivity was obtained by using Square Wave Stripping

Voltammetry with a 5 minute deposition time. The use of ASV with samples exposed to a ion exchange resin were unsuccessful. Colloidal analysis showed that most of the Zn, Cd and Pb were not present in the free ionic form, but were bound the colloids or organic matter whose bonds could be broken by exposure to UV light. Only Cu occurred in mostly the ionic form.

Recommendations for future research include work with the new toxicity test system, decreasing the detection limit of Zn measured by ASV, and developing the use of ASV for samples digested in nitric acid and for those exposed to the Chelex-100 ion exchange resin.

ABSTRACT OF DISSERTATION

The University of Alabama Graduate School

Degree: Doctor of Philosophy **Major Subject**: Civil Engineering

Name of Candidate: Renee E. Morquecho

Title of Dissertation: Pollutant Associations with Particulates in Stormwater

Many studies have identified metals in urban runoff as a major contributor to the degradation of urban streams and rivers. Metals of most concern are copper, cadmium, chromium, lead, mercury, and zinc. Metals in urban runoff can occur as dissolved, colloidal and particulate-bound species. Therefore, it is important to measure all forms of heavy metals, especially the particulate and filterable fractions, when determining their fate and effects.

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Recommendations for future research include work with the new toxicity test system, decreasing the detection limit of Zn measured by ASV, and developing the use of ASV for samples digested in nitric acid and for those exposed to the Chelex-100 ion exchange resin.

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CHAPTER 1

LITERTURE REVIEW

1.1 Heavy Metal Pollution of Stormwater

Many studies have identified heavy metals in urban runoff as a major contributor to the degradation of urban streams and rivers (Pitt *et al*, 1995; Drapper *et al*, 2000). Metals of most concern are copper, cadmium, chromium, lead, mercury, and zinc. Of these metals, copper and zinc are currently receiving the most attention due to their effects and their occurrence and concentrations in urban runoff. Metals in urban runoff can occur as dissolved, colloidal and particulate-bound species. Therefore, it is important to measure all forms of heavy metals, especially the particulate and filterable fractions, when determining their fate and effects. If possible, associations of the metals with different particle sizes should also be determined. Finally, to obtain the most meaningful data on either bioavailability or toxicity, it is important that chemical speciation techniques be applied (Florence and Bately, 1980). Chemical speciation is the determination of the individual concentrations of the various chemical forms of an element that together make up the total concentration of that element in a sample. Speciation of metals is dependent upon chemical and physical parameters such as pH, temperature and the presence of ligands and particulates. Depending upon the chemical form of the metal, a water with a high total metal concentration may be less toxic than another water with a lower total metal concentration (Florence and Batley, 1980).

The threat from metals to humans and aquatic life is due to their toxicity, persistence and bioaccumulation. It is important to determine the speciation of a metal because of the toxicity of many metals is related to their speciation and valence state. Most metals are essential nutrients for living cells, but only in small quantities. When metals are present in excess, they can become cumulative toxins. Some metals, such as mercury and lead, have no nutritional value and are considered dangerous, even in small concentrations.

1.2 Characteristics of Stormwater Affecting Treatability of Heavy Metals

1.2.1 Dissolved and Particulate Forms of Pollutants

Table 1 summarizes the filterable fraction of heavy metals found in stormwater runoff sheet flows from many urban areas (Pitt, *et al*. 1995). Constituents that are mostly in filterable forms have a greater potential of affecting groundwater and are more difficult to control using conventional stormwater control practices that mostly rely on sedimentation and filtration principles. Luckily, most of the metals are associated with the non-filterable (suspended solids) fraction of stormwater. Likely exceptions include zinc which may be mostly found in the filtered sample portions. However, dry-weather flows in storm drainage tend to have much more of the heavy metals associated with filtered sample fractions.

Table 1: Reported filterable fractions of stormwater heavy metals from source areas.

Constituent	**Filterable Fraction (%)**
Cadmium	20 to 50
Chromium	<10
Copper	<20
Iron	small amount
Lead	<20
Nickel	small amount
Zinc	>50

Source: Pitt, *et al*. 1995

Pitt, et al. (1998) analyzed 550 samples for a broad list of constituents, including the total and filtered observations shown in Table 2. The samples were collected from telecommunication manhole vaults that were mostly affected by stormwater. However, some other contaminating water and groundwater sources likely also influenced these samples. Most of the copper and lead were associated with the particulates, whereas most of the zinc was found in the filterable fractions. These data are very similar to cold and warm season stormwater data collected during other projects. This is the largest data base available that contains both total and filtered analyses. These samples were obtained throughout the US and represent all seasons.

Table 2: Average Particulate Fraction of Selected Constituents from 550 Nationwide Samples (mg/L, unless otherwise noted).

Constituents	**Total Concentration**	**Filtered Concentration (after a 0.45 µm membrane filter)**	**Percent Associated with Filterable Fraction**	**Percent Associated with Particulates**
Turbidity (NTU)	13	1.2	8%	91%
COD	25	22	86%	14%
Color (HACH)	34	20	59%	41%
Copper (µg/L)	29	9.5	33%	67%
Lead (µg/L)	14	3	21%	79%
Zinc (µg/L)	230	160	70%	30%

Source: Pitt, *et al.* (1998)

Harrison and Wilson (1985) examined the chemical associations of Cd, Cu, Pb, Mn and Fe in roadside drainage and receiving stream waters. Samples were taken during different stages of a storm event. They found that the water-soluble or dissolved metals were subject to a “first-flush” effect, while the metals which were substantially particle-associated were dependent upon flow capable of mobilizing particles from the road surface and drainage system. Fe and Pb were particle-associated, while Cd and Cu were associated more with colloidal material.

Sansalone (1996) investigated the forms of heavy metals in stormwater and snowmelt. It was found that Zn, Cd, and Cu were mainly dissolved in stormwater, while only Pd was mainly dissolved in snowmelt. Pb was associated with the finer particulate fractions in both stormwater and snowmelt. The authors suggested that the dissolved fraction of the metals be immobilized by sorption, while the particulate bound metals should be immobilized by filtration in a partial exfiltration trench. Another study by

Sansalone and Buchberger (1997a) analyzed lateral pavement sheetflow for five events on a heavily traveled roadway in Cincinnati, Ohio. They found that the event-mean concentrations (EMC) of Zn, Cd, and Cu were relatively high. Further, it was noted that Zn, Cd, and Cu were mainly in the dissolved form while other metals, i.e., Pb, Fe, and Al were mainly bound to particles.

Sansalone and Glenn (2000) analyzed stormwater for eight events during 1996 and 1997 from the same highway in Cincinnati, Ohio. Their results indicated that Zn, Cd and Cu masses were predominately dissolved in pavement sheetflow and that chemical treatment will be required in order to immobilize the dissolved metal mass.

Dean *et al* (2005) examined speciation of Pb, Cd, Cu and Zn in four samples from an elevated section of I-10 transversing City Park Lake in Baton Rouge, LA. They found that Cd and Cu partitioned nearly equally between particulate and dissolved phases while Zn was generally particulate-bound and Pb was highly particulate-bound. Using water quality anlalyses, measured ion balances and speciation modeling, results for Cd and Zn indicated that divalent ionic forms of these metals dominated the dissolved species for all events, while Pb was predominately associated with dissolved organic matter (DOM), and Cu was predominately associated with carbonate species or DOM.

Morrison and Diaz-Diaz (1988) looked at the association of copper with dissolved organic matter in urban runoff using gel filtration chromatography. Their results indicated that Cu preferentially associates with organic matter in stormwater. Spokes, *et al*. (1996) found that copper was largely bound to organic ligands in rainwater samples in Norwich, England.

Grout, *et al*. (1999) studied the colloidal phases in urban stormwater runoff entering Brays Bayou (Houston, Texas). Colloids in the filtrate (after 0.45 µm filtering) and further separation by ultracentrifuging, accounted for 79% of the Al, 85% of the Fe, 52% of the Cr, 43% of the Mn, and 29% of the Zn present in the filtrates. Changes in the colloidal composition were caused by changes in colloidal morphologies, varying from organic aggregates to diffuse gel-like structures rich in Si, Al, and Fe. Colloids were mostly composed of silica during periods of dry weather flow and at the maximum of the stormwater flow, while carbon dominated the colloidal fraction at the beginning and declining stages of the storm events. Garnaud, *et al.* (1999) examined the geochemical speciation of particulate metals using sequential extraction procedures for different runoff sources in Paris, France. They found that most metals were bound to acid soluble particulates in the runoff but that Cu was almost entirely bound to oxidizable and residual fractions.

Barry, *et al*. (1999) identified salinity effects on the partitioning of heavy metals in the stormwater canals entering Port Jackson (Sydney), Australia. Cu, Pb, and Zn were found increasingly in dissolved phases as the salinity increased in the lower sections of the canals. During high flows, most of the metals seemed to be rapidly exported from the estuary as a discrete surface layer, while low flows contributed most of the metals to the estuary.

Water quality and particle-size distribution were characterized from urban stormwater runoff from four sites in the Galveston Bay area of Texas (Characklis and Wiesner, 1997). Results indicated a potential relationship between Zn and organic carbon and Fe and macrocolloids (0.45 – 20 µm size range) Results also indicated that concentrations of particle ion number, organic carbon, suspended solids, Fe and Zn increased during storm events, but showed no evidence of a “first flush” effect.

Shafer, *et al*. (1999) investigated the partitioning of trace metal levels (Al, Cd, Cu, Pb, and Zn) in Wisconsin rivers and found that the concentrations in the rivers were comparable to recent data collected in the Great Lakes and other river systems where ‘modern’ clean methods were used for sampling and analysis. They also found that the variation in the partitioning coefficients of each metal between sampling locations could be explained by the amount of anthropogenic disturbance in the watershed and by the concentration of dissolved organic carbon (DOC) in the water.

Parker, *et al*. (2000) analyzed the particulates found in urban stormwater in the Phoenix, Arizona, metropolitan area. They found that the inorganic content of the particulates was similar to that in soils that were not impacted by urban runoff. The metals concentrations (Cd, Cu, Pb, and Zn) were higher, but below levels that may require remediation. Arsenic concentrations were above recommended levels; however, this contribution likely was geologic and not anthropogenic. Sediment toxicity was seen, but could not be explained based on their chemical results.

Krein and Schorer (2000) investigated heavy metals and PAHs in road runoff and found that, as expected, an inverse relationship existed between particle size and particle-bound heavy metals concentrations. Sutherland, *et al*. (2000) investigated the potential for road-deposited sediments in Oahu, Hawaii, to bind contaminants, and thus transport these bound contaminants to the receiving water as part of the runoff load. In the sediment fractions less than 2 mm in diameter, the origins of the Al, Co, Fe, Mn and Ni were determined to be geologic. Three of the metals concentrations (Cu, Pb and Zn) were found to be enhanced by anthropogenic activities. Sequential extraction of the sediment determined the associations of the metals with the following fractions: acid extractable, reducible, oxidizable, and residual.

The fate and transport of metallic pollutants through a watershed were related to the characteristics of the solid particles to which they are bound (Magnuson, *et al*. 2001). Because the particles most often associated with metal pollution have nominal diameters of < 50 µm, split-flow thin-cell (SPLITT) fractionation was investigated as a means to study the metal loading as a function of particle settling rate. Sansalone, *et al*. (2001) showed that urban stormwater levels of Zn, Cu, Cd, Pb, Cr, and Ni can be significantly above ambient background levels for both dissolved and particulate-bound fractions. The authors advocated a multiple-unit-operation approach to stormwater treatment.

Glenn, *et al.* (2001) described their research at highway test sites in Cincinnati, OH, investigating the effects of traffic activities and winter maintenance on the behavior of particulates in the runoff. They found that urban snow has a much greater capacity to accumulate traffic-related pollutants, as compared to stormwater, due to longer residence times before melting, and the snow's porous matrix. Parameters such as residence time, solids loadings, alkalinity, hardness and pH influence the heavy metal partitioning in the snow. They found that Pb, Cu, Cd, Zn, Al, Mg, and Fe were mostly particulate bound, while Na and Ca were mostly dissolved. Partition coefficients for most heavy metals in snowmelt water ranged from 103 to 106 L/kg.

Significant amounts of non-point source runoff were shown to enter the Santa Monica Bay (CA) from the Ballona Creek Watershed during wet weather flow during monitoring by Buffleben, *et al.* (2001). The watershed is developed mostly with residential, commercial and light industrial land uses. They found that the suspended solids phase primarily transported the mass for five of the six metals studied: Cd, Cr, Cu, Pb, and Ni. Arsenic was found primarily in the aqueous phase.

Mosley and Peake (2001) characterized urban runoff from a catchment in Dunedin, New Zealand, during base flows and storm flows from five rainfall events. Fe and Pb were found to be predominantly particle-associated (>0.4 μm) with concentrations increasing significantly at the beginning of storm runoff. In contrast, the majority of Cu and Zn was found in the <0.4 μm fraction prior to rain, but a significant proportion was present in the >0.4 μm fraction during the initial period of storm flows. The results indicate that Cu and Zn may be more bioavailable, and more difficult to remove by stormwater treatment than Pb. The pH level and the concentration of major ions (Ca^{+2}, Na^{+}, Mg^{+2}, K^{+}), dissolved PO_4^{-3}, and NO_3 generally decreased during storm flows due to rainwater dilution. Concentrations of total N and P often increased during the initial period of storm runoff, likely because of wash-off of particulate plant material.

Fan, *et al.* (2001) reviewed the transport of toxic pollutants through multiple media and drainage systems in the urban watershed during wet-weather periods. Field studies have identified that a major portion of hazardous waste priority pollutants including benzene, polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, and heavy metals (e.g., arsenic, cadmium, chromium, copper, lead, mercury, and zinc) contained in urban stormwater runoff are in particulate form, or sorbed onto particles.

Tobiason (2004) studied the removal of metals from roof runoff through media filtration. In particular, he looked at zinc runoff from a 1-acre metal-roofed building and tested different media for the ability to remove zinc from the roof runoff. He found that the concentration of zinc in the runoff ranged from 0.42 mg/L to 14.7 mg/L and averaged 86% dissolved.

DeCarlo *et al* (2004) studied the composition of water and suspended sediment in streams of urbanized watersheds in Hawaii. They found that suspended particulate matter controlled most of the trace element transport and that Pb, Zn, Cu, Ba and Co exhibited increased concentrations with urbanized portions of the watershed. Colich (2004) in his study of stormwater runoff from the Evergreen Point Floating Bridge in Seattle, WA found elevated concentrations of metals, especially copper and zinc, when compared to the water body. During high-volume traffic times, the concentrations were up to three times higher than at the low-traffic volume times.

Deletic and Orr (2005) collected sediment from an urban road in Aberdeen, Scotland using a “wet” technique that involved washing the designated surfaces. They measured heavy metals (Zn, Cu, Pb and Cd) only in their particulate forms. They found the highest concentrations of heavy metals in the smallest particle size fraction analyzed (<63 µm).

Tables 3 through 5 summarize the particulate and filterable fraction of stormwater heavy metals from a number of studies. In almost all cases, the heavy metals are mostly associated with particulates, except for Zn which is mostly associated with the filterable fraction. Interesting exceptions are noted, however. Zinc stormwater concentrations from Birmingham industrial storage areas were found to be almost completely associated with the particulate fraction. These samples were apparently not affected by runoff from areas having galvanized metals, but were affected by heavy truck traffic, where the particulate forms of Zn would be mostly from tire wear.

Table 3: Filterable Fraction of Heavy Metals Observed at the Inlet to the Monroe St. Wet Detention Pond, Madison, WI (average and standard deviation).

	Copper	Lead	Zinc
Number of observations	60 to 64	59 to 64	57 to 64
Average total concentration (µg/L)	50 (14)	85 (52)	152 (136)
Average filtered concentration (µg/L)	6.4 (3.3)	3.5 (1.7)	51 (34)
Average percentage filterable	13%	4.1%	34%
Average percentage associated with particulates	87%	96%	66%

Data from: House, *et al*. 1993.

Table 4: Milwaukee and Long Island NURP Source Area Heavy Metal Associations (based on mean concentrations observed).

	Residential roof runoff % filt	 % part	Commercial parking runoff % filt	 % part
Arsenic[b]			25	75
Cadmium[b]			18	82
Chromium[b]			24	76
Lead[a]	8	92	3	97
Lead[b]			16	84

[a] Bannerman, *et al*. 1983 (Milwaukee) (NURP)

[b] STORET Site #596296-2954843 (Huntington-Long Island, NY) (NURP)

Table 5: Birmingham, AL, Source Area Heavy Metal Particulate Associations (based on mean concentrations observed)

	Roof areas (12 samples)		Parking areas (16 samples)		Storage areas (8 samples)		Street runoff (6 samples)		Loading docks (3 samples)		Vehicle service areas (5 samples)		Landscaped areas (6 samples)		Urban creeks (19 samples)		Detention ponds (12 samples)	
	% filt	% part	% filt	% part	% filt	% part	% filt	% part	% filt	% part	% filt	% part	% filt	% part	% filt	% part	% filt	% part
Aluminum	3.4	97	13	87	7.8	92	29	71	na[a]	na	25	75	52	48	31	69	47	53
Cadmium	12	88	9.5	90	36	64	1	99	29	71	3.2	97	na	na	2.4	98	25	75
Copper	2.6	97	9.5	90	86	14	1.4	99	40	60	6.2	94	5.1	95	2.8	97	47	53
Chromium	2.1	98	4.1	96	15	85	18	82	na	na	na	na	2.5	97	2.5	97	5.4	95
Lead	2.7	97	4.6	95	2.5	97	4.6	95	na	na	3.8	96	na	na	7.0	93	5.3	95
Nickel	na	na	11	89	Na	na	na	na	na	na	na	na	na	na	7.9	92	13	87
Zinc	88	12	78	22	1.3	99	53	47	60	40	70	30	61	39	100	0	100	0

[a] na: not available, too few detectable observations for calculation

Pitt, *et al.* 1999

The University of Alabama and the Center for Watershed Protection has collected and reviewed Phase I NPDES (National Pollutant Discharge Elimination System) MS4 (municipal separate storm sewer system) stormwater data. The National Stormwater Quality Database (NSQD) contains more than 3700 data sets from 66 municipalities in 17 states (Pitt, R. *et al.*, 2003). Table 6 summarizes the total and filtered Cd, Cu, Pb and Zn data from four landuses included in the database. Cd, Zn and Cu had larger filtered fractions, whereas most of the Pb was non-filterable

Table 6: Summary of available heavy metal stormwater data included in the NSQD, version 1.1

	Cd, total (µg/L)	**Cd, filtered (µg/L)**	**Cu, total (µg/L)**	**Cu, filtered (µg/L)**	**Pb, total (µg/L)**	**Pb, filtered (µg/L)**	**Zn, total (µg/L)**	**Zn, filtered (µg/L)**
Overall (3765)								
Number of observations	2575	389	2724	411	2950	446	3008	382
Median	1.0	0.50	16	8.0	17.0	3.0	117	52
Coefficient of variation	3.7	1.1	2.2	1.6	1.8	2.0	3.3	3.9
Residential (1069)								
Number of observations	723		799	90	788	108	810	88
Median	0.5		12	7.0	12.0	3.0	73	31.5
Coefficient of variation	3.4		1.8	2.0	1.9	1.9	1.3	0.8
Commercial (497)								
Number of observations	358	47	387	48	377	59	392	49
Median	0.89	0.30	17	7.57	18.0	5.0	150	59
Coefficient of variation	2.7	1.34	1.5	0.8	1.6	1.6	1.2	1.4
Industrial (524)								
Number of observations	395	42	416	42	412	51	433	42
Median	2.0	0.60	22	8.0	25.0	5.0	210	112
Coefficient of variation	2.3	1.1	2.0	0.7	1.8	1.6	2.3	3.6
Freeways (185)								
Number of observations	95	114	97	130	107	126	93	105
Median	1.0	0.68	34.7	10.9	25	1.8	200	51
Coefficient of variation	0.9	1.0	1.0	1.5	1.5	1.7	1.0	1.9

1.1.2 Particle Size

Knowing the settling velocity characteristics associated with stormwater particulates is necessary when designing controls relying on sedimentation controls, such as wet detention ponds. Particle size is directly related to settling velocity and is usually used in the design of detention facilities. Particle size can also be much more rapidly measured in the laboratory than settling velocities. Settling tests for stormwater particulates need to be conducted for about three days in order to quantify the smallest particles that are of interest in the design of stormwater controls. If designing rapid treatment systems (such as grit chambers or vortex separators for CSO treatment), then much more rapid settling tests can be conducted. Probably the earliest description of conventional particle settling tests for stormwater samples was made by Whipple and Hunter (1981).

Whipple and Hunter (1981) contradict the assumption sometimes used in modeling detention pond performance that pollutants generally settle out in proportion to their concentrations. However, Grizzard and Randall (1986) have shown a relationship between particulate concentrations and particle size distributions. High particulate concentrations were found to be associated with particle size distributions that had relatively high quantities of larger particulates, in contrast to waters having low particulate concentrations. The high particulate concentration water would therefore have increased particulate removals in detention ponds. This relationship is expected to be applicable for pollutants found mostly in particulate forms (such as suspended solids and most heavy metals), but the relationship between concentration and settling would be much poorer for pollutants that are mostly in soluble forms (such as filterable residue, chlorides and most nutrients). Therefore, the partitioning of specific pollutants between the "particulate" and "dissolved" forms, and eventually for different particulate size fractions, is needed.

Smith (1982) also states that settleability characteristics of the pollutants, especially their particle size distribution, is needed before detention pond analyses can be made. Kamedulski and McCuen (1979) report that as the fraction of larger particles increase, the fraction of the pollutant load that settles also increases. Randall, *et al.* (1982), in settleability tests of urban runoff, found that non-filterable residue (suspended solids) behaves liked a mixture of discrete and flocculant particles. The discrete particles settled out rapidly, while the flocculant particles were very slow to settle out. Therefore, simple particle size information may not be sufficient when flocculant particles are also present. Particle size analyses should include identification of the particle by microscopic examination to predict the extent of potential flocculation.

Figure 1 shows approximate stormwater particle size distributions derived from several upper Midwest and Ontario analyses, from all of the NURP data (Driscoll, 1986), and for several eastern sites that reflect various residue concentrations (Grizzard and Randall, 1986). Pitt and McLean (1986) microscopically measured the particles in selected stormwater samples collected during the Humber River Pilot Watershed Study in Toronto. The upper Midwest data sources were two NURP projects: Terstriep, *et al.* (1982), in Champaign/Urbana, IL, and Akeley (1980) in Washtenaw County, MI.

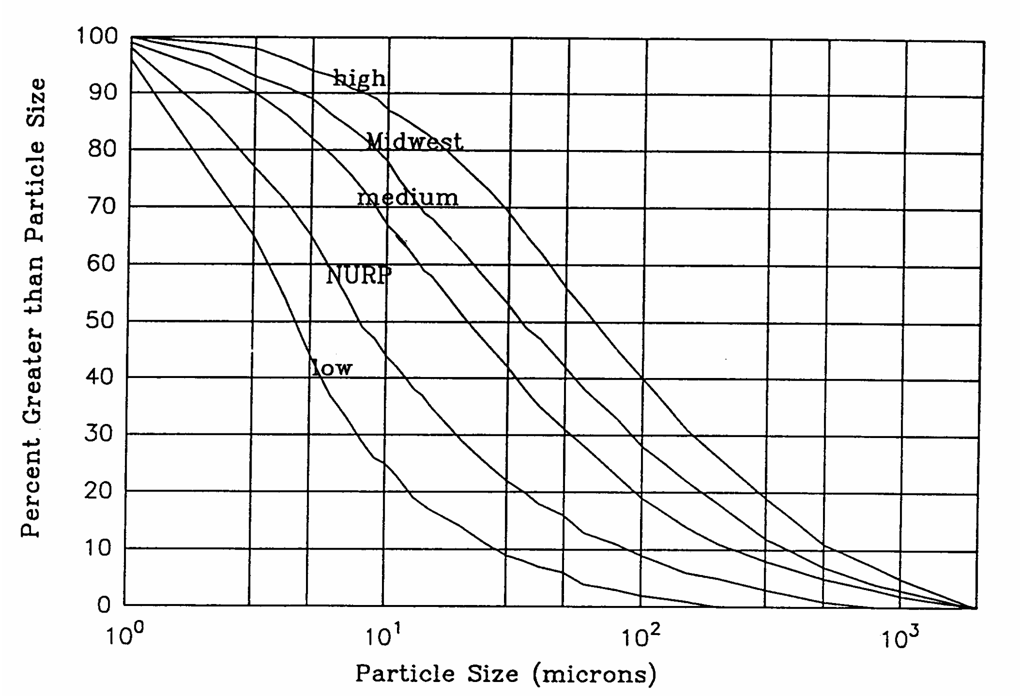

Figure 1: Particle size distributions for various stormwater sample groups.

Relatively few samples have been analyzed for stormwater particle sizes (compared to the much more common TSS measurements) and no significant trends have been identified relating the particle size distribution to land use or storm condition. However, the work by Grizzard and Randall (1986) does indicate significantly different particle size distributions for stormwaters from the same site having different suspended solids concentrations. The highest suspended solids concentrations were associated with waters having relatively few small particles, while the low suspended solids concentration waters had few large particles. The particle size distribution for the upper Midwest urban runoff samples falls between the medium and high particulate concentration particle size distributions.

Specific conditions (such as source area type, rain conditions and upstream controls) have been shown to have dramatic effects on particle size distributions. Randall, *et al.* (1982) monitored particle size distributions in runoff from a shopping mall that was cleaned daily by street cleaning. Their data (only collected during the rising limb of the hydrographs) showed that about 80 percent of the particles were smaller than 25 µm, in contrast to about 40 percent that were smaller than 25 µm during the outfall studies. They also only found about two percent of the runoff particles in sizes greater than 65 µm, while the outfall studies found about 35 percent of the particles in sizes greater than 65 µm. This shopping mall runoff would therefore be less effectively treated by sedimentation controls because of the relatively smaller fraction of large particles present.

Tests have also been conducted to examine the routing of particles through the Monroe Street detention pond in Madison, Wisconsin (House, L.B. *et al*., 1993). This detention pond serves an area that is mostly comprised of medium residential, with some strip commercial areas. This joint project of the Wisconsin Department of Natural Resources and the U.S. Geological Survey has obtained a number of inlet and outlet particle size distributions for a wide variety of storms. The observed median particle sizes ranged from about 2 to 26 µm, with an average of 9 µm. Table 7 shows the average particle sizes corresponding to various distribution percentages for the Monroe St. outfall. These distributions included bedload material that was also sampled and analyzed during these tests. This distribution is generally comparable to the "all NURP" particle size distribution presented previously.

Table 7: Average particle sizes for Monroe Street outfall in Madison, WI.

Percent larger than size	Particle Size (μm)
10	450
25	97
50	9.1
75	2.3
90	0.8

The particle size distributions of stormwater at different locations in an urban area greatly affect the ability of different source area and inlet controls in reducing the discharge of stormwater pollutants. Pitt, R. (1995) examined the sources and treatability of urban stormwater pollutants. This research has included particle size analyses of 121 stormwater inlet samples from three states (southern New Jersey; Birmingham, Alabama; and at several cities in Wisconsin) in the U.S. that were not affected by stormwater controls. Particle sizes were measured using a Coulter Counter Multisizer IIe and verified with microscopic, sieve, and settling column tests. Figures 2 through 4 are grouped box and whisker plots showing the particle sizes (in μm) corresponding to the 10th, 50th (median) and 90th percentiles of the cumulative distributions. If 90 percent control of suspended solids (by mass) was desired, then the particles larger than the 90th percentile would have to be removed, for example. In all cases, the New Jersey samples had the smallest particle sizes (even though they were collected using manual "dipper" samplers and not automatic samplers that may miss the largest particles), followed by

Wisconsin, and then Birmingham, AL, which had the largest particles (which were collected using automatic samplers and had the largest rain intensities). The New Jersey samples were obtained from gutter flows in a residential neighborhood that was xeroscaped. The Wisconsin samples were obtained from several source areas, including parking areas and gutter flows mostly from residential, but from some commercial areas, and the Birmingham samples were collected from a long-term parking area on the University of Alabama at Birmingham campus.

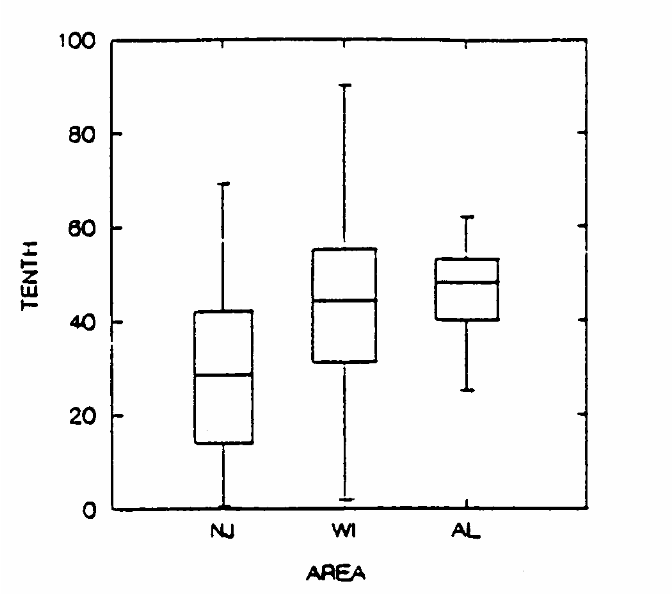

Figure 2: Tenth percentile particle sizes for stormwater inlet flows (Pitt, et al. 1997).

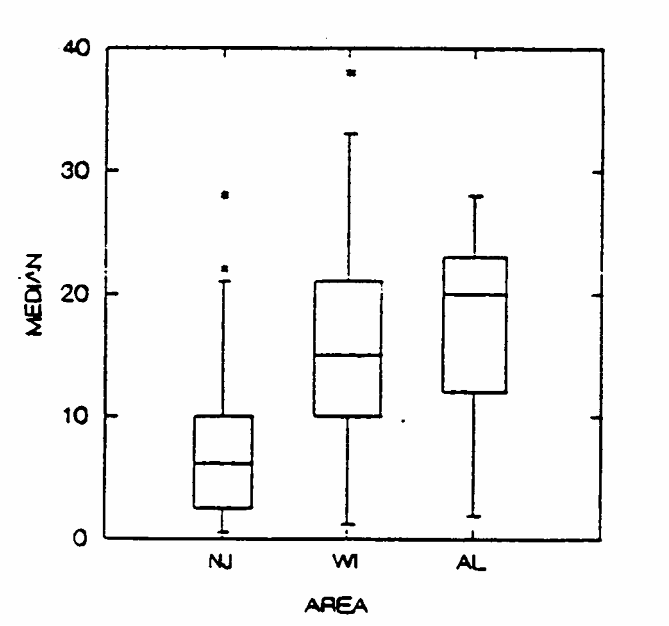

Figure 3: Fiftieth percentile particle sizes for stormwater inlet flows (Pitt, *et al.* 1997).

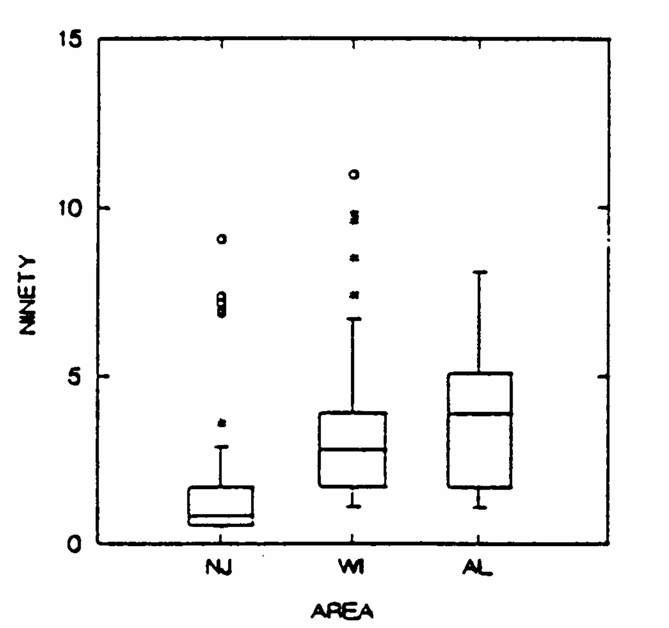

Figure 4: Ninetieth percentile particle sizes for stormwater inlet flows (Pitt, *et al.* 1997).

The median particle sizes ranged from 0.6 to 38µm and averaged 14µm. The 90th percentile sizes ranged from 0.5 to 11µm and averaged 3µm. These particle sizes are all substantially smaller than have been typically assumed for stormwater. Stormwater particle size distributions typically do not include bed load components because automatic sampler intakes are usually located above the bottom of the pipe where the bed load occurs. During the Monroe St. (Madison, WI) detention pond monitoring, the USGS and WI DNR installed special bed load samplers that trapped the bed load material for analysis (House, *et al*. 1993). Figure 5 shows the particle size distribution for the inflow events, including bed load, for the influent water at the Monroe St. detention pond site in Madison, WI. The additional bed load comprised about 10 percent of the annual total solids loading. This is not a large fraction of the solids, but it represents the largest particle sizes flowing in the stormwater and it can be easily trapped in most detention ponds or catchbasins. The bed load component in Madison was most significant during the early spring rains when much of the traction control sand that could be removed by rains was being washed from the streets. The median size was about 8 µm, but it ranged from about 2 to 30 µm.

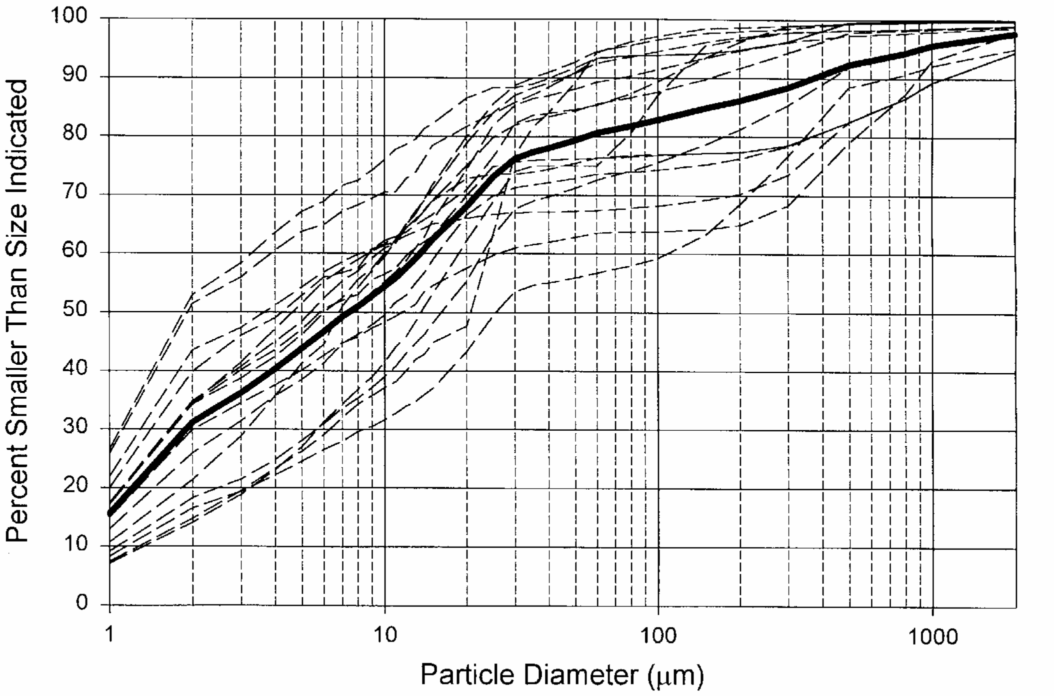

Figure 5: Inlet particle size distributions observed at the Monroe Street wet detention pond.

Additional data obtained by Pitt, *et al.* (1997) for the USEPA described particle sizes from many different source flows in the Birmingham, AL, area. These data did not indicate any significant differences in particle size distributions for different source areas or land uses, except that the roof runoff had substantially smaller particle sizes than the other areas sampled.

The settling velocities of discrete particles can be predicted using Stoke's and Newton's settling equations. Probably more than 90% of all stormwater particulates (by volume and mass) are in the 1 to 100 μm range, corresponding to Laminar flow conditions. In most cases, stormwater particulates have specific gravities in the range of 1.5 to 2.5 (determined by conducting settling column, sieving, and microscopic evaluations of the samples, in addition to particle counting), corresponding to a relatively narrow range of settling rates for a specific particle size.

1.1.3 Particle Settling Velocities

The settling velocities of discrete particles are shown in Figure 6, based on Stoke's and Newton's settling relationships. This figure also illustrates the effects of different specific gravities on the settling rates. In most cases, stormwater particulates have specific gravities in the range of 1.5 to 2.5. This corresponds to a relatively narrow range of settling rates for a specific particle size. Particle size is much easier to measure than settling rates and it is generally recommended to measure particle sizes using automated particle sizing equipment and to conduct periodic settling column tests to determine the corresponding specific gravities. If the particle counting equipment is not available, then small scale settling column tests (using 50 cm diameter Teflon™ columns about 0.7 m long) can be easily used.

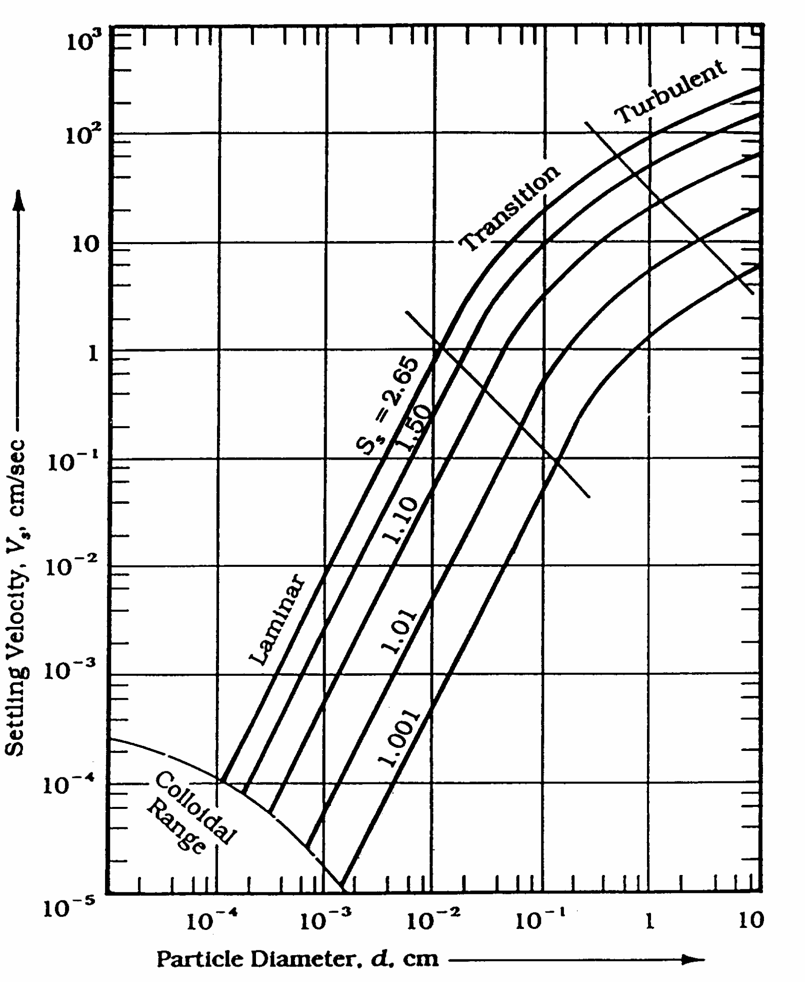

Figure 6: Type 1 (discrete) settling of spheres in water at 10° C.

1.2 Pollutant Associations with Stormwater Particulates

Randall, *et al.* (1982), recognized the strong correlation between pollutant removal effectiveness in wet detention ponds and pollutant associations with suspended solids. High lead removals were related to lead's affinity for suspended solids, while much smaller removals of BOD_5 and phosphorus were usually obtained because of their significant soluble fractions.

Wet detention ponds also are biological and chemical reactors. Dally, *et al.* (1983) monitored heavy metal forms in runoff entering and leaving a wet detention pond serving a bus maintenance area. They found that metals entering the monitored pond were generally in particulate (nonfilterable) forms and underwent transformations into filterable (smaller than 0.2 µm in size) forms. The observed total metal removals by the pond were generally favorable, but the filterable metal outflows were much greater than the filterable metal inflows. This effect was most pronounced for Cd and Pb. Very little changes in Zn were found, probably because most of the Zn entering the pond was already in filterable forms. These metal transformations may be more pronounced in wet detention ponds that in natural waters because of potentially more favorable (for metal dissolution) pH and ORP conditions in wet pond sediments. Other studies have found similar transformations in the forms and availability of nutrients in wet detention ponds, usually depending on the extent of algal growth and algal removal operations.

Vignoles and Herremans (1995) examined heavy metal associations with different particles sizes in stormwater samples from Toulouse, France. They found that the vast majority of the heavy metal loadings in stormwater were associated with particles less than 10 µm in size, as shown on Table 8. They concluded that stormwater control practices must be able to capture the very small particles.

Table 8. Percentages of Suspended Solids and Distribution of Heavy Metal Loadings Associated with Various Stormwater Particulate Sizes (Toulouse, France) (Percentage associated with size class, concentration in mg/kg).

	>100 µm	**50 - 100 µm**	**40 - 50 µm**	**32 - 40 µm**	**20 - 32 µm**	**10 - 20 µm**	**<10 µm**
Suspended solids	15%	11%	6%	9%	10%	14%	35%
Cadmium	18 (13)	11 (11)	6 (11)	5 (6)	5 (5)	9 (6)	46 (14)
Cobalt	9 (18)	5 (16)	4 (25)	6 (20)	6 (18)	10 (22)	60 (53)
Chromium	5 (21)	4 (25)	2 (26)	6 (50)	3 (23)	9 (39)	71 (134)
Copper	7 (42)	8 (62)	3 (57)	4 (46)	4 (42)	11 (81)	63 (171)
Manganese	8 (86)	4 (59)	3 (70)	3 (53)	4 (54)	7 (85)	71 (320)
Nickel	8 (31)	5 (27)	4 (31)	5 (31)	5 (27)	10 (39)	63 (99)
Lead	4 (104)	4 (129)	2 (181)	4 (163)	5 (158)	8 (247)	73 (822)
Zinc	5 (272)	6 (419)	3 (469)	5 (398)	5 (331)	16 (801)	60 (1,232)

Source: Vignoles and Herremans (1995)

Sansalone and Buchberger (1997b) also examined heavy metal associations with particles sizes in Cincinnati, Ohio. The solids in this study were separated mechanically using sieves from 9500µm to 25µm. Their results indicated a similar trend as that found by Vignoles and Herremans in that most of the heavy metal loadings were associated with the smallest particulate sizes.

Particulate pollutant strength (or potency factor) is the ratio of a particulate pollutant concentration to the suspended solid concentration, expressed in mg/kg. The strengths of stormwater particulates were calculated for each pollutant with a particulate form and plotted on a probability versus strength chart for the Madison, WI, data from House, *et al*. (1993) shown in Figure 7 for Zn. All pollutants had higher outlet than inlet strength values due to preferential removals of large particles in the detention pond, leaving relatively more small particles in the discharge water. The small particles in stormwater have higher pollutant strengths than the large particles.

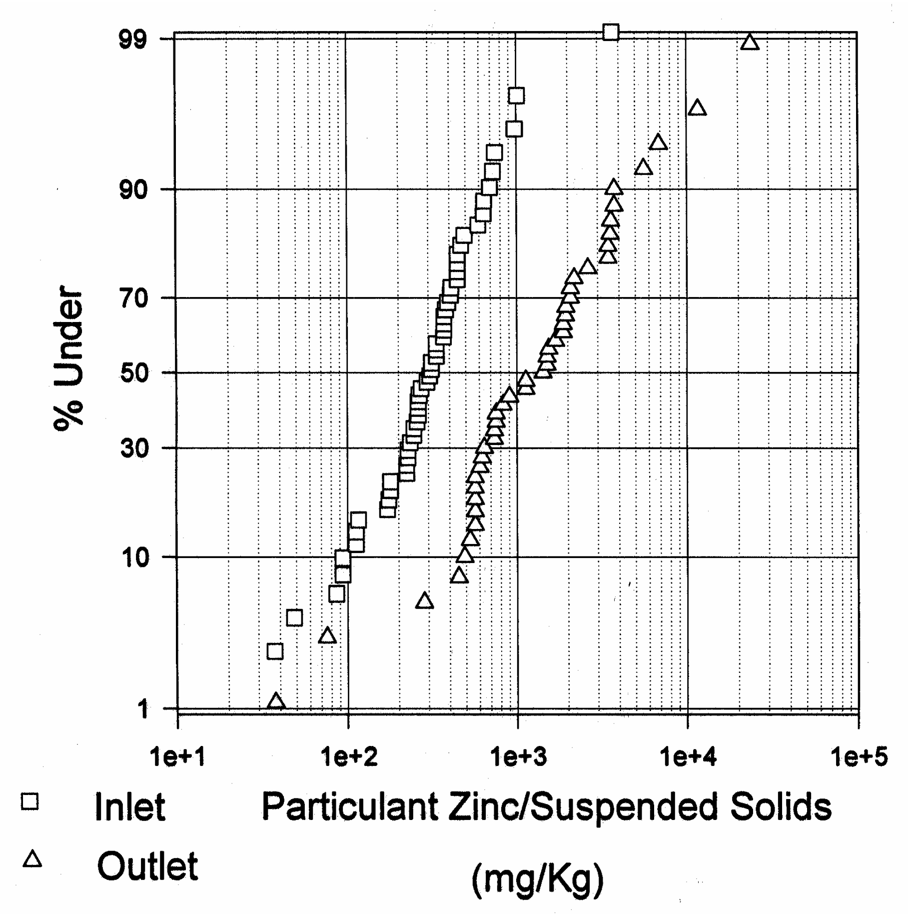

Figure 7 Particulate pollutant strengths for zinc (data from House, et al. 1993).

1.3 Development of Analytical Techniques

Measurement of the total metal concentration in a water sample provides little information about the bioavailability and/or toxicity of the metal. It has become more apparent that metal speciation is essential to understanding the fate of a metal and its availability to biota. In natural waters, only a small portion of the overall dissolved metal may be present as the free hydrated cations because metal ions form stable complexes with a large variety of inorganic and organic ligands, which influence the bioavailability, toxicity, and mobility of the metal (Mota and Correia Dos Santos, 1995). In the case of metal toxicity, it is generally accepted that the free metal ion is the form most toxic to aquatic life. Strongly complexed metal, or metal associated with colloidal particles, is much less toxic (Florence and Batley, 1980). To obtain meaningful data on either bioavailability or toxicity, it is essential that chemical speciation techniques be applied.

The development of analytical techniques which can reliably measure the concentration of the various chemical forms of a trace metal in a water sample is a challenging problem. Florence (1977) proposed a trace metal speciation scheme for determining the chemical forms of Cu, Pb, Cd and Zn in natural fresh waters (Figure 8). This scheme utilizes the chelating resin Chelex-100 to separate ionic and colloidal metal fractions and involves both ultraviolet irradiation and chelating resin separation steps, along with anodic stripping voltammetry (ASV) for measurements of labile and total metal in the separated fractions. For natural fresh waters using the new scheme, measurements showed that 1) copper was associated mainly with organic matter, probably organic colloids; 2) lead was divided between stable inorganic and organic forms; 3) cadmium existed almost entirely as labile ionic forms; and 4) zinc was divided between labile ionic species and a stable inorganic form. Very little zinc was associated with organic colloids.

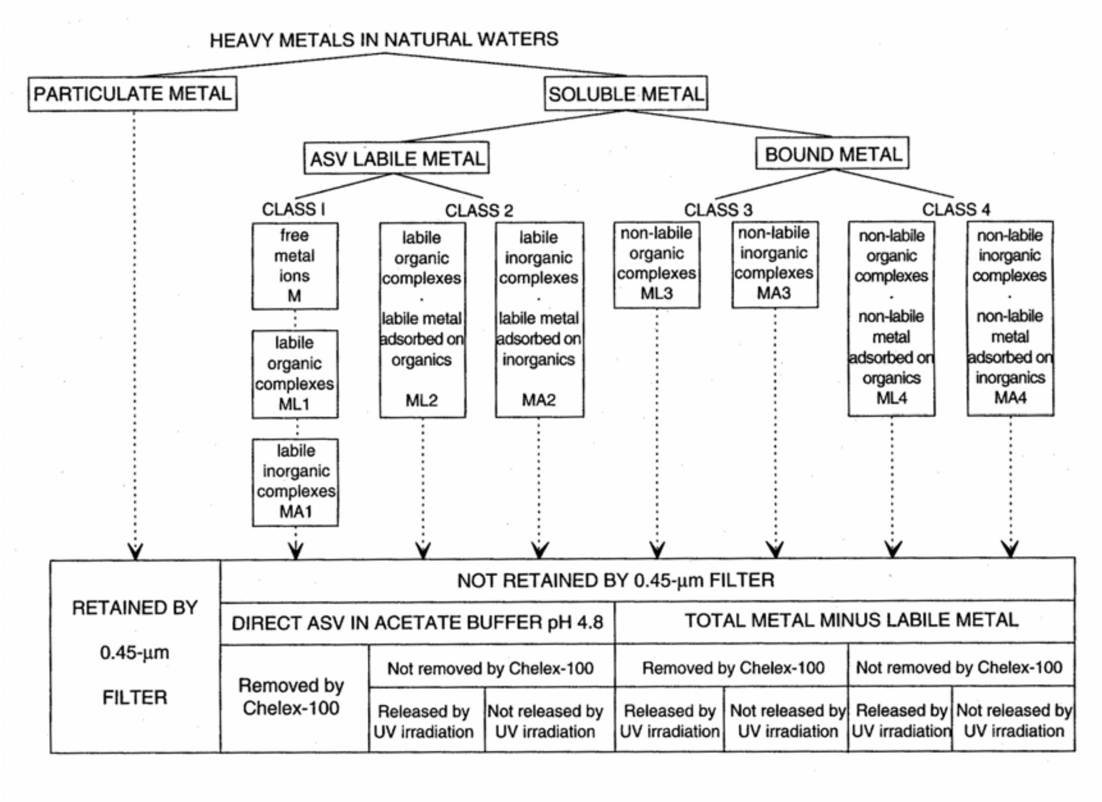

Figure 8: Diagram of sequential extraction scheme proposed by Florence (1977) and Florence and Batley (1980).

Figura and McDuffie (1980) used a modified version of the Florence and Batley scheme to determine labilities of Cd, Cu, Pb and Zn in river, estuary and secondary sewage effluent water samples (Figure 9). The “ASV-inert” fraction was divided into three groups based on the rate of metal dissociation on Chelex columns: “moderately-labile”, “slowly-labile”, and “inert”. The ASV-labile fraction was described as “very labile”. They found that Cd and Zn were almost entirely in the “very” and “moderately” labile fractions, Cu existed primarily in the “moderately” and “slowly” labile fractions, and Pb existed in the “slowly labile” and “inert” fractions

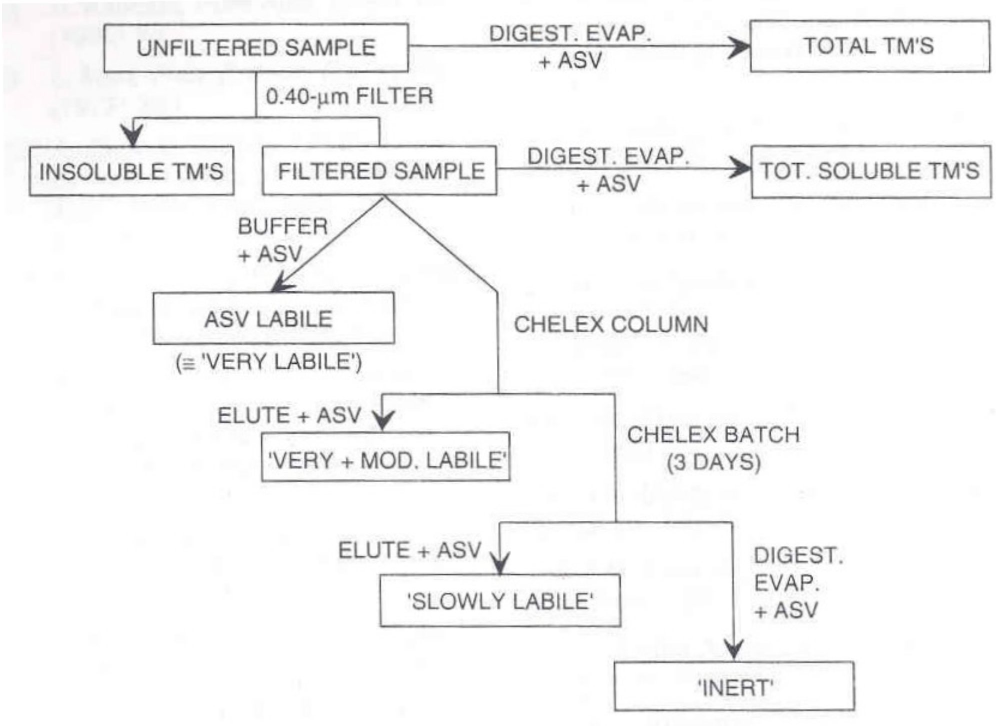

Figure 9: Diagram of Figura-McDuffie (1980) scheme for speciation of trace metals in natural waters.

A modification of both the Florence and Batley and Figura and McDuffie schemes has been used by Chakrabarti *et al*. (1993) and Cheng *et al*. (1994) in river, rain and snow samples (Figure 10). These researchers combined physical speciation by size using ultrafiltration with chemical characterization of the metal species by their dissociation kinetics. The kinetics of metal complex dissociation was studied by ASV and ionic exchange using the Chelex-100 cation-exchange resin. This scheme differed from others in that graphite platform furnace atomic adsorption spectrometry was used to measure all but the "ASV-labile" trace metals in the samples.

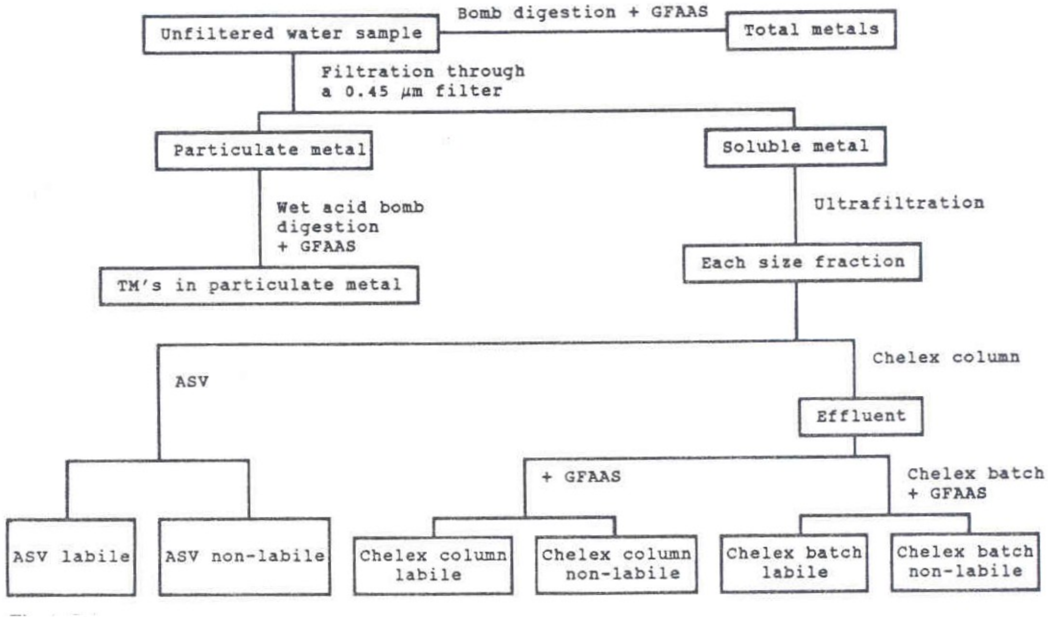

Figure 10: Chakrabarti et al. (1993) scheme for metal speciation.

More recently, Santos et al. (2002) studied the speciation of Zn, Cd, Pb and Cu in groundwater contaminated by a mining accident near Sevilla, Spain. They were able to determine four metal fractions using ASV: labile, H^+ exchangeable, strongly inert and forms associated with suspended matter. Their results showed that Zn and Cd were present in great extent in available forms (labile and H+ exchangeable), while Pb and Cu were found mostly in the less available forms (strongly inert).

CHAPTER 2

ASSOCIATION OF POLLUTANTS AND TOXICITY WITH PARTICULATES IN STORMWATER

2.1 Introduction

Many studies have identified metals in urban runoff as a major contributor to the degradation of urban streams and rivers. Metals of most concern in urban runoff are copper, cadmium, chromium, lead, mercury, and zinc. Of these metals, copper and zinc are currently the most prevalent in terms of occurrence and concentration in urban runoff with trace quantities of lead, nickel, cadmium and chromium commonly found in all areas of the United States. Metals in urban runoff can occur as dissolved, colloidal and particulate-bound species. Therefore, it is important to measure all forms of heavy metals, especially the particulate and filterable fractions, when determining their fate and effects. If possible, associations of the metals with different particle sizes should also be determined.

The objectives of this study were to determine the associations of chemical oxygen demand, total phosphorus, and heavy metals with different-sized particulates in stormwater using cascade sieves and filters.

2.2 Methodology

2.2.1 Sample Collection

For each sample, six liters of stormwater was collected manually into acid washed HDPE or LDPE sample bottles. Immediately following each event, samples were transported to the laboratory within one hour and then stored at 4^{o}C until further processing and analysis. A total of fourteen samples were collected and are described in Table 9. Collection sites were either roof runoff, sheetflow runoff, or a combination of the two from the Tuscaloosa, Alabama area. Two sets of samples (samples 11-14) were taken in order to analyze the function of an upflow stormwater filter located in a storm drain inlet at the Courhouse in Tuscaloosa, AL. For each set of samples, one was taken in front of the inlet and the other at the filter outlet. A 500mL plastic dipper was used and the collector alternated between the inlet and outlet until the desired volume was collected. Figure 11 shows the use of the dipper to collect stormwater from the storm drain inlet.

Table 9: Sample collection information.

Sample ID	**Sampling Date**	**Site Description**	**Type of Sample**
Inlet 1	7/25/2004	Local mall parking lot	Sheetflow runoff in front of storm drain inlet
Roof 1	7/26/2004	Department store roof runoff	Grab sample
Inlet 2	8/20/2004	Courthouse parking lot	Sheetflow runoff in front of storm drain inlet
Roof 2	8/20/2004	Roof runoff from courthouse	Grab sample
Mixed 1	8/20/2004	Mixed drainage from upper parking deck and roof of courthouse	Grab sample
Roof 3	8/20/2004	Roof runoff from building next to courthouse	Grab sample
Inlet 3	1/13/2005	courthouse parking lot	Sheetflow runoff in front of storm drain inlet
Roof 4	1/13/2005	Roof runoff from courthouse	Grab sample
Mixed 2	1/13/2005	Mixed drainage from upper parking deck and roof of courthouse	Grab sample
Roof 5	1/13/2005	Roof runoff from back of engineering building	Grab sample
Inlet 4	3/22/05	Filter Inlet	Grab sample
Outlet 1	3/22/05	Filter Outlet	Grab sample
Inlet 5	4/1/05	Filter Inlet	Grab sample
Outlet 2	4/1/05	Filter Outlet	Grab sample

Figure 11: Storm drain inlet sampling at Tuscaloosa Courthouse site using dipper.

2.2.2 Sample Processing

The processing and analysis scheme for each stormwater sample is shown in Figures 12 and 13. Each water sample was first processed by splitting the sample into homogenous fractions using a Delrin$^{®}$ cone splitter. The cone splitter was tested for its ability to equally split samples by first using a water blank and measuring the resultant volumes. The cone splitter has ten outlets, since we were interested in producing five homogeneous fractions, two outlets were inserted into each 1L bottle. Then 5L of water was poured through the top of the cone splitter and the resultant volumes collected in each bottle measured. This trial was performed three times. The results of these tests are show in Table 10. The trials produced errors of 6.2%, 4.9% and 3.4%.

Table 10: Delrin® cone splitter trials.

	Trial		
Outlet#	1	2	3
1,2	930mL	930mL	940mL
3,4	985	950	980
5,6	910	1050	1030
7,8	940	950	995
9,10	1060	950	970
AVERAGE	965.00mL	966.00mL	983.00mL
STDEV	59.79	47.75	33.09
COV	0.062	0.049	0.034

Screening material with 1500µm openings was used at the top of the cone splitter to capture large particles such as leaves, twigs and insects. The screening material was washed/soaked in hot soapy water for one hour before use. One split sample was set aside as the "unfiltered/unsieved" fraction, three others for sieving through the 250, 106 and 45µm sieves, and the last for use in filtering the sample through the 10, 2, 1 and 0.45µm filters. The use of separate split samples for sieving is designed to minimize particulate losses that can occur if one sample is used and then sieved through each sieve in succession. It also minimizes the introduction of contamination that may occur when one sample is sequentially processed from 250µm all the way to 0.45µm. The filtered fraction (<0.45µm) of each sample was subjected to a sequential extraction procedure which will be described in Chapter 3.

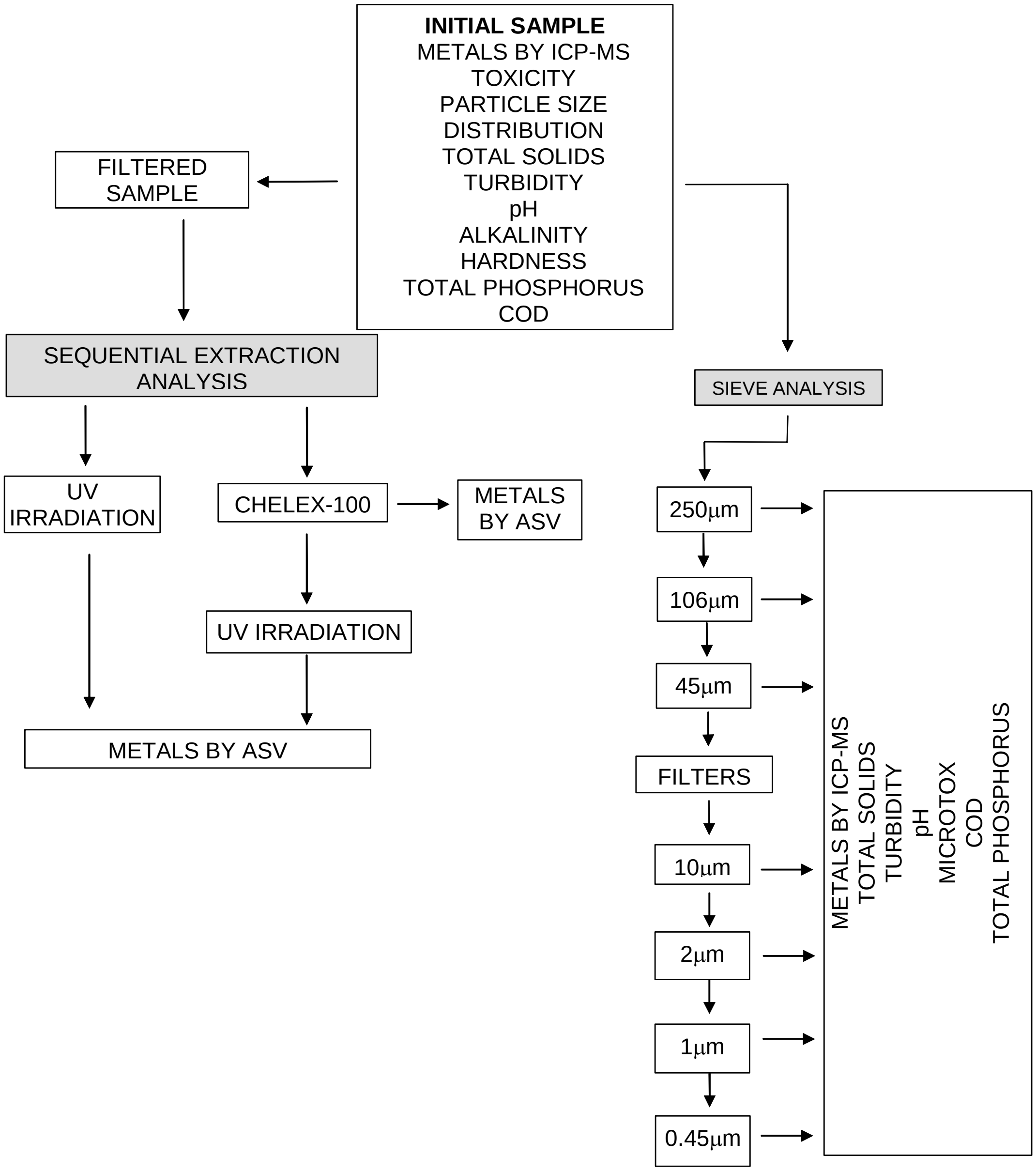

Figure 12: Sample Processing Scheme.

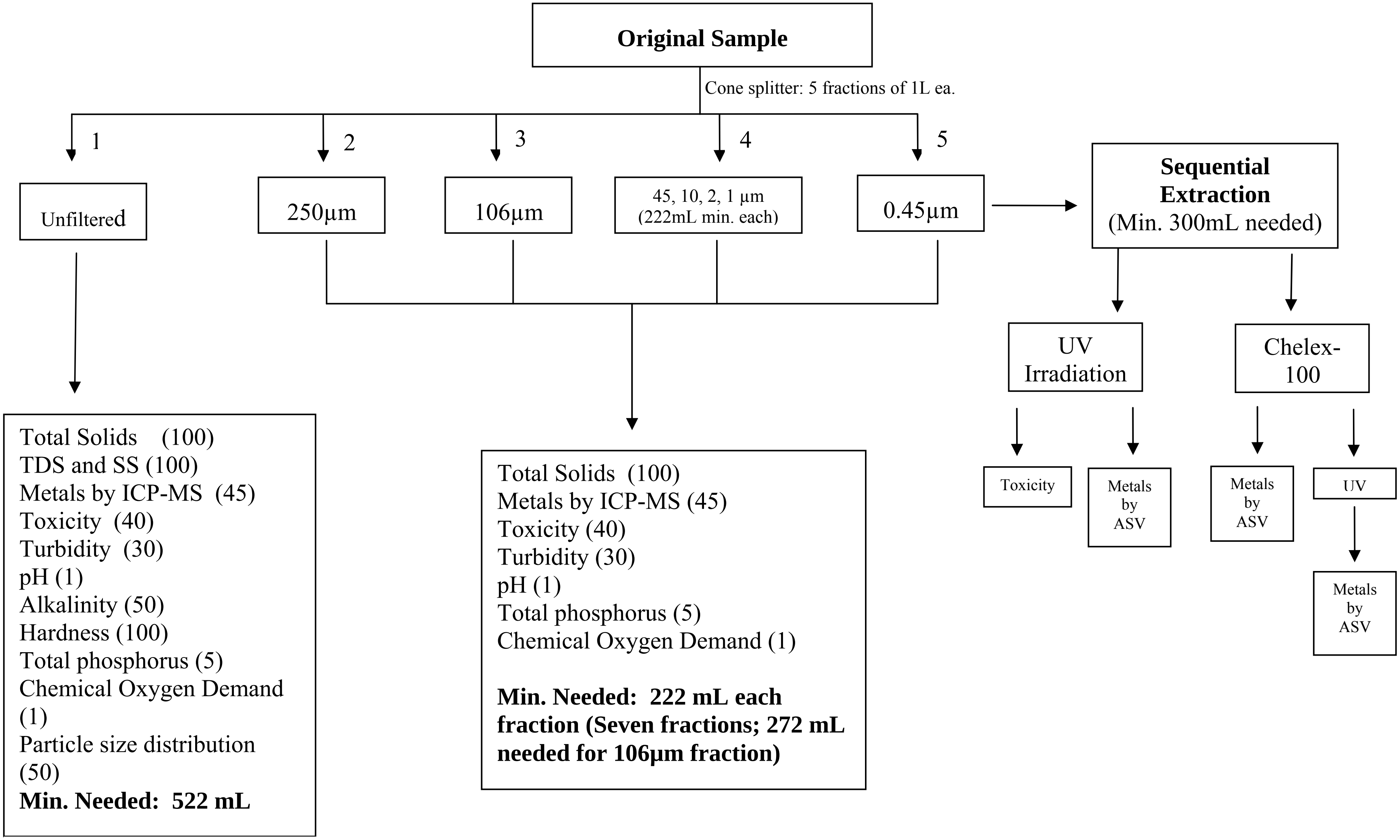

Figure 13: Sample analyses scheme by fraction.

2.2.3 Laboratory Analyses

Each unfiltered/unsieved water sample was analyzed for total solids, turbidity, pH, alkalinity, hardness, total phosphorus, and chemical oxygen demand using the standard procedures listed in Table 10. Each sample was also analyzed for toxicity using the Microtox® Test System. Particle distributions were determined using a Beckman Coulter Multisizer™ 3 Coulter Counter with the 400 µm, 100 µm and 30 µm aperture tubes. The sieved and filtered fractions were also analyzed for total solids, turbidity, pH, total phosphorus and chemical oxygen demand according to the methods listed in Table 10. In addition, they were analyzed for toxicity using the Microtox® Test System and heavy metals using an Inductively Coupled Plasma Mass Spectrometer (PerkinElmer Elan 6000).

Table 11: Analytical procedures for analysis of water samples.

Analytical Parameter	**Analysis Method**
pH	EPA Method 150 (Standard Methods 4500-H^+.B.)
Turbidity	EPA Method 180.1 (Standard Methods 2130.B.)
Total Phosphorus	EPA Method 365.2 (Standard Methods 4500-P B, 5 and P.E.)
Chemical Oxygen Demand	EPA Method 410.4 (Standard Methods 5220.D.)
Hardness, Total – titrimetric EDTA	EPA Method 130.2 (Standard Methods 2340C)
Alkalinity (Titrimetric, pH 4.5)	EPA Method 310.1
Solids, Total	EPA Method 160.3 (Standard Methods 2540B)

2.3 Quality Assurance/Quality Control

The techniques used in sample collection, preparation and storage are critical in any analyses being carried out at trace or ultratrace concentrations. In order to avoid heavy metal contamination, all labware that came in contact with samples was made of polyethylene or Teflon® and acid soaked in 10% nitric acid (Fisher Chemical) for at least 24 hours before use. Any glassware used was also cleaned and stored in a 10% nitric acid bath at least overnight before use. Only ultrapure 18mΩ water was used for method blanks and for rinsing labware. All labware was also thoroughly rinsed with ultrapure water after acid soaking/rinsing. Water sampling bottles were also rinsed with the water being sampled before taking a final sample for analysis. Water samples were stored in polyethylene containers at 4^{o}C until analysis. Bacterial activity can be reduced by storage at this temperature and can decrease the losses of heavy metals (Batley, G.E., 1989). Instrument performance was checked with external standards when applicable. Method blanks were run through all analyses. Periodically, samples were analyzed in triplicate to determine precision of analytical performance. Each measurement for toxicity was performed in triplicate. For the ICP-MS, QA/QC data were obtained by analyzing at least seven matrix matched blanks, finding the standard deviation of the blanks, multiplying by three to determine the limit of detection (lod), adding the average (if positive), multiplying the standard deviation by 10 to determine the limit of quantification (loq) and then adding the average (if positive).

2.4 Results and Discussion

2.4.1 Particle Size Distributions

Figures 14 and 15 are the particle size distributions for all samples and of the samples by type (excluding the outlet samples). For most samples, the median particle size falls between 20 and 90 µm. There were a few samples for which larger particles dominated. Sample 6 was a roof runoff sample after a few weeks of no rain from a flat roofed building neighboring the Tuscaloosa Courthouse. This sample had the largest number of solids greater than 1500µm. It is easier to see the difference between the samples in Figure 15. The particle distributions for the storm drain inlet samples were variable and could depend upon when the sample was taken during the storm event and the length of the antecedent dry period. If the sample is taken at the beginning of the storm and there has been a long dry period, then more particulates will be captured in the sample. The mixed samples, which consisted of roof and some parking lot runoff were virtually the same and contained mostly small particulates (<90 µm). The roof runoff samples were variable, with some samples having less particulates >90 µm.

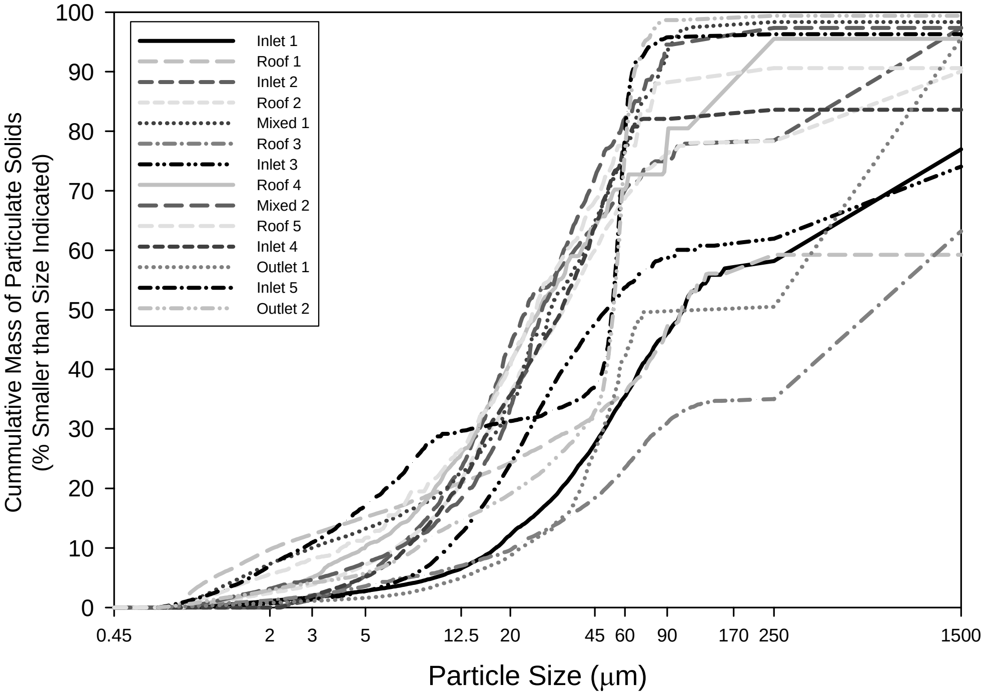

Figure 14: Particle size distributions for all samples.

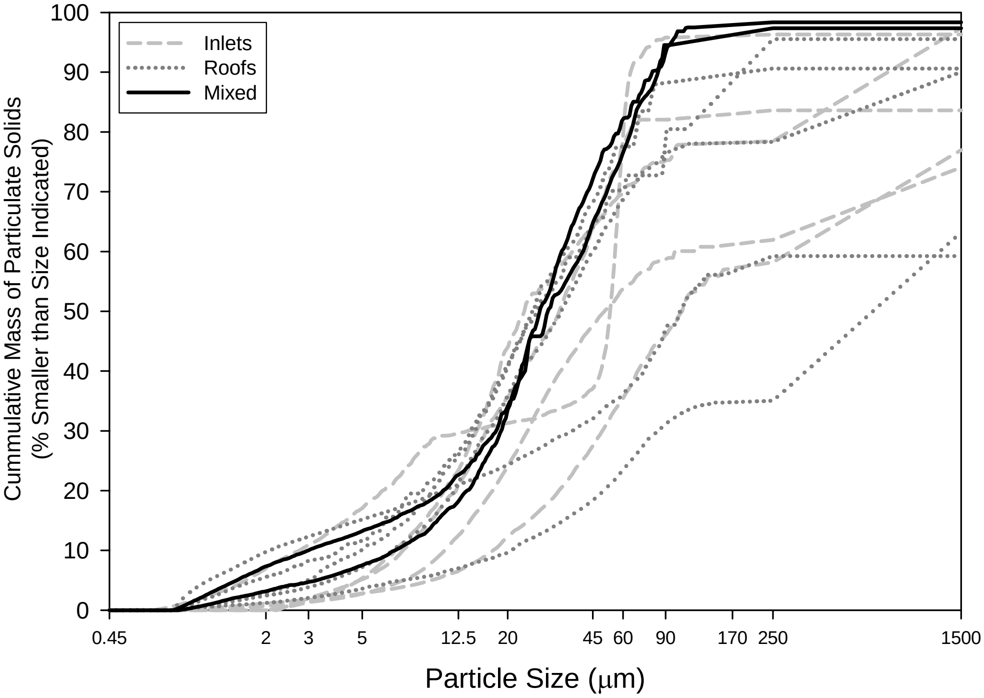

Figure 15: Particle size distributions by sample type.

In Figure 16, the particle size distributions for the stormwater filter inlet and outlet samples are compared. For one pair, the distributions are almost identical, and for the other, the median size for the outlet sample was larger than for the inlet sample. This type of information was helpful in determining if the filter was removing particulates and if the media that was being tested needed to be changed/altered. The test media in the upflow filter at the time was a mixture of 45% Bone Char, 45% Mn-coated Zeolite and 10% Peat Moss.

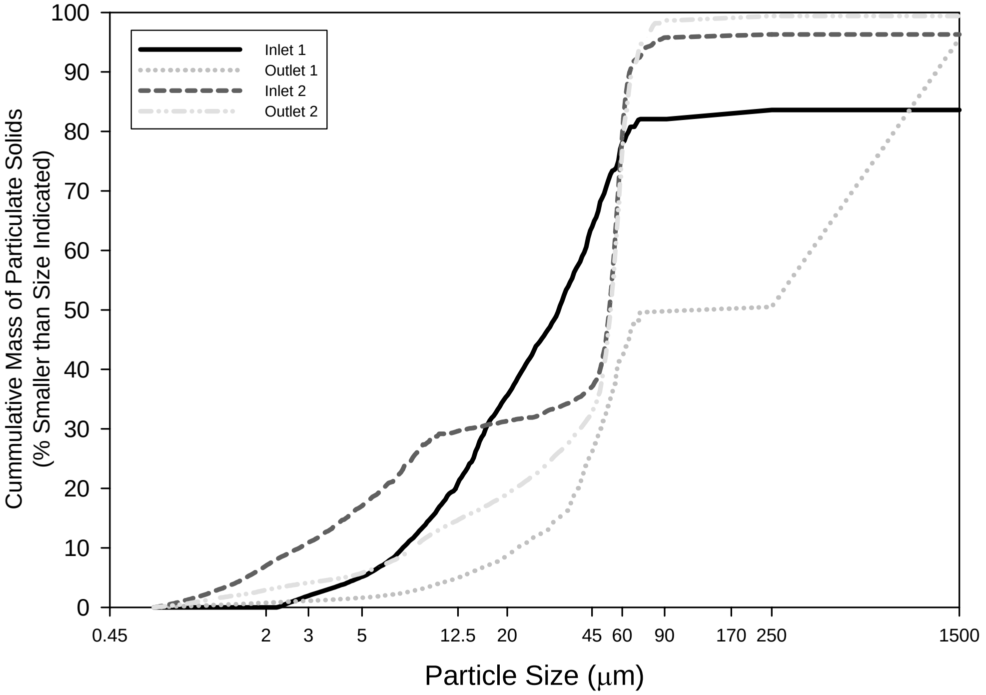

Figure 16: Particle size distributions for stormwater filter inlet and outlet samples.

2.4.2 Nutrients

Figures 17 and 18 show the results of chemical oxygen demand and total phosphorus, respectively, for all fourteen samples. The general trend in both these figures, is a decrease with removal of more particulates. There is a point around 10 µm where it appears no more COD or total phosphorus is being removed and that the pollutant concentration is all in the dissolved form.

In Figures 19 and 20, the association of COD with particulates can be seen for inlet samples and roofs, respectively. The trend of a decrease in COD concentration with the removal of particulates is more obvious in Figure 19 than was seen in Figure 17. On average, the unfiltered roof runoff samples appear to have a lower concentration of COD compared to the inlet samples, with samples 8 and 10 having concentrations close to zero.

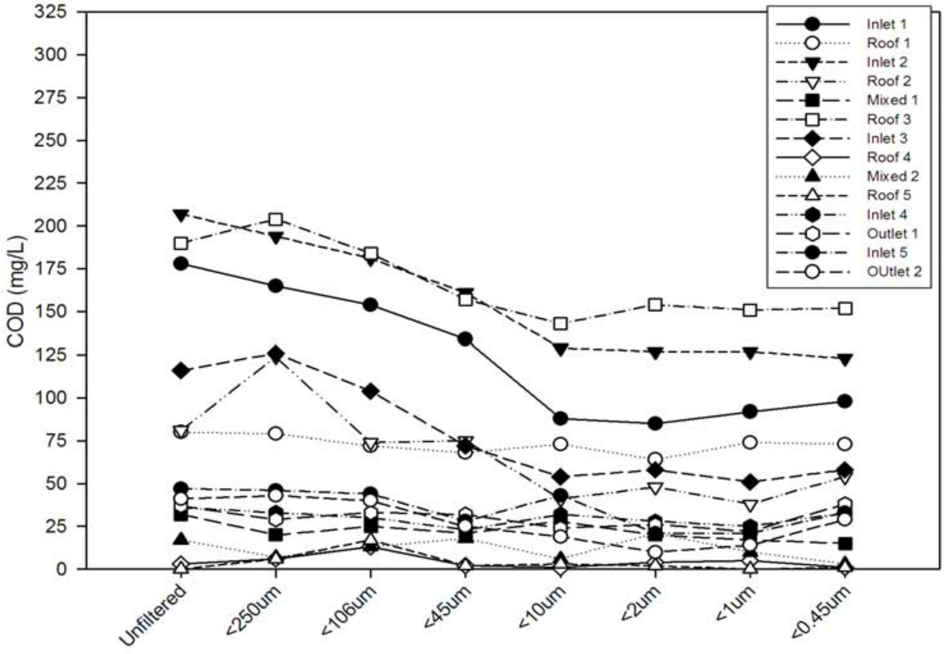

Figure 17: Chemical oxygen demand by particle size for all samples.

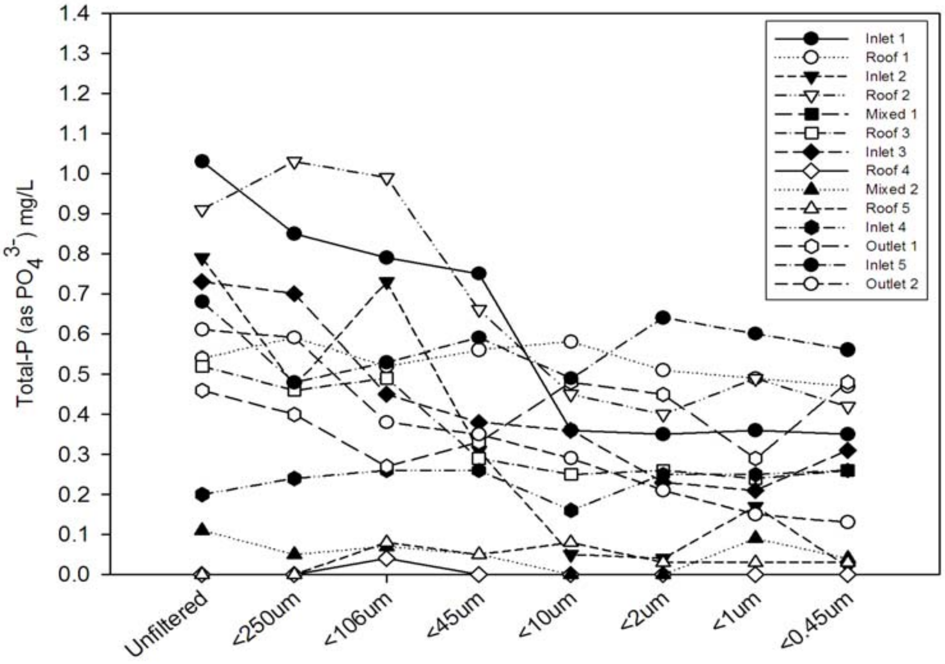

Figure 18: Total phosphorus by particle size for all samples.

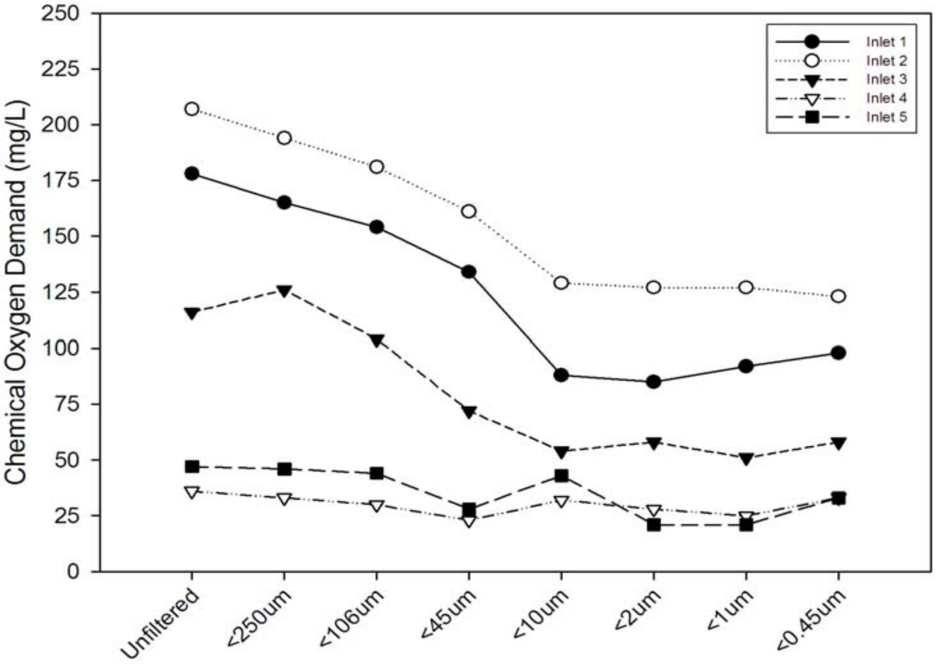

Figure 19: Chemical oxygen demand by particle size for inlet samples.

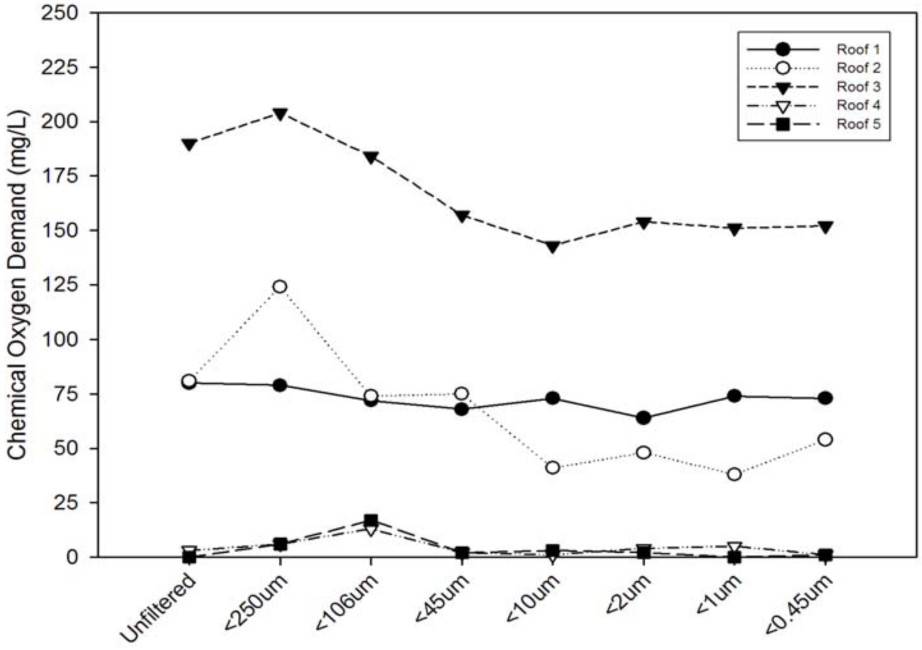

Figure 20: Chemical oxygen demand by particle size for roof samples.

Figures 21 and 22 are total phosphorus concentrations for inlets and roof runoff samples, respectively. Although the concentrations are variable for both roof and inlet samples, the general trend is a decrease in concentration with removal of particulates. The concentrations in general were higher for the inlet samples compared to the roof runoff samples. It also seems that most of the roof runoff concentration was dissolved, as there was less of a decrease in concentration with the sequential removal of particulates.

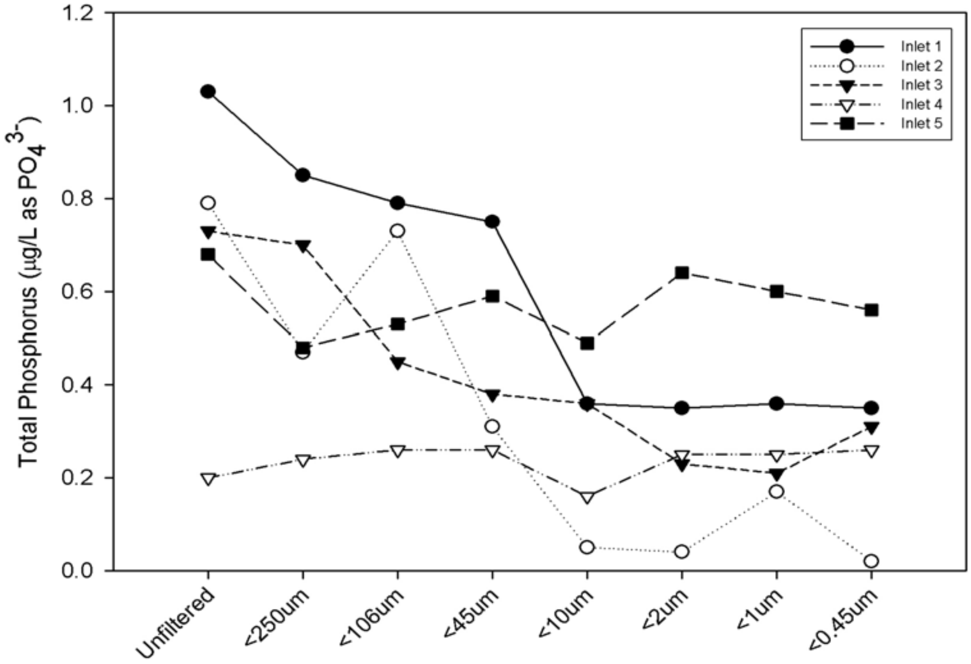

Figure 21: Total phosphorus by particle size for storm drain inlet samples.

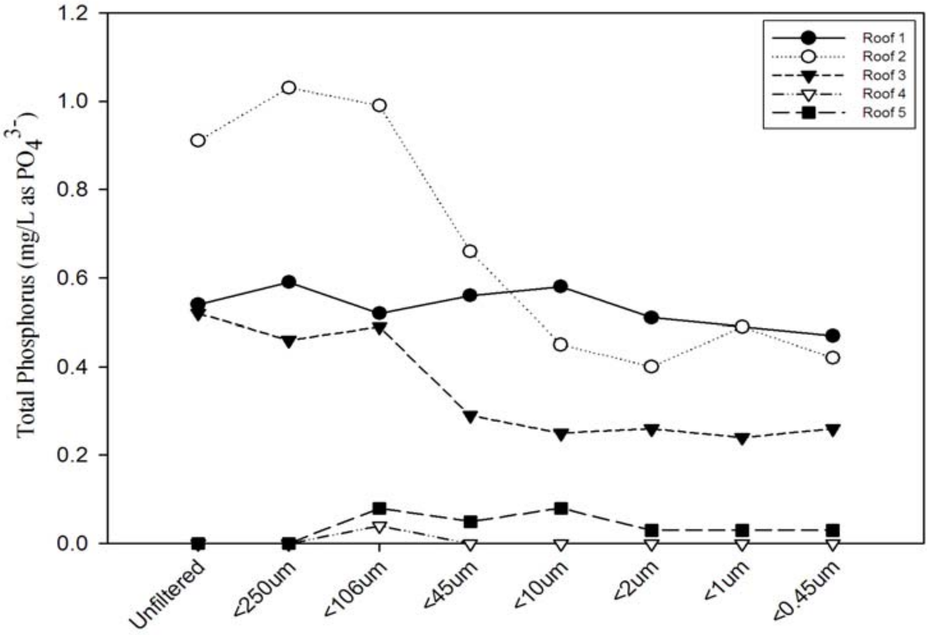

Figure 22: Total phosphorus by particle size for roof runoff samples.

Figure 23 shows the pH for all fourteen stormwater samples. None of the pH numbers were outside the range of what would be considered normal for stormwater or rainwater. In addition, the pH would not be expected to change with the removal of particulates in the stormwater since pH is dependent on the concentration of H^+ ions. One would expect roof runoff water to have a lower pH than inlet samples because roof water would be similar to rainwater. The pH of rainwater would normally be around 5-5.5. Rainwater that has flowed over concrete in a parking lot or on a road would have a higher pH than rainwater because of the buffering capacity of the concrete. In Figure 24, the pH for the inlet samples show that they are all very similar and centered around a pH of 6.5. The pH of roof runoff samples shown in Figure 25 are more variable, but most are below 6.0 except for the Courthouse roof runoff samples. There was little or no difference in the pH of storm drain filter inlet and outlet samples and can be seen in Figure 26.

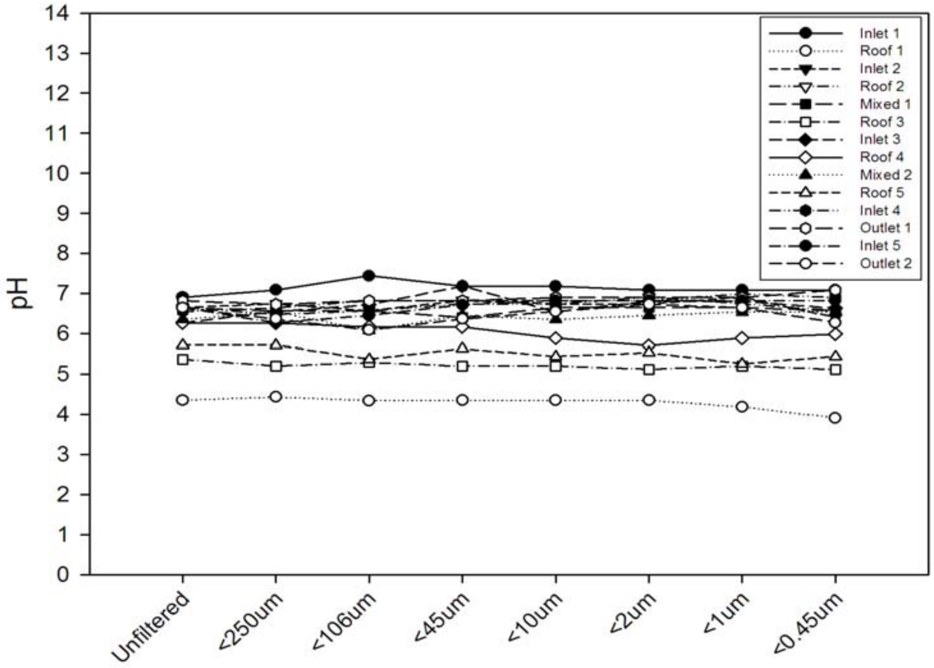

Figure 23: pH by particle size for all stormwater samples.

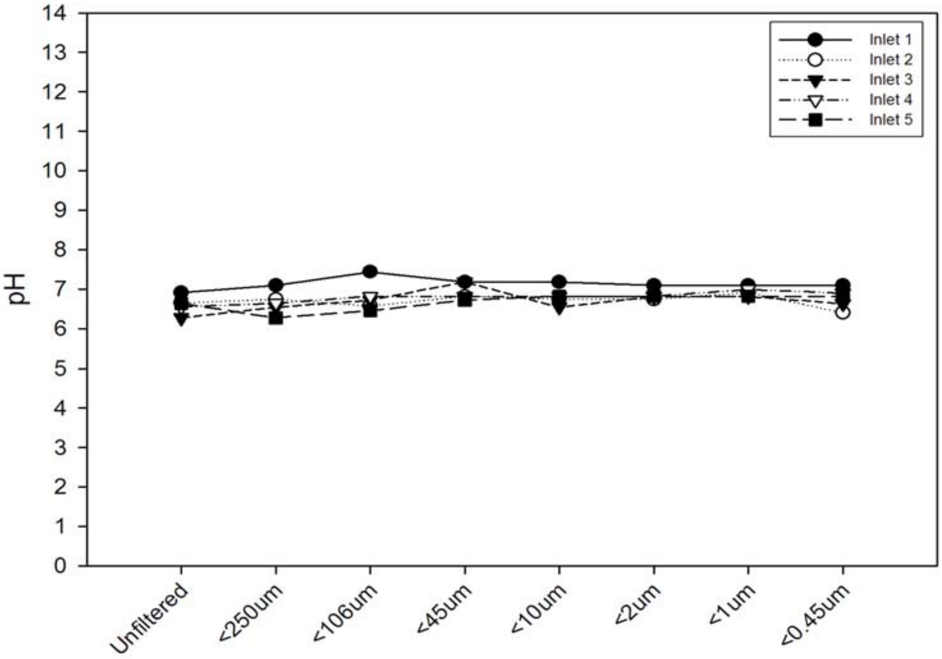

Figure 24: pH by particle size for storm drain inlet samples.

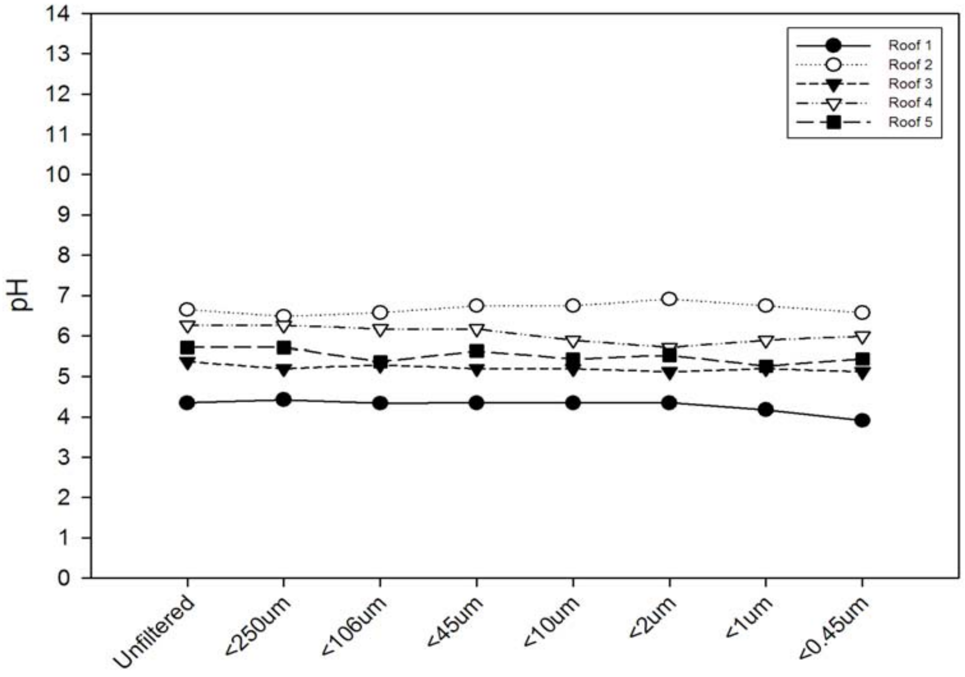

Figure 25: pH by particle size of roof runoff samples.

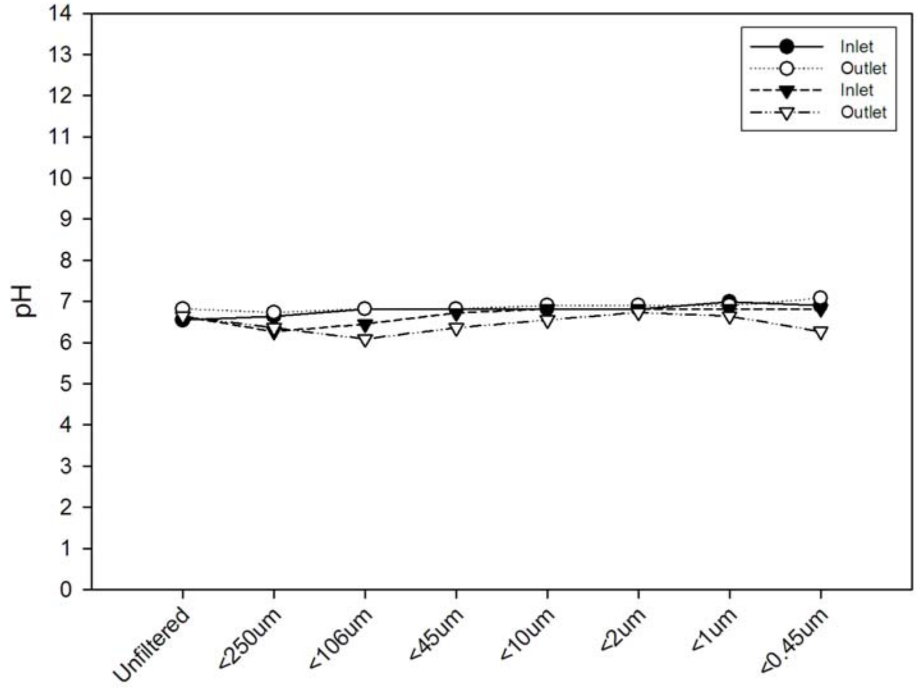

Figure 26: pH by particle size for storm drain filter inlet and outlet samples.

2.4.3 Solids and Turbidity

In Figures 27-29, total solids are presented for all samples and then for storm drain inlets and roof runoff samples separately. As expected, the total solids concentrations decreased with increased removal of particulates from the samples. The decrease was more dramatic for the inlet samples as shown in Figure 28 than for the roof runoff samples (Figure 29). Normally, there are more solids found in the inlet samples as compared to roof runoff because the water taken in front of inlets has already run across a parking lot or other street area. Sample 6 from a building next to the Courthouse was a flat roof after a long period (approximately 2 weeks) without rain. There was more than the expected amount of leaves and other debris in that sample.

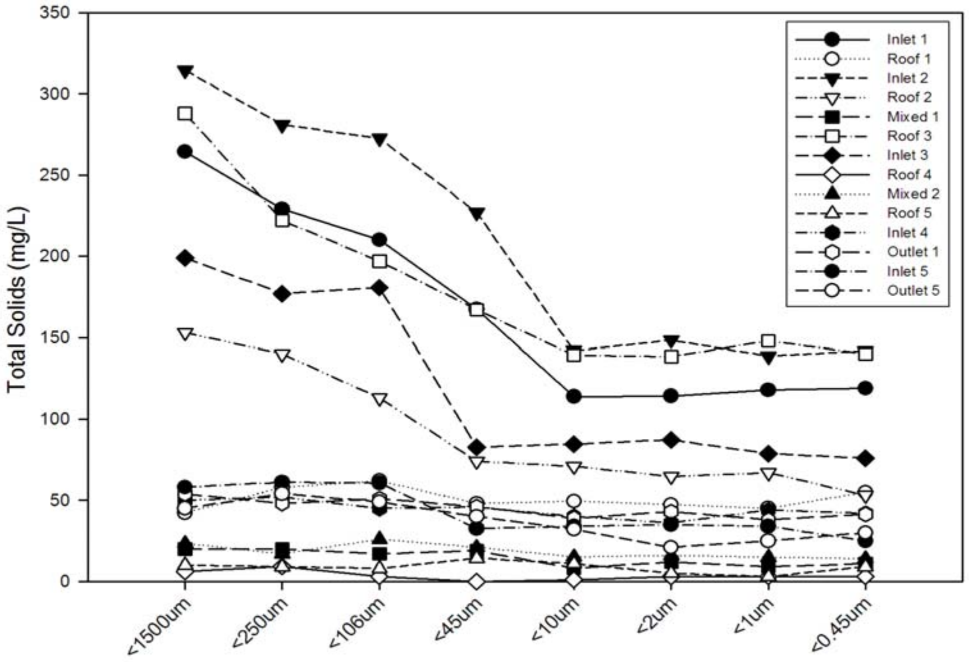

Figure 27: Total solids by particle size for all samples.

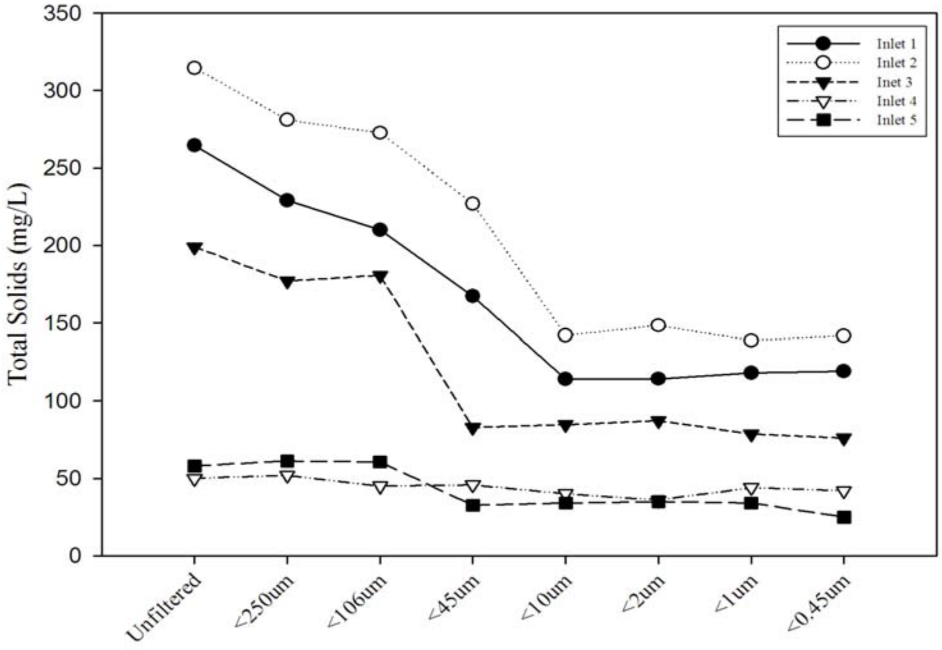

Figure 28: Total solids by particle size for storm drain inlet samples.

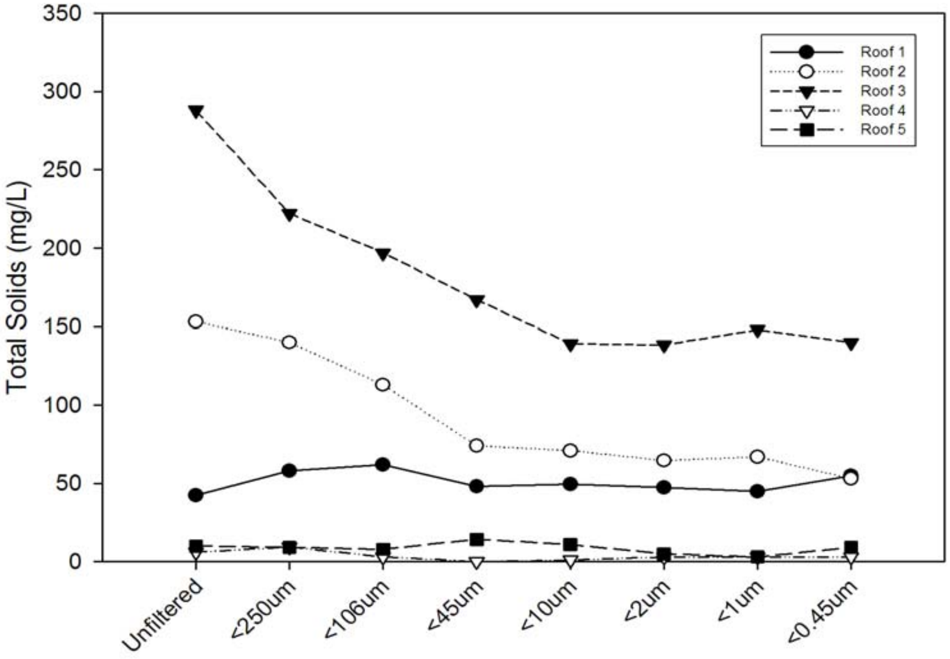

Figure 29: Total solids by particle size for roof runoff samples.

In Figure 30, the total solids concentrations of the storm drain filter inlet and outlet samples can be compared. Unfortunately, there was little difference in the total solids concentrations between inlet and outlet samples. These tests have been very helpful to those designing the filter and modifications are being made accordingly in order to improve the treatment the filter may provide.

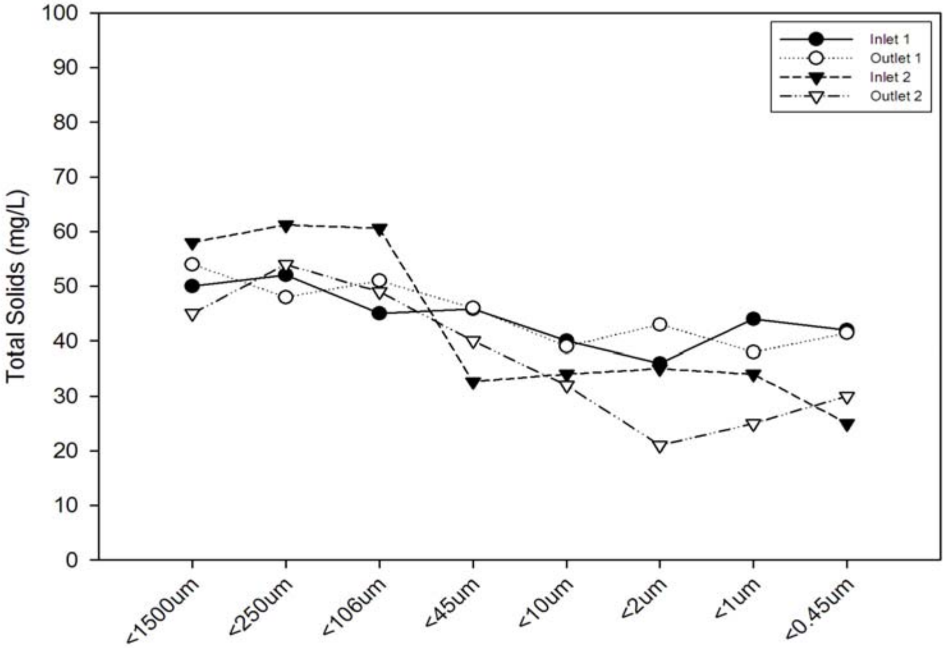

Figure 30: Total solids by particle size for stormwater upflow filter inlet and outlet samples.

After removing the dissolved solids (<0.45 μm), only the suspended solids remain. Figure 31 shows the suspended solids for all samples. The vertical scale has been kept the same for comparison with the figures for total solids. There was a drop in solids concentrations for all samples. Some dropped to almost zero, indicating that most of the solids present were dissolved. This is better seen in Figures 32 and 33 which show the suspended solids concentrations for inlet and roof runoff samples respectively. There were a few inlet samples and roof runoff samples that consisted mostly of dissolved solids. After removal of the dissolved solids, the solids concentrations were greatly reduced. The two inlet samples that had a lot of dissolved solids were not taken at the beginning of the storm, so many of the larger solids had already been washed off the pavement before collection. The roof runoff samples would not be expected to have a large concentration of suspended solids. Most solids would come from atmospheric deposition and deposits of materials carried by the wind. Roof 2 and roof 3 samples were collected on the same day from two different buildings after a long period of dry weather. These samples were more turbid than the other roof runoff samples (Figure 36)

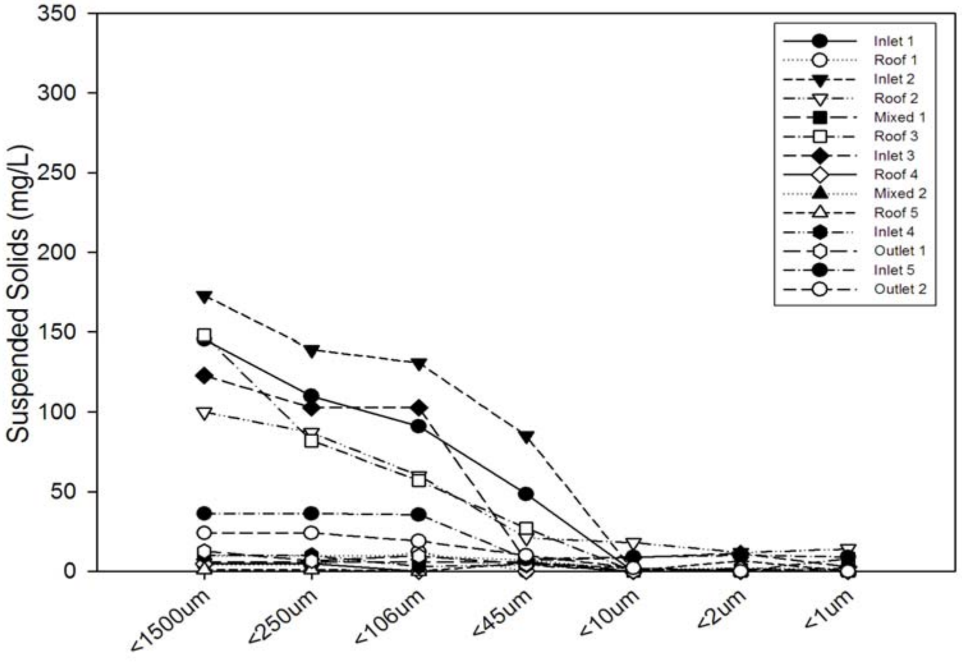

Figure 31: Suspended particles by particle size for all samples.

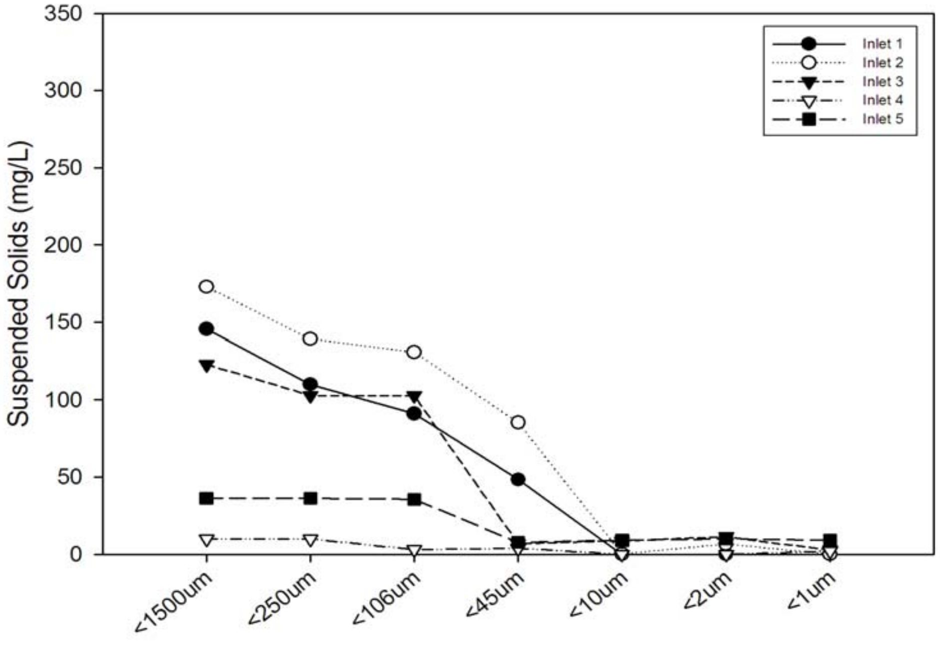

Figure 32: Suspended solids by particle size for storm drain inlet samples.

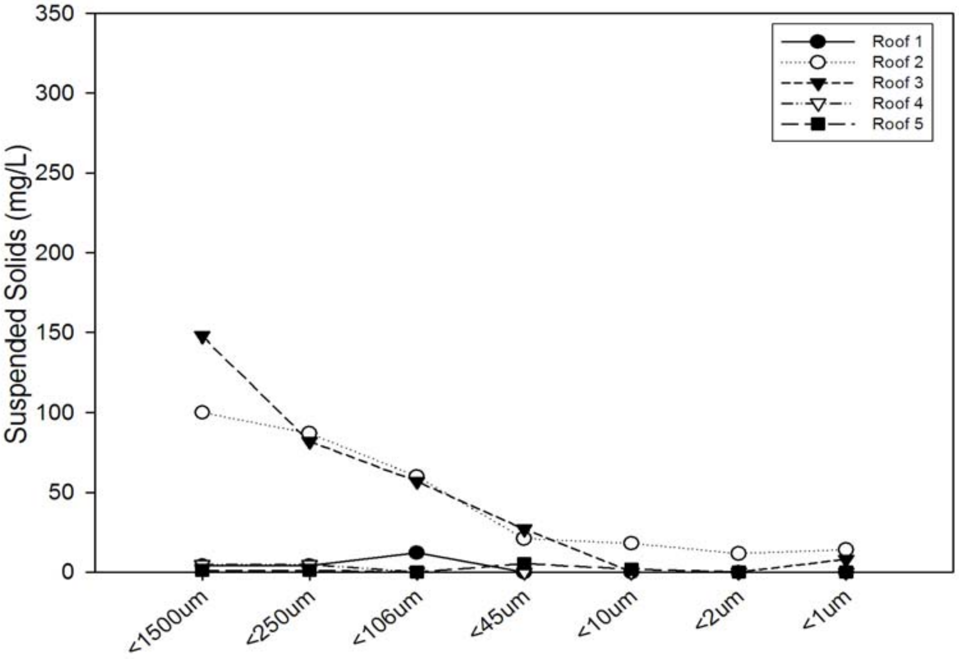

Figure 33: Suspended solids by particle size for roof runoff samples.

The results for turbidity show the same decrease as shown for total solids (Figure 34). Since turbidity is an indication of the number of particulates in a sample, one would expect a decrease in turbidity with the sequential removal of particulates in the samples. In Figure 35, the turbidity for the storm drain inlet samples were higher as compared to the roof runoff samples shown in Figure 36. This again would be expected because roof runoff would on average be "cleaner" than the storm drain inlet runoff.

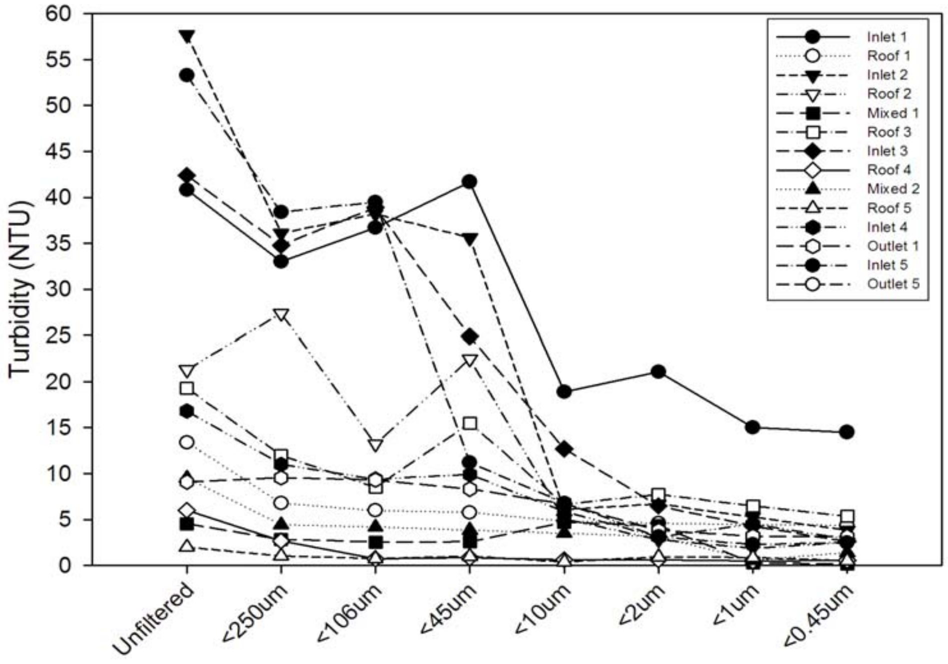

Figure 34: Turbidity of all stormwater samples by particle size.

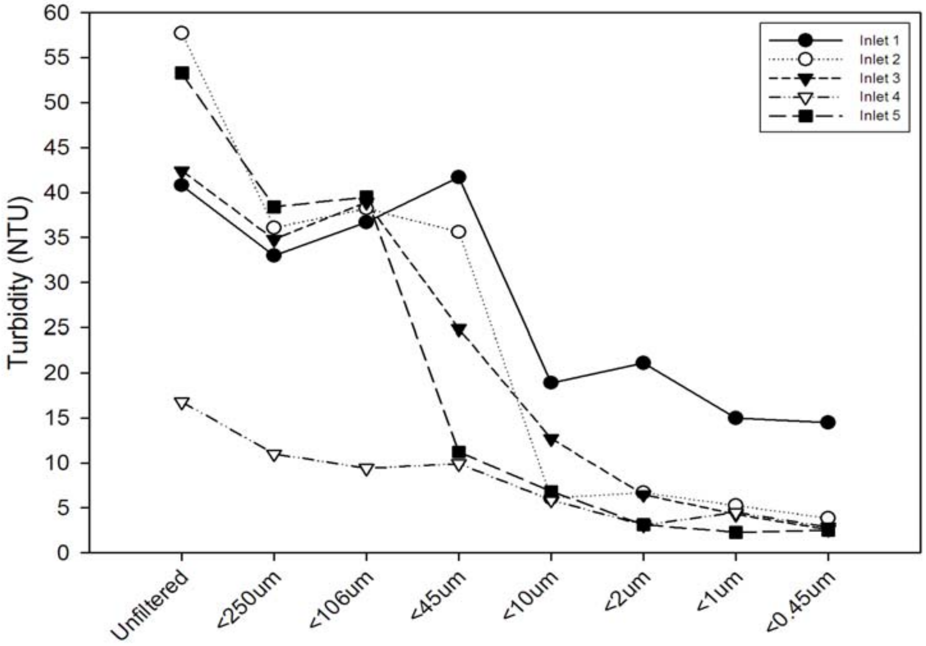

Figure 35: Turbidity by particle size for storm drain inlet samples.

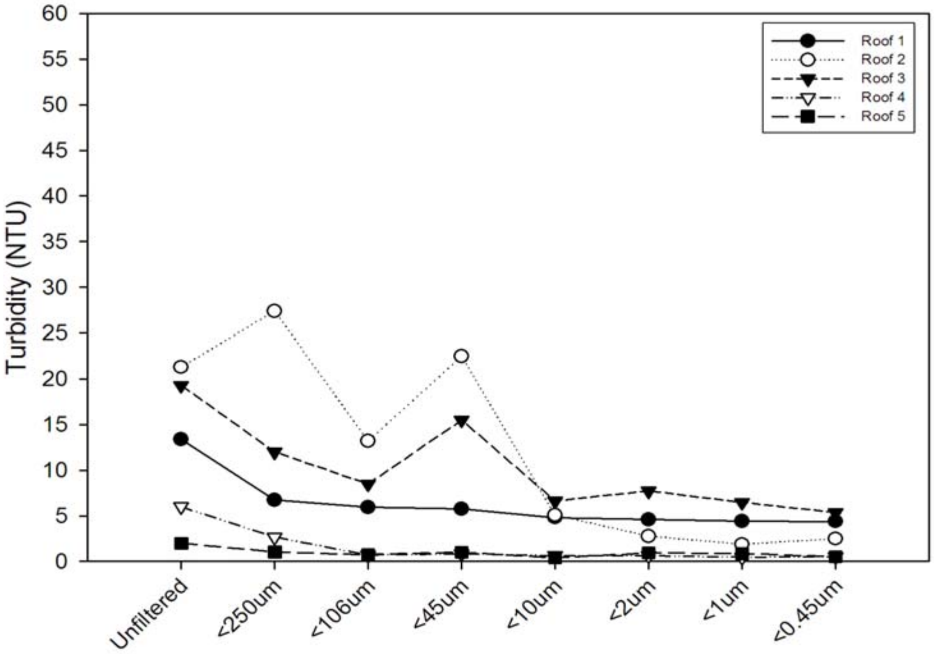

Figure 36: Turbidity by particle size for roof runoff samples.

For the storm drain filter samples shown in Figure 37, like that shown in Figure 30 for total solids, there was little difference between the inlet and outlet samples. For those particular events, the filter was not successfully removing particulates from the runoff.

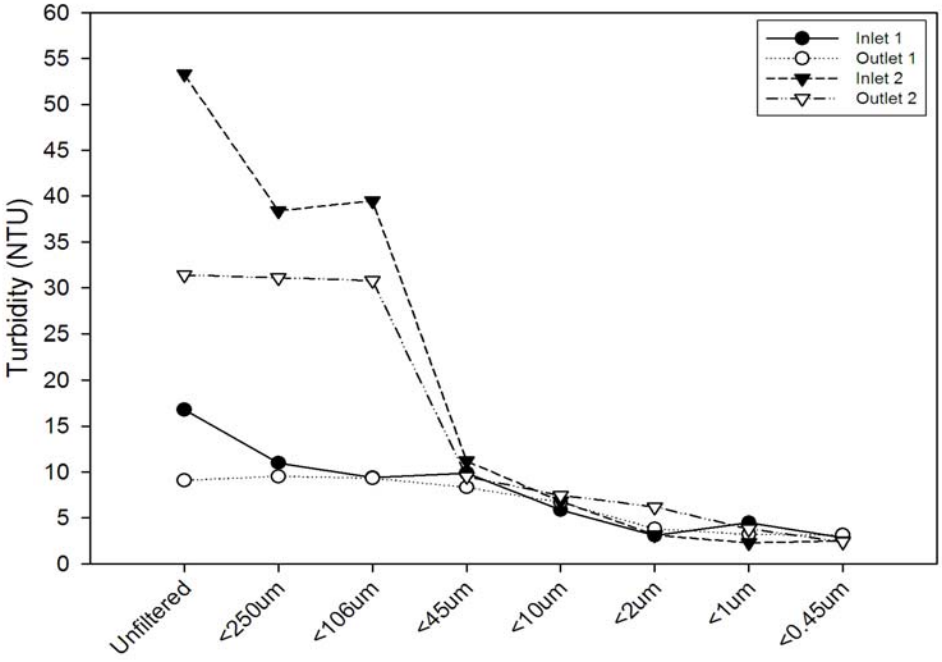

Figure 37: Turbidity by particle size for storm drain filter inlet and outlet samples.

2.4.4 Toxicity

New equipment was purchased for performing toxicity tests using the Microtox® Test System (Stragetic Diagnostics, Inc.). This test exposes luminescent organisms (*Vibrio fischeri*) in the Microtox Acute Reagent to aqueous samples, and measures the increase or decrease in light output by the test organisms. The reagent contains living luminescent bacteria that have been freeze-dried and are rehydrated with Reconstitution Solution provided by the manufacturer. The Reconstitution Solution is a specially prepared nontoxic ultra pure water. One vial of freeze-dried reagent contains approximately one million test organisms. The test system measures the light output of the luminescent bacteria after they have been challenged by a sample and compares it to the light output of a control (reagent blank) that contains no sample. A difference in light output is attributed to the effect of the sample on the organisms.

Before performing tests with actual samples, the new equipment and bacteria were tested for a variety of factors including mixing, salt concentration and repeatability. First, the effect of mixing of the bacteria was tested. Previous instructions using an older model test system advised mixing the sample 20 times with a 500 µL pipettor after addition of the bacteria. The protocol of the new instrument advised mixing the sample only three times after adding the bacteria. Because of this discrepancy and a possible change in the behavior of the bacteria now being supplied with the Microtox® Test System, the effect of mixing was tested by running a 10 µg/L standard of $ZnSO_4$ ten times mixing either three times or 20 times and comparing the effect on fluorescence of the bacteria. Zinc sulfate is commonly used as a reference toxicant to check the performance of the test system. As can be seen in Figure 38, mixing the bacteria 20 times was unnecessary and may actually have caused a decrease in the fluorescence of the bacteria. For all future testing, the samples were mixed three times with a 500 µL pipettor after the addition of the bacteria.

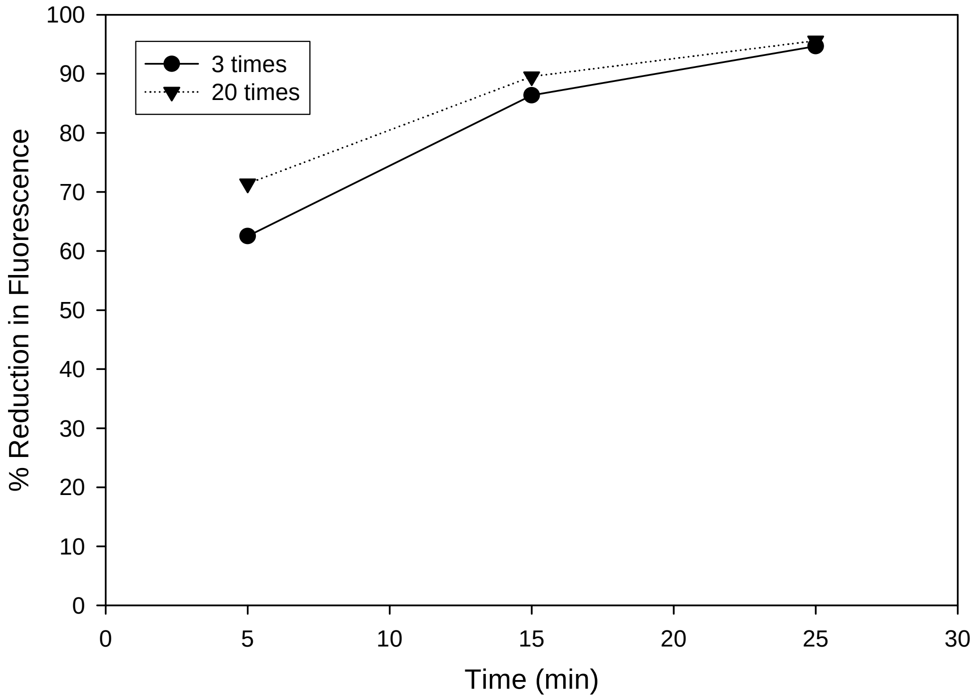

Figure 38: Effect of mixing on 15min fluorescence of Microtox® acute bacteria.

In the past, a protocol had been developed that used granular NaCl to adjust the salinity (osmotic pressure) of the samples to 2% instead of using the Osmotic Adjusting Solution (OAS) provided by the manufacturer. The OAS is a specially prepared nontoxic 22% sodium chloride solution used to adjust the osmotic pressure of the sample to approximately 2% NaCl. A preliminary test was performed to first determine if there was a difference in fluorescence with the test bacteria if the NaCl concentration was different than the recommended 0.2g per 10mL sample. Figure 39 is a plot of three different NaCl concentrations. Each point is an average of the reduction in fluorescence at 15 minutes for 5 replicates. Preliminarily, is was obvious that changing the salinity of the samples to above or below 2% could have a dramatic effect on the fluorescence of the test organisms.

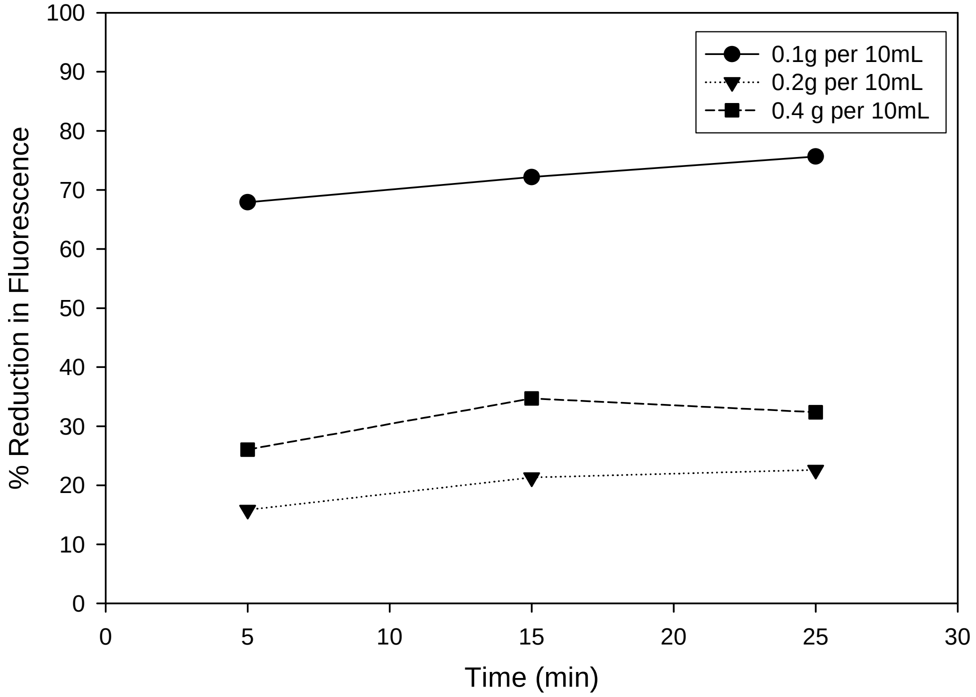

Figure 39: Preliminary tests of bacterial fluorescence using three different NaCl conentrations. Each point is an average of 5 replicates at 15min.

Tests were also needed to determine if the use of NaCl was still acceptable and if there would be a difference in the results compared to using OAS to adjust salinity. Figure 40 is a plot of the average of three replicates for varying $ZnSO_4$ concentrations using both the OAS and NaCl to adjust the osmotic pressure to 2% NaCl. There was an obvious difference in the average reduction in fluorescence of the test organisms between OAS and NaCl. Granular NaCl appeared to have an IC_{50} of around 1.0 mg/L and with OAS the IC_{50} is around 5.5 mg/L. These results are similar to what was obtained using NaCl to adjust salinity in previous tests using earlier model testing equipment.

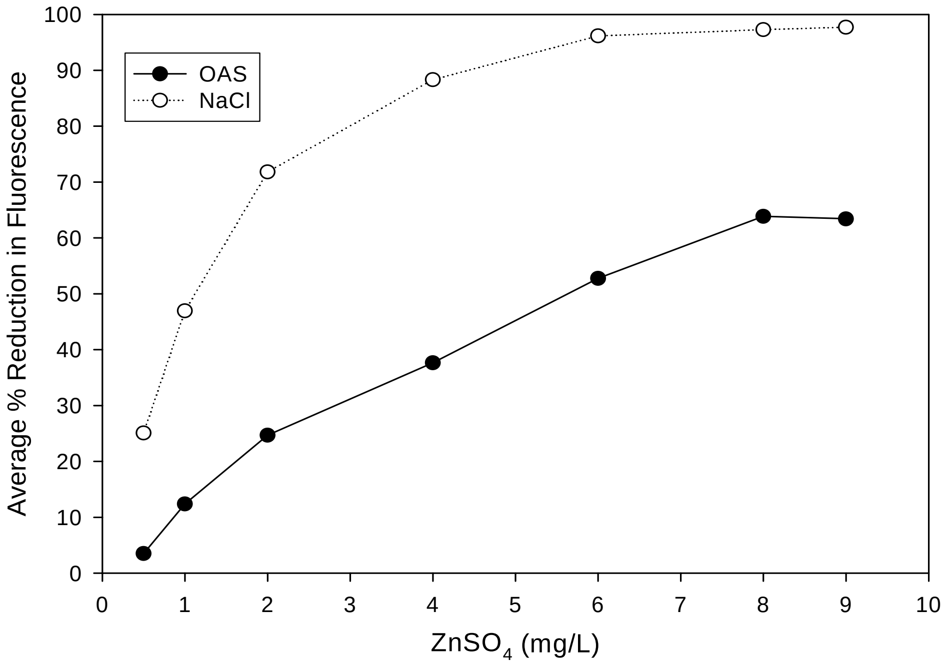

Figure 40: Reduction in fluorescence (15min) averaged for three replicates of varied ZnSO4 concentrations using OAS and NaCl to adjust salinity to 2%.

The next test was to determine how precise the addition of NaCl needed to be when adjusting the salinity of a sample. Was there a range of salinity that would be acceptable to the test organisms? A composite of two stormwater samples collected in June 2004 were used to test for an acceptable range of salinity using 20mL aliquots. As can be seen in Figure 41, the light reduction is minimum at 0.50g (2.5% salinity) then starts to rises again at 6.5g (3.3% salinity). The recommended salinity is 2% which in this case resulted in a 34% reduction in fluorescence. From these results it was determined that the additions of salt to the samples must be measured carefully. A difference of a hundredth of a gram can change the osmotic pressure of the organisms sufficiently to result in a change in their fluorescence.

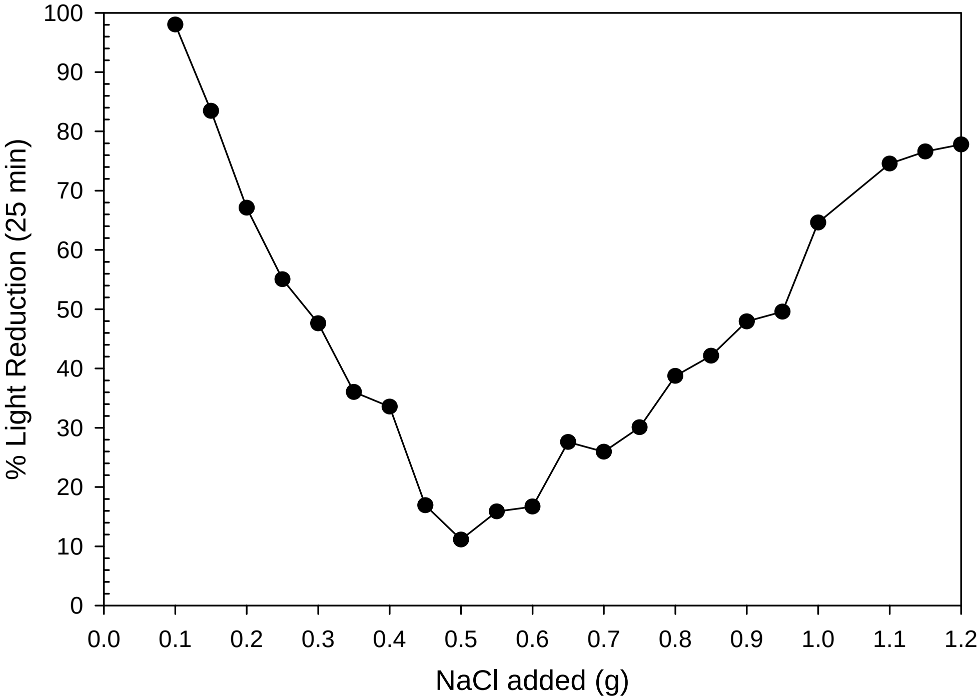

Figure 41: Light reduction at 25min of 20mL stormwater samples with varying salinity using granular NaCl.

The final tests were to determine an appropriate IC_{50} for $ZnSO_4$ using NaCl to adjust salinity and to test for repeatability of the test system using the approximate IC_{50}. The IC_{50} is the approximate concentration required for 50% inhibition of bacterial fluorescence. Figure 42 is a graph of the average of three replicates of varied $ZnSO_4$ concentrations using granular NaCl to adjust the salinity of the samples to 2 percent versus fluorescence. From this plot, it appears that the IC_{50} is approximately 0.75 mg/L $ZnSO_4$. Using the results from these tests and previous results (Figure 40), repeatability of the test system was analyzed using 0.75 and 1.0 mg/L $ZnSO_4$. Table 12 shows the results from running ten replicates of the two $ZnSO_4$ concentrations. A concentration of 0.75 mg/L $ZnSO_4$ had an average reduction in fluorescence of 51.03% compared to an average reduction of 71.66% for 1.0 mg/L $ZnSO_4$. The error for 0.75 mg/L $ZnSO_4$ was

6.3% and that of 1.0 $ZnSO_4$ was 4.7%. These are acceptable errors and show that the testing system can provide repeatable results with an error below 10%. All subsequent tests used a $ZnSO_4$ concentration of 0.75 mg/L as a test toxicant to run along with samples.

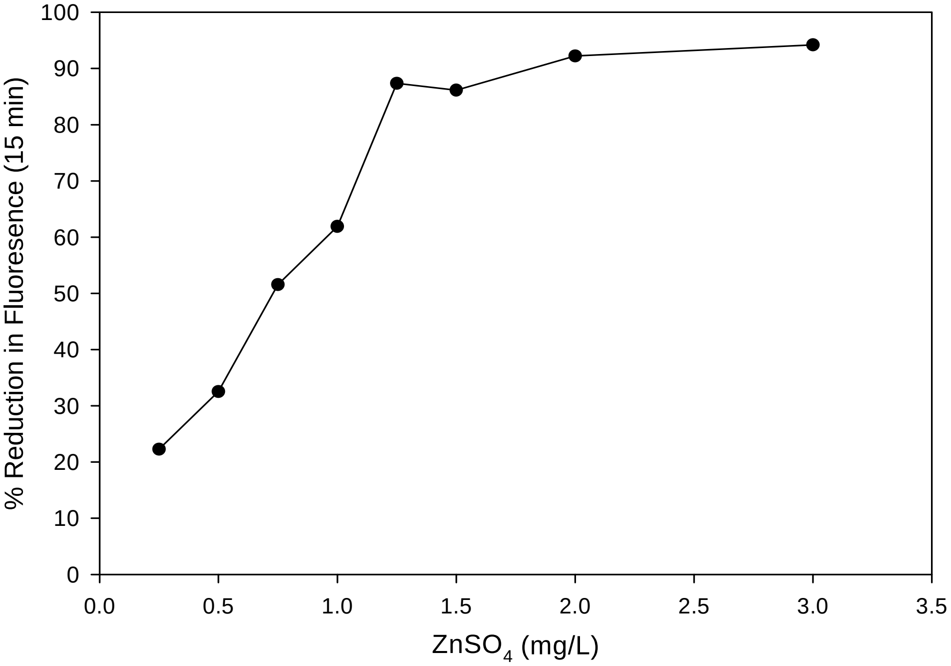

Figure 42: Tests for IC_{50} at 15 min using varied concentrations of $ZnSO_4$ and NaCl to adjust salinity to 2%.

Table 12: Test for repeatability of Microtox test system using 10 replicates of two concentrations of $ZnSO_4$.

$ZnSO_4$ conc. (mg/L)	% Reduction in flouorescence	$ZnSO_4$ conc. (mg/L)	% Reduction in fluorescence
0.75	53.33%	1.00	69.14%
0.75	51.22%	1.00	68.63%
0.75	47.69%	1.00	71.14%
0.75	55.85%	1.00	75.00%
0.75	46.59%	1.00	66.56%
0.75	51.95%	1.00	74.32%
0.75	52.78%	1.00	70.55%
0.75	47.36%	1.00	69.95%
0.75	49.02%	1.00	74.02%
0.75	54.50%	1.00	77.28%
Average	51.03%		71.66%
STDEV	0.032		0.034
COV	0.063		0.047
MAX	55.85%		77.28%
MIN	46.59%		66.56%

Previous results had shown a reduction in toxicity with the sequential removal of particulates in stormwater (Pitt *et al*, 1999a). In Figure 43, the toxicity by particle size is shown for all stormwater samples. Unlike before, no trend is seen by particle size. It appears that a removal of particulates did not decrease the toxicity of these stormwater samples. No trend is seen for inlet or roof runoff samples (Figures 44 and 45, respectively).

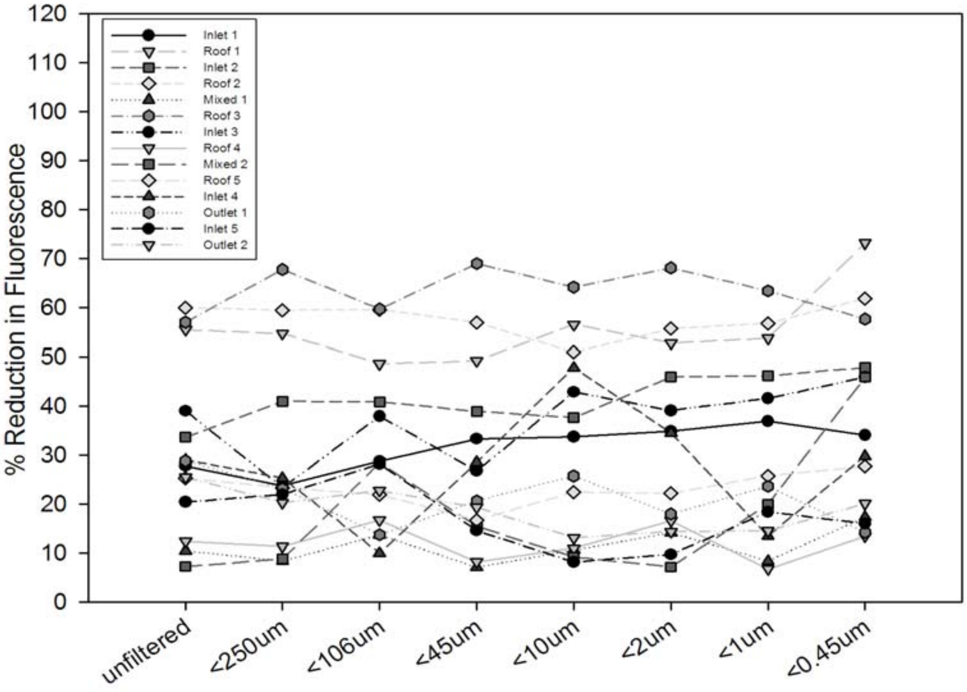

Figure 43: Toxicity by particle size for all stormwater samples.

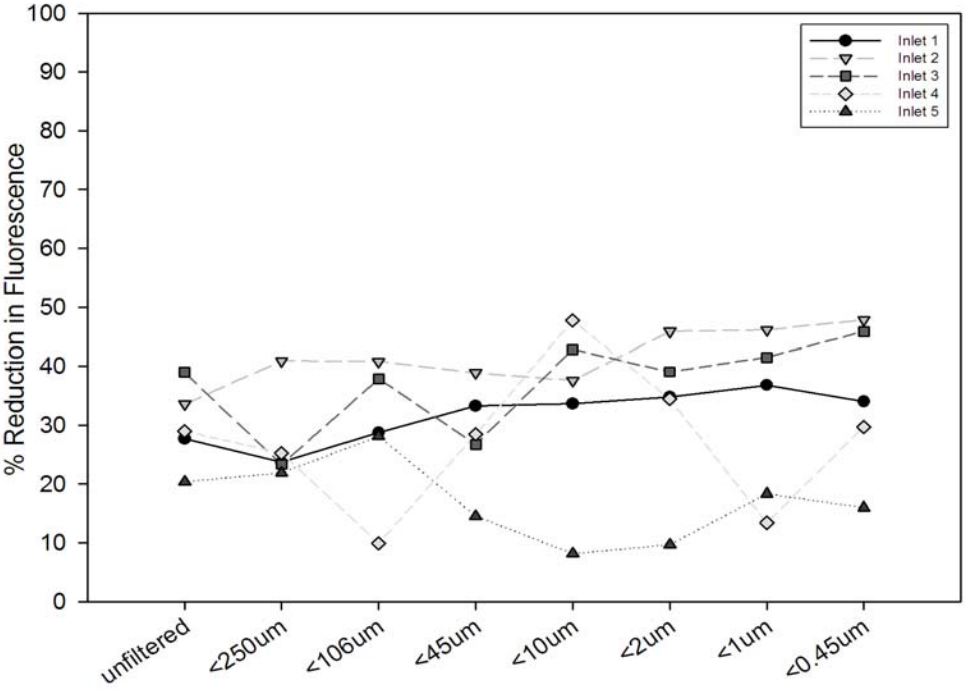

Figure 44: Toxicity by particle size for storm drain inlet samples.

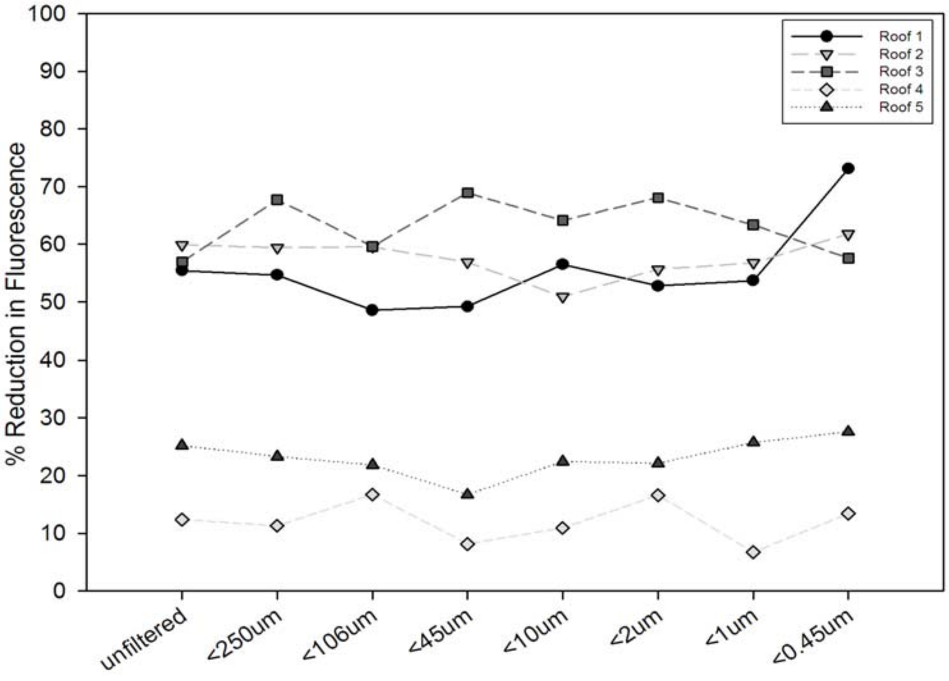

Figure 45: Toxicity by particle size of roof runoff samples.

Because of the discrepancy with previous results, tests were run on a method blank and on a standard concentration of $ZnSO_4$ (0.75 mg/L). The results of these tests are shown in Figure 46. There was a small amount of toxicity with the laboratory blank (water) sample. But there does not appear to be any particular step that is adding toxicity to the samples. The level of toxicity was consistent through all sieve/filter sizes. For the $ZnSO_4$ standard, the percent reduction in toxicity was close to the expected 50% at each particle size. Therefore, the results for the stormwater samples are not erroneous and appear to be valid.

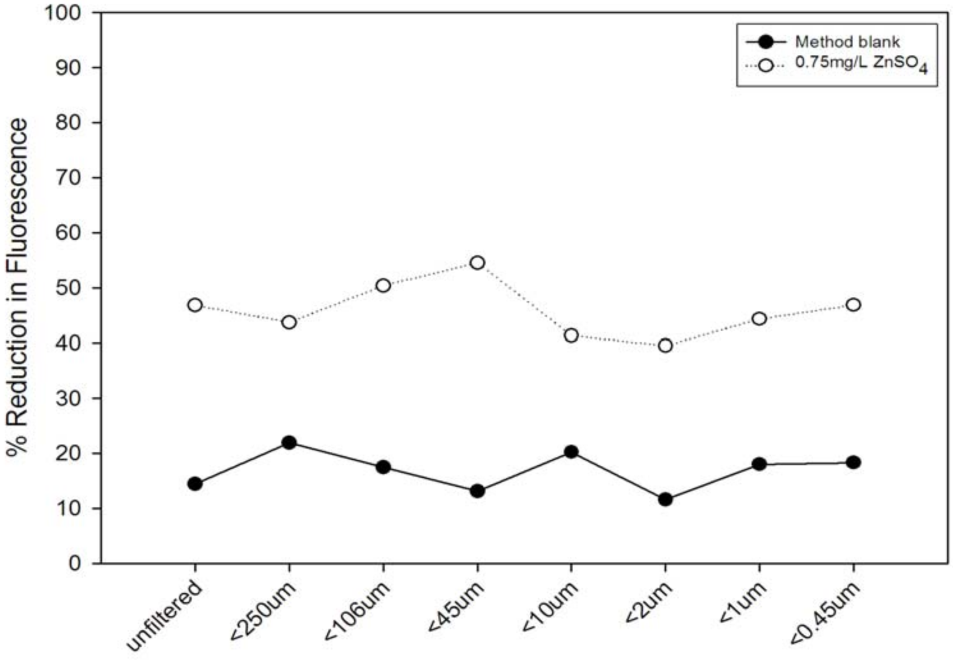

Figure 46: Toxicity by particle size of method blank and $ZnSO_4$ standard.

It is difficult to explain why the results have changed. No samples are the same and the Microtox® testing procedure has changed as well as the bacteria used to perform the test. Perhaps before the pollutants associated with the particulates in the samples were more toxic than the pollutants in these samples. We have found good repeatability with this new testing equipment and procedures. As shown in Table 12, repeatability tests with standard concentrations of 0.75 mg/L and 1.00 mg/L $ZnSO_4$ resulted in errors of 6.3 and 4.7%, respectively. Therefore, we would not expect a large error in the test results to account for a change from previous results. For these fourteen samples, toxicity did not appear to be associated with the particulates.

The toxicity of the storm drain filter inlet and outlet samples in shown in Figure 47. In general, when compared to a method blank sample, these samples were not highly toxic and little or no difference was seen between the inlet and outlet samples. For the first inlet sample, there was a strange jump in toxicity at 45, 10 and 2 µm that could not be explained. Perhaps some contamination occurred in that particular sample split because the 45, 10, 2 and 1 µm fractions are processed from the same 1L bottle split.

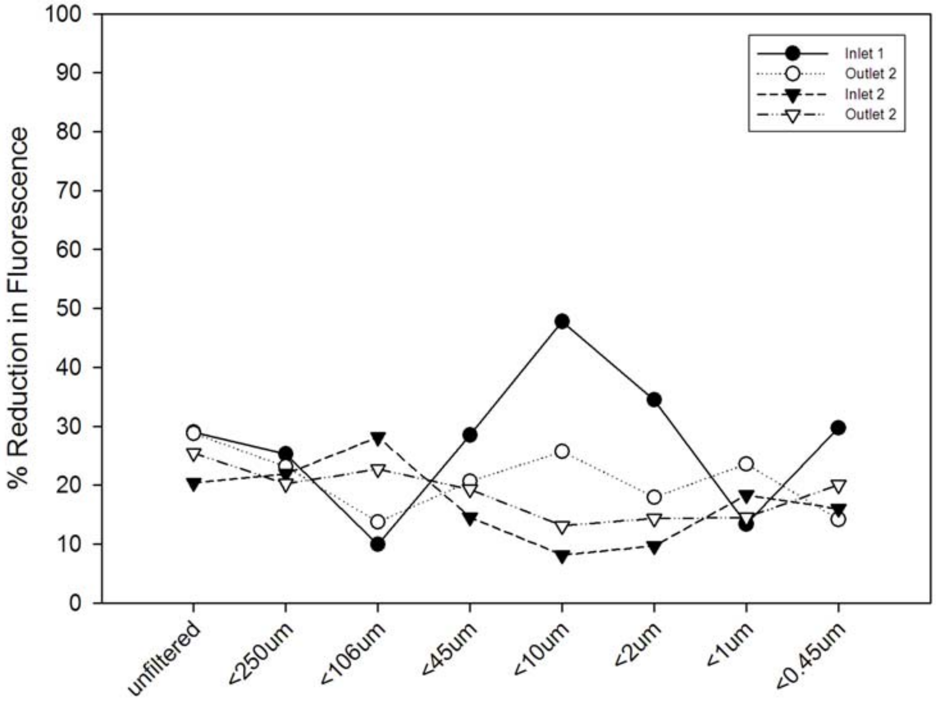

Figure 47: Toxicity by particle size for storm drain filter inlet and outlet samples.

2.4.5 Heavy Metals

2.4.5.1 Zinc and Copper

In Figure 48, zinc concentrations for all samples by particle size are shown as measured by ICP-MS. There were a few roof runoff samples that were higher than the majority of the other samples. This is not unusual since many roofs are now made of metallic materials. In this case, roof 2 and roof 3 were collected on the same day and during the same storm. The dry period before this storm was approximately two weeks. Therefore there may have been a higher concentration of zinc in these samples due to atmospheric deposition. The roof from the Tuscaloosa Courthouse is relatively new and appears to be constructed of aluminum. Zinc is a common contaminant of roof runoff. In addition, samples from these two events were taken at the beginning of the storm (first flush) whereas subsequent roof samples were taken later during the storm. There is a slight, but noticeable trend of decreasing Zn concentration as more particulates are removed from the stormwater samples. As seen in the previous plots for solids and nutrients, the decrease in pollutant concentration levels out around 10 µm. Below 10µm, most of the pollutants are dissolved. It should be noted that problems with analysis of the samples by ICP-MS resulted in some Zn concentrations being biased +20% compared to other samples. Since trends were important and not the exact concentration, the values were left as given and not corrected.

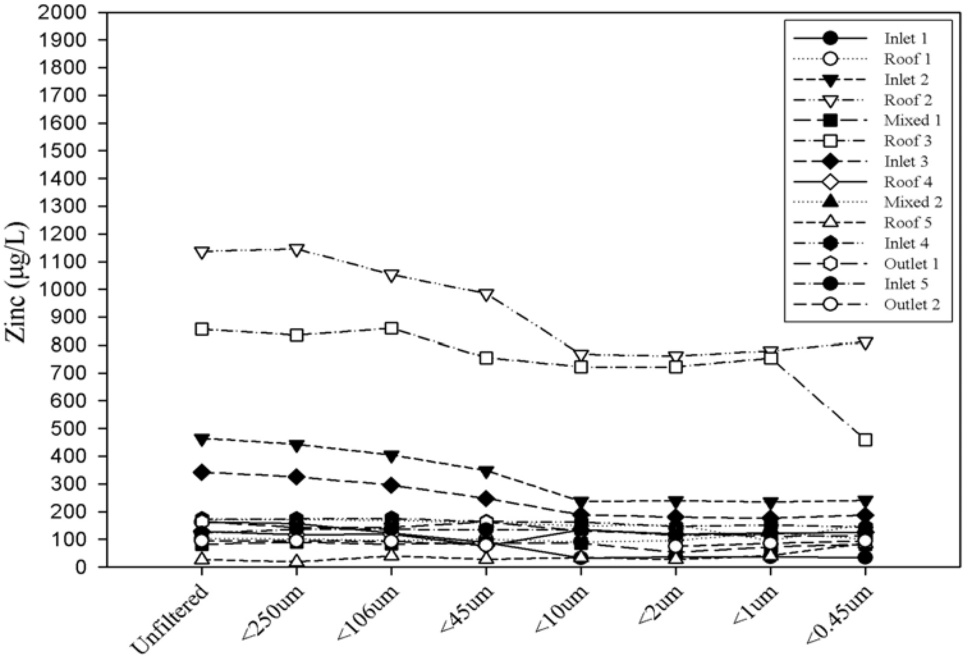

Figure 48: Zinc concentrations by particle size for all stormwater samples.

The same overall trend with particle size is not seen for copper. In Figure 49, copper concentration is given by particle size for all samples as measured by ICP-MS. There is a strange increase in Cu for the roof 3 sample at 106 µm. It is difficult to explain this discrepancy. Not all samples were analyzed together at the same time and there were analysis problems using the ICP-MS instrument. Nevertheless, it is possible that some contamination occurred during the processing of that particular sample.

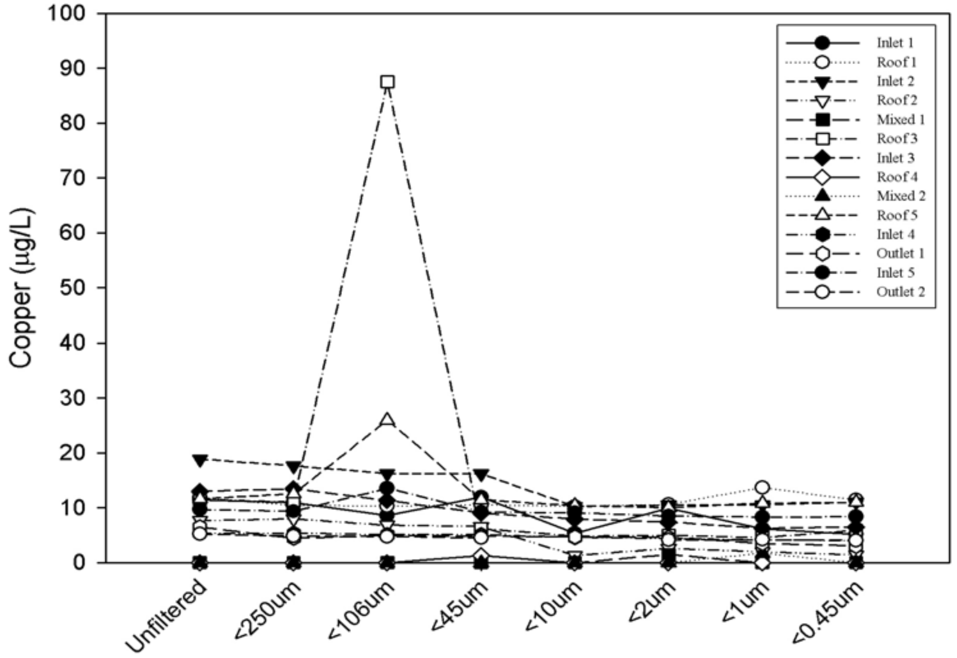

Figure 49: Copper concentrations by particle size for all stormwater samples.

Trends with particle size can better be seen by looking at the samples separated by type. In Figures 50, the trends by particle size are a little more obvious. All of the inlet samples showed a decrease in zinc concentration with sequential removal of particulates down to 10 µm. Two of the more polluted roof runoff samples showed the same decrease in zinc with particle size. For the other three roof runoff samples, most of the zinc was not associated with particulates. The mixed samples behaved mostly like roof runoff samples with little association of zinc with particle size.

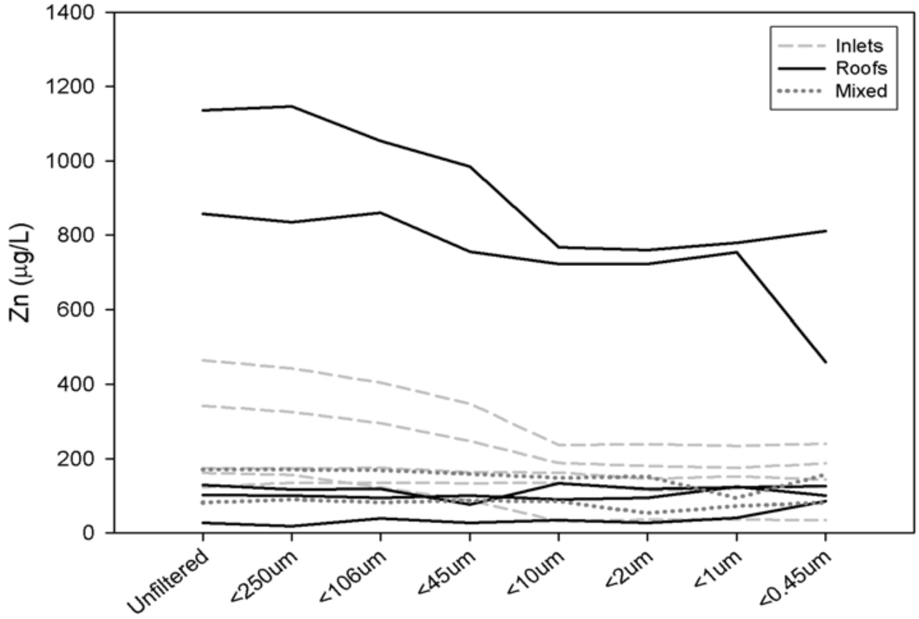

Figure 50: Zinc concentrations by type and particle size as measured by ICP-MS.

For copper, it is better to look at the inlet and roof runoff samples separately. In Figure 51, a slight trend of decrease copper with sequential removal of particulates can be seen for inlet samples. It is difficult to see this trend in Figure 49 because of the outlying data point for roof 3. If this point is removed from the plot, the trends by type can more easily be seen as shown in Figure 52. The concentration from inlets and roofs were similar with the mixed samples having the lowest concentrations.

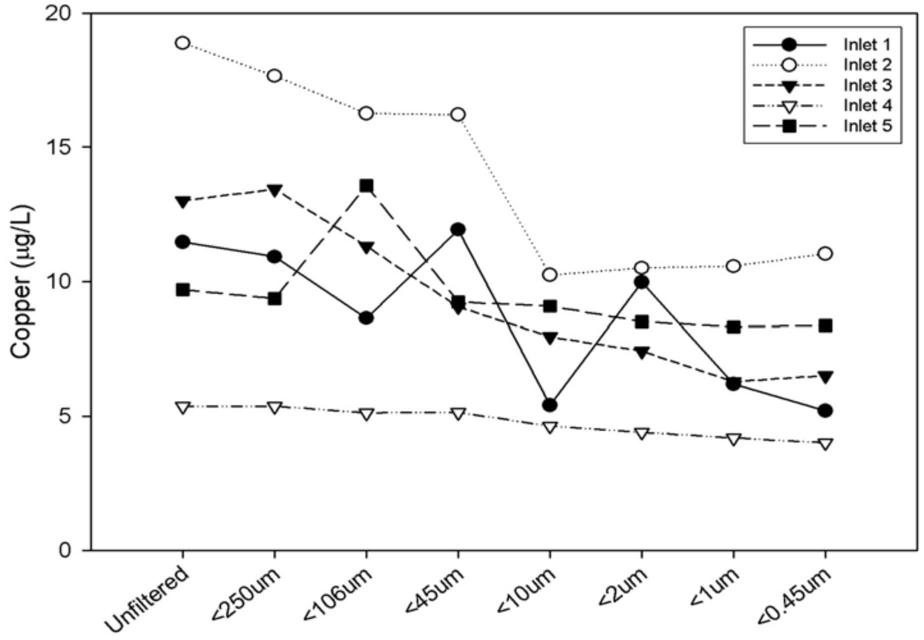

Figure 51: Copper concentrations by type and particle size for storm drain inlet samples.

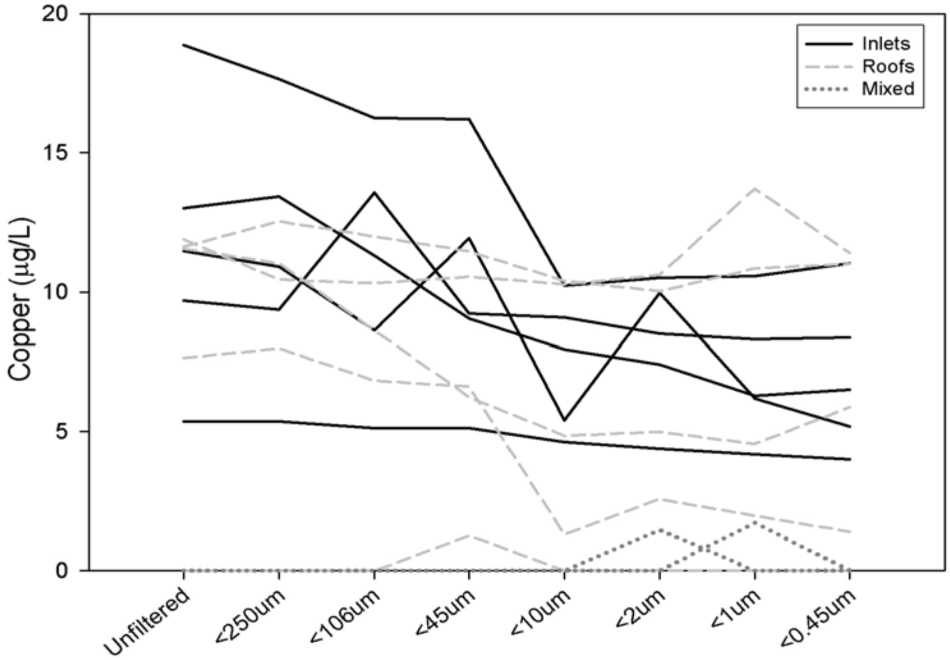

Figure 52: Copper concentration by type and particle size as measured by ICP-MS after removal of outlying data point.

2.4.5.2 Lead and Cadmium

For lead and cadmium, few samples showed a trend of decreasing concentration with the sequential removal of particulates. Figure 53 shows cadmium concentration by particle size for all samples. From this plot, there does not appear to be a trend of pollutant removal with sequential removal of particulates. Most of the cadmium is dissolved and not associated with particulates. There is one data point that is much larger than the others for the mixed 2 sample at 250 microns. Again, as for copper, it is difficult to determine why one fraction would show such a high concentration in comparison to other samples. Contamination of that fraction is possible (an air-borne particulate or something on the sieve) as is a problem with the ICP-MS measurements. There was a problem with the ICP-MS measurements for many of the sample batches. The technician had to run many samples 3 or 4 times. Ultimately, the data that was produced had to be used, but some values were elevated and some may not be correct. Unfortunately, there was not time to correct the problem with the ICP-MS. The concentrations by particle size are more easily seen in Figure 54 where the outlying value for the mixed 2 sample was removed. For some samples there is a slight decrease in cadmium concentration with the removal of particulates, but for most, the cadmium seems to be mostly dissolved.

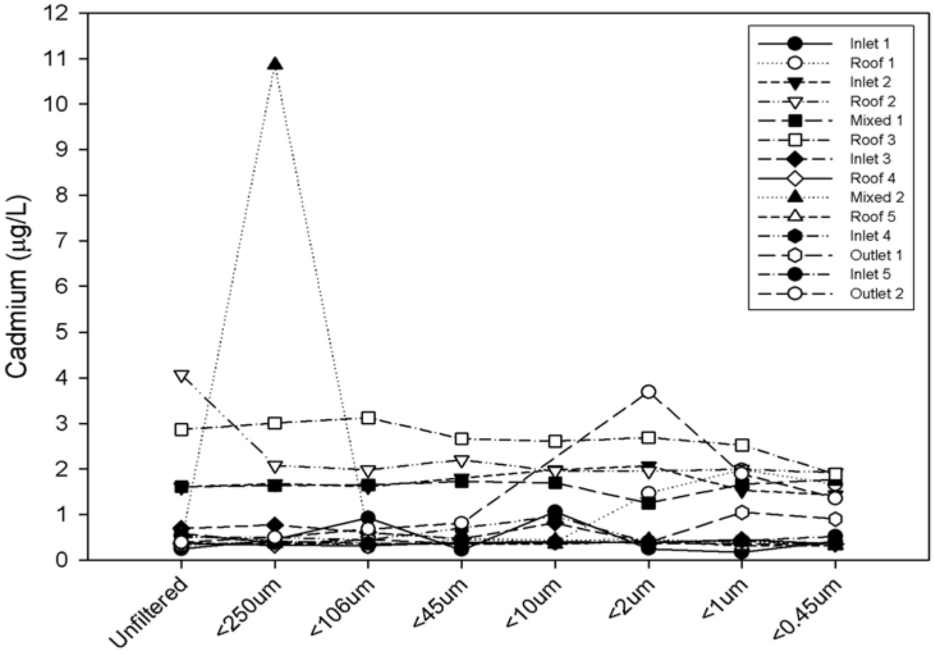

Figure 53: Cadmium concentrations by particle size for all samples.

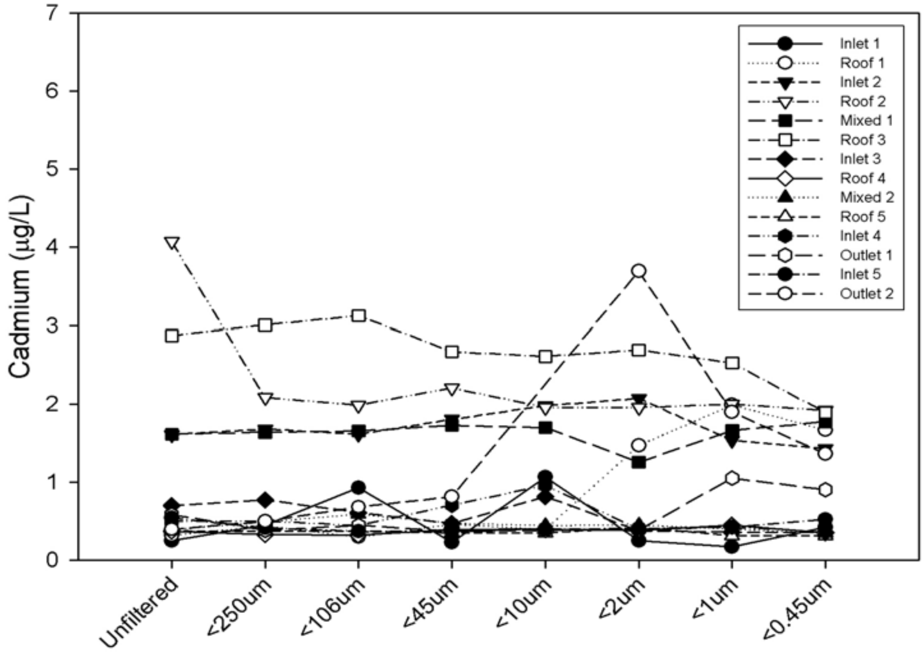

Figure 54: Cadmium concentrations by particle size after removal of outlying data point.

Lead concentrations by particle size are shown in Figure 55. For some samples, there was a decrease in concentration with removal of particulates. For others, most of the lead was dissolved and not removed with the removal of particulates.

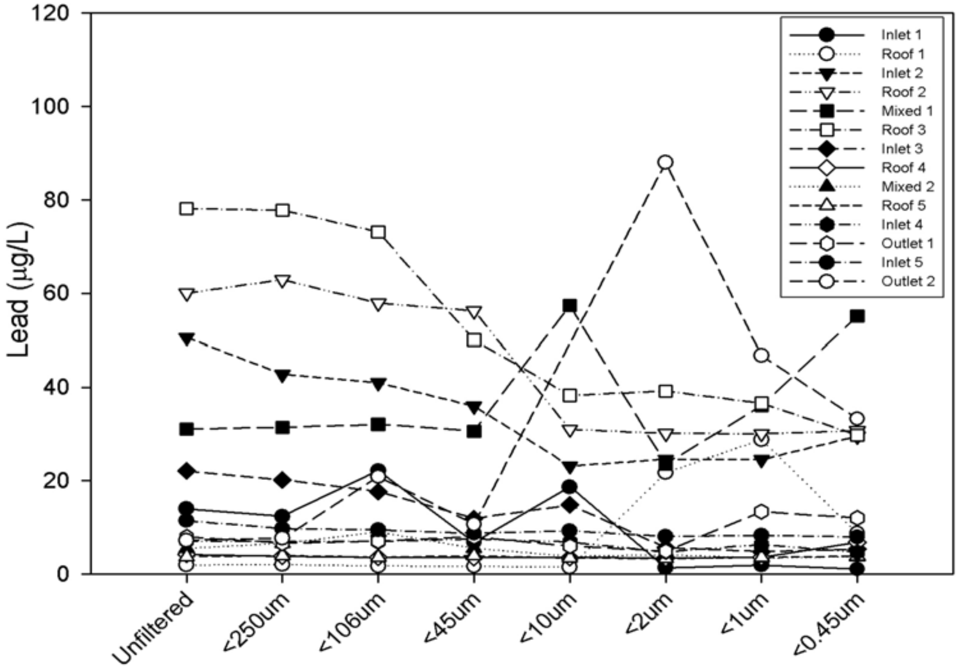

Figure 55: Lead concentration by particle size for all samples.

The difference between sample types can be seen in Figure 56. There were jumps in concentration for some fractions demonstrating the innate variability in these analyses, but in general, most samples showed a decrease in lead with removal of particulates.

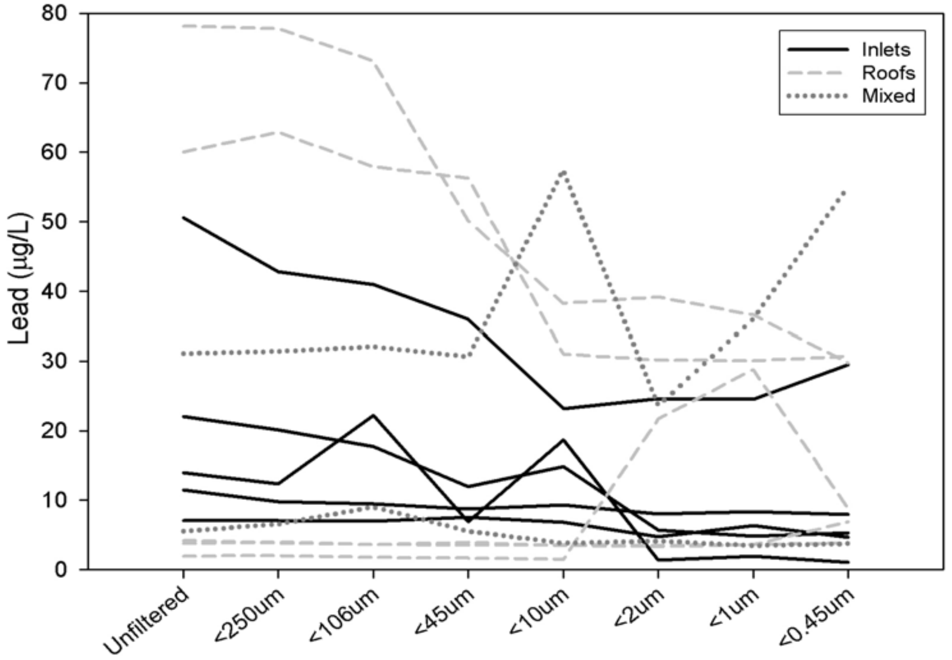

Figure 56: Lead concentration by sample type and particle size.

Inlet and roof runoff samples can be seen separately in Figures 57 and 58, respectively. For the most polluted samples, a decrease in lead occurred with the sequential removal of particulates. Again, like for zinc, the roof 2 and roof 3 samples had the highest concentrations of lead. Much of this may be due to atmospheric deposition because of the long antecedent dry period. The highest inlet sample (inlet 2) was sampled at the same time as roof 2 and 3. The antecedent dry period allowed for a larger accumulation of particulates and pollutants in the parking lot where this inlet was located. Subsequent samples at the same location showed lower concentrations of lead.

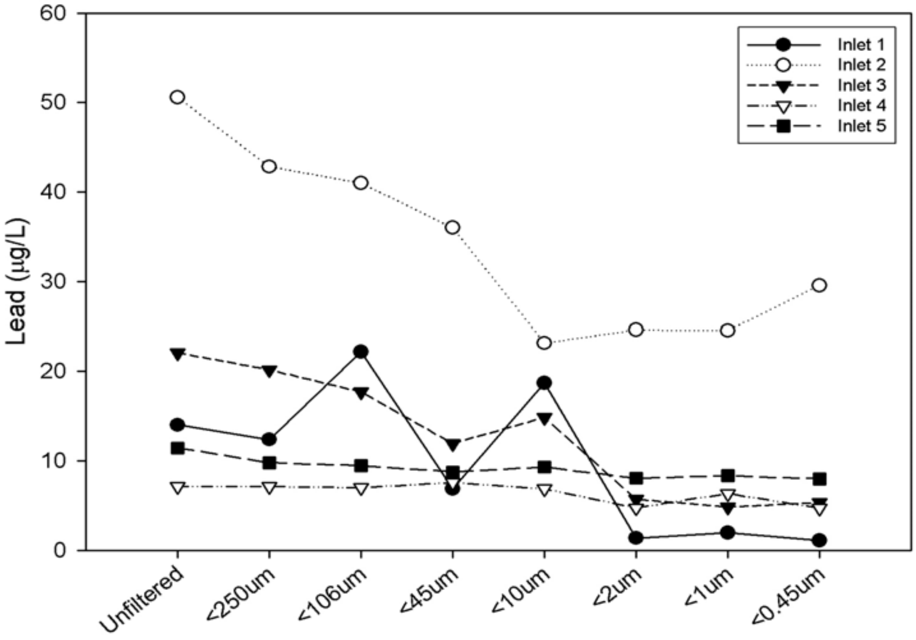

Figure 57: Lead by particle size for storm drain inlet samples.

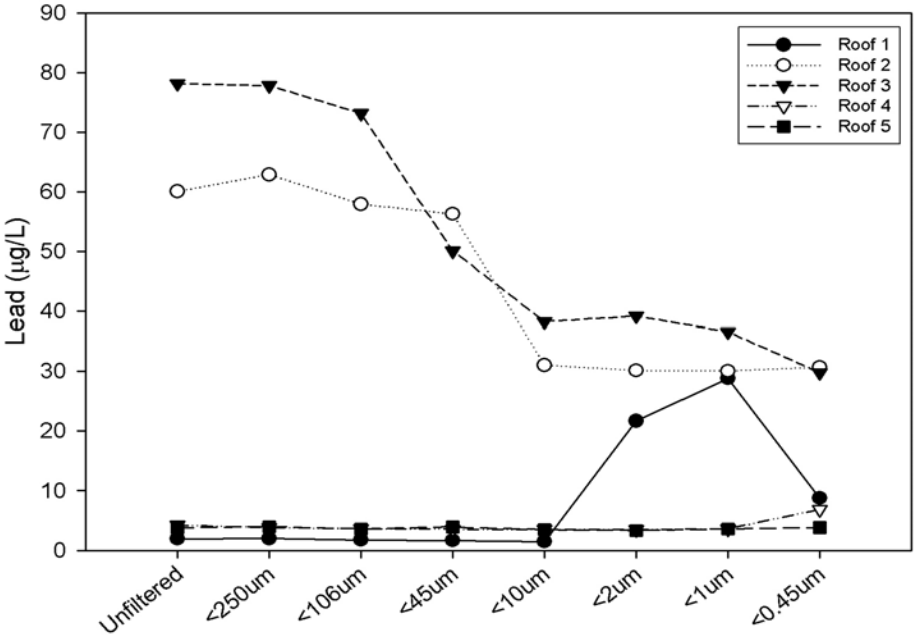

Figure 58: Lead by particle size for roof runoff samples.

2.4.5.3 Inlet versus Outlet Samples

Metal concentrations for storm drain upflow filter inlet and outlet paired samples are shown in Figures 59-62. With the exception of zinc, most metals were not reduced with use of this storm drain filter. Both pairs of samples showed a reduction in zinc with filtration (Figure 59). The second pair showed the larger reduction. Only the second pair of samples showed a reduction in copper (Figure 60). No differences were seen for cadmium and lead (Figures 61 and 62). There appears to have been some contamination of the 2 µm fraction of both cadmium and lead. There is a large increase in both cadmium and lead in that particular fraction.

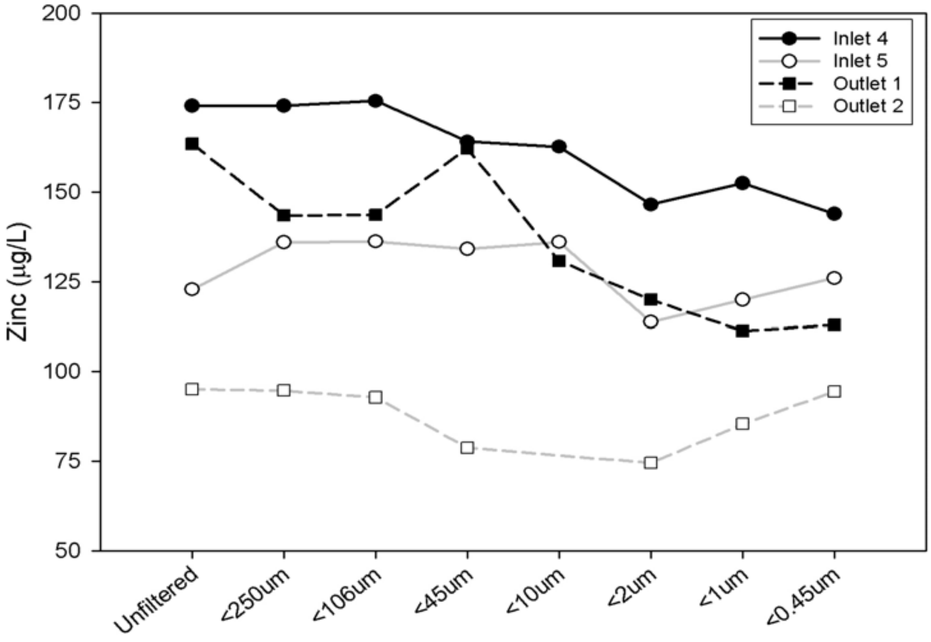

Figure 59: Zinc by particle size for storm drain upflow filter inlet and outlet samples.

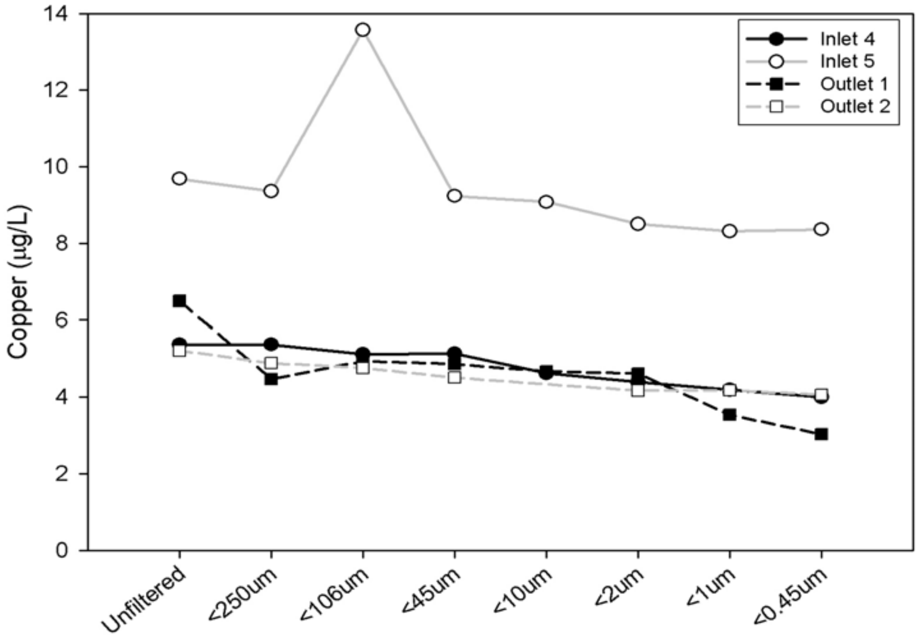

Figure 60: Copper by particle size for storm drain upflow filter inlet and outlet samples.

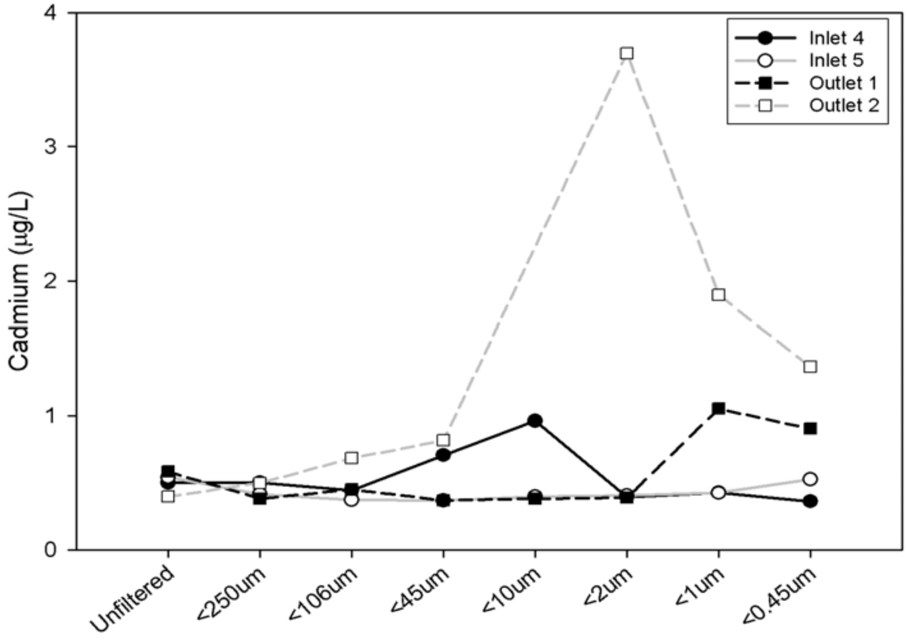

Figure 61: Cadmium by particle size for storm drain upflow filter inlet and outlet samples.

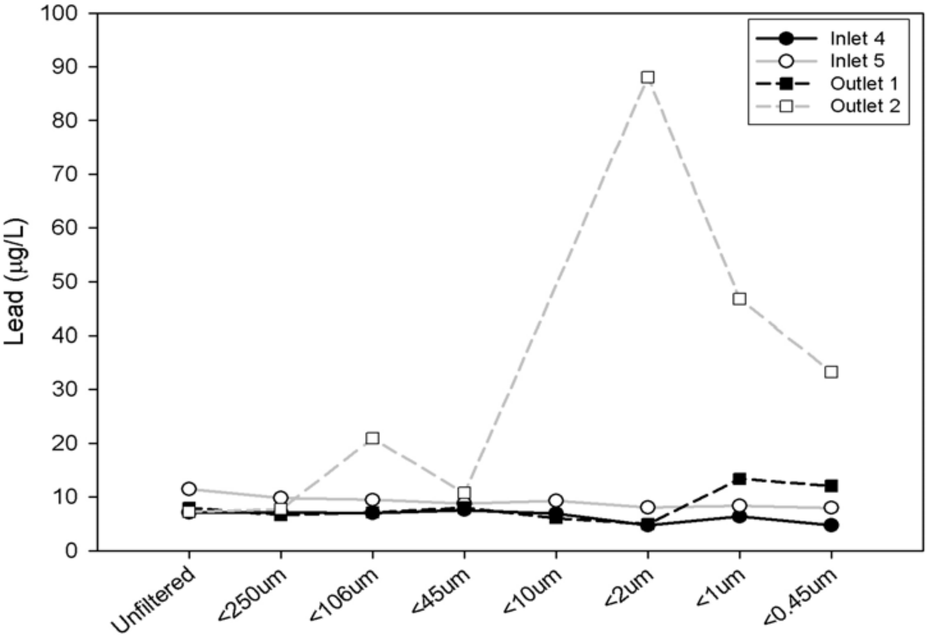

Figure 62: Lead by particle size for storm drain upflow filter inlet and outlet samples.

CHAPTER 3

USE OF ANODIC STRIPPING VOLTAMMETRY TO MEASURE DISSOLVED HEAVY METALS IN STORMWATER

3.1 Introduction

Measurement of the total metal concentration in a water sample provides little information about the bioavailability and/or toxicity of the metal. It has become more apparent that metal speciation is essential to understanding the fate of a metal and its availability to biota. In natural waters, only a small portion of the overall dissolved metal may be present as the free hydrated cations because metal ions form stable complexes with a large variety of inorganic and organic ligands, which influence the bioavailability, toxicity, and mobility of the metal (Mota and Correia Dos Santos, 1995). In the case of metal toxicity, it is generally accepted that the free metal ion is the form most toxic to aquatic life. Strongly complexed metal, or metal associated with colloidal particles, is much less toxic (Florence and Batley, 1980). To obtain meaningful data on either bioavailability or toxicity, it is essential that chemical speciation techniques be applied.

Florence (1977) proposed a trace metal speciation scheme for determining the chemical forms of Cu, Pb, Cd and Zn in natural fresh waters. This scheme utilizes the chelating resin Chelex-100 to separate ionic and colloidal metal fractions and involves both ultraviolet irradiation and chelating resin separation steps, along with anodic stripping voltammetry (ASV) for measurements of labile and total metal in the separated fractions. The use of a chelating resin such as Chelex-100, in combination with ASV, have been utilized by many researchers, and various forms of the resin have been characterized (Figura and McDuffle 1977, 1979, 1980; Yousef, *et al* 1985). The methods used during this project were modified, based on the Florence and Batley scheme.

One of the major applications of voltammetry in environmental analysis has been speciation studies (Bott, 1995). Anodic stripping voltammetry (ASV) can provide a direct method for the study of trace metals at low concentration levels because it does not require, as an initial step, preconcentration of the water sample by physical methods. ASV can also be used to measure Zn, Cd, Pb and Cu all at the same time.

ASV is the most widely used form of stripping analysis (Wang, J., 2000). In ASV, metal ions in solution are concentrated onto a hanging mercury drop electrode by reduction to the metallic state. During deposition, the metals dissolve in the mercury by diffusion and convection and form an amalgam:

$$M^{n+} + ne^{-} + Hg \rightarrow M(Hg)$$

where n is the number of electrons and M is the metal being reduced. The convective transport is achieved by stirring of the solution. The duration of the deposition step is selected according to the concentration level of the metal ion(s) in question. The total amount of metal plated represents a small (but reproducible) fraction of the metal present in the bulk solution. Following the preselected time of deposition, the forced convection is stopped, and a short rest period on the order of several seconds is observed. During this rest period, the deposition current drops to near zero, the concentration of metal in the amalgam becomes more uniform, and the solution is allowed to become quiescent. A positive-going potential scan is then applied to oxidize (strip) the metal from the amalgam back into solution to its original state:

$$M(Hg) \rightarrow M^{n+} + ne^{-} + Hg$$

The resulting anodic peak currents are proportional to the concentration of the metal ions in the sample (Dewald, H.D., 1996). This entire process must be carried out in an oxygen-free solution, therefore the solution is purged for 5-10 minutes with highly pure nitrogen or argon gas before deposition.

A typical voltammogram produced using ASV with the Epsilon™ Electrochemical Analyzer and the CGME is shown in Figure 63 for Zn, Cd, Cu and Pb at a concentration of 20µg/L and analyzed by square wave stripping Voltammetry (SWSV).

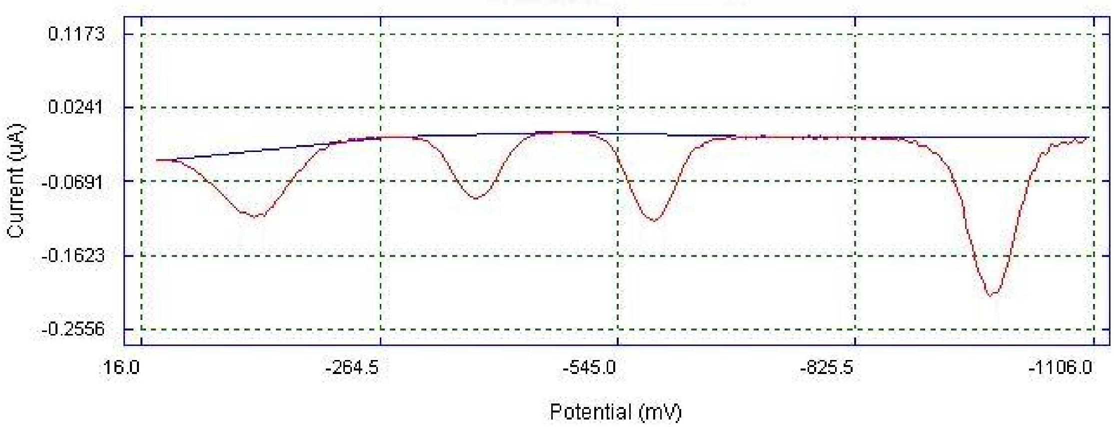

Figure 63: Typical ASV voltammogram using square wave stripping voltammetry at a concentration of 20µg/L. From left to right the peaks are: Cu, Pb, Cd and Zn.

Multiple voltammograms can be combined and overlayed to produce a plot showing the background and successive increases in concentration. Figure 64 displays multiple voltammograms using SWSV. The uppermost line is the background solution of 0.1M KCl followed by a 10µg/L solution of Zn, Pb, Cu and Cd in 0.1M KCl. The successive voltammograms are in order from top to bottom: 20, 30 and 40 µg/L solutions of Zn, Pb, Cu and Cd. Again, from left to right, the peaks are Cu, Pb, Cd and Zn.

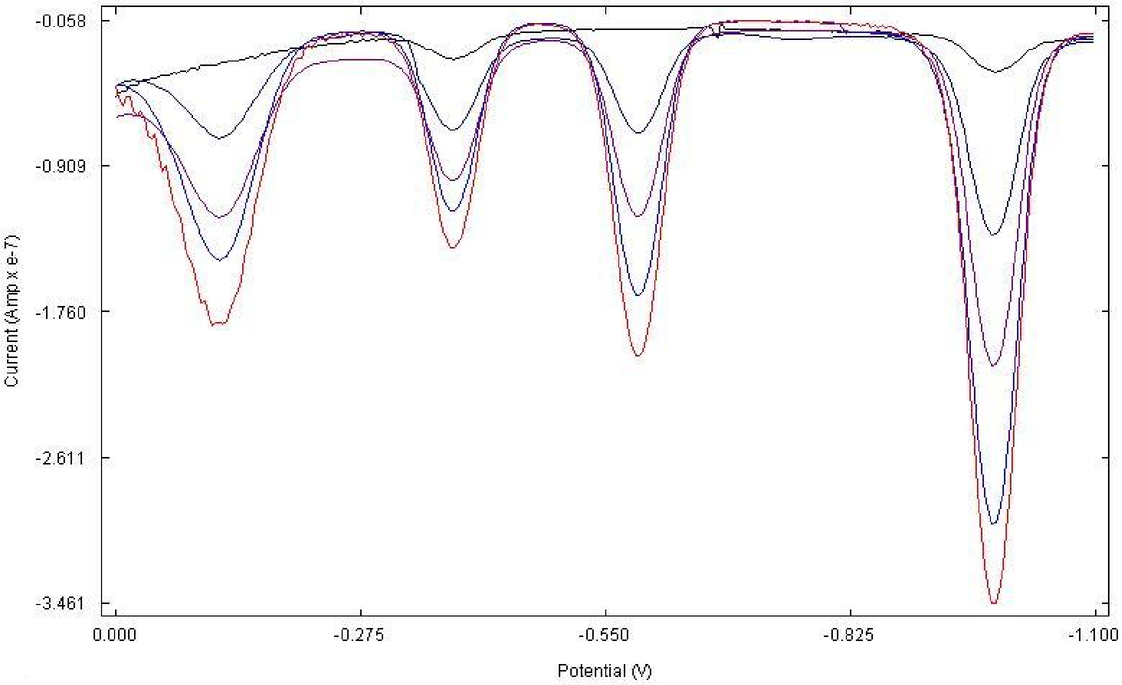

Figure 64: File overlay of multiple SWSV voltammograms in 0.1M KCl for 10, 20, 30 and 40µg/L concentrations of Zn, Cd, Pb and Cu.

3.2 Methodology

For each sample, six liters of stormwater was collected manually into acid washed HDPE or LDPE sample bottles. Immediately following each event, samples were transported to the laboratory within one hour and then stored at 4°C until further processing and analysis. A total of fourteen samples were collected. Collection sites were either roof runoff, sheetflow runoff, or a combination of the two from the Tuscaloosa, Alabama area. Two sets of samples (samples 11-14) were taken in order to analyze the function of an upflow stormwater filter located in a storm drain inlet at the Courhouse in Tuscaloosa, AL

For each sample, the filtered fraction (<.0.45µm), dissolved Zn, Cu, Cd and Pb were measured using voltammetric methods with an Epsilon™ Electrochemical Analyzer and Controlled Growth Mercury Electrode (CGME). In addition, the filtered fractions were subjected to a sequential extraction procedure. Each fraction was exposed to ultraviolet light for six hours while continuously being stirred in a Rayonet Chamber Reactor™ in order to cause dissociation of metals from organic complexes or colloids. The portion of the same filtered sample was also be exposed to Chelex-100 ion exchange resin using a batch procedure in order to separate ionic metals from metals strongly bound to metal-ligand complexes or those strongly adsorbed to colloidal particles. For each 100mL of filtered sample, 5g of Chelex-100 resin is added and the sample is gently shaken for one hour on a shaking table. After the Chelex exposure, the sample is again filtered through a 0.45µm filter and a portion put aside for metals analysis using ASV. After Chelex exposure, the rest of the sample is then UV irradiated for 6 hours and processed for metals analysis by ASV.

3.3 Results and Discussion

3.3.1 Development of ASV for use with stormwater samples

The first step in using voltammetric techniques for this study was to develop the optimal settings for the metal concentrations that were expected in the stormwater samples. At first the plan was to try and use voltammetric techniques to measure metals in all size fractions of the samples. In order to do so, it would necessary to use 10% nitric acid as the electrochemical medium for measuring the metals since all fractions will first be acid digested in 10% tracemetal grade nitric acid (Fisher Chemical). Unfortunately, there was a problem getting a clean voltammagram using nitric acid as the electrochemical medium. There was too much noise in the region of Zn. It was thought that perhaps raising the Ph of the acid would result in a cleaner voltammogram. NaOH was used to raise the Ph of the HNO_3, but there was no change in the resulting voltammogram. Next, it was thought that the quality of the acid could play a factor and so ultrapure nitric acid from Mallinckrodt-Baker was purchased and run through the same procedures. Again, no change in the results. In order to rule out a problem with the equipment or technique, 0.1M KCl was used as the electrochemical solution (a common electrochemical medium) and resulted in a clean voltammogram (although there is a very small amount of Pb and Zn contamination of the KCl). In order to reduce the amount of Pb and Zn contamination, samples were run at a 5:1 dilution of sample:0.1M KCl (8Ml sample to 2Ml 0.1M KCl). Next, varying combinations of HNO_3 and KCl were tried with no success. At this point, the decision was made to only use the ASV for samples that are not acid-digested and to use the ICP-MS to measure heavy metals for the acid-digested samples.

Using previous results of heavy metal concentrations in stormwater measured by ICP-OES, the decision was made to test a range of metals from 0.5 to 1000 µg/L in 0.1M KCl. Square Wave Stripping Voltammetry (SWSV) was chosen as the technique because it was more rapid than the other option of Differential Pulse Stripping Voltammetry (DPSV).

First, the optimal plating time needed to be determine to measure the lowest concentrations of metals desired. A five minute deposition time worked well for 0.5 to 5 µg/L concentrations of Zn, Cd, Pb and Cu. A 1-minute deposition time could be used for concentrations above 5 µg/L. The results of these tests are shown in Table 13. The peak heights in µA are listed for each metal tested according to concentration. This table was useful for determining the approximate concentration of metals in stormwater samples. An approximate concentration was needed because the standard additions procedure was used to quantitate the metals in samples.

Table 13: Tests of varying metals concentrations using SWSV and 1min or 5min deposition times.

Concentration (µg/L)	**Peak Height (µA)**			
	Zn	Cd	Pb	Cu
Background (5min deposition)	0.291	0	0.04	0
0.5	0.241	0.331	0.045	0.026
1	0.255	0.342	0.053	0.035
2	0.297	0.379	0.072	0.052
3	0.321	0.389	0.083	0.067
4	0.346	0.397	0.093	0.081
5	0.395	0.432	0.11	0.102
Background (1min deposition)	0.0203	0	0.0131	0
10	0.113	0.056	0.049	0.040
20	0.195	0.106	0.078	0.078
30	0.280	0.157	0.106	0.113
40	0.331	0.192	0.127	0.144
Background (1min deposition)	0.082	0	0.011	0
50	0.490	0.250	0.160	0.170
100	0.890	0.500	0.315	0.340
200	1.740	1.010	0.610	0.640
300	2.395	1.420	0.850	0.835
400	3.050	1.800	1.100	1.000
Background (1min deposition)	0.010	0	0.010	0
500	4.550	2.750	1.650	1.400
600	5.400	3.300	2.000	1.600
700	6.000	3.700	2.200	1.700
800	7.000	4.300	2.600	1.900
900	7.900	4.900	2.900	2.000
1000	8.500	5.300	3.100	2.100

Next, the method detection limit for each metal was determined using SWSV, a deposition time of 5 minutes, drop size of 8, stirring at 300 rpm and purging time of 300 seconds. A concentration of 0.5 µg/L was chosen as the estimated detection limit for the above ASV settings. Seven aliquots of a 0.5 µg/L solution containing each metal was run as if it was a stormwater sample. Two standard additions of 0.5 µg/L each were added to each aliquot in order to calculate the measured concentration of the standard solution. The MDL for each metals is listed in Table 14. The MDL is the standard deviation

(St.Dev.) multiplied by Student's t-value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. For seven replicates, the Student's t-value is 3.143. The highest variability was for Zn, giving a MDL of 3.3 µg/L. The least variable concentration was Cd with an MDL of 0.34 µg/L.

Table 14: Method Detection Limits for all metals using an estimated 0.5 µg/L detection limit and 7 replicates for a deposition time of 5 minutes.

Aliquot #	Zn	Cd	Pb	Cu
1	3.7152	0.4651	1.5238	1.1429
2	2.8613	0.2155	1.9647	0.6124
3	3.1415	0.3651	0.7152	0.9000
4	2.3871	0.3965	0.9740	1.1014
5	1.5206	0.4213	1.3853	1.6105
6	1.9252	0.3990	0.9635	1.7625
7	0.5890	0.1356	1.5446	0.7079
Average	2.31	0.34	1.30	1.12
St. Dev.	1.06	0.12	0.43	0.43
MDL	3.32	0.38	1.36	1.36

3.3.2 Dissolved Metal Concentrations

For each sample, the concentration of metal ions was measured in the dissolved fraction (<0.45 µm) before and after exposure to UV light. The UV exposure breaks down organic complexes or colloids and can release the associated heavy metals that before were not available in the ionic form.

Table 15 shows the concentrations of Zn, Cu, Cd and Pb in the dissolved fractions before and after exposure to UV light. Zinc was present in the highest concentrations ranging from less than 0.5 µg/L to over 800 µg/L. There was a consistent increase in both zinc and copper after UV light exposure, indicating a dissociation of those metals from organic complexes and/or colloids. The zinc concentrations after UV light exposure increased an average of 69% while Cu increased an average of 62%.

The increase in Zn concentrations after UV exposure is shown graphically in Figure 65. In Figure 66, the lines are grouped by sample type showing roofs, inlets and mixed area samples. The sample with the highest concentrations was a roof runoff sample from the Tuscaloosa Courthouse during the summer of 2004. That same roof produced a much lower concentration of dissolved Zn when sampled in the winter of 2005. The flat roofs (samples 6 and 10) produced much lower concentrations of Zn.

Table 15: Dissolved metal concentrations for all samples as measured by ASV before and after UV light exposure.

	Zinc (µg/L)		Copper (µg/L)		Cadmium (µg/L)		Lead (µg/L)	
Sample	Before	After	Before	After	Before	After	Before	After
1	0.26	4.48	0.00	0.55	1.36	0.05	1.08	3.17
2	71.07	569.01	14.20	12.36	0.00	0.00	5.35	19.72
3	112.80	562.00	0.00	10.00	0.39	0.72	3.27	4.10
4	815.08	1891.92	0.00	0.00	37.43	1.31	6.80	1.56
5	27.58	62.09	0.00	0.00	2.72	0.72	0.00	0.00
6	0.00	0.00	1.93	4.40	1.64	1.84	7.74	5.18
7	33.96	898.81	0.00	3.57	0.00	0.85	5.93	1.44
8	28.59	43.98	1.90	2.63	0.64	0.83	0.00	1.19
9	202.00	387.38	0.00	4.50	0.00	0.21	1.06	1.22
10	0.14	16.94	12.25	28.33	0.00	0.39	0.00	0.26
11	55.96	211.88	0.00	3.05	1.99	1.19	18.60	0.00
12	42.94	135.54	0.69	3.09	0.74	3.86	5.94	0.00
13	8.69	243.08	0.00	6.97	0.99	1.90	6.42	0.00
14	23	97.8	0	4.67	0.75	0.77	8.13	0.00

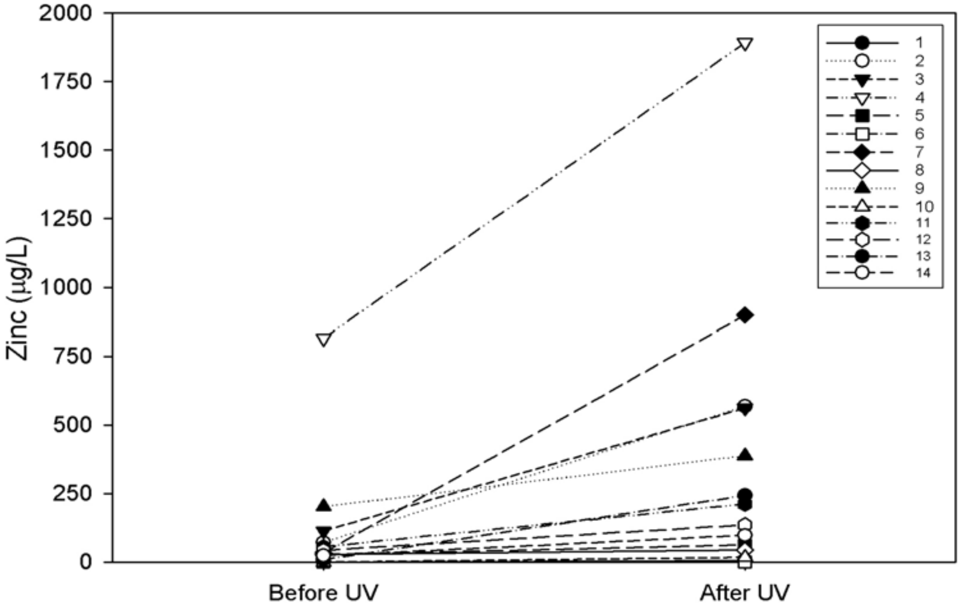

Figure 65: Dissolved zinc concentrations as measured by ASV before and after UV light exposure.

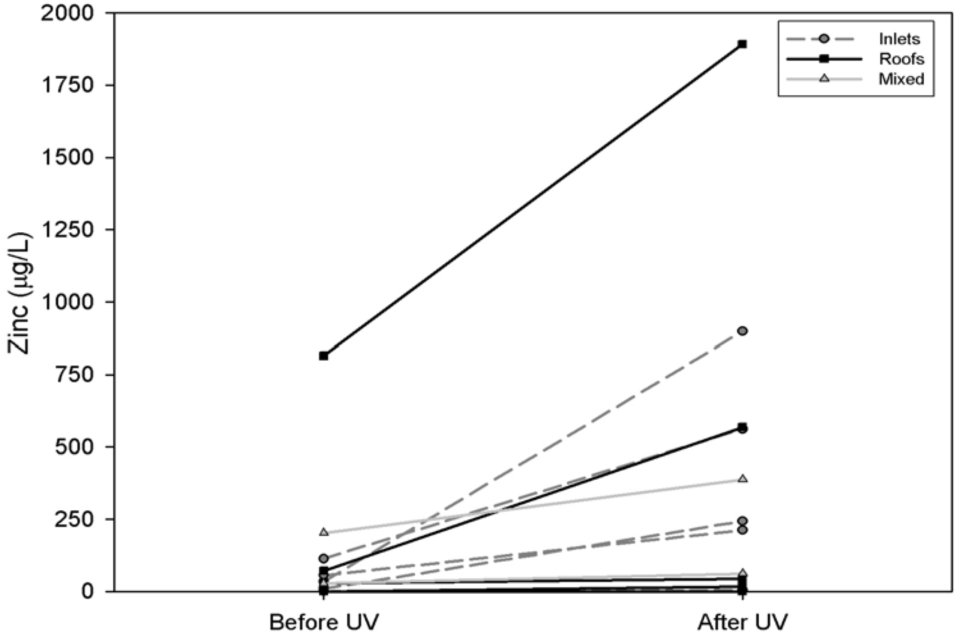

Figure 66: Dissolved zinc concentrations as measured by ASV before and after UV light exposure, broken down by sample type.

The increase in Cu concentrations after UV light exposure is shown graphically in Figure 67. Most of the samples before UV light exposure had little, if any, dissolved copper that could be measured by ASV. After UV light exposure all but one sample showed an increase in dissolved Cu concentration. Overall, the concentrations of dissolved Cu were surprisingly low. Only roof runoff samples had any level of dissolved Cu before UV light exposure. Given that the inlet samples were samples of parking lot runoff with regular traffic flow, it is surprising not to see more dissolved Cu. Results from previous studies has varied with some showing Cu mostly associated with particulates and others where Cu is mostly dissolved. In Figure 68, the concentrations of Cu are broken down by sample type. The largest increases in Cu after UV-exposure were for the inlet samples, indicating an association of Cu with organics and/or colloids in those samples.

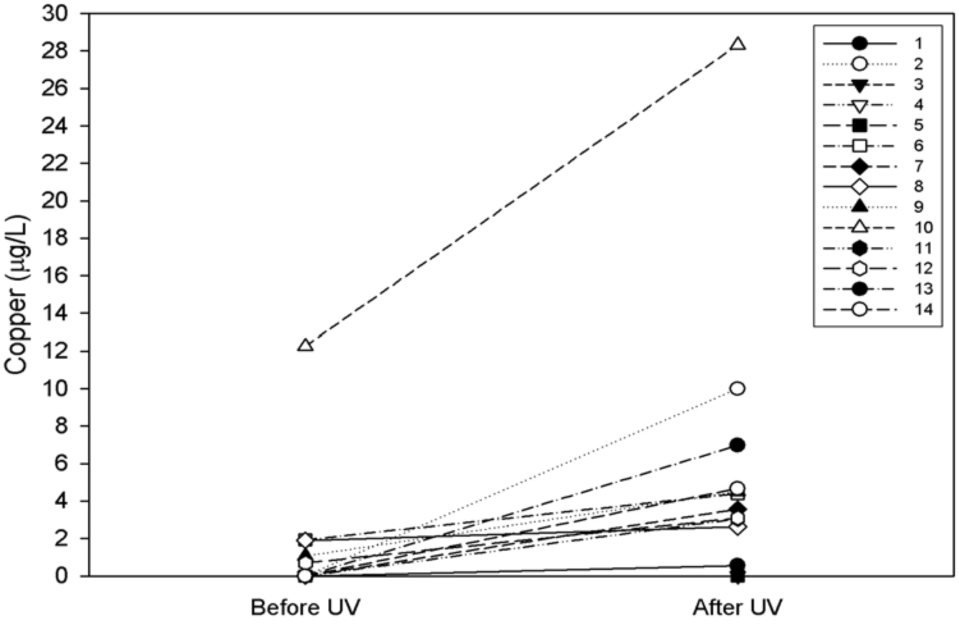

Figure 67: Dissolved copper concentrations as measured by ASV before and after exposure to UV light.

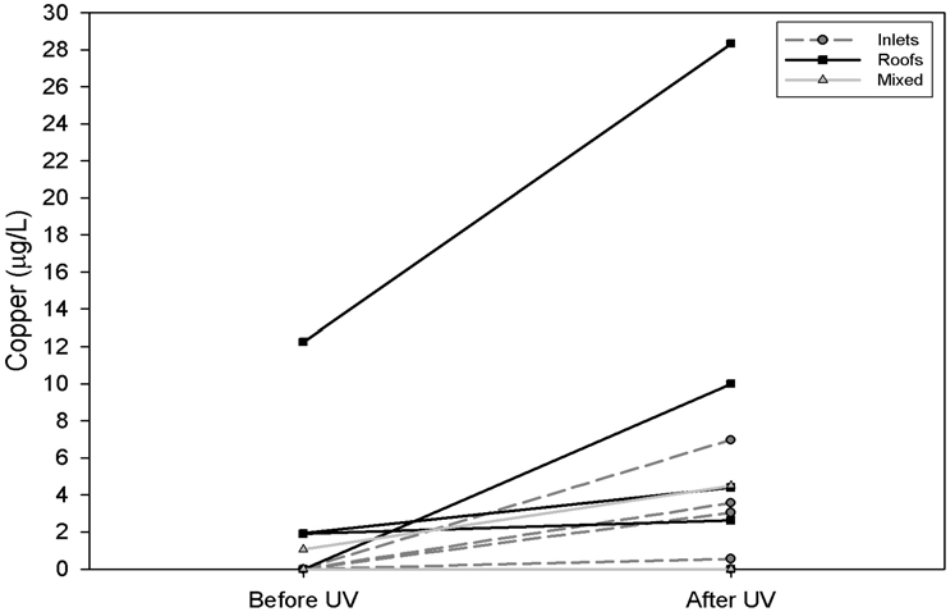

Figure 68: Dissolved concentrations of copper as measured by ASV before and after exposure to UV light, broken down by sample type.

Concentrations of Cd and Pb were less consistent with some samples showing an increase in concentrations after UV light exposure and others indicating a decrease. The concentrations before and after UV exposure for Pb and Cd are shown graphically in Figures 69 and 70, respectively. Since the metals could not be disappearing from the samples during UV light exposure, the apparent decrease in concentrations was most likely due to the difficulty in measuring the lower concentrations of Cd and Pb and also because of the ability of Cd to co-precipitate with Zn on the mercury drop. Pb was particularly difficult to detect in the last four samples after UV light exposure. Figure 71 (without Zn) is an overlay of three voltammograms for inlet 5 before UV light exposure. The top line is the sample and the bottom two lines are the standard additions of known concentrations. The peak for lead at around -0.37 V is in the correct spot for the sample and lines up with the peaks for the standard additions. But after UV light exposure, there is no longer a peak where Pb should be, but one at around -0.40 V (Figure 72 without Zn). This peak was not counted as a peak for Pb and that is why the concentrations for dissolved Pb after UV exposure listed in Table 14 are zero for samples 11-14. Most probably this new peak is another metal, not of interest, that is being released with UV-exposure and is overwhelming the Pb concentration or possibly Pb is co-precipitating with another metal and therefore no longer being seen as a separate peak on the voltammogram.

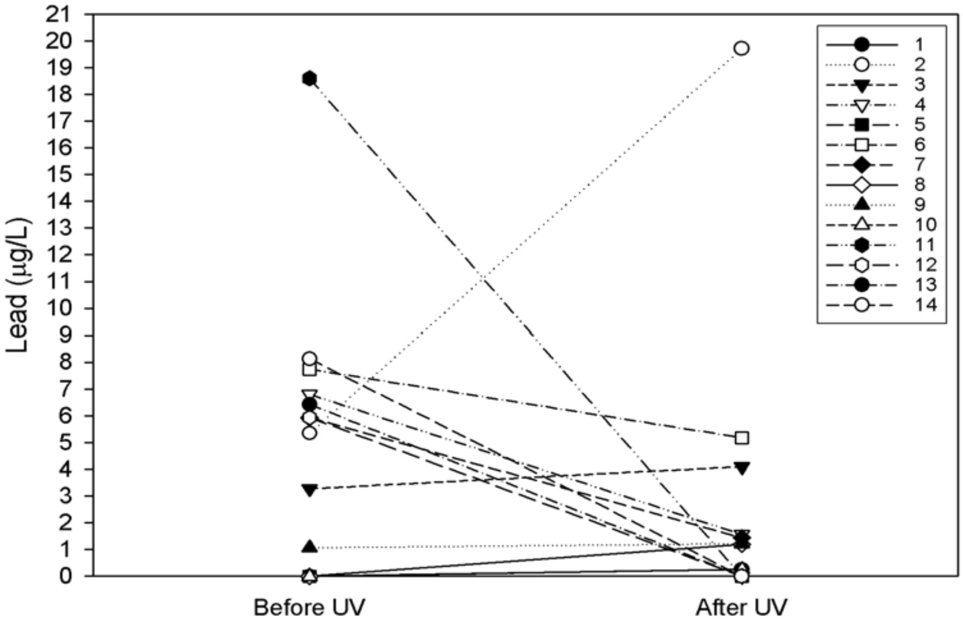

Figure 69: Dissolved Pb concentrations as measured by ASV before and after exposure to UV light.

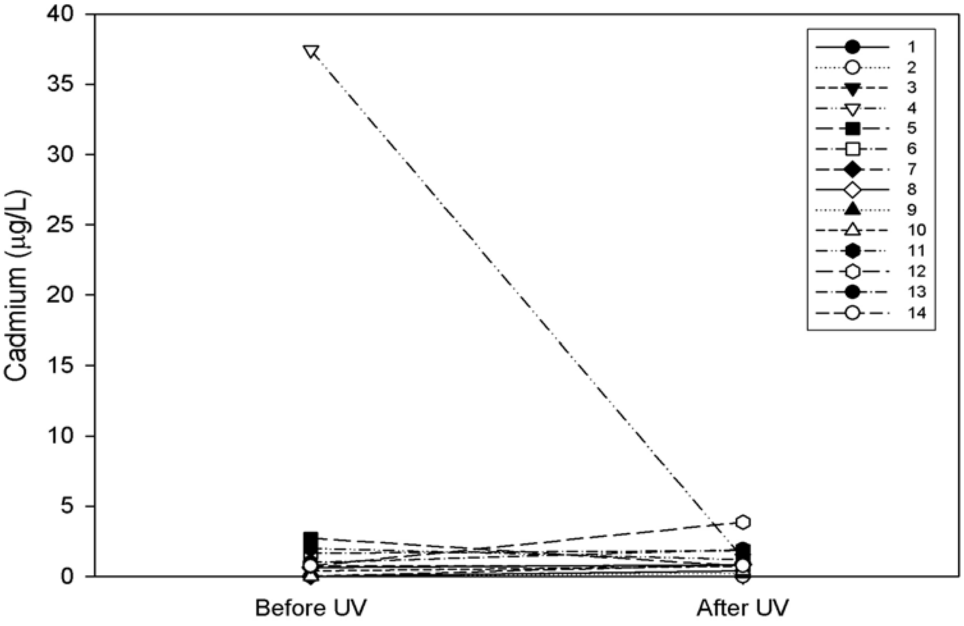

Figure 70: Dissolved cadmium concentrations as measured by ASV before and after exposure to UV light.

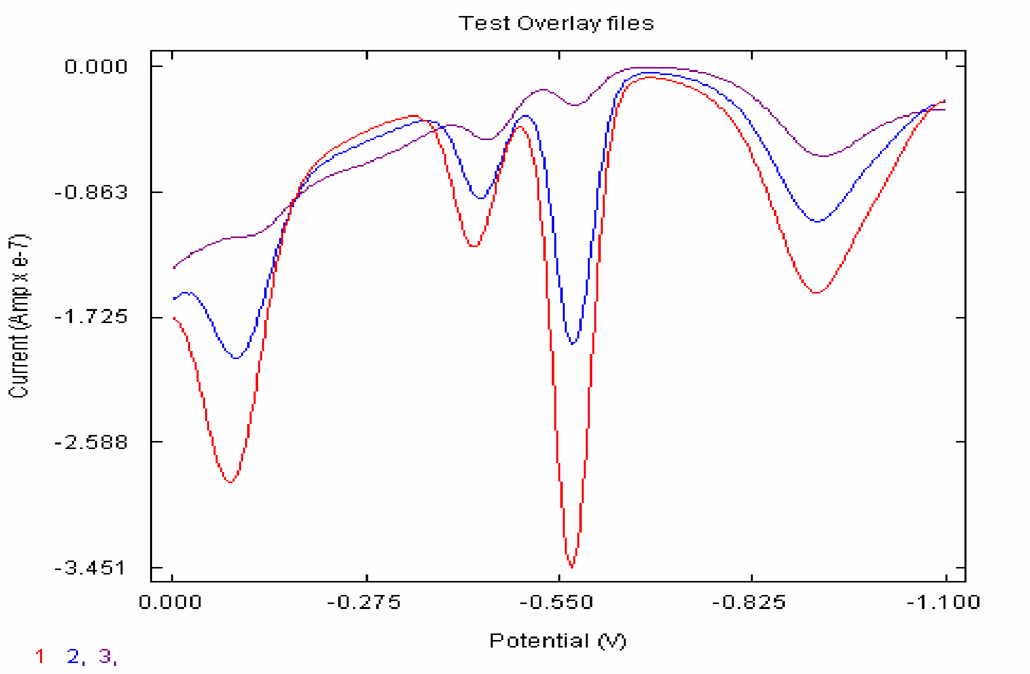

Figure 71: Overlay of voltammograms for inlet 5 before exposure to UV light (Zn not shown).

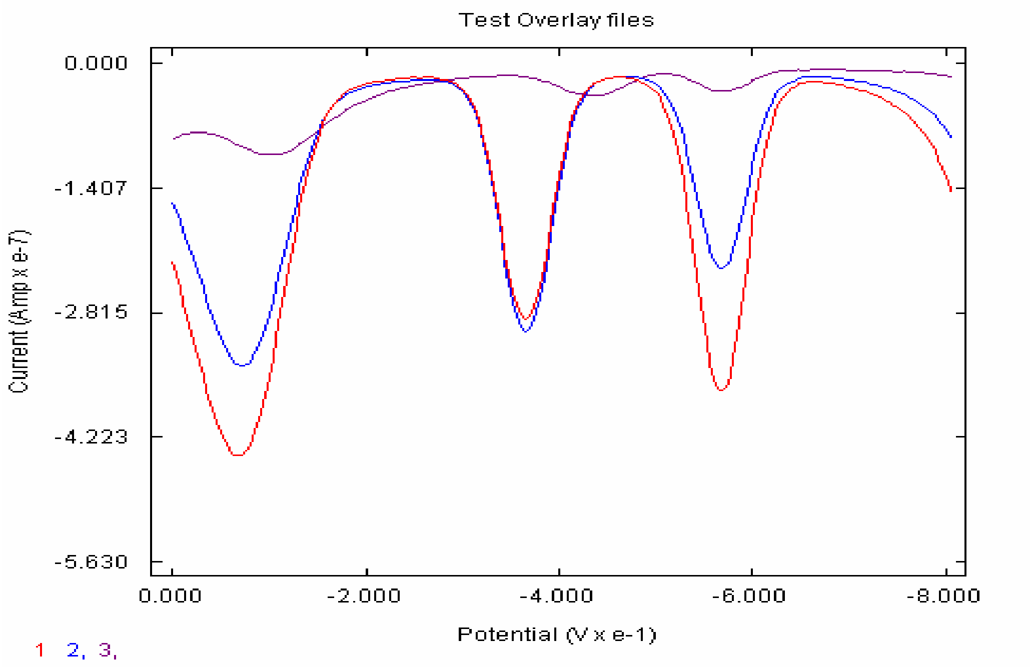

Figure 72: Overlay of voltammograms for inlet 5 after exposure to UV light (Zn not shown).

3.3.3 Use of ASV with Samples Exposed to Chelex-100 Resin

The purpose of using the Chelex-100 ion exchange resin was to be able to determine the concentration of metals in their ionic forms versus those associated with particulates. The Chelex resin selectively removes only the ionic forms of metals by an exchange with another cation. In this case, the cation was sodium. Therefore, by measuring the concentration of heavy metals before and after exposure to the Chelex ion exchange resin, the concentration of metals in their ionic form can be calculated by difference. Then, by exposure the sample to UV light after the use of the Chelex resin, one could determine the concentration of non-labile metals (not easily removed from organics or colloids and difficult to measure by ASV).

Since previous studies indicated that ASV was used to measure metals after the use of the Chelex-100 resin, but with little detail given on the methodology, an attempt to use ASV to measure metals after the use of Chelex-100 in the stormwater samples was made. At first, it appeared that there would be no problem in using ASV to measure the heavy metals in these samples after the use of Chelex-100 resin. Blanks exposed to the resin and analyzed by SWSV gave smooth peaks with no background noise (Figure 73). Problems arose w hen standard concentrations were added to a Chelex-exposed method blank. The ASV was unable to pick out peaks at the same detections limits that were found when using 0.1M KCl. There seemed to be some kind of interference or perhaps left over Chelex that was removing the added metals.

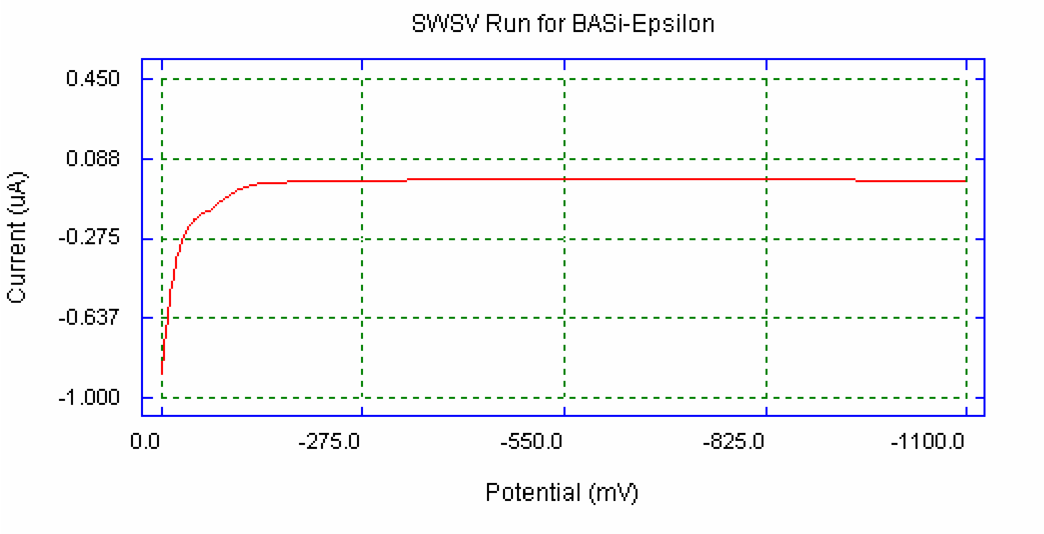

Figure 73: Method blank exposed to Chelex-100 ion exchange resin and analyzed by SWSV (5 min deposition).

Figure 74 is a voltammogram of blank exposed to the Chelex-100 resin with a standard addition of 10 µg/L of all four metals of interest. There is a lack of the four peaks that can be seen in Figure 75 which is a solution of 0.10 KCl with a standard addition of the same concentration of metals. In this voltammogram, there is a distinct peak for Zn, Cd, Pb and Cu (reading right to left). For samples exposed to the Chelex-100 resin, clean, distinct peaks such as those shown in Figure 75 could not be obtained until a standard concentration of around 900 µg/L was added (Figure 76). Even at this high concentration, the peaks were not as large as those obtained using KCl as the electrochemical solution (Figure 77) and the peak for Pb was not in the correct location (-360Mv). This would indicate an inability to detect the entire concentration of metals added to the solution and perhaps some contamination or problem distinguishing Pb in the solution.

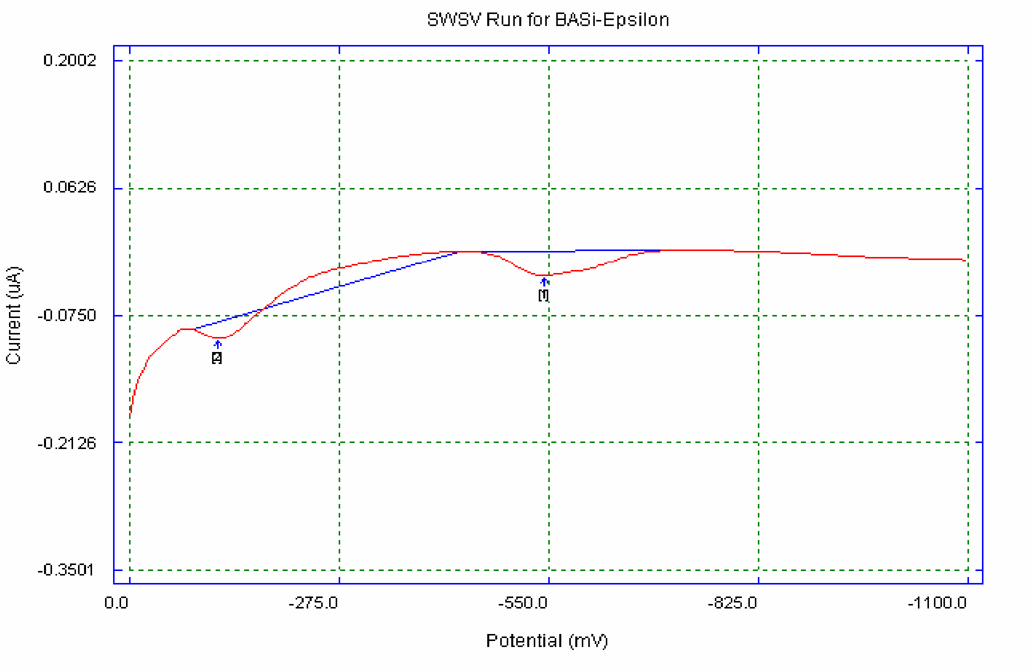

Figure 74: Voltammogram using SWSV and 5 min deposition of blank exposed to Chelex-100 resin and a 10 µg/L standard addition of all metals of interest.

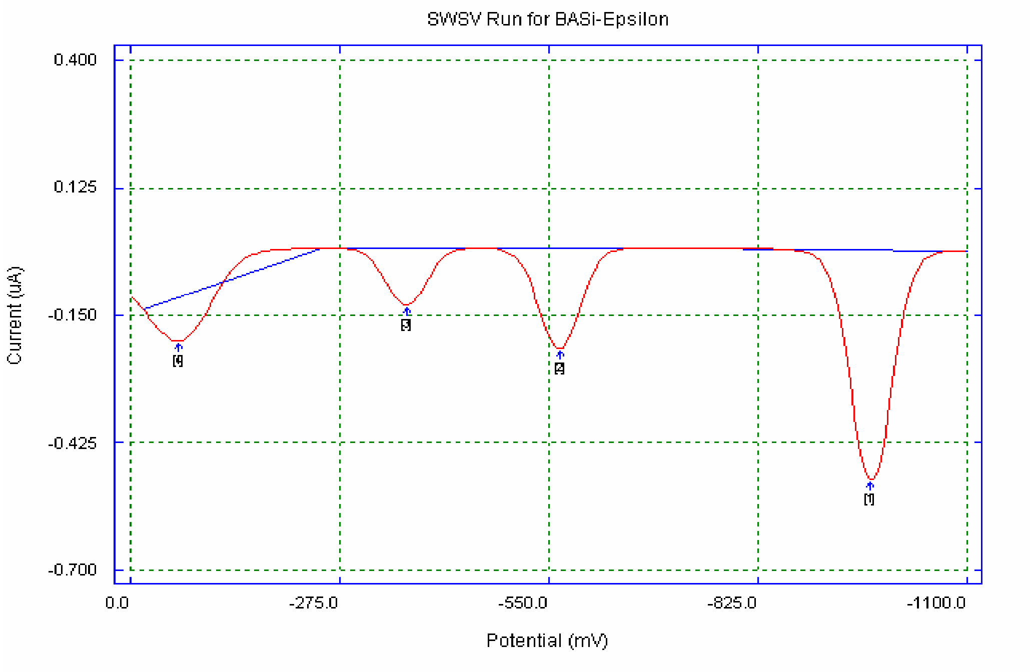

Figure 75: Voltammogram using SWSV and 5 min deposition time of 0.10M KCl and a 10 µg/L standard addition of all metals of interest.

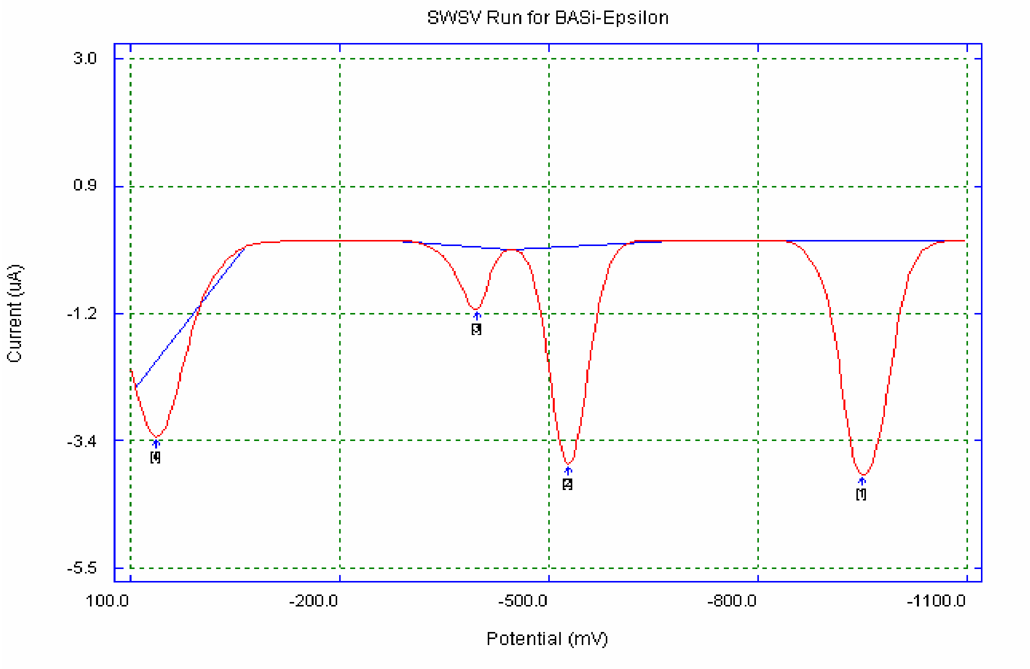

Figure 76: Voltammogram using SWSV and 1 min deposition of blank exposed to Chelex-100 resin and a 900 µg/L standard addition of all metals of interest.

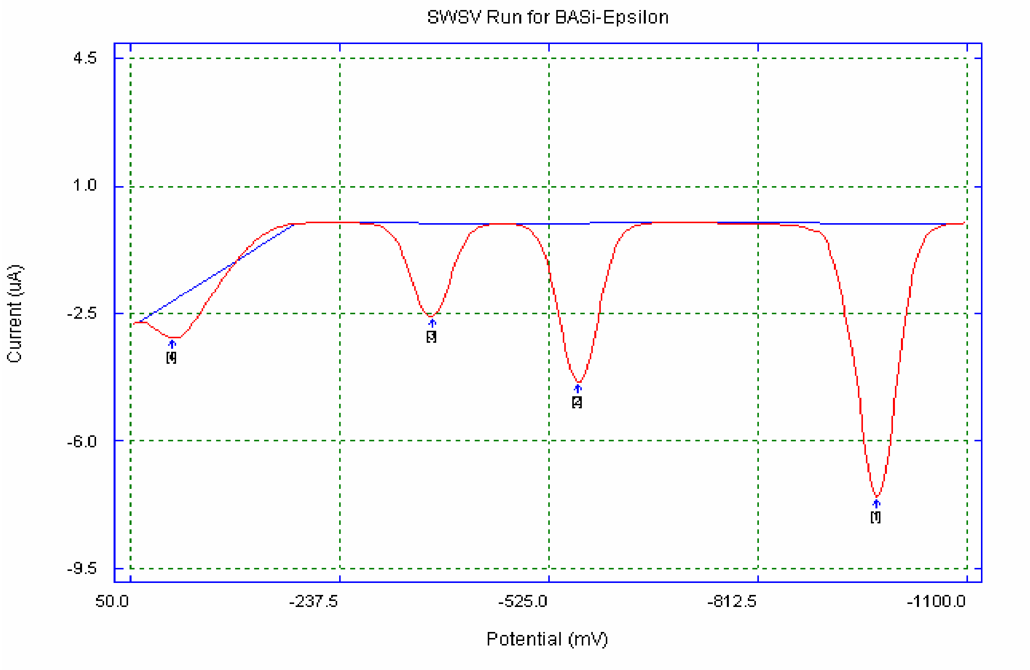

Figure 77: Voltammogram using SWSV and 1 min deposition in 5:1 dilution of water:0.10M KCl and a 900 µg/L standard addition of all metals of interest.

Next, tests were run on combinations of the Chelex method blank and water or 0.10M KCl. Mixtures of 1:10, 1:5, and 1:1 Chelex solution: water were tried, but clean voltammograms could not be obtained. Figure 78 is a voltammogram of 2mL Chelex method blank and 8mL water (1:5 dilution). The line obtained should be flat like that seen in Figure 73. In this case there was a lot of noise in this voltammogram.

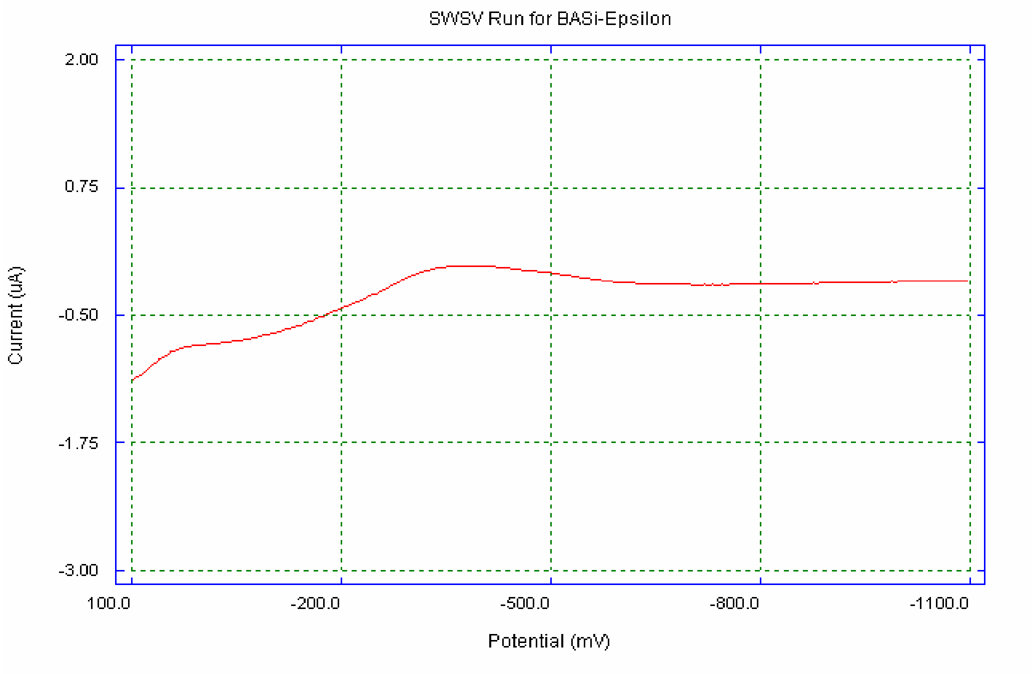

Figure 78: Voltammogram of a 1:5 mixture of Chelex method blank and water, 1 min deposition using SWSV.

A decision was made at this point to do some standard additions to a Chelex method blank and try and determine at what concentrations the metals are discernible in a sample exposed to Chelex. Figures 79 and 80 are overlays of voltammograms for standard additions of 1-9 μg/L in water:0.1M KCl mixture and Chelex method blank, respectively. The top line in each of these overlays is the background solution. It is clear at these low concentration levels, the response for the Chelex blank is very different from the response seen in the water:0.1MKCl solution. The peaks in Figure 79 are very distinct for all four metals of interest and can clearly be identified at each concentration level. In comparison, the peaks in Figure 80 are not distinct and are questionable as to whether they can be used to indicate the presence of any of the metals of interest. It is possible that the peaks seen in Figure 80 are those for Cu (far left) and Cd. But it is not clear at this point.

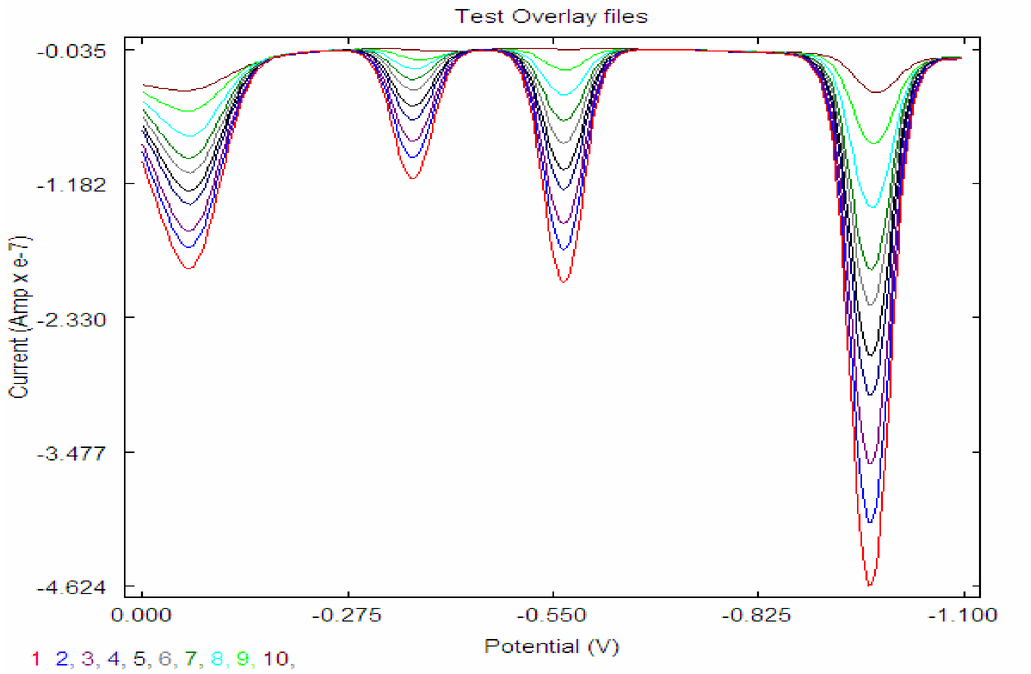

Figure 79: Overlay of voltammograms for 1-9 µg/L all metals (in increments of 1 µg/L) using SWSV and 5min deposition in a 5:1 mixture water:0.1M KCl.

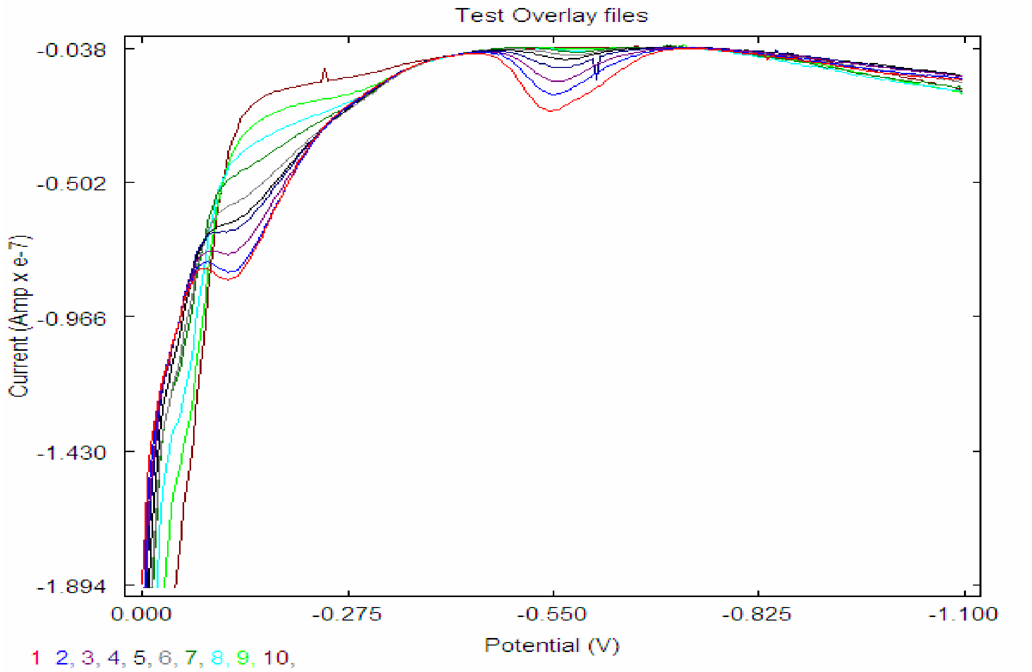

Figure 80: Overlay of voltammograms for 1-9 μg/L all metals in increments of 1 μg/L) using SWSV and 5min deposition in Chelex method blank.

In Figures 81 and 82, the concentrations of standards are increased in 20 μg/L increments from 20-180 μg/L. Again, in the water:0.1M KCl solution, the peaks are distinct and can easily be distinguished, but in Figure 82, the Chelex method blank solution still does not show four distinct peaks. The peaks are better than those in Figure 80 (there is now a peak for Zn at the far right), but Cd and Pb peaks are not showing up as separate peaks and the peak for Cu is truly is not in the correct spot when compared to Figure 81.

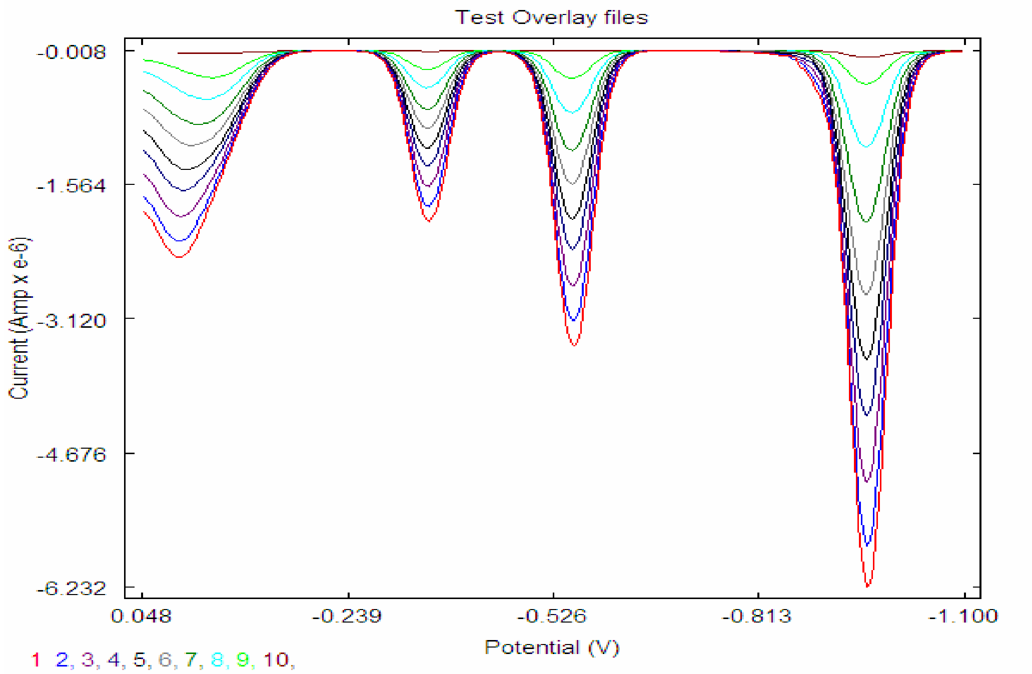

Figure 81: Overlay of voltammograms for 20-180 µg/L (in increments of 20 µg/L) all metals using SWSV and 5min deposition in a 5:1 mixture water:0.1M KCl.

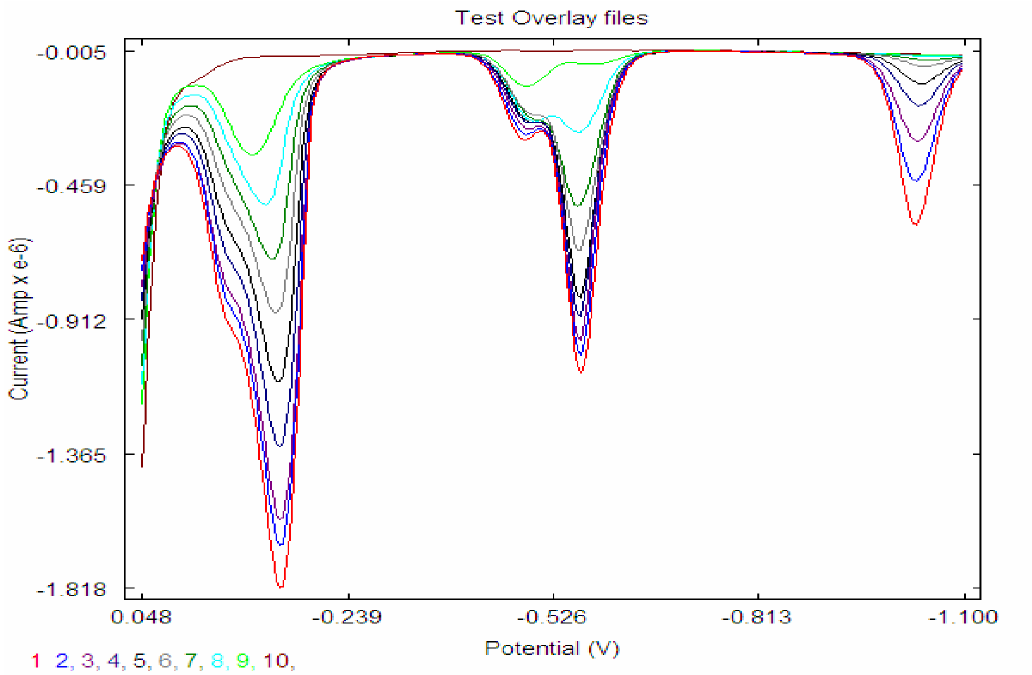

Figure 82: Overlay of voltammograms for 20-180 µg/L (in increments of 20 µg/L) all metals using SWSV and 5min deposition in Chelex method blank.

In Figures 83 and 84, the standard addition concentrations are increased further in 100 µg/L increments from 200-400 µg/L. The peaks for the Chelex method blank sample in Figure 84 are still not distinct and not as distinct as those in Figure 83. Even at a concentration of 1.0 mg/L, the peaks for the Chelex method blank are not clean, even though there are now four peaks (Figure 85). The cleanest peaks are for Cd and Cu, which seem to be in the correct spot and give a similar peak height as the Cd and Cu peaks in Figure 86. But the peaks for Zn and Pb are not clean and are not at the same heights as the peaks in Figure 86.

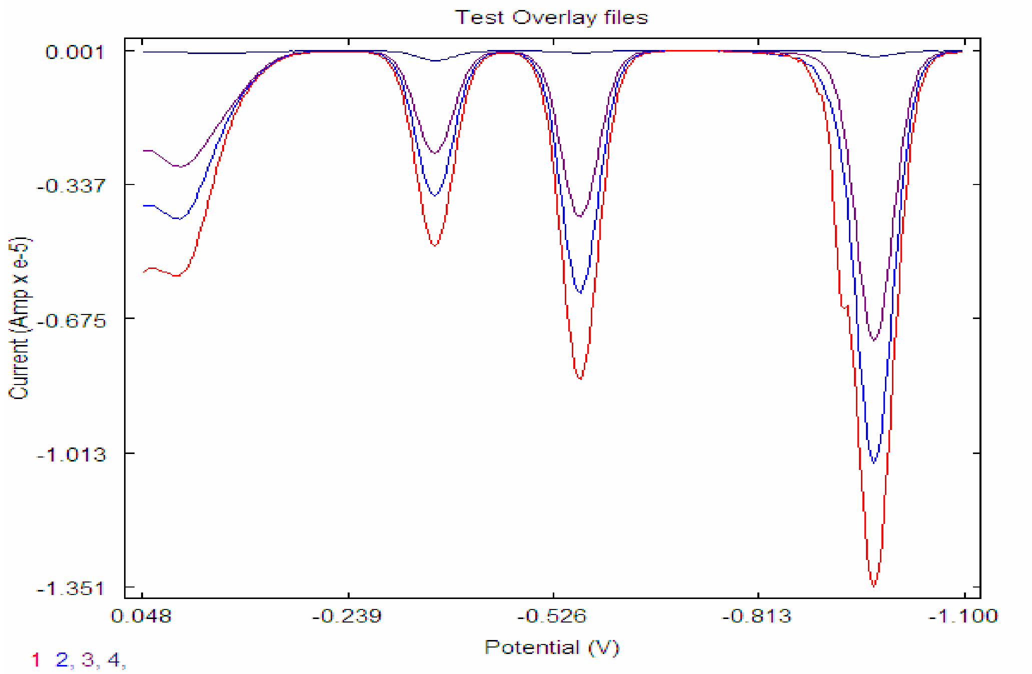

Figure 83: Overlay of voltammograms for 200-400 µg/L (in increments of 100 µg/L) all metals using SWSV and 5min deposition in a 5:1 mixture water:0.1M KCl.

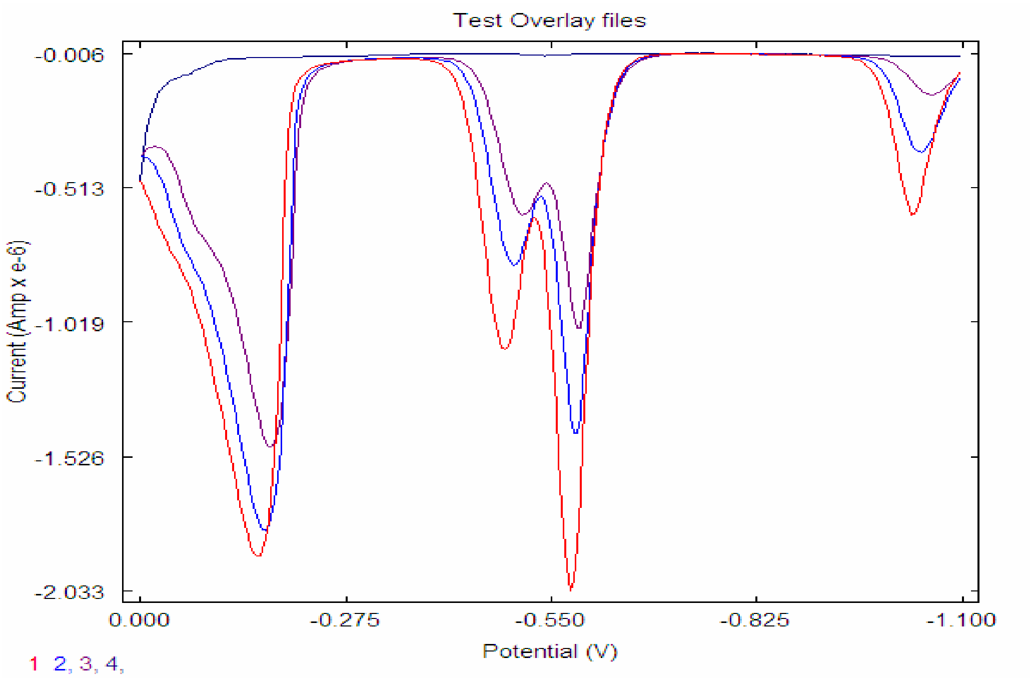

Figure 84: Overlay of voltammograms for 200-400 µg/L (in increments of 100 µg/L) all metals using SWSV and 5min deposition in Chelex method blank.

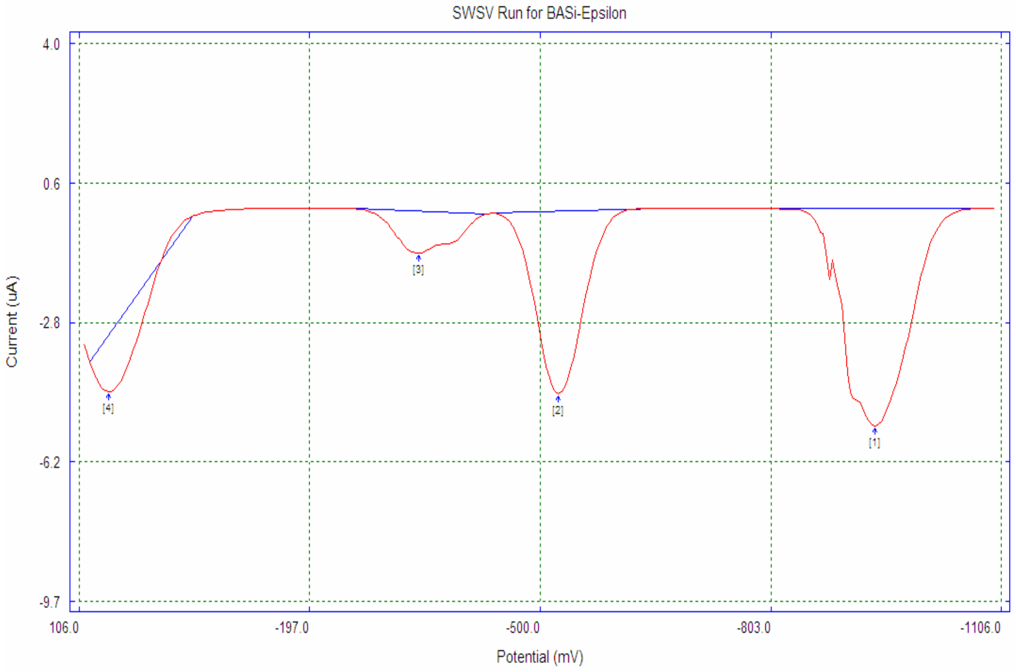

Figure 85: Voltammogram of Chelex method blank and 1mg/L standard addition of all metals, 1 min deposition using SWSV.

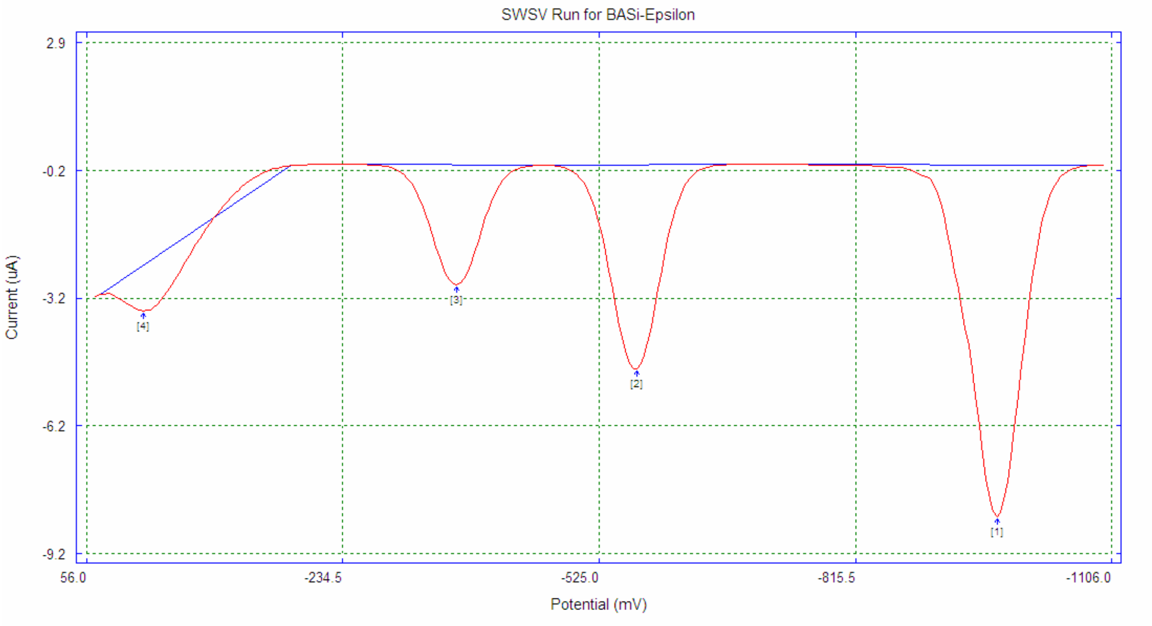

Figure 86: Voltammogram using SWSV and 1 min deposition in 5:1 dilution of water:0.10M KCl and a 1.0 mg/L standard addition of all metals of interest.

After all of these tests with varying metals concentrations, an estimate had to be made as to the sensitivity of ASV using the Chelex-100 ion exchange resin. A rough estimate is that Cu can be detected at around 8 µg/L, Cd at 7 µg/L, Zn at 100 µg/L and Pb at 300 µg/L. All samples that had been exposed to the Chelex resin and before UV exposure gave no peaks using SWSV and 5 minute deposition. This would indicate that all ionic forms of the metals had been removed by the ion exchange resin. After exposure to UV, some samples showed possible metal peaks. By plotting peak height versus concentration added, regression equations were obtained for each metal and estimates were made as to the concentrations of metals present in solution after a Chelexed sample had been exposed to UV light. Table 16 list the estimated concentrations of samples after use of Chelex resin and exposure to UV light. Almost all samples showed a possible increase in Zn after UV exposure with few samples measuring Cu, Cd or Pb.

Table 16: Estimates of metals concentrations in µg/L using SWSV and 5 min deposition of samples after use of Chelex resin and exposure to UV light.

Sample ID	Zn	Cu	Cd	Pb
Inlet 1	78.7	0.0	0.0	0.0
Roof 1	81.4	0.0	0.0	0.0
Inlet 2	114.0	0.0	56.1	203.4
Roof 2	86.0	0.0	0.0	174.0
Mixed 1	77.7	5.2	5.4	0.0
Roof 3	88.9	0.0	14.9	179.2
Inlet 3	83.4	0.0	5.8	0.0
Roof 4	0.0	0.0	0.0	0.0
Mixed 2	77.8	0.0	0.0	0.0
Roof 5	75.0	0.0	0.0	0.0
Inlet 4	95.1	0.0	0.0	0.0
Outlet 1	88.8	0.0	0.0	0.0
Inlet 5	95.6	0.0	0.0	0.0
Outlet 2	84.5	0.0	0.0	0.0

After all the work in trying to use voltammetric techniques to determine the metals concentrations after use of the Chelex-100 resin and being disappointed in the lack of sensitivity provided by the technique, the last four samples collected also were analyzed by ICP-MS for metals after use of the Chelex resin. An increase in metals after exposure to UV light was not seen for all samples or metals as can be seen in Table 17. Most actually showed a decrease in concentration indicating few metals to be strongly bound to colloids or other ligands. Colloidal-bound metals or metals strongly bound to ligands will not be removed by Chelex and may be liberated by exposure to UV light. Therefore, no increase in metals concentrations after UV exposure would indicate that the metals all occurred in their ionic forms and were removed by the Chelex-100 ion exchange resin.

Table 17: Increase or decrease in metals after use of Chelex-100 ion exchange resin and subsequent UV light exposure (metals measured by ICP-MS).

	% Increase or Decrease			
	Zn	Cu	Cd	Pb
Inlet 4	13.8	-7.4	-34.6	-25.5
Outlet 1	-27.0	9.2	-33.6	-33.5
Inlet 5	-23.2	-30.6	-39.2	-12.5
Outlet 2	-44.9	30.8	-24.7	-28.7

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDY

4.1 Associations with particle sizes

Most stormwater treatment efforts involve the physical removal of particulates. In order to better design sedimentation stormwater treatment devices, it is important to understand which pollutants are associated with different sized particulates and how they may be controlled during the removal of the particulates. Table 18 shows the average percentage of pollutants associated with either the particulate or filterable fractions of all samples analyzed broken down by sample type. As expected, most of the turbidity will be removed by removal of particulates because turbidity is caused by particulate matter. Surprisingly much of the COD was associated with the filterable fraction, except for the two mixed samples. In previous work from this laboratory, COD was reduced almost 50% by removal of particulates to 0.45 um (Johnson et al. 2003). Total phosphorus showed a similar pattern to COD with a surprising amount associated with the filterable fractions. Before, over 90% of total phosphorus could be removed by removal of particulates. Heavy metals were in general found more in the filterable fraction. Only 30% of zinc for roof samples was associated with the particulate fraction, 42% for inlets and 6% for mixed samples. Almost all of the cadmium was in the filterable fraction with copper and lead more evenly divided between the two fractions.

Table 18: Average particulate and filterable fractions of pollutants analyzed.

	Roofs		Inlets		Mixed	
Constituent	Ave % Particulate	Ave % Filterable	Ave % Particulate	Ave % Filterable	Ave % Particulate	Ave % Filterable
Turbidity	79	21	88	12	89	11
COD	21	79	39	61	63	37
Total Phosphorus	44	56	59	41	64	36
Zinc	30	70	42	58	6	96
Copper	44	56	40	60	0.0	100
Cadmium	23	77	14	86	0.0	100.0
Lead	46.0	54.0	53.8	46.2	0.0	100.0

Table 19 lists the percentage reduction in pollutants after controlling for particle sizes ranging from 10 to 0.45 µm. For these samples, most of the pollutants were not controlled by a reduction in particulates. Only total solids, turbidity and total phosphorus were reduced more than 50% by a reduction in particulates. The other pollutants, especially the heavy metals were reduced much less, even after filtration down to 0.45 µm.

Table 19: Average percent reduction in pollutants after controlling for particle size indicated.

	10 µm	2 µm	0.45 µm
Total Solids	48%	50%	52%
Turbidity	72	77	86
COD	36	37	40
Total Phosphorus	48	51	52
Zinc	23	30	31
Copper	34	30	36
Cadmium	0.1	0.1	7
Lead	23	23	24

The percentage of zinc and COD associated with the filterable fraction was similar to that obtained when Pitt et al. (1998) looked at over 550 nationwide samples from telecommunication manhole vaults mostly affected by stormwater. They found 70% of zinc and 86% of COD associated wit the filterable fraction. However, results for heavy metals were quite different from those seen at the inlet to the Monroe Street wet detention pond (House et al. 1993). In that study, 87% of copper, 96% of lead and 66% of zinc were associated with the particulate fraction. Even previous results from this laboratory resulted in greater reductions in lead and zinc with removal of particulates (Johnson et al. 2003). Results for copper and cadmium reductions though were similar.

Most well designed wet detention ponds remove most particulates down to about 1 to 5 µm, depending on the rain conditions and drainage area. Smaller ponds may not be able to remove small particulates. No pond can remove the filterable fraction by physical processes alone. Keeping this in mind and looking again at Table 19, results from these samples indicate that solids, turbidity and total phosphorus would achieve a greater than 50% removal for a pond that could remove particulates down to 2 µm. For ponds that could not achieve this level of control, only turbidity would be removed more than 50% for particulate removal down to 10 µm. Much of the pollutant concentrations in these samples was associated with the filterable fraction and would not be removed by physical processes alone.

4.2 Colloidal Analysis

The Chelex-100 ion exchange resin was used to determine how much of the heavy metals occurred in the ionic form, considered more toxic to aquatic life, and those bound to colloids or other organic matter in solution. Because of the problems obtaining reliable data using voltammetric techniques, only the results obtained using the ICP-MS on the last four samples (the inlet and outlet pairs) could be used for analysis. Table 20 lists the average percentage of the heavy metals analyzed that occurred as either ionic or bound forms. Most of the zinc, cadmium and lead were not present in the free ionic form, but were bound the colloids or organic matter whose bonds could be broken by exposure to UV light. Only copper occurred in mostly the ionic form. These results differ from previous results from this laboratory (Johnson et al. 2003), in which only cadmium was mostly particulate bound (70%) and about 50% of copper was in ionic forms. Results from these types of tests can be highly variable due to low metals concentrations in the filterable fractions.

Table 20: Average percentage of metals occurring as ionic or bound forms for last four samples (metals measured by ICP-MS).

	Average % Ionic	Average % Bound
Zinc	15	85
Copper	70	30
Cadmium	10	90
Lead	12	88

4.3 Use of ASV to measure dissolved heavy metals

The use of Anodic Stripping Voltammetry (ASV) to measure dissolved heavy metals in stormwater has been used infrequently in the past. One of the main objectives of this research was to develop a method for using ASV with stormwater.

Using Square Wave Stripping Voltammetry (SWSV) to measure the ionic forms of the heavy metals in the filterable fractions was a quick and relatively easy method. Using a five minute deposition time provide great detection limits for Cu, Cd and Pb. The detection limit for Zn, which was around 3 µg/L was higher than preferred and seemed to be more variable than the other metals. This may be due to the ubiquitous nature of Zn and also its ability to co-amalgamate with other metals in solution. A lower detection limit could probably be obtained by simply increasing the deposition time.

Results from the use of ASV to measure metals in samples that had been exposed to the Chelex-100 ion exchange resin were disappointing. The size of the resin is over 100 microns and should be removed with simple decantation from the sample. In this case, removal of the resin was done by filtration through a 0.45 µm nylon membrane.

The inability to measure metals in a solution which has been exposed to the Chelex resin with the same sensitivity as a 0.1M KCl electrochemical solution was something not expected. An explanation for the reduced sensitivity is lacking. Some ideas are that the resin is not completely removed from solution, even by filtration or that there is something else in the resin that interferes with the voltammetric technique. Phone calls to the manufacturer of the resin did not solve the problem. Recommendation is that any samples for which Chelex-100 ion exchange resin is used to not measure metals by voltammetric techniques.

4.4 Recommendations for future study

There are many areas that still need more work. First, the toxicity results from these samples were much different than the results from previous studies. Although the new equipment and bacteria were thoroughly tested for repeatability and correct NaCl addition, more questions remain unanswered. Has there been a change in the sensitivity of the bacteria? Have other changes been made to the acute reagent? Second, more work needs to be done with the use of ASV for measuring metals in stormwater. The detection limit for zinc should be lowered if possible. In addition, perhaps someone can find a way to use ASV along with the Chelex-100 ion exchange resin. It still remains a mystery as to why those tests failed. There are also other options for electrochemical solutions and other voltammetric techniques that could be tried such as Differential Pulse Stripping Votammetry. There is almost an endless combination of solutions, techniques, and deposition times that could be tested. Ultimately, the goal would be to use voltammetric techniques to measure the ionic forms of the metals in all the stormwater fractions. This would entail finding a way to measure the metals in a solution of acid. Nitric acid is typically used for microwave digestion, but perhaps another acid would be suitable, such as HCl that would also provide the optimal electrochemical solution for the voltammetric techniques.

REFERENCES

AZUR Environmental MicrotoxOmni™ Software for Windows® 95/98/NT User Manual and Test Templates. 1999 (available from Strategic Diagnostics, Inc.).

Akeley, R.P. "Retention ponds for control of urban stormwater quality." In *Proceedings National Conference on Urban Erosion and Sediment Control: Institutions and Technology*, EPA-905/9-80-002, Chicago, January 1980.

Bannerman, R., K. Baun, M, Bohn, P.E. Hughes, and D.A. Graczyk. *Evaluation of Urban Nonpoint Source Pollution Management in Milwaukee County, Wisconsin*. U.S. Environmental Protection Agency, PB 84-114164, Chicago, Ill., 1983.

Barry, S.C.; Taylor, S.E.; and Birch, G.F. Heavy Metals in Urban Stormwater Canals Entering Port Jackson, Australia and Their Impact on the Estuarine Environment. *Proc. The Eighth International Conference on Urban Storm Drainage*. August 30 – September, 3 1999, Sydney, Australia. Edited by IB Joliffe and JE Ball. The Institution of Engineers Australia, the International Association for Hydraulic Research, and The International Association on Water Quality, 1825. 1999.

Batley, G.E. "Collection, Preparation, and Storage of Samples for Speciation Analysis." In *Trace Metal Speciation: Analytical Methods and Problems*. G.E. Batley, Ed. CRC Press, Inc., Boca Raton, Florida. 1989.

Bechman Coulter. Multisizer 3 Operator's Manual. 2001.

Bott, A.W. Voltametric determination of trace concentrations of metals in the environment. *Current Separations* 14:1, 24-30. 1995.

Buffleben, M.S.; Zayeed, K.; Kimbrough, D.; Stenstrom, M.K.; and Suffet, I.H. Evaluation of Urban Non-Point Source Runoff of Hazardous Metals that Enters Santa Monica Bay, California. *5th International Conf.: Diffuse/Nonpoint Pollution and Watershed Management.* CD-ROM. 2001.

Burton, G.A. and R. Pitt. *Handbook for Evaluating Stormwater Runoff Effects, A Tool Box of Procedures and Methods to Assist Watershed Managers.* CRC/Lewis Publishers, New York. 2002.

Burton, G.A., Jr., R. Pitt, and S. Clark. The role of whole effluent toxicity test methods in assessing stormwater and sediment contamination. *CRC Critical Reviews in Environmental Science & Technology*. 30: 413-447. 2000.

Chakrabarti, C.L., Lu, Y., and Cheng, J. Studies on Metal Speciation in the Natural Environment. *Anal. Chim. Acta*. Vol. 276, pp. 47-64. 1993.

Characklis, G.W., and Wiesner, M.R. Particles, Metals, and Water Quality in Runoff from Large Urban Watershed. *J. Environ. Eng.* Vol. 123, No. 8, pp. 753. 1997.

Cheng, J., Chakrabarti, C.L., Back, M.H., and Schroeder, W.H. Chemical Speciation of Cu, Zn, Pb and Cd in Rain Water. *Anal. Chim. Acta.* Vol. 288, pp. 141-156. 1994.

Clark, S., R. Pitt, and S. Burian. "Urban Wet Weather Flows – 2002 Literature Review." *Water Environment Research*. Vol. 75, No. 5, Sept./Oct. 2003 (CD-ROM).

Clark, S., R. Pitt, and S. Burian. "Urban Wet Weather Flows – 2001 Literature Review." *Water Environment Research*. Vol. 74, No. 5, Sept./Oct. 2002 (CD-ROM).

Clark, S., R. Rovansek, L. Wright, J. Heaney, R. Field, and R. Pitt. "Urban Wet Weather Flows 2000 Literature Review." *Water Environment Research*. Vol. 73, No. 5, Sept./Oct. 2001. (CD-ROM).

Colich, F. "Trace metals concentrations in stormwater runoff from the Evergreen Point Floating Bridge in the Seattle, Washington area." *2003 Georgia Basin/Puget Sound Research Conference Proceedings*, 2004.

Dally, L.K., D.P. Lettenmaier, S.J. Burges, and M.M. Benjamin. *Operation of Facilities for Urban Stream Quality Enhancement*. University of Washington, Department of Civil Engineering, Water Resources Series Technical Report No. 79, Seattle, Washington, July 1983.

Dean, C.M., J.J. Sansalone, F.K. Cartledge and J.H. Pardue. "Influence of hydrology on rainfall-runoff metal element speciation." *J. Environ. Eng*. Vol. 141. No. 4. 2005.

Deletic, A. and D.W. Orr. "Pollution on road surfaces." *J. Environ. Eng*. Vol. 131, No. 1. 2005.

DeCarlo, E.H., V.L. Beltran and M.S. Tomlinson. "Composition of water and suspended sediment in streams of urbanized subtropical watersheds in Hawaii." *Applied Geochemistry*. 19(7):1001-1037. 2004.

Dewald, H.D. "Stripping Analysis." In *Modern Techniques in Electroanalysis*. P. Vanysek, Ed. Chemical Analysis Series, Vol. 139. John Wiley and Sons, Inc. New York. 1996.

Drapper, D., R. Tomlinson and P. Williams. "Pollutant Concentrations in Road Runoff: Southeast Queensland Case Study". *J. Environ. Eng*. Vol. 124, No. 4, April 2000.

Driscoll, E. D. "Detention and retention controls for urban stormwater." *Engineering Foundation Conference: Urban Runoff Quality – Impact and Quality Enhancement Technology*, Henniker, New Hampshire, edited by B. Urbonas and L. A. Roesner, published by the American Society of Civil Engineers, New York, June 1986.

Fan, C.-Y.; Field, R.; Sullivan, D.; and Lai, F.-h. Toxic Pollutants in Urban Wet-Weather Flows: An Overview of the Multi-Media Transport, Impacts, and Control Measures. *Proc. ASCE EWRI Conf. – Bridging the Gap: Meeting the World's Water and Environmental Resources Challenges*. CD-ROM. 2001.

Ferarra, R. A. "Stormwater detention and nonpoint source pollution control." *1982 International Symposium on Urban Hydrology, Hydraulics and Sediment Control*, University of Kentucky, Lexington, Kentucky, July 1982.

Figura, P. and B. McDuffle. "Determination of labilities of soluble trace metal species in aqueous environmental samples by anodic stripping voltammetry and chelex column and batch methods." *Anal. Chem*. 52:1433-1439. 1980.

Florence, T.M. "Trace metal species in fresh water." *Water Research*. Vol. 11, pp. 681-687. 1977.

Florence, T.M., and G.E. Bately. "Chemical speciation in natural waters." *CRC Crit. Rev. Anal. Chem*. Vol. 9, pp. 219-296. 1980.

Garnaud, S.; Mouchel, J.M.; Chebbo, G.; and Thevenot, D.R. Heavy Metal Concentrations In Dry And Wet Atmospheric Deposits In Paris District: Comparison With Urban Runoff. *Sco. Total Environ.* Vol. 235, No. 1-3, pp. 235. 1999a.

Garnaud, S.; Mouchel, J-M.; and Thevenot, D.R. Mobility Evolution of Particulate Trace Metals in Urban Runoff: From Street Deposits and Road Runoff to Combined Sewer Deposits and Catchment Outlet. *Proc. The Eighth International Conference on Urban Storm Drainage*. August 30 – September 3 1999, Sydney, Australia. Edited by IB Joliffe and JE Ball. The Institution of Engineers Australia, the International Association for Hydraulic Research, and The International Association on Water Quality, 1511. 1999b.

Gietz, R. J. *Urban Runoff Treatment in the Kennedy-Burnett Settling Pond*. For the Rideau River Stormwater Management Study, Pollution Control Division, Works Department, Regional Municipality of Ottawa-Carleton, Ottawa, Ontario, March 1983.

Gilbert R.O. *Statistical Methods for Environmental Pollution Monitoring*. John Wiley & Sons, Inc. New York, NY. 1987.

Glenn, D.W.; Tribouillard, T.; and Sansalone, J.J. Temporal Deposition of Anthropogenic Pollutants in Urban Snow as Generated by Traffic. *WEFTEC 2001 Conf. Proc*. CD-ROM. 2001.

Grizzard, T. J., C. W. Randall, B. L. Weand, and K. L. Ellis. "Effectiveness of extended detention ponds." *Engineering Foundation Conference: Urban Runoff Quality – Impact and Quality Enhancement Technology*, Henniker, New Hampshire, edited by B. Urbonas and L. A. Roesner, published by the American Society of Civil Engineers, New York, June 1986.

Grout, H.; Wiesner, M.R.; and Bottero, J.Y. Analysis of Colloidal Phases in Urban Stormwater Runoff. *Environ. Sci. Technol.* (G.B.). Vol. 33, No. 6, pp. 831. 1999.

Harrison, R.M. and Wilson, S.J. The Chemical Composition of Highway Drainage Waters III. Runoff Water Metal Speciation Characteristics. *Sci. Total Environ*. Vol. 43, pp. 89-102. 1985.

House, L.B., R.J. Waschbusch, and P.E. Hughes. *Water Quality of an Urban Wet Detention Pond in Madison, Wisconsin, 1987-1988*. U. S. Geological Survey, in cooperation with the Wisconsin Department of Natural Resources. USGS Open File Report 93-172, 1993.

Kamedulski, G. E. and R. H. McCuen. "The effect of maintenance on storm water detention basin efficiency." *Water Resources Bulletin*, Vol. 15, No. 4, pg. 1146, August 1979.

Krein, A., and Schorer, M. "Road runoff pollution by polycyclic aromatic hydrocarbons and its contribution to river sediments." *Water Res. (G.B.)*. Vol. 34, pp. 4110. 2000.

Johnson, P.D., R. Pitt, S.R. Durrans, M. Urrutia, and S. Clark. *Metals Removal Technologies for Urban Stormwater*. Water Environment Research Foundation. WERF 97-IRM-2. ISBN: 1-94339-682-3. Alexandria, VA. 701 pgs. Oct. 2003.

Magnuson, M.L.; Kelty, C.A.; and Kelty, K.C. Trace Metal Loading on Water-Borne Soil and Dust Particles Characterized Through the Use of Split-Flow Thin Cell Fractionation. *Analytical Chemistry*. 73:3492. 2001.

Morrison, G.M.P. and Diaz-Diaz, G. Size Distribution and Copper Association of Dissolved Organic Material in Urban Runoff. *Environmental Technology Letters*. Vol. 9, pp. 109-116. 1988.

Mosley, L.M., and Peake, B.M. Partitioning of Metals (Fe, Pb, Cu, Zn) in Urban Run-Off From the Kaikorai Valley, Dunedin, New Zealand. *New Zealand J. Marine Freshwater Res*. 35:615. 2001.

Mota, A.M. and Correia dos Santos, M.M. Trace Metal Speciation of Labile Chemical Species in Natural Waters: Electrochemical Methods in *Metal Speciation and Bioavailability in Aquatic Systems.* A. Tessier and D.R. Turner, Eds. John Wiley and Sons, Ltd. 1995.

Parker, J.T.C.; Fossum, K.D.; and Ingerssol, T.L. Chemical Characteristics of Urban Stormwater Sediments and Implications for Environmental Management, Maricopa County, Arizona. *Environ. Manage.* 26, 99. 2000.

Pisano, W.C. and H. Brombach. Solids settling curves: Wastewater solids data can aid design of urban runoff controls. *Water Environment & Technology*. Vol. 8, no. 4, pp. 27-33. April 1996.

Pitt, R. *Demonstration of Nonpoint Pollution Abatement Through Improved Street Cleaning Practices*. EPA-600/2-79-161, U.S. Environmental Protection Agency, Cincinnati, Ohio, August 1979.

Pitt, R. *Characterizing and Controlling Urban Runoff through Street and Sewerage Cleaning*. U.S. Environmental Protection Agency, Storm and Combined Sewer Program, Risk Reduction Engineering Laboratory. EPA/600/S2-85/038. PB 85-186500. Cincinnati, Ohio. 467 pgs. June 1985.

Pitt, R. “Receiving water impacts associated with urban runoff.” In: *Handbook of Ecotoxicology*, 2nd edition (Edited by D.J. Hoffman, B.A. Rattner, G.A. Burton, Jr. and J.Cairns, Jr.). Lewis Publishers/CRC Press, Boca Raton. Publication in 2002.

Pitt, R. and J. McLean. *Toronto Area Watershed Management Strategy Study: Humber River Pilot Watershed Project*. Ontario Ministry of the Environment, Toronto, Ontario, 1986.

Pitt, R.E., R. Field, M. Lalor, and M. Brown. Urban Stormwater Toxic Pollutants: Assessment, Sources, and Treatability. *Water Environment Research*. Vol. 67, No. 3, pp. 260-275. May/June 1995.

Pitt, R. “Unique Features of the Source Loading and Management Model (SLAMM).” In: *Advances in Modeling the Management of Stormwater Impacts, Volume 6*. (Edited by W. James). Computational Hydraulics International, Guelph, Ontario and Lewis Publishers/CRC Press. Pp. 13 – 37. 1997.

Pitt. R. S. Clark, J. Lantrip, and J. Day. *Telecommunication Manhole Water and Sediment Study*. Bellcore, Inc. (now Telcordia), Special Report SR-3841. Morriston, NJ. With further support from NYNEX, BellSouth, Bell Atlantic, GTE, SNET, Pacific Bell, US West, Ameritech and AT&T. *Vol. 1: Evaluation of Field Test Kits* (483 pgs); *Vol. 2: Water and Sediment Characteristics* (1290 pgs); *Vol. 3: Discharge Evaluation Report* (218 pgs); *Vol. 4: Treatment of Pumped Water* (104 pgs). December 1998.

Pitt, R., B. Robertson, P. Barron, A. Ayyoubi and S. Clark. 1999a. "*Stormwater treatment at critical areas: the Multi-Chambered Treatment Train (MCTT).*" U.S. Environmental Protection Agency, Water Supply and Water Resources Division. National Risk Management Research Laboratory. EPA 600/R-99/017. Cincinnati, OH. 169 pgs. March 1999.

Pitt, R., J. Lantrip, R. Harrison, C. Henry, and D. Hue. 1999b. *Infiltration through Disturbed Urban Soils and Compost-Amended Soil Effects on Runoff Quality and Quantity*. U.S. Environmental Protection Agency, Water Supply and Water Resources Division, National Risk Management Research Laboratory. EPA 600/R-00/016. Cincinnati, Ohio. 231 pgs. December. 1999.

Pitt, R., Maestre, A., and Morquecho, R. Compilation and Review of Nationwide MS4 Stormwater Quality Data. *WEFTEC 2003 Conf. Proc.* CD-ROM 2003.

Randall, C. W., K. Ellis, T. J. Grizzard, and W. R. Knocke. "Urban runoff pollutant removal by sedimentation." *Urban Runoff Pollutant Removal by Sedimentation", Proceedings of the Conference on Stormwater Detention Facilities, Planning, Design, Operation, and Maintenance*, Henniker, New Hampshire, Edited by W. DeGroot, published by the American Society of Civil Engineers, New York, August 1982.

Rose, S., M.S. Crean, D.K. Sheheen, and A.M. Ghazi. "Comparative Zinc Dynamics in Atlanta Metropolitan Region Stream and Street Runoff". *Environ. Geol*. 40:983-992.

Sansalone, J.J. Immobilization of Metals and Solids Transported in Urban Pavement Runoff. *North American Water and Environ. Congress '96*, Anaheim, CA, ASCE, NY. 1996.

Sansalone, J.J. and Glenn III, D.W. Temporal Variations in Heavy Metal Partitioning and Loading in Urban Highway Pavement Sheet Flow. *Transportation Research Record* #1720. 2000.

Sansalone, J. J., and Buchberger, S.G. Partitioning and First Flush of Metals in Urban Roadway Storm Water. *J. Environ. Eng*., Vol. 123, No. 2, p. 134. 1997a.

Sansalone, J.J. and Buchberger, S.G. Characterization of Solid and Metal Element Distributions in Urban Highway Stormwater. *Wat. Sci. Tech.* Vol. 36, No. 8-9, pp. 155-160. 1997b.

Sansalone, J.J.; Mishra, S.K.; and Singh, V.P. The Role of Anthropogenic Hydrology on the Transport, Partitioning and Solid-Phase Distribution of Heavy Metals in Urban Storm Water – Implications for Treatment. *WEFTEC 2001 Conf. Proc*. CD-ROM. 2001.

Santos, A., Alonso, E., Callejón, M. and Jiménez, J.C. Heavy Metal Content and Speciation in Groundwater of the Guadiamar River Basin. *Chemosphere*. Vol. 48, pp. 279-285. 2002.

Shafer, M.M.; Overdier, J.T.; Phillips, H.; Webb, D.; Sullivan, J.R.; and Armstrong, D.E. Trace Metal Levels and Partitioning in Wisconsin rivers. *Water, Air, Soil Pollut.*. Vol. 110, No. 3-4, p. 273. 1999.

Smith, W.G. "Water Quality Enhancement through Stormwater Detention." *Proceedings of the Conference on Stormwater Detention Facilities, Planning, Design, Operation, and Maintenance*, Henniker, New Hampshire, Edited by W. DeGroot, published by the American Society of Civil Engineers, New York, August 1982.

Spokes, J.J.; Lucia, M.; Campos, A.M.; and Jickells, T.D. The Role of Organic Metter in Controlling Copper Speciation in Precipitation. *Atmospheric Environment*. Vol. 30, No. 23, pp. 3959-3966. 1996.

Sutherland, R.A.; Tack, F.M.G.; Tolosa, C.A.; and Verloo, M.G. Operationally Defined Metal Fractions in Road Deposited Sediment, Honolulu, Hawaii. *J. Environ. Qual*. 29, 1431. 2000.

Terstriep, M.L., G.M. Bender, and D.C. Noel. *Final Report – NURP Project, Champaign, Illinois: Evaluation of the Effectiveness of Municipal Street Sweeping in the Control of Urban Storm Runoff Pollution*. State Water Survey Division, Illinois Dept. of Energy and Natural Resources, Champaign-Urbana, Illinois, December 1982.

Tobiason, S. "Stormwater metals removal by media filtration: Field assessment case study." *Watershed 2004 Conference Proceedings*. Water Environment Federation. CD-ROM, 2004.

Vignoles M., and L. Herremans. "Metal pollution of sediments contained in runoff water in the Toulouse city." (in French). *NOVATECH 95, 2nd International Conference on Innovative Technologies in Urban Storm Drainage*. May 30 – June 1, 1995. Lyon, France. Pp. 611-614. Organized by Eurydice 92 and Graie. 1995.

Wang, J. Controlled-Potential Techniques in *Analytical Electrochemistry*. John Wiley and Sons, Inc., New York. 2nd ed. 2000.

Whipple, W. and J. V. Hunter. Settleability of urban runoff pollution. *Journal WPCF*, Vol. 53, No. 12, pg. 1726, 1981.

APPENDIX A

NUTRIENTS, SOLIDS AND HEAVY METALS DATA TABLES

A.1: Total Solids (mg/L)

Sample ID	>1500µm	<1500µm	<250µm	<106µm	<45µm	<10µm	<2µm	<1µm	<0.45µm
Inlet 1	43.5	264.5	229.0	210.0	167.3	114.0	114.3	118.0	119.0
Roof 1	2.8	54.1	54.1	62.0	48.0	49.5	47.4	50.0	50.0
Inlet 2	4.7	314.6	281.0	272.6	227.0	142.0	148.4	138.7	141.8
Roof 2	11.1	153.0	140.0	113.0	74.0	71.0	64.6	67.0	53.0
Mixed 1	0.1	17.0	17.0	17.0	17.0	8.0	12.0	9.0	11.0
Roof 3	86.2	288.0	222.0	196.9	167.0	139.2	138.4	148.0	140.0
Inlet 3	43.0	198.9	178.8	178.8	82.8	84.7	87.2	78.7	76.0
Roof 4	0.2	7.7	7.7	3.1	0.0	1.0	3.0	3.0	3.0
Mixed 2	0.3	23.6	23.6	23.6	21.0	15.2	16.0	15.0	14.0
Roof 5	0.1	10.3	10.3	8.0	14.3	11.0	5.0	3.0	9.1
Inlet 4	1.96	52.00	52.00	45.00	45.83	40.00	36.00	44.00	42.00
Outlet 1	0.58	54.00	48.00	51.00	46.00	39.00	43.00	38.00	41.41
Inlet 5	1.4	61.2	61.2	60.6	32.7	34.0	35.0	34.0	25.0
Outlet 2	0.1	54.0	54.0	49.0	40.0	32.0	21.0	25.0	30.0

A. 2: Turbidity (NTU)

Sample ID	<250µm	<106µm	<45µm	<10µm	<2µm	<1µm	<0.45µm	<250µm
Inlet 1	40.8	33	36.7	41.7	18.9	21.1	15	14.5
Roof 1	13.4	6.76	5.97	5.77	4.81	4.6	4.42	4.38
Inlet 2	57.7	36.1	38.2	35.6	6.09	6.69	5.26	3.84
Roof 2	21.3	27.4	13.2	22.5	5.08	2.78	1.88	2.5
Mixed 1	4.55	2.84	2.55	2.58	4.7	4.33	0.273	0.155
Roof 3	19.3	12	8.49	15.5	6.64	7.74	6.47	5.36
Inlet 3	42.400	34.800	38.900	24.900	12.700	6.480	4.280	2.590
Roof 4	5.990	2.660	0.705	0.850	0.618	0.625	0.467	0.529
Mixed 2	9.490	4.430	4.180	3.850	3.490	3.140	0.557	1.410
Roof 5	1.990	1.030	0.745	1.000	0.390	0.939	0.855	0.520
Inlet 4	16.800	11.000	9.390	9.900	5.870	3.100	4.490	2.850
Outlet 1	9.090	9.530	9.320	8.320	6.690	3.810	3.180	3.150
Inlet 5	53.300	38.400	39.500	11.200	6.810	3.130	2.280	2.500
Outlet 2	31.400	31.100	30.800	9.500	7.460	6.200	3.780	2.390

A. 3: Total Phosphorus (mg/L as PO_4^{3-})

Sample ID	<250µm	<106µm	<45µm	<10µm	<2µm	<1µm	<0.45µm	<250µm
Inlet 1	0.87	0.69	0.63	0.59	0.2	0.19	0.2	0.19
Roof 1	0.38	0.43	0.36	0.4	0.42	0.35	0.33	0.31
Inlet 2	0.79	0.47	0.73	0.31	0.05	0.04	0.17	0.02
Roof 2	0.91	1.03	0.99	0.66	0.45	0.4	0.49	0.42
Mixed 1	0	0	0	0	0	0	0	0
Roof 3	0.52	0.46	0.49	0.29	0.25	0.26	0.24	0.26
Inlet 3	0.73	0.7	0.45	0.38	0.36	0.23	0.21	0.31
Roof 4	0	0	0.04	0	0	0	0	0
Mixed 2	0.11	0.05	0.07	0.05	0	0	0.09	0.04
Roof 5	0	0	0.08	0.05	0.08	0.03	0.03	0.03
Inlet 4	0.2	0.24	0.26	0.26	0.16	0.25	0.25	0.26
Outlet 1	0.46	0.4	0.27	0.33	0.48	0.45	0.29	0.48
Inlet 5	0.68	0.48	0.53	0.59	0.49	0.64	0.6	0.56
Outlet 2	0.61	0.59	0.38	0.35	0.29	0.21	0.15	0.13

A. 4: Chemical Oxygen Demand (mg/L)

Sample ID	<250µm	<106µm	<45µm	<10µm	<2µm	<1µm	<0.45µm	<250µm
Inlet 1	178	165	154	134	88	85	92	98
Roof 1	80	79	72	68	73	64	74	73
Inlet 2	207	194	181	161	129	127	127	123
Roof 2	81	124	74	75	41	48	38	54
Mixed 1	32	20	25	21	28	20	17	15
Roof 3	190	204	184	157	143	154	151	152
Inlet 3	116	126	104	72	54	58	51	58
Roof 4	3	6	13	2	1	4	5	1
Mixed 2	17	7	13	18	6	21	10	3
Roof 5	0	6	17	2	3	2	-5	1
Inlet 4	36	33	30	23	32	28	25	33
Outlet 1	37	29	33	32	24	26	22	38
Inlet 5	47	46	44	28	43	21	21	33
Outlet 2	41	43	40	25	19	10	14	29

A. 5: pH

Sample ID	<250µm	<106µm	<45µm	<10µm	<2µm	<1µm	<0.45µm	<250µm
Inlet 1	6.91	7.09	7.44	7.18	7.18	7.09	7.09	7.09
Roof 1	4.35	4.43	4.34	4.35	4.35	4.35	4.18	3.91
Inlet 2	6.65	6.74	6.57	6.82	6.74	6.74	6.91	6.4
Roof 2	6.65	6.48	6.57	6.74	6.74	6.91	6.74	6.57
Mixed 1	6.65	6.57	6.57	6.4	6.65	6.65	6.65	6.57
Roof 3	5.37	5.2	5.29	5.2	5.2	5.12	5.2	5.12
Inlet 3	6.27	6.54	6.72	7.18	6.54	6.81	6.81	6.63
Roof 4	6.26	6.26	6.17	6.17	5.89	5.71	5.89	5.99
Mixed 2	6.35	6.54	6.08	6.45	6.35	6.45	6.54	6.54
Roof 5	5.72	5.72	5.37	5.63	5.44	5.53	5.26	5.44
Inlet 4	6.55	6.64	6.82	6.82	6.82	8.82	6.99	6.9
Outlet 1	6.82	6.73	6.82	6.82	6.9	6.9	6.9	7.08
Inlet 5	6.64	6.27	6.45	6.72	6.82	6.82	6.82	6.82
Outlet 2	6.64	6.36	6.09	6.36	6.55	6.73	6.64	6.27

A.6: Zinc (µg/L)

Sample ID	>250µm	<250µm	<106µm	<45µm	<10µm	<2µm	<1µm	<0.45µm
Inlet 1	162.11	156.22	122.62	88.36	31.38	36.10	36.58	34.32
Roof 1	102.74	101.29	95.19	100.82	90.27	95.67	125.03	100.62
Inlet 2	465.19	443.02	404.81	348.16	236.62	239.55	234.62	240.75
Roof 2	1136.76	1146.32	1053.79	984.23	766.95	760.50	779.85	811.40
Mixed 1	82.20	90.33	82.83	87.44	85.16	53.39	72.44	82.20
Roof 3	857.35	835.30	860.12	755.10	722.33	722.38	753.84	459.85
Inlet 3	342.61	325.73	295.58	247.82	188.51	180.68	175.96	187.57
Roof 4	129.40	117.11	118.70	76.98	134.13	119.33	122.97	125.87
Mixed 2	171.51	170.79	168.86	159.27	148.96	151.89	94.44	157.27
Roof 5	27.11	18.84	39.96	28.16	34.24	27.66	41.01	85.70
Inlet 4	174.10	174.10	175.45	164.06	162.65	146.49	152.41	143.87
Outlet 1	163.44	143.41	143.62	162.12	130.74	119.94	111.31	112.92
Inlet 5	122.81	135.92	136.19	134.07	136.04	113.79	119.95	125.95
Outlet 2	95.08	94.68	92.78	78.72		74.48	85.35	94.45
Method Blank	26.12	15.08	28.53	17.60	13.94	16.15	24.66	35.30

A.7: Copper (µg/L)

Sample ID	>250µm	<250µm	<106µm	<45µm	<10µm	<2µm	<1µm	<0.45µm
Inlet 1	11.46	10.91	8.63	11.93	5.41	9.97	6.19	5.19
Roof 1	11.88	10.44	10.31	10.55	10.27	10.61	13.71	11.40
Inlet 2	18.88	17.65	16.25	16.21	10.23	10.50	10.56	11.03
Roof 2	7.65	7.98	6.83	6.61	1.32	2.58	1.98	1.41
Mixed 1	<lod	<lod	<lod	<lod	<lod	1.47	<lod	<lod
Roof 3	11.55	11.03	87.52	6.24	4.85	4.99	4.56	5.88
Inlet 3	13.01	13.43	11.30	9.05	7.95	7.42	6.28	6.51
Roof 4	<lod	<lod	<lod	1.26	<lod	<lod	<lod	<lod
Mixed 2	<lod	<lod	<lod	<lod	<lod	<lod	1.73	<lod
Roof 5	11.63	12.54	25.97	11.46	10.40	10.03	10.84	11.01
Inlet 4	5.37	5.37	5.12	5.14	4.63	4.39	4.19	4.00
Outlet 1	6.49	4.47	4.94	4.86	4.67	4.62	3.53	3.03
Inlet 5	9.68	9.36	13.57	9.23	9.08	8.51	8.31	8.36
Outlet 2	5.21	4.89	4.76	4.51		4.17	4.18	4.06
Method Blank	<lod	0.22	<lod	0.96	<lod	<lod	<lod	2.16

*lod = 0.151 ug/L

A.8: Cadmium (μg/L)

Sample ID	>250μm	<250μm	<106μm	<45μm	<10μm	<2μm	<1μm	<0.45μm
Inlet 1	0.25	0.45	0.93	0.23	1.07	0.25	0.17	0.42
Roof 1	0.32	0.44	0.30	0.46	0.39	1.47	1.99	1.67
Inlet 2	1.61	1.68	1.61	1.80	1.98	2.07	1.54	1.43
Roof 2	4.07	2.08	1.99	2.20	1.96	1.95	2.00	1.92
Mixed 1	1.61	1.64	1.65	1.73	1.70	1.26	1.66	1.77
Roof 3	2.87	3.01	3.13	2.67	2.61	2.69	2.53	1.89
Inlet 3	0.70	0.77	0.61	0.47	0.82	0.38	0.36	0.35
Roof 4	0.37	0.33	0.32	0.39	0.40	0.38	0.45	0.35
Mixed 2	0.39	10.86	0.59	0.47	0.44	0.45	0.40	0.35
Roof 5	0.38	0.37	0.37	0.35	0.35	0.42	0.31	0.31
Inlet 4	0.50	0.50	0.44	0.71	0.96	0.39	0.43	0.36
Outlet 1	0.58	0.38	0.45	0.37	0.38	0.39	1.05	0.90
Inlet 5	0.54	0.42	0.37	0.37	0.40	0.41	0.42	0.52
Outlet 2	0.40	0.50	0.68	0.81		3.69	1.89	1.36
Method Blank	1.45	1.57	1.52	1.49	1.67	1.54	1.52	1.44

A.9: Lead (µg/L)

Sample ID	>250µm	<250µm	<106µm	<45µm	<10µm	<2µm	<1µm	<0.45µm
Inlet 1	14.01	12.38	22.20	6.88	18.72	1.37	1.97	1.08
Roof 1	1.96	2.02	1.77	1.67	1.50	21.70	28.82	8.76
Inlet 2	50.56	42.82	40.98	35.99	23.16	24.60	24.53	29.54
Roof 2	60.05	62.89	57.93	56.27	31.04	30.16	30.08	30.70
Mixed 1	31.10	31.43	32.08	30.63	57.42	23.62	36.04	55.13
Roof 3	78.15	77.78	73.15	50.09	38.26	39.20	36.60	29.77
Inlet 3	22.09	20.17	17.70	11.94	14.84	5.70	4.83	5.34
Roof 4	4.22	3.81	3.63	3.55	3.54	3.48	3.62	6.88
Mixed 2	5.56	6.58	9.03	5.55	3.81	4.15	3.47	3.76
Roof 5	3.78	3.98	3.62	3.92	3.47	3.34	3.61	3.83
Inlet 4	7.11	7.11	7.00	7.55	6.87	4.74	6.33	4.69
Outlet 1	7.97	6.63	7.10	7.99	6.03	4.95	13.37	12.03
Inlet 5	11.44	9.78	9.45	8.76	9.29	8.05	8.33	7.98
Outlet 2	7.26	7.70	20.87	10.72		88.05	46.77	33.26
Method Blank	9.29	8.05	8.33	7.98	7.26	7.70	20.87	10.72

APPENDIX B

TOXICITY TEST DATA

B.1: Effect of mixing Microtox® acute testing bacteria on fluorescence.

	5 min	15 min	25 min
Sample	% effect	% effect	% effect
10 mg/L $ZnSO_4$ mixed 3x	59.61	85.03	94.28
10 mg/L $ZnSO_4$ mixed 3x	58.73	85.02	94.29
10 mg/L $ZnSO_4$ mixed 3x	60.26	86.61	94.95
10 mg/L $ZnSO_4$ mixed 3x	60.25	85.82	94.53
10 mg/L $ZnSO_4$ mixed 3x	60.87	86.06	94.57
10 mg/L $ZnSO_4$ mixed 3x	61.93	86.09	94.47
10 mg/L $ZnSO_4$ mixed 3x	62.81	86.18	94.6
10 mg/L $ZnSO_4$ mixed 3x	66.60	87.57	95
10 mg/L $ZnSO_4$ mixed 3x	67.59	87.89	95.09
10 mg/L $ZnSO_4$ mixed 3x	66.64	87.38	94.89
Average	62.53	86.37	94.67
St. Dev.	3.26	1.00	0.29
COV	0.0521	0.0116	0.0031
10 mg/L $ZnSO_4$ mixed 20x	68.41	87.87	95.04
10 mg/L $ZnSO_4$ mixed 20x	67.02	88.24	95.25
10 mg/L $ZnSO_4$ mixed 20x	68.58	88.71	95.19
10 mg/L $ZnSO_4$ mixed 20x	70.21	89.14	95.49
10 mg/L $ZnSO_4$ mixed 20x	71.37	89.05	95.61
10 mg/L $ZnSO_4$ mixed 20x	72.72	89.90	95.64
10 mg/L $ZnSO_4$ mixed 20x	73.04	90.00	95.69
10 mg/L $ZnSO_4$ mixed 20x	71.32	90.44	95.98
10 mg/L $ZnSO_4$ mixed 20x	73.92	90.47	95.97
10 mg/L $ZnSO_4$ mixed 20x	77.47	91.45	96.15
Average	71.41	89.53	95.60
St. Dev.	3.0755	1.1171	0.3666
COV	0.0431	0.0125	0.0038

B.2: Effect of different NaCl concentrations on fluorescence of bacteria.

	5 min	15 min	25 min
Sample	% effect	% effect	% effect
0.1 g NaCl per 10mL	66.92	71.13	75.26
0.1 g NaCl per 10mL	67.94	71.99	75.7
0.1 g NaCl per 10mL	71.29	75.01	78.6
0.1 g NaCl per 10mL	66.48	71.19	74.29
0.1 g NaCl per 10mL	66.96	71.57	74.5
Ave	67.918	72.178	75.67
St.Dev.	1.959112	1.62016	1.734013
COV	0.028845	0.022447	0.022915
0.2 g NaCl per 10mL	15.23	20.71	21.76
0.2 g NaCl per 10mL	15.49	20.88	22.65
0.2 g NaCl per 10mL	14.85	20.33	22.02
0.2 g NaCl per 10mL	15.49	20.56	22.12
0.2 g NaCl per 10mL	18.1	24.09	24.45
Ave	15.832	21.314	22.6
St.Dev.	1.294651	1.564938	1.083674
COV	0.081774	0.073423	0.04795
0.4 g NaCl per 10mL	27.16	35.44	33.38
0.4 g NaCl per 10mL	29.2	36.4	34.1
0.4 g NaCl per 10mL	24.87	33.91	31.18
0.4 g NaCl per 10mL	25.42	34.12	32.07
0.4 g NaCl per 10mL	23.55	33.65	31.1
Ave	26.04	34.704	32.366
St.Dev.	2.190514	1.172659	1.335283
COV	0.084121	0.03379	0.041256

B.3: Difference in use of Osmotic Adjusting Solution or NaCl to adjust osmotic pressure of bacteria using varying concentrations of $ZnSO_4$.

% Effect $ZnSO_4$ w/OAS 15min

	Concentration						
Replicate	0.5 mg/L	1.0 mg/L	2.0 mg/L	4.0 mg/L	**6.0 mg/L**	8.0 mg/L	9.0 mg/L
1	1.90%	13.83%	24.49%	36.26%	**53.52%**	60.93%	63.03%
2	4.11%	11.47%	23.86%	39.20%	**52.16%**	65.38%	63.01%
3	4.55%	11.91%	25.73%	37.52%	**52.64%**	65.31%	64.25%
Ave	3.52%	12.40%	24.69%	37.66%	**52.77%**	63.87%	63.43%
St.Dev.	0.01	0.01	0.01	0.01	**0.01**	0.03	0.01
COV	0.40	0.10	0.04	0.04	**0.01**	0.04	0.01

% Effect $ZnSO_4$ w/NaCl 15min

	0.5 mg/L	**1.0 mg/L**	2.0 mg/L	4.0 mg/L	6.0 mg/L	8.0 mg/L	9.0 mg/L
1	23.43%	**43.89%**	71.30%	91.01%	96.10%	97.43%	97.60%
2	26.78%	**46.59%**	70.30%	82.62%	95.89%	97.29%	97.97%
3	25.12%	**50.43%**	73.85%	91.37%	96.54%	97.18%	97.64%
Ave	25.11%	**46.97%**	71.82%	88.33%	96.18%	97.30%	97.74%
St.Dev.	0.02	**0.03**	0.02	0.05	0.00	0.00	0.00
COV	0.07	**0.07**	0.03	0.06	0.00	0.00	0.00

B.4: Effect of varying NaCl concentration on bacterial fluorescence.

Sample Size (mL)	NaCl added (g)	% light reduction	Salinity (%)	Conductivity (mS/cm)
20	0.10	98.02	0.5	8.2
20	0.15	83.46	0.8	11.5
20	0.20	67.12	1.0	14.7
20	0.25	55.05	1.3	18.5
20	0.30	47.62	1.5	25.4
20	0.35	36.03	1.8	28.4
20	0.40	33.57	2.0	32.2
20	0.45	16.93	2.3	37.4
20	0.50	11.13	2.5	48
20	0.55	15.88	2.8	56.1
20	0.60	16.7	3.0	58.8
20	0.65	27.6	3.3	65.2
20	0.70	25.95	3.5	72.4
20	0.75	30.08	3.8	72.5
20	0.80	38.75	4.0	82.5
20	0.85	42.14	4.3	84.5
20	0.90	47.93	4.5	90
20	0.95	49.58	4.8	100.2
20	1.00	64.62	5.0	103.2
20	1.10	74.57	5.5	114.6
20	1.15	76.61	5.8	124.6
20	1.20	77.8	6.0	122.4

B.5: Average reduction in fluorescence using varying ZnSO4 concentrations and NaCl to adjust salinity to 2%. Approximate IC_{50} in bold.

	0.25mg/L	0.50mg/L	**0.75mg/L**	1.00mg/L	1.25mg/L	1.50mg/L	2.00mg/L	3.00mg/L
1	22.18%	33.20%	**47.37%**	60.65%	88.01%	85.33%	92.42%	93.95%
2	21.25%	30.67%	**53.62%**	62.80%	87.90%	85.61%	92.34%	94.41%
3	23.44%	33.71%	**53.69%**	62.24%	86.13%	87.48%	91.94%	94.27%
Ave	22.29%	32.53%	**51.56%**	61.90%	87.35%	86.14%	92.23%	94.21%
St.Dev.	0.011	0.016	**0.036**	0.011	0.011	0.012	0.003	0.002
COV	0.049	0.050	**0.070**	0.018	0.012	0.014	0.003	0.003