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Pollutant Associations with Particulates in Stormwater

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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 (along with some major constituents 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).

Preliminary results show that total phosphorus and chemical oxygen demand are associated with the particulates and in general decrease with a decrease in particle size. Obviously, concentrations should all decrease with filtration. However, there were periodic jumps in concentrations for some conditions, reflecting variability in the analytical method and the sample handling. Results using ASV show the metals of concern (Zn, Cd, Pb and Cu) all present in the dissolved (<0.45µm) fraction of the stormwater samples with Zn normally present in the highest concentration. Exposure of the samples to UV light increases the concentration of most of the metals, indicating a dissociation of metals from organic complexes or colloids.

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. 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 may be defined as the determination of the individual concentrations of the various chemical forms of an element when 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 Bately 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 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. Other metals, such as lead and mercury, have no nutritional value and are always considered dangerous, even at relatively small concentrations. Associations with fine particulates also affect heavy metal toxicity to many forms of aquatic life.

Pitt, *et al.* (1998) analyzed 550 samples for a broad list of constituents, including the total and filtered observations shown in Table 1. The samples were collected from telecommunication manhole vaults that were mostly affected by stormwater. 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 United States and represent all seasons.

Table 1. 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%

Pitt, *et al.* (1998)

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. The analytical schemes developed by Florence and Batley (1980), and Florence (1977) and Bott (1995) enable associations of metals to different categories to be measured. Their schemes do not provide a detailed species distribution, but rather an estimation of the fraction of the metal present in toxic forms. Florence and Bately (1980) used Anodic Stripping Voltammetry (ASV) with a chelating resin separation and UV irradiation to examine the dissolved (<0.45 micron) metal fractions, as shown in Figure 1. A chelating resin (Chelex-100) was used to separate ionic metals from metals strongly bound in metal-ligand complexes, or strongly adsorbed to colloidal particles. The UV-irradiation was applied to the water at a pH of 4.8 to cause dissociation of the metals from organic complexes, or colloids. The use of a chelating resin such as Chelex-100, in combination with ASV, has 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 Bately scheme.

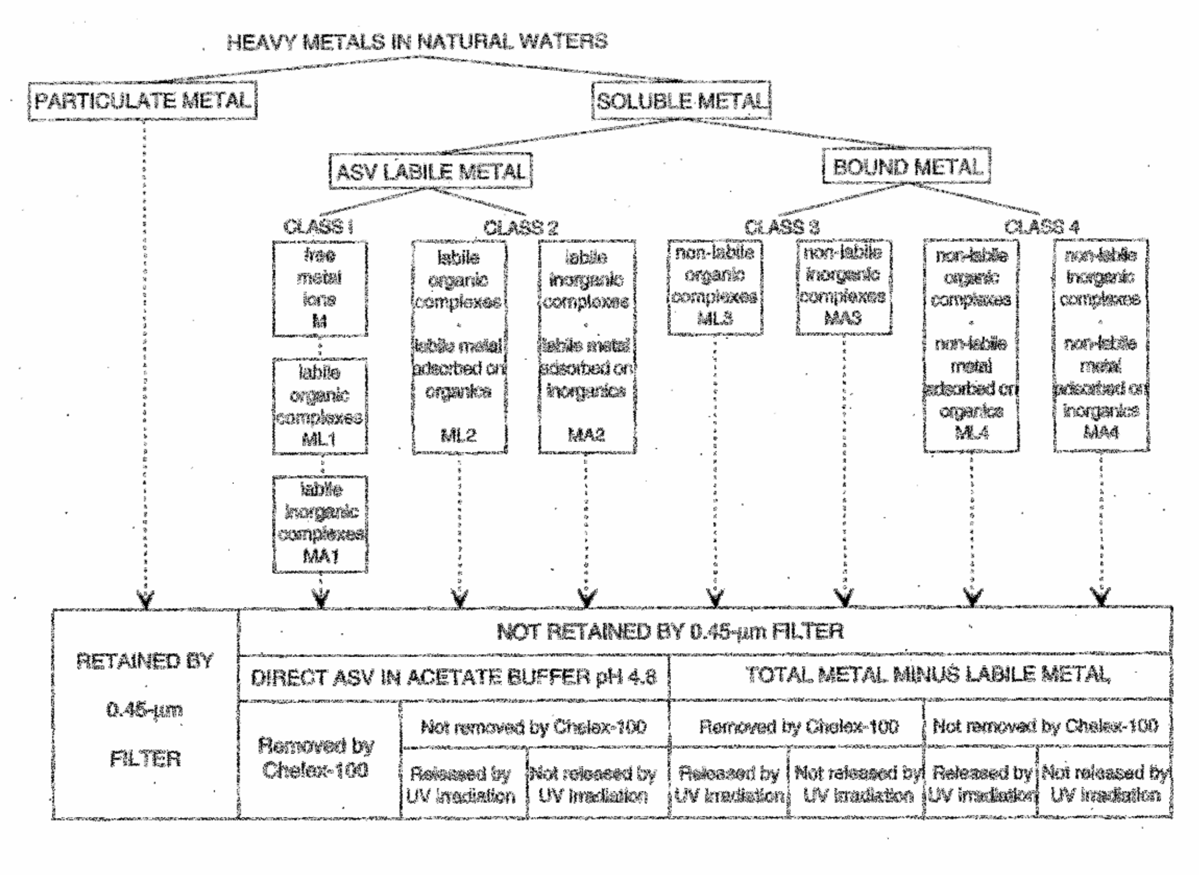

Figure 1. Diagram of sequential extraction (Florence and Batley 1980), as presented by Bott (1995).

The main purpose of treating stormwater is to reduce its adverse impacts on receiving waters. One of the most important characteristics affecting the treatability and fate of heavy metals in stormwater is their association with different particle sizes. Most stormwater treatment methods include the physical removal of particulates. Since many pollutants of interest are associated with particulates in stormwater, knowledge of the critical size of these particulates is crucial for the design of stormwater treatment. Basic particle size distributions of stormwater need to be known as well as the associations of the pollutants with the different sizes.

Methodology

Sampling

For each sample, six liters of stormwater was collected manually into acid washed HDPE or LDPE sample bottles and then stored at 4°C until further processing and analysis. To date, ten samples have been collected and are described in Table 3. Collection sites were either roof runoff or sheetflow runoff from the Tuscaloosa, Alabama area.

Table 2: Sample collection information.

Sample No.	Sampling Date	Site Description	Type of Sample
1	7/25/2004	Local mall parking lot	sheetflow runoff in front of storm drain inlet
2	7/26/2004	Department store roof runoff	Grab sample
3	8/20/2004	Courthouse parking lot	sheetflow runoff in front of storm drain inlet
4	8/20/2004	Roof runoff from courthouse	Grab sample
5	8/20/2004	Drain from upper parking deck and roof of courthouse	Grab sample
6	8/20/2004	Roof runoff from building next to courthouse	Grab sample
7	1/13/2005	courthouse parking lot	sheetflow runoff in front of storm drain inlet
8	1/13/2005	Roof runoff from courthouse	Grab sample
9	1/13/2005	Drain from upper parking deck and roof of courthouse	Grab sample
10	1/13/2005	Roof runoff from back of engineering building	Grab sample

Sample Processing

The processing and analysis scheme for each stormwater sample is shown in Figure 2. Each water sample was first processed by splitting the sample into homogenous fractions using a Delrin® cone splitter. 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.

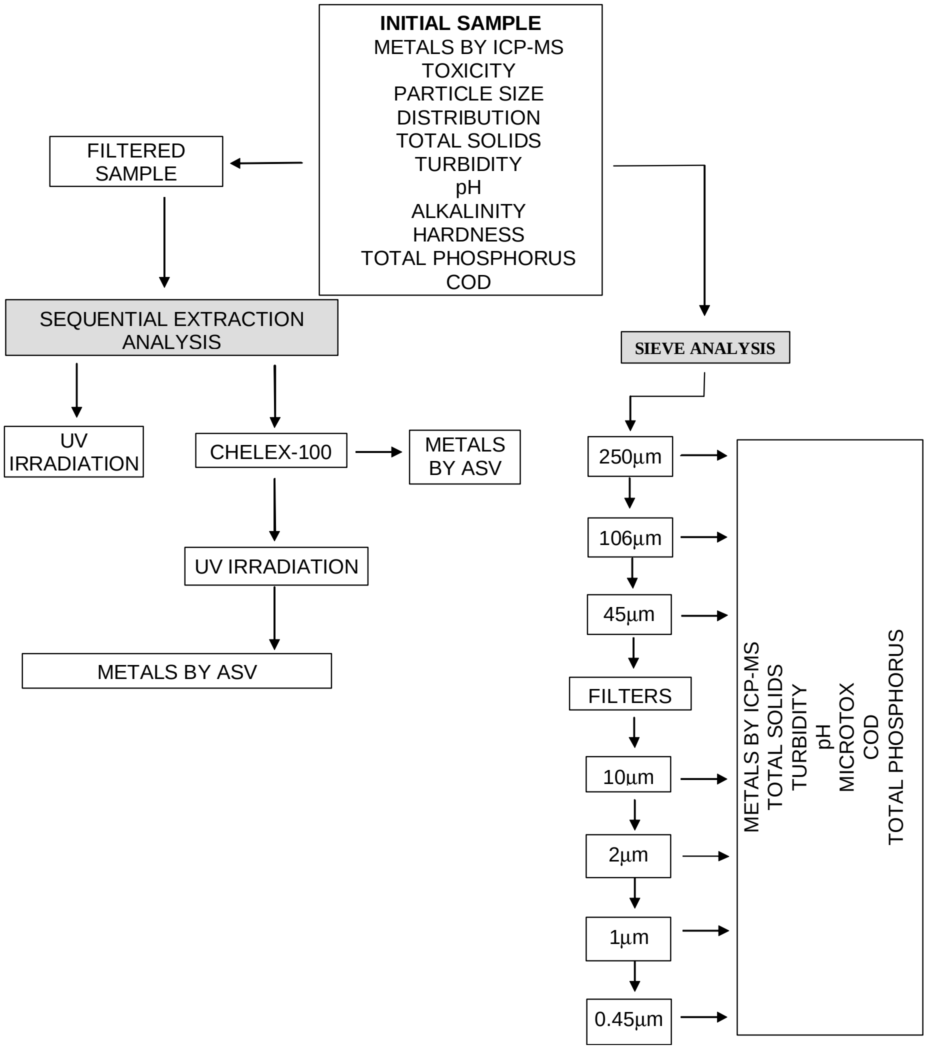

Figure 2: Sample processing scheme

Stormwater 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 3. Each sample was also analyzed for toxicity using the Microtox® Test System and for metals using voltammetric methods with an Epsilon™ Electrochemical Analyzer and Controlled Growth Mercury Electrode (CGME). Particle distributions were determined using a Beckman Coulter Multisizer™ 3 Coulter Counter. 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 3. In addition, they were analyzed for toxicity and heavy metals using ICP-MS.

Table 3: 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)

The filtered fraction of each sample was 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 will 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. After Chelex exposure, the rest of the sample is then UV irradiated for 6 hours and processed for metals analysis.

Results

Figures 3-5 are representative preliminary plots from the first 10 samples collected showing concentrations after filtering the samples through the different sized sieves and polycarbonate membrane filters. Figures 3 and 4 show the decrease in the concentration of total phosphorus and chemical oxygen demand, respectively. The general trend is towards a decrease in pollutant concentration with a decrease in particle size. Obviously, concentrations should all decrease with filtration. However, there were periodic jumps in concentrations for some conditions, reflecting variability in the analytical method and the sample handling. Figures 5 and 6 show the measured changes in total solids after sieving and filtering through different sizes apertures. As expected, the general trend is a lower concentration of total solids as the particle size decreases. All samples were analyzed using three different apertures of the coulter counter that then could be combined to cover the entire size range of 0.45 to over 250 µm.

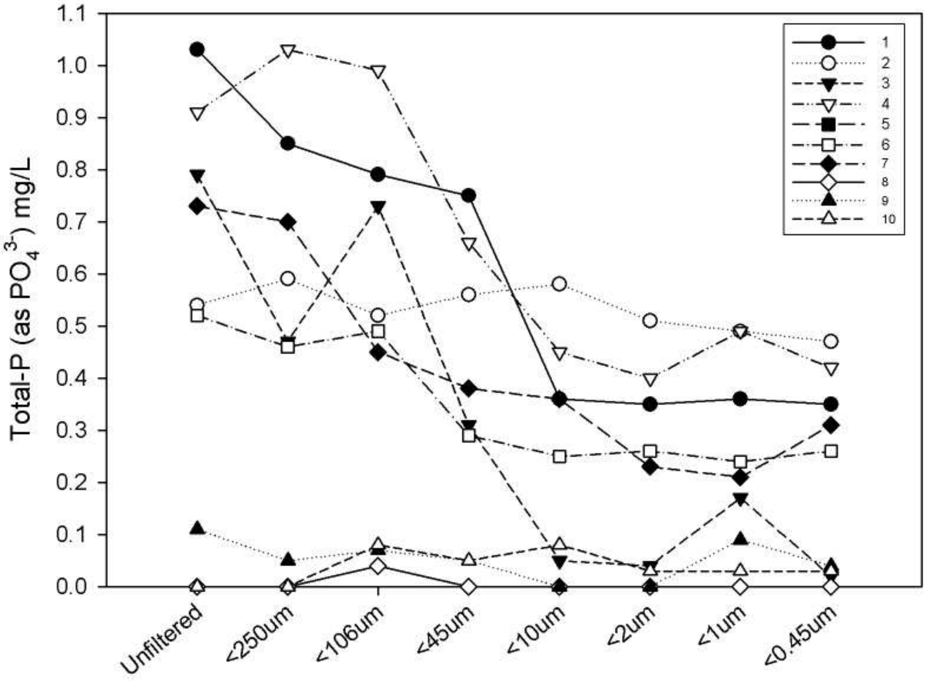

Figure 3: Total phosphorus associations with particle sizes for preliminary samples (separations with sieves and membrane filters).

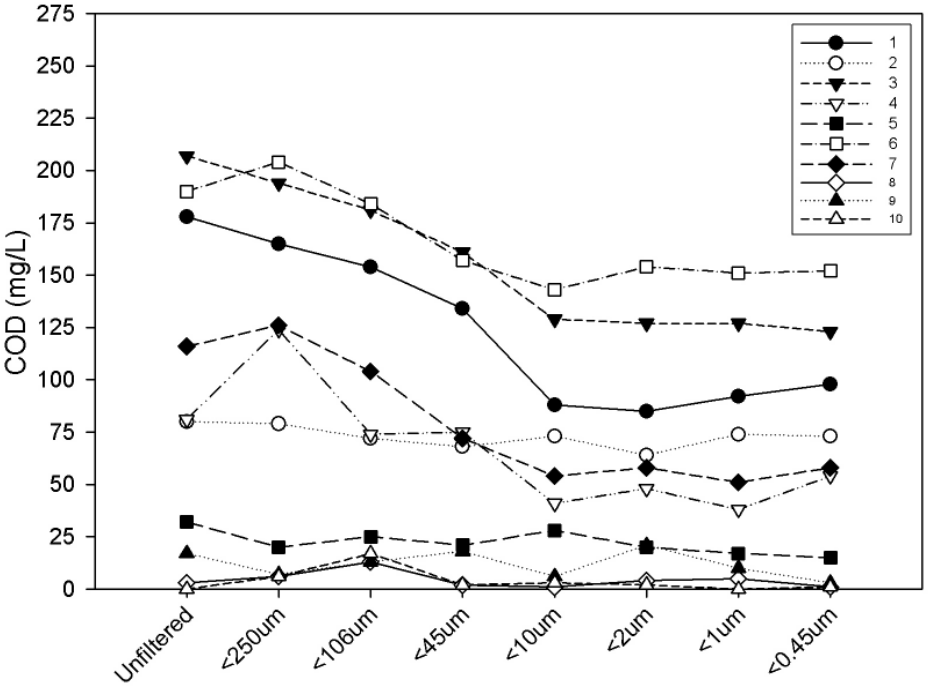

Figure 4: Association of chemical oxygen demand with particle size for preliminary samples (separations with sieves and membrane filters).

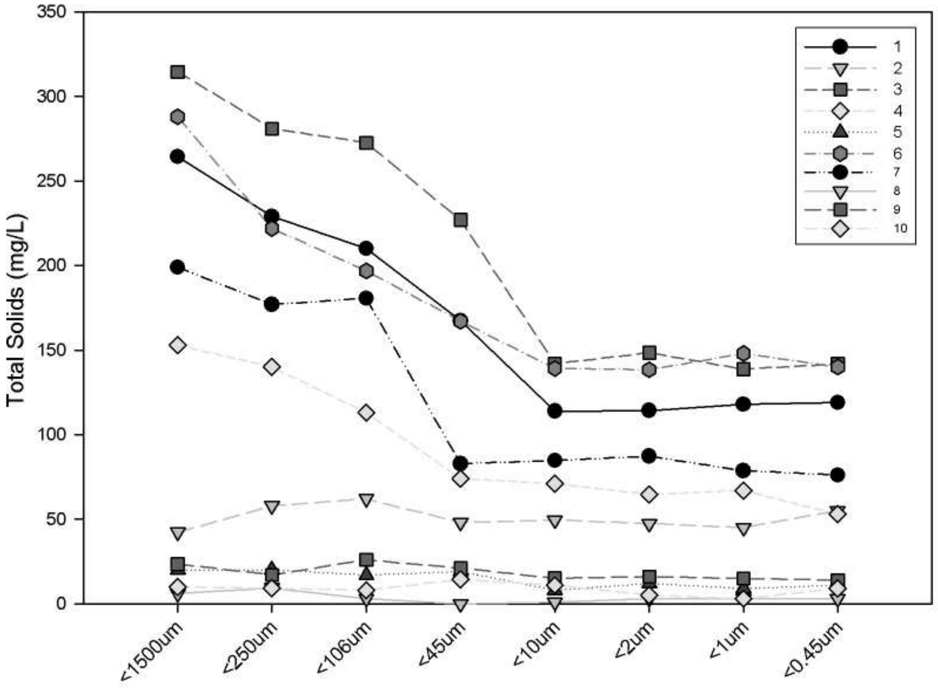

Figure 4: Total solids concentrations after filtering through sieves and membrane filters.

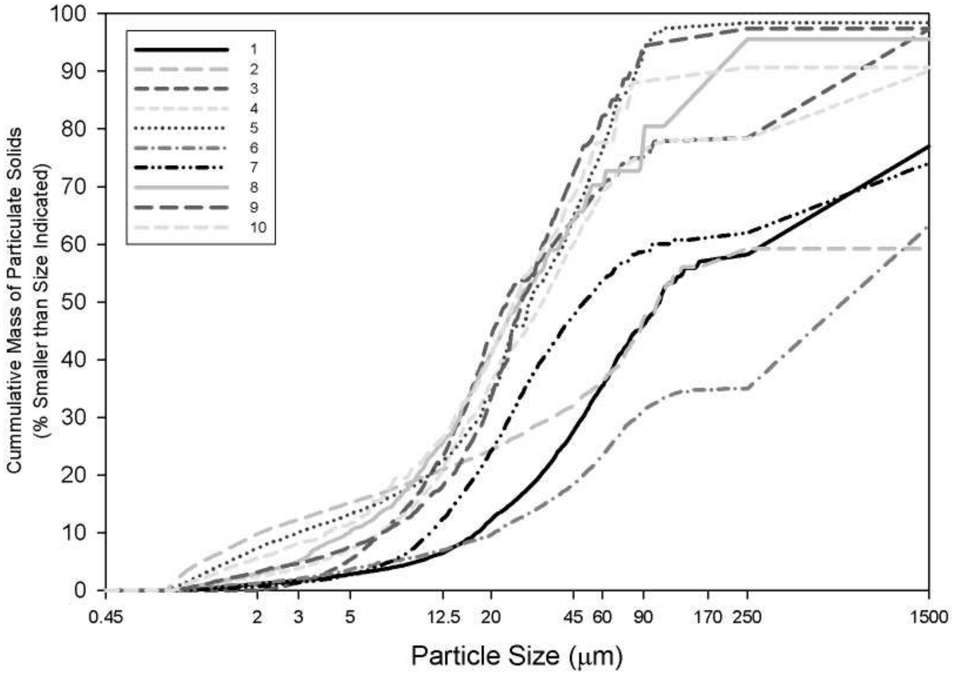

Figure 5: Particle size distributions of preliminary samples.

Preliminarily, results using Anodic Stripping Voltammetry to measure dissolved metals in solution have found all four metals of interest still present in the 0.45µm - filtered fractions, with Zn normally being present in the highest concentration. The range of Zn concentrations so far has been less than 0.5 µg/L to almost 1 mg/L. After exposure of the same fractions to ultraviolet light, the concentrations of most of the metals increase slightly, and in the case of Zn, can concentration can double indicating a dissociation of metals from organic complexes or colloids. Results using the Chelex-100 ion exchange resin have not fully been analyzed at this time. Previous results using the Chelex-100 resin showed that most of the Zn, Pb and Cd were present in ionic forms and removed by the ion-exchange resin whereas only around 30% of copper was ionic and removed from solution.

Discussion

Most stormwater treatment efforts involve the physical removal of particulates. In order to better design sedimentation stormwater treatment devices, it is important to understand what pollutants are associated with different sized particulates and how they may be controlled during the removal of the particulates. Although results from our most recent samples have not yet been fully analyzed at this time, previous results from this laboratory have been used to show the concentrations of pollutants remaining after controlling for particle sizes ranging from 20 to 0.45µm. These concentrations are shown in Table 4. The corresponding percentage reductions are shown in Table 5.

Table 4. Average Remaining Concentrations after Controlling for Different Sized Particles

	Residual Concentration after Removing all Particulates Greater than Size Shown (mg/L, unless otherwise noted)				
	Unfiltered	**20 µm**	**5 µm**	**1 µm**	**0.45 µm**
Total Solids	178	106	102	86	84
Suspended Solids	94	22	18	2	0
Turbidity (NTU)	53	30	24	4	2
Total-P	0.38	0.12	0.07	0.04	0.03
Total-N	2.13	1.50	1.25	1.38	1.63
Nitrate	0.6	0.60	0.60	0.53	0.50
Phosphate	0.8	0.23	0.18	0.15	0.10
COD	99	51	48	47	52
Ammonia	0.26	0.17	0.14	0.12	0.11
Cadmium (µg/L)	4.9	3.9	3.8	3.8	3.8
Copper (µg/L)	24.6	18.3	16.2	17.8	15.6
Lead (µg/L)	15.7	9.2	6.0	3.7	2.8
Zinc (µg/L)	179	64	53	53	51

Table 5. Average Percentage Reduction in Pollutants after Controlling for Different Particle Sizes

	Percent Pollutant Reduction after Removing all Particulates Greater than Size Shown			
	20 µm	5 µm	1 µm	0.45 µm
Total Solids	40%	43%	52%	53%
Suspended Solids	76	81	98	100
Turbidity	43	55	92	96
Total-P	68	82	89	92
Total-N	30	41	35	23
Nitrate	0	0	12	17
Phosphate	71	78	81	88
COD	48	52	52	47
Ammonia	35	46	54	58
Cadmium	20	22	22	22
Copper	26	34	34	37
Lead	41	62	76	82
Zinc	64	70	70	72

Some pollutants can be reduced by a reduction in particulates, such as suspended solids, total phosphorus and most heavy metals. Other pollutants, such as nitrates, are reduced much less, even after filtration down to 0.45 µm.

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 only be able to remove the particulates down to about 20 µm, while no pond can remove the filterable fraction by physical removal processes alone. Of course, samples for other locations and situations would likely result in different levels of control. However, the predicted level of control associated with particulate control at least to 1 to 5 µm are close to what is expected for a well-designed wet detention pond designed for the control of these particulates, with the exception of copper which would normally be better controlled than indicated with this data. These data enable us to specify the level of treatment of particulates to obtain specific pollutant treatment goals.

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