EVALUATION OF RETENTION POND AND CONSTRUCTED WETLAND BMPs FOR TREATING PARTICULATE-BOUND HEAVY METALS IN URBAN STORMWATER RUNOFF

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ABSTRACT

The sources of heavy metals in urban stormwater runoff are diverse (e.g., highways, road surfaces, roofs) and the release of metals into the environment is governed by several complex mechanisms. Heavy metals in stormwater are associated with suspended particulate materials that vary from coarse (>75 µm) and fine particulates (<75 to 1 µm), to colloids (<1µm). Stormwater runoff investigations increasingly focus on evaluating quality and the effectiveness of adopting best management practices (BMPs) to minimize pollutant input, including heavy metals, to receiving waters. Heavy metals in stormwater are primarily removed by sedimentation in BMPs such as retention ponds and constructed wetlands; these sediments may be toxic to benthic invertebrates and aquatic microorganisms. Information on heavy metals-particulate association is therefore a fundamental requirement prior to using wetland and pond BMPs for treatability studies. Research is being conducted at the U.S. EPA's Urban Watershed Research Facility in Edison, NJ to evaluate the effectiveness of retention pond and constructed wetland BMP mesocosms to remove particulate-bound heavy metals from roof and parking-lot stormwater runoff. The research objectives include: (i) investigating the association of selected heavy metals (Al, Cr, Cu, Fe, Mn, Pb, and Zn) with fine particulates (20 to 0.4 µm) in stormwater runoff; (ii) evaluating the relative removal of particulate-bound as well as dissolved heavy metals in retention ponds and cattail-wetland mesocosms; and, (iii) investigating the solid-phase chemical associations of heavy metals in cattail wetland sediments and assessing the potential for sediment toxicity and heavy metal bioavailability. This investigation comprises the study of eight separate storm events; six sampling events have been completed to date. Preliminary results show that Al, Cr, Fe, and Pb are primarily particulate-bound (>20 µm) and Mn is mostly soluble. Cu and Zn are primarily associated with fine particulates (10 to 1 µm) and the dissolved fraction (<0.4 µm) in stormwater runoff. Also, the retention pond and cattail wetland mesocosms are effective in attenuating heavy metals, especially, Cu, Zn, Al, Cr, and Pb. Preliminary results are also presented for the chemical fractionation of cattail wetland sediments.

Keywords: urban stormwater runoff, heavy metals, retention ponds, constructed wetlands, suspended particulates, sediments, chemical speciation, selective sequential extraction

INTRODUCTION

Urban wet-weather flow discharges have been recognized as significant sources of pollutants that adversely impact the quality of receiving waters (Deletic, 2001; Lee et al., 2004; Nordeidet et al., 2004; Sansalone et al., 1996). Land-use changes coinciding with urbanization result in detrimental changes to stormwater runoff quality, and subsequently, impervious surfaces in urban and urbanizing areas have been implicated in the decline of watershed integrity (Bannerman et al., 1993; Brattebo and Booth, 2003). The chemical composition of urban runoff is influenced by watershed characteristics such as land-use, traffic volume, and percent impervious cover (Chang et al., 2004; Karouna-Renier et al., 2001; Nelson and Booth, 2002; Van Metre and Mahler, 2003). Urban stormwater runoff contains significant concentrations of heavy metals, nutrients, persistent organic pollutants, pathogens, sediments, and other anthropogenic compounds (McPherson et al., 2002).

The presence of heavy metals in stormwater runoff is a major concern due to their toxicity, bioavailability, and persistence in the environment. The sources of heavy metals are varied and their concentrations in the dissolved and particulate phases in stormwater runoff are significantly influenced by the land-use pattern. Some specific sources include rooftops, building materials, asphalt surfaces, traffic activities, automobile wear, atmospheric deposition, and accidental spills (Davis et al., 2001; Farm, 2002; Herngren et al., 2005). Levels of Zn, Cu, Cd, Pb, Cr, and Ni in urban stormwater runoff often exceed ambient background levels, and for many urban and transportation land uses, often exceed surface water discharge criteria on an event basis (Sansalone and Buchberger, 1997). Heavy metals are either dissolved in the stormwater or are bound to particulates; the degree of binding is a function of pH, average pavement residence time, and the nature and quantity of solids present (Charlesworth and Lees, 1999). A significant portion of the heavy metals is associated with suspended particulate materials that vary from coarse (>75 µm) and fine particulates (<75 to 1 µm), to colloids (<1µm) (Sansalone, 2003). The partitioning of heavy metals between the particulate and dissolved phases has a major effect on the occurrence, transport, fate, and biological effects of heavy metals in aquatic systems (Mungur et al., 1995; Ran et al., 2000).

The use of best management practices (BMPs) for stormwater management has been practiced in the U.S. for the last two decades and is becoming more widespread in urban areas in Europe; e.g., the UK and France (Dechesne et al., 2004; Hares and Ward, 1999). Current research investigations focus on runoff quality and the effectiveness of adopting stormwater BMPs to minimize pollutant input, including heavy metals, to receiving waters. Detention systems such as ponds and constructed wetlands increasingly form a part of an integrated stormwater management strategy and aim at reducing the levels of suspended solids and heavy metals in runoff (Persson and Wittgren, 2003). Sedimentation appears to be the primary means by which these structural BMPs reduce the heavy metal load associated with particulate matter and improve runoff quality (Mazer et al., 2001). Vegetated BMPs such as natural and constructed wetlands have been used for the treatment of heavy metals in road runoff (Farm, 2002) and have been shown to significantly reduce the concentration of metals such as Zn, Pb, and Cu (Walker and Hurl, 2002). The differences in removal observed for different metals in wetlands could be due to various factors such as organic matter (Wood and Shelley, 1999) and redox potential (Walker and Hurl, 2002). In wetland BMPs, in addition to sedimentation, macrophytes could provide a major removal mechanism by providing sites for metal precipitation and/or sedimentation. Above-ground plant parts (stems, stolons, leaves) are thought to induce sedimentation of particulates and their sorbed pollutants; plant roots stabilize sediment deposits and prevent sediment re-suspension (Bavor et al., 2001; Mazer et al., 2001). Emergent plants such as the common reed (*Phragmites australis*) and reed mace (*Typha latifolia*) have been shown to effectively remove particulate and soluble heavy metals in wetland BMPs (Shutes et al., 1999; Sriyaraj and Shutes, 2001).

The reported pollutant removal efficiencies of BMPs are often erratic, partly contributed by the inherent uncertainties in the temporal and spatial characteristics of stormwater runoff (Park et al., 2006). An in-depth understanding of the processes involved is essential for applying these BMP systems to stormwater management measures. The partitioning of heavy metals into different particle size classes in terms of their adsorption to particulates has major implications for urban water quality management (Herngren et al., 2005). Since metals are primarily removed by the removal of suspended solids in stormwater BMPs, the geochemical partitioning of metals should be an important consideration for BMP selection (Lee et al., 2004; Lau and Stenstrom, 2006). Previous studies on stormwater BMPs have not focused on either the lower or upper practical size limit for the removal of particulate-bound heavy metals from stormwater runoff. The investigation presented in this paper is addressing this growing research need.

The different removal pathways for heavy metals in BMPs lead to a concentration of various heavy metal compounds in pond and wetland sediments, which can therefore be considered as the sink for heavy metals. The continued accumulation of heavy metals in these sediments can lead to their migration and increase the risk for ground and surface water quality deterioration downstream. Heavy metals accumulated in BMP sediments may also be toxic to benthic invertebrates and aquatic microorganisms downstream of the BMPs (Wood and Shelley, 1999; Karouna-Renier and Sparling, 2001). These accumulated sediments have to be routinely removed to minimize the risk of contamination and maximize the operational efficiency of these BMPs. However, the frequency of such maintenance practices and the handling of sediments require a full understanding of the quantity and quality of the deposits, especially with reference to their heavy metal content (Yousef et al., 1994). It is well known that the mobility, bioavailability, and toxicity of heavy metals depend on their physicochemical form. Consequently, heavy metal characterization in BMP sediments should include speciation studies in addition to determining total metal content. It is imperative to assess the types of chemical associations between heavy metals and the sediment solid phase to evaluate their possible toxicity and also for understanding and controlling the behavior of these elements in the environment (Clozel et al., 2006; Gumgum and Ozturk, 2001; Jong and Parry, 2004). Very few studies have been done on the solid-phase speciation of heavy metals accumulated in wetland sediments (Lim et al., 2001); this study also addresses this research need.

OBJECTIVES

The overall objectives of this study were:

i. Characterize the heavy metals in stormwater runoff in several size ranges (>20µm, and between 20 and 0.4 µm) generated from parking lots and roof-runoff;
ii. Evaluate the effects of two types of structural BMPs (cattail wetland and wet pond) on the removal of particulate-bound and dissolved heavy metals from stormwater;
iii. Determine if the distribution of heavy metals in particulates exhibits a seasonal variability, and determine the effects of BMP type, water column chemistry as well as the season, on the removal of dissolved and particulate heavy metals in BMP mesocosms; and,
iv. Assess the chemical associations between heavy metals and wetland sediments in the solid phase by selective sequential chemical fractionation techniques and thereby predict heavy metal mobility and toxicity.

STUDY AREA AND EXPERIMENTAL DESIGN

This investigation was performed in U.S. EPA's Urban Watershed Research Facility (UWRF) in Edison, NJ using urban stormwater runoff generated from a parking lot and rooftop of the adjacent county college campus (9.75 acres). A meso-scale approach was used to simulate two different BMP treatments: (i) retention pond and (ii) constructed wetland, in order to study the various objectives. The two mesocosms were circular tanks of the same size, and were lined with gravel, sand, and topsoil. Each tank was designed with a perforated drain at the bottom. The two BMP treatments differed in their water depth and the presence of a macrophytic community (*T.latifolia*) in the wetland. A small orifice (0.2-cm diameter) set in a riser pipe was used to control the overflow rate for each mesocosm. Under normal conditions, the mesocosms were fed with tap water to simulate baseflow conditions and prevent surface water stagnation. A stormwater storage tank (7500 L) near the mesocosms was used to collect the runoff which was routed from an onsite storm sewer outfall that drains the adjacent county college. Flow-weighted technique was adopted to collect the runoff during real storm events conforming to recommended guidelines (NJDEP). The collected runoff was used to "simulate" storm events to the mesocosms within 72 h of the actual rain event. During a "simulated" storm event, stormwater in the storage tank was mixed thoroughly and pumped to an elevated "supply" tank (3000 L) which acted as the stormwater feed for the mesocosms. After mixing, stormwater from the supply tank was routed by gravity flow to the two mesocosms (225 L), with a 24-h storm-event drain time. Time-weighted composite samples were collected over 24 h, and these were representative of the mesocosm effluent produced by the simulated stormwater event. During each event, the stormwater runoff was characterized for selected heavy metals and water quality constituents prior to, and after passing through, the two BMP treatments. To understand the particulate association of heavy metals, the outfall samples and the influent and effluents from the two mesocosms were sequentially filtered through five different pore sizes: 20, 10, 5, 1, and 0.4 µm, using Millipore polycarbonate membrane filters. Major physico-chemical parameters such as pH, oxidation reduction potential (ORP), total suspended solids (TSS), and total and dissolved organic carbon (TOC and DOC) were determined in the unfiltered and filtered samples. The seven heavy metals that were investigated were aluminum (Al), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), lead (Pb), and zinc (Zn). These were determined in the unfiltered fraction as well as in samples filtered through the different pore sizes. Other parameters that were analyzed included: particle size distribution (unfiltered samples), cations (unfiltered and 0.4 µm filtrate), and anions (chloride and sulphate in samples filtered through 0.4 µm) (APHA, 1998; U.S. EPA, 1983; 1985). In order to assess seasonal variability, this investigation comprises the study of eight separate storm events (two rain events per season – spring, summer, fall, and winter) of which six stormwater sampling events (three events each in 2005, and 2006) have been completed to date.

Sediments from the wetland mesocosms were sampled in spring 2005 and 2006. For the purposes of this investigation, sediments were defined as those mineral and organic materials situated beneath the aqueous layer of the cattail wetland mesocosm (0 to 5 cm). The sediments were collected and processed according to guidelines recommended by the USGS (Shelton and Capel, 1994) and the U. S. EPA (U. S. EPA, 2001). The sampling procedure specifically targeted depositional zones near and below the inlet and outlet of the mesocosm. Collected sediments were composited, homogenized, and wet-sieved through 2 mm (U.S. sieve size no. 10) and 63 µm (U.S. sieve size no. 230) nylon-mesh. The pH, ORP, and TOC were determined in both size fractions of the sediment. The sequential chemical fractionation technique recommended by the Standards, Measurements and Testing Programme (SM&T) (formerly known as the Bureau Commun de Reference or BCR) of the European Commission was used. This procedure yielded four "operationally" defined species: (i) water soluble, exchangeable, and carbonate bound (exch); (ii) Fe-Mn oxide bound (red); (iii) organic matter and sulfide bound (oxid); and, (iv) residual (resid).

Yellow Springs Instruments (YSI) data sondes were installed in the mesocosms and the control tank to monitor essential water quality parameters (pH, dissolved oxygen (DO), temperature, conductivity, and ORP on a 12-min time step before, during, and after each experimental event to assess the temporal variation and the dynamics of mesocosm-to-mesocosm water chemistry.

PRELIMINARY RESULTS AND DISCUSSION

Stormwater Characteristics

Six stormwater events were investigated during the spring, summer, and fall in 2005 and 2006. Preliminary results for four events conducted during spring and summer between 2005 and 2006 are discussed here. Continuous monitoring of the weather and flow during the sampling events in 2005 showed that rainfall intensities varied from 2.39 mm/h to 5.89 mm/h. Total storm runoff volumes ranged from 3,491 m^3 to 21,253 m^3. The peak storm flows varied from 0.04 m^3/s to 0.16 m^3/s during different events.

The pH of unfiltered stormwater runoff was neutral (7.07 to 7.49) as determined during the spring and summer sampling events. With regard to the mesocosms, the retention pond exhibited a higher pH compared to the wetland. The pH of the retention pond averaged 7.56 to 7.60, consistently. The wetland exhibited a slightly lower pH that varied from 7.12 to 7.32. The redox potential of stormwater varied from 658.9 to 660.0 mV during sampling events conducted in 2005. However, it was lower at 408.7 mV during the summer sampling event in July 2006. The redox potentials of the two mesocosms were quite similar and did not vary much from the outfall or from one another as observed from their unfiltered effluents. Effluents from the retention pond and the wetland exhibited a redox potential varying from 610.5 to 630.8 mV in the pond, and between 570.0 and 671.3 mV in the wetland. Again, for the summer sampling event in 2006, consistent with the observation for the stormwater runoff from the outfall, the two BMPs exhibited lower ORP between 393.0 and 400 mV. Organic carbon was present mostly in the dissolved fraction (67 to 97%). Chloride, Ca, and Mg concentrations were very high in stormwater analyzed during spring 2005, possibly due to contribution from road salt application during the preceding winter months. The physico-chemical characteristics of stormwater runoff from the outfall are shown in Table 1.

Table 1 - Physicochemical Characteristics of Runoff from Roofs and Parking Lot

UWRF Outfall	April '05	June '05	Aug '05	Jul '06
pH	7.49 ± 0.097	7.32 ± 0.06	7.33 ± 0.05	7.07 ± 0.061
Temp (°C)	20.1	25.0	23.1	22.0
ORP (mV)	685.3 ± 10.9	658.9 ± 4.55	631.7 ± 50.1	408.7 ± 9.50
TSS (mg/l)	11.9 ± 0.832	221.7 ± 2.91	329.6 ± 4.54	69.33 0.977
sulphate (mg/l)	28.2 ± 0.12	32.7 ± 0.10	24.8 ± 0.62	29.7 ± 0.722
chloride (mg/l)	333.9 ± 2.94	336.7 ± 2.89	56.4 ± 1.40	48.41 ± 1.40
TOC (mg/l)	18.67 ± 0.00	32.15 ± 2.33	17.95 ± 0.35	13.12 ± 0.07
DOC (mg/l)	18.1 ± 0.05	26.1 ± 0.14	16.3 ± 0.00	8.81 ± 0.512
Ca (mg/l)	46.1 ± 0.55	50.1 ± 0.14	16.3 ± 0.28	16.06 ± 0.094
Mg (mg/l)	6.98 ± 0.07	7.54 ± 0.01	2.40 ± 0.05	2.36 ± 0.075
Na (mg/l)	149.3 ± 0.55	156.0 ± 1.41	33.85 ± 0.28	34.91 ± 0.321
K (mg/l)	3.84 ± 0.07	3.1 ± 0.03	1.69 ± 0.00	2.59 ± 0.018

Heavy Metals and Their Partitioning in Urban Stormwater Runoff

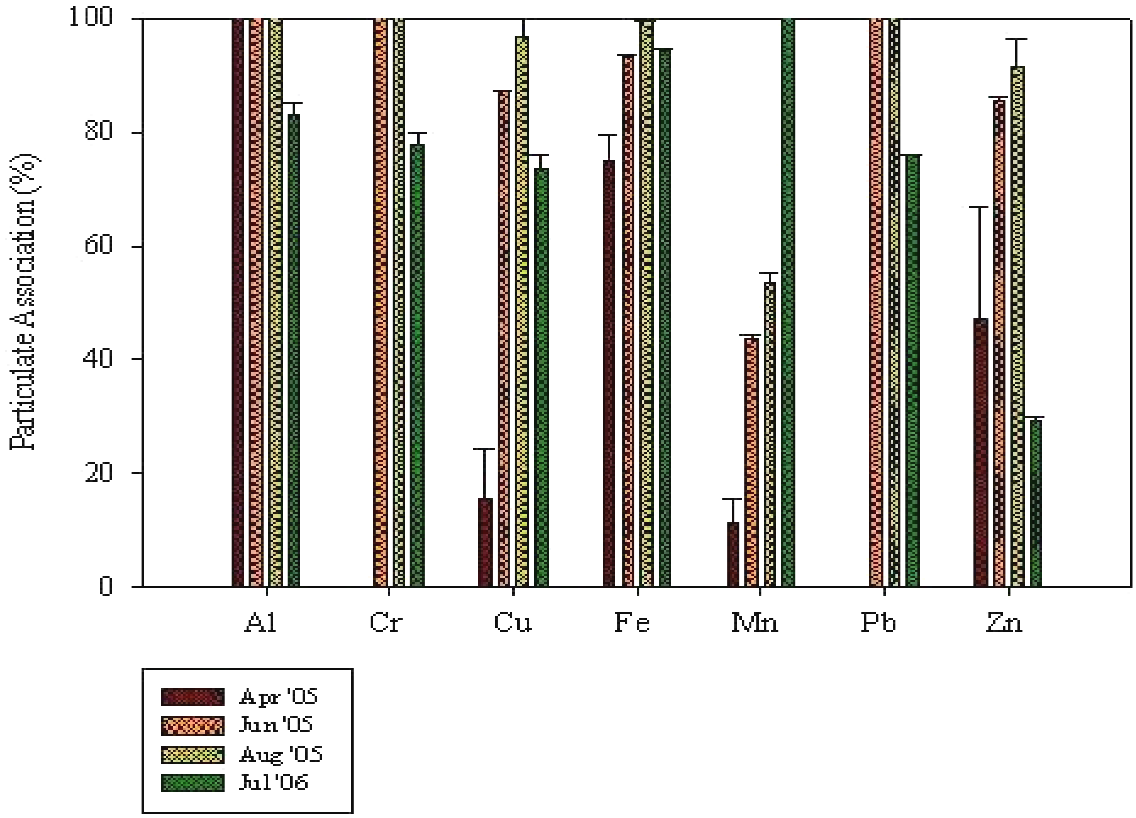
The concentrations of heavy metals in parking lot and roof runoff were highly variable between different events (Table 2). Studies conducted elsewhere have reported similar variability for both heavy metals and suspended solids in urban runoff (Stone and Marsalek, 1996). The differences in concentrations between storm events could be attributed to a variety of contaminant sources in the watershed, and also due to the complex wash-off dynamics of the contaminated materials (Brown and Peake, 2006). Concentrations of all heavy metals increased significantly, especially between the spring and summer storm events in 2005. Most of the metals studied (Cu, Zn, Fe, Mn, and Al) were routinely detected in stormwater runoff during all sampling events; Pb and Cr, while absent during the spring event in 2005, were regularly detected in runoff during subsequent events. It is believed that ongoing land-use changes due to massive housing construction activity in the vicinity in mid-2005 have altered the stormwater characteristics and contributed to the presence of these heavy metals in runoff. While the concentrations of heavy metals varied between events, the results were largely consistent with observations made in similar studies (Maestre and Pitt, 2005; Tuccillo, 2006). In addition to concentration variations, the degree of association of these metals with the particulate and soluble fractions was different for different events, and was more pronounced for Cu and Zn.

Table 2 - Concentration of Heavy Metals in Runoff from Roofs and Parking lot

UWRF Outfall	April '05	June '05	Aug '05	July '06
Al_{tot} (mg/L)	0.271 ± 0.096	4.23 ± 0.400	4.79 ± 0.460	3.18 ± 0.518
$Al_{0.4\mu m}$ (µg/L)	NA	NA	NA	529.7 ± 57.6
Cr_{tot} (µg/L)	NA	15.85 ± 0.071	14.2 ± 0.849	5.569 ± 0.128
$Cr_{0.4\mu m}$ (µg/L)	NA	NA	NA	1.26 ± 0.132
Cu_{tot} (µg/L)	17.03 ± 1.40	58.2 ± 1.98	45.9 ± 1.70	17.52 ± 1.37
$Cu_{0.4\ \mu m}$ (µg/L)	13.97 ± 1.27	7.45 ± 0.212	NA	4.64 ± 0.110
Fe_{tot} (mg/L)	1.009 ± 0.166	11.25 ± 0.353	40.65 ± 2.33	1.594 ± 0.0595
$Fe_{0.4\ \mu m}$ (µg/L)	249.3 ± 11.24	757.5 ± 0.707	241.0 ± 56.6	92.9 ± 8.23
Mn_{tot} (µg/L)	413.3 ± 12.2	769.5 ± 10.61	494.5 ± 26.2	109.6 ± 0.367
$Mn_{0.4\ \mu m}$ (ug/L)	369.1 ± 10.2	433 ± 0.00	230.5 ± 3.54	115.8 ± 6.46
Pb_{tot} (µg/L)	NA	44.5 ± 2.55	41.2 ± 2.83	16.9 ± 0.160
$Pb_{0.4\ \mu m}$ (µg/L)	NA	NA	NA	3.19 ± 1.52
Zn_{tot} (ug/L)	32.97 ± 8.82	272.5 ± 21.92	504.0 ± 32.5	106.3 ± 3.89
$Zn_{0.4\ \mu m}$ (µg/L)	16.33 ± 3.15	39.2 ± 1.20	42.40 ± 21.8	87.4 ± 19.3

The association of heavy metals with particulate materials in stormwater runoff was investigated between 20 µm and 0.4 µm. It was observed that the particulate associations varied for each metal studied, and the nature and type of solid-phase partitioning exhibited by the heavy metal varied for different storm events. Of the metals studied, Al, Cr, and Pb were 100% particulate bound, and no dissolved forms were detected for any of these metals during the first three events (Figure 1). Stormwater characteristics such as pH, conductivity, and total organic carbon appeared to have a negligible effect, if any, on the concentration and particulate distribution of heavy metals. Heavy metal associations with particulate material in the 0.4 to 20 µm range and the occurrence of dissolved metals (< 0.4 µm) appeared to be greatly influenced by the storm characteristics and the TSS loads in the runoff; this observation supported the hypothesis of heavy metal – particulate associations in urban stormwater runoff. Herngren et al. (2005) also reported strong relationships between stormwater TSS and heavy metals such as Al, Fe, Pb, and Cr.

Figure 1 - Particulate Fractions of Heavy Metals in Urban Stormwater Runoff



Aluminum in runoff was primarily associated with particles > 20 µm and between 5 and 20 µm. Copper was associated with the soluble fraction and also bound to fine particulates, primarily 1to 5 µm; associations with particles > 5 µm as well as 10 – 20 µm were also observed during different events. Iron, Mn, and Zn existed as both particulate-bound and soluble species; however, with an increase in TSS concentrations in the runoff during different events (Figure 2), these metals exhibited a higher distribution in the particulate fractions, especially with particles in sizes >20 µm and between 5 and 20 µm. The storm event monitored during April showed that 80% of the observed TSS was due to the presence of particles larger than 20 µm, and particles smaller than 20 µm contributed to less than 20% of the TSS in runoff. However, the size distribution of TSS was different during events in June and August, and was characterized by an increase in particles smaller than 20 µm. During these events, particles between 5 and 20 µm contributed to 41% of the TSS in runoff, and the presence of larger particles (>20 µm) were reduced to around 50%. On the other hand, during the event in July 2006, the TSS concentrations was more due to the presence of particles <10 µm. This event was characterized by the dominance of particles smaller than 5 µm which contributed to 42% of the observed TSS. This was significantly different from earlier events where these particles contributed to less than 10% of the TSS in runoff. This variation in the size distribution of TSS and the resulting changes observed in heavy metal-particulate associations further support the influence of TSS on the particulate distribution of heavy metals in stormwater runoff. Figures 3 and 4 show the variation in heavy metal-particulate associations for four events.

Figure 2 – Distribution of Total Suspended Solids in Urban Stormwater Runoff

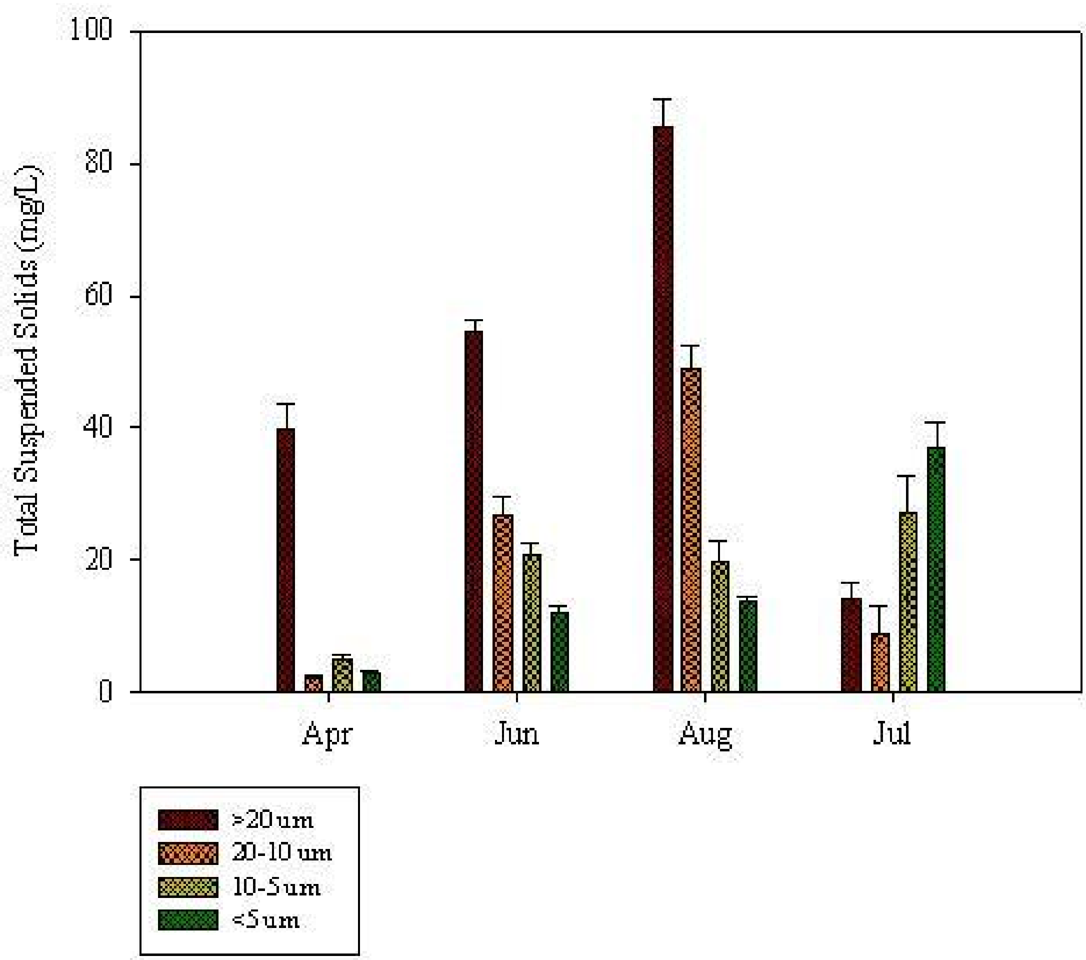


Figure 3 – Particulate Associations of Al, Fe, and Mn in Urban Stormwater Runoff

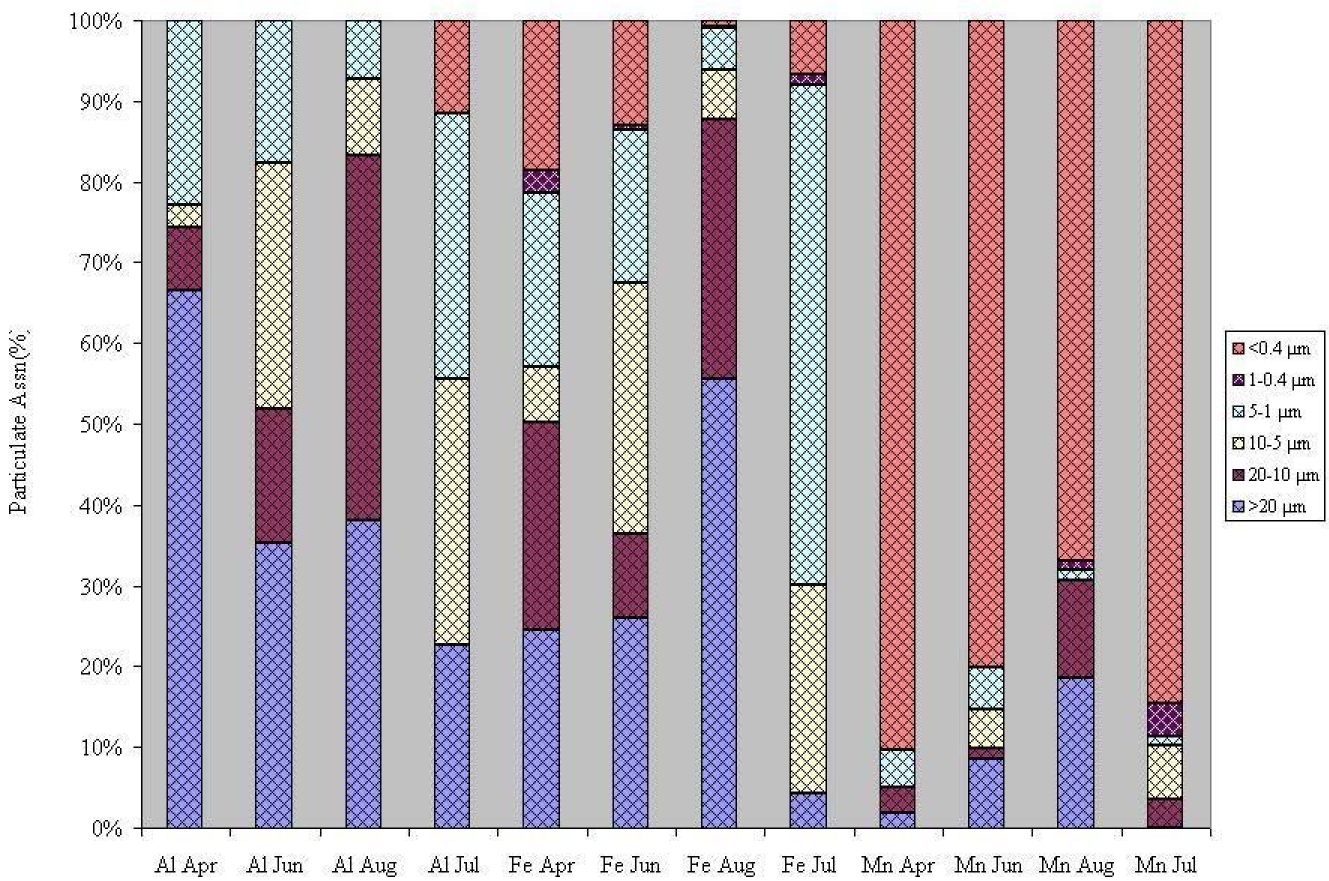
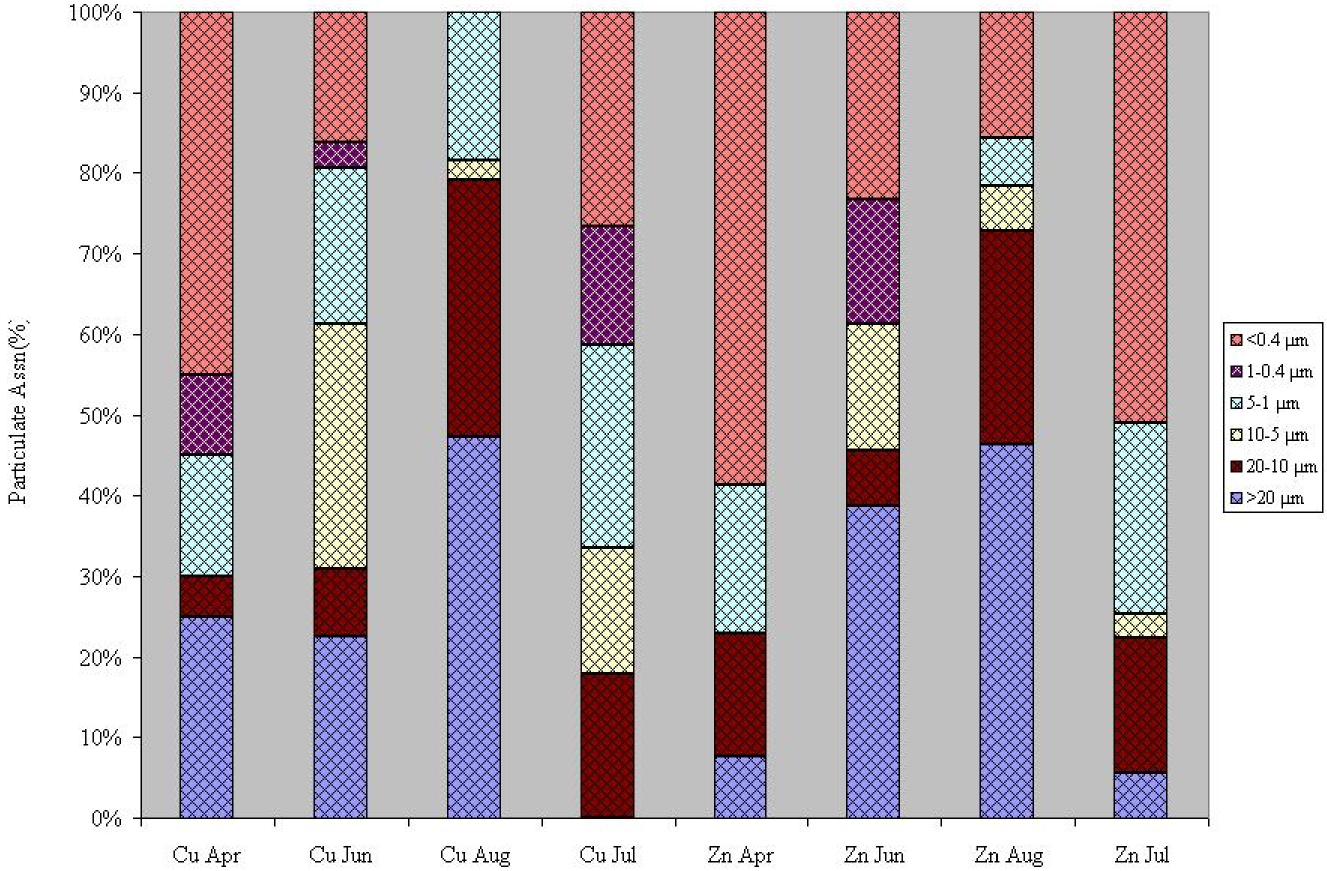


Figure 4 – Particulate Associations of Cu and Zn in Urban Stormwater Runoff



It was observed that antecedent conditions and the nature of the rain event, both of which are highly variable, appeared to influence heavy metal and TSS loads in stormwater runoff. For example, the storm during June was characterized by a prolonged drought and resulted in a runoff similar to what is known as the "first flush". This resulted in a higher washing off of heavy metals and suspended solids leading to elevated concentrations in the runoff. Except for Mn, event mean concentrations of all other metals were significantly higher ($P<0.001$) during this event. Linear regression analysis on heavy metals associations in stormwater runoff yielded significant associations ($P<0.001$) between Cu, Al, TOC, and TSS in runoff; significant associations were also observed for Zn ($P<0.001$) with Fe, Al, and TSS. The influence of TSS on heavy-metal particulate associations was more pronounced during the events in June and August, 2005, as observed from the regression analysis ($P < 0.001$).

Heavy Metals Removal in Retention Pond and Cattail Wetland Mesocosms

The effects of the two BMP mesocosms on heavy metals removal from urban stormwater runoff are shown for the three events in 2005 in Tables 3 and 4. Values shown in the tables represent the total heavy metal concentration (i.e., unfiltered fraction) of each sample. Results for Al, Cu, Fe, Mn, and Zn are presented and discussed. The attenuation of Cu concentrations was significant in both the retention pond ($P = 0.013$) and the wetland ($P = 0.047$) during the first event. In the case of Fe, the difference in concentration in runoff varied significantly between events ($P < 0.05$) and reduction in Fe loads was significant for both mesocosms ($P < 0.05$) in the second event. Unfortunately, there were some errors in the analytical measurement of Fe during the first event leading to a few questionable results and as a result, parametric tests could not be verified for the April event. The influent concentration of Al varied significantly between April and June ($P < 0.05$) and was attenuated considerably ($P = 0.027$) on passing through the retention pond. The 24 h detention appeared to effectively result in the complete removal of Al, which was all particulate-bound, in the wetland due to sedimentation; Al was not detected in the wetland effluent during these events. An increase in particulate-associated Cu and Zn in stormwater runoff during the second and third event was accompanied by an improved efficiency of removal of these metals from the two BMP mesocosms. This was especially significant for Zn ($P<0.001$) and supported the hypothesis that sedimentation of particulate-associated metals is an effective means of removing heavy metals from stormwater runoff.

Table 3 – Removal of Heavy Metals in Retention Pond

Event	Metal	Influent Conc. (µg/L)*	Retention Pond: Effluent. Conc. (µg/L)*	Retention Pond: Reduction in Conc. (µg/L)*	Retention Pond: Removal Efficiency (%)
Apr	Al	0.745 ± 0.042	0.113 ± 0.007	0.632 ± 0.035	84.82 ± 0.10
	Cu	18.3 ± 1.44	7.33 ± 0.569	11.0 ± 1.82	59.7 ± 5.80
	Fe	1.69 ± 0.207	0.386 ± 0.004	1.31 ± 0.207	76.95 ± 2.91
	Mn	297.7 ± 8.96	107.3 ± 5.77	190.3 ± 13.05	63.97 ± 2.72
	Zn	68.3 ± 2.27	50.1 ± 4.24	18.2 ± 2.12	26.7 ± 3.83
June	Al	2.18 ± 0.085	0.254 ± 0.0064	1.93 ± 0.091	88.36 ± 0.75
	Cu	31.5 ± 0.495	5.60 ± 0.566	25.9 ± 1.06	82.18 ± 2.08
	Fe	6.06 ± 0.099	1.18 ± 0.057	4.88 ± 0.042	80.53 ± 0.62
	Mn	726.0 ± 15.6	468.5 ± 9.19	257.5 ± 6.36	35.47 ± 0.12
	Zn	232.5 ± 3.54	72.7 ± 1.56	159.8 ± 5.09	68.7 ± 1.14
August	Al	2.85 ± 0.219	0.340 ± 0.042	2.51 ± 0.261	87.97 ± 2.40
	Cu	37.95 ± 2.76	9.55 ± 1.63	28.4 ± 4.38	74.61 ± 6.13
	Fe	17.1± 1.27	1.70 ± 0.325	15.4 ± 1.60	89.96 ± 2.65
	Mn	343.0 ± 12.7	143.5 ± 2.12	199.5 ± 14.8	58.12 ± 2.17
	Zn	316.0 ± 19.8	90.6 ± 3.82	225.4 ± 23.6	71.23 ± 3.01

Note: *Al and Fe conc. are reported in mg/L

Table 4 – Removal of Heavy Metals in Cattail Wetland

		Influent Conc. (µg/L)*	Cattail Wetland		
			Effluent. Conc. (µg/L)*	Reduction in Conc. (µg/L)*	Removal Efficiency (%)
Apr	Al	0.684 ± .11	ND	0.684	100.0
	Cu	18.3 ± 1.44	5.87 ± 0.153	12.47 ± 1.29	67.91 ± 1.77
	Fe	1.69 ± 0.207	0.378 ± 0.001	1.32 ± 0.208	77.42 ± 2.89
	Mn	297.7 ± 8.96	148.0 ± 0.00	149.7 ± 8.97	50.3 ± 1.47
	Zn	68.3 ± 2.27	54.10 ± 1.42	14.1 ± 0.896	20.7 ± 0.64
June	Al	2.85 ± 0.219	0.126**	2.78 ± 0.130	97.9 ± 2.97
	Cu	31.5 ± 0.495	4.6**	29.2 ± 2.76	85.5 ± 10.2
	Fe	6.06 ± 0.099	1.38 ± 0.042	4.68 ± 0.141	77.2 ± 1.07
	Mn	726.0 ± 15.6	525.5 ± 16.3	200.5 ± 31.8	27.6 ± 3.79
	Zn	232.5 ± 3.54	69.4 ± 2.69	163.1± 0.849	70.2 ± 0.70
August	Al	2.84 ± 0.219	ND	ND	100.0
	Cu	37.95 ± 2.76	3.20 ± 0.00	34.75 ± 2.76	91.55 ± 0.61
	Fe	17.1± 1.27	0.804 ± 0.012	16. 30 ± 1.28	95.29 ± 0.42
	Mn	343.0 ± 12.7	231.0 ± 1.41	112.0 ± 14.1	32.60 ± 2.84
	Zn	316.0 ± 19.80	33.9 ± 1.48	282.2 ± 21.3	89.3 ± 1.14

Note: *Al and Fe conc. are reported in mg/L
** Standard deviation was not determined

Pair-wise multiple comparison using Tukey's Test showed that events in June and August resulted in a higher removal of Cu in both the retention pond and wetland, and this was significantly different ($P < 0.001$) from the attenuation behavior observed during April.
The removal of Cu in these BMPs appeared to be related to the particulate association exhibited by Cu during the different events. Cu was predominantly related to the soluble fraction (50%) during the event in April, and during subsequent events, occurred primarily as bound to particles larger than 5 µm. This reinforces the assumption that sedimentation is the primary removal mechanism in these BMP systems and they may not be effective in retaining soluble metal species in stormwater runoff. However, it is not clear if vegetation plays a major role in heavy metals uptake as no significant difference was observed between the retention pond and wetland with regard to Cu removal. A similar removal pattern was observed for Zn in both the wetland and the retention pond. A higher removal of Zn was observed from these systems with an increase in particulate-bound Zn in the runoff. Again, the removal was significantly higher and different ($P<0.05$) between April, which had 79% of Zn in the soluble phase, and August, which had <10% of Zn less than 0.4 µm. As was the case with Cu, there were no significant differences in the way Zn was removed from runoff in the pond and wetland.

Chemical Fractionation of Heavy Metals in Wetland Sediments

The surface sediments in the wetland were sampled during spring 2005 to assess the background concentration and speciation of heavy metals accumulated in this mesocosm since its establishment in 2002. As the underlying soil layer in the mesocosm was not analyzed previously, results from this study were assumed to account for heavy metal inputs from both the soil and the incoming stormwater runoff during the last three years. These sediments were subsequently sampled in spring 2006 to assess changes if any to the heavy metal concentration and speciation. Results from the background assessment conducted in 2005 are discussed here. The pH of the wetland was near neutral, 6.49 ± 0.46, and the organic matter content varied between 2.27 and 2.32%. These characteristics were similar in the two size fractions investigated, i.e. <63 µm (silt and clay fraction), and 63 to 2000 µm (sand). However the redox potential was lower (733.5 ± 11.7 mV) in the clay fraction and significantly different (P<0.05) from the silt and clay fraction (892.5 ± 17.5 mV).

Mean concentrations of the seven heavy metals in wetland sediment samples sieved through 0.063 mm and 2 mm are shown in Table 5. The silt and clay fraction (<0.063 mm) held the highest concentrations of the seven heavy metals compared to the sand fraction (0.063 – 2mm). The differences in concentrations between the two fractions were significant (P < 0.05) for all the metals investigated, and especially for Al, Cr, Fe, and Mn (P < 0.001). The large variations in heavy metal concentrations, especially for Cu, Pb, and Zn, have been observed in similar studies on wetland sediments (Langan, 1999). An analysis of the wetland sediments for the heavy metals showed slight variation in pattern between silt and clay-sized fraction (<0.063 mm) and the sand fraction (63 to 2000 µm). While Al was the most dominant metal in samples sieved through 0.063 mm, followed by Fe, Fe was more abundant than Al in samples sieved through 2 mm (63 to 2000 µm fraction). The order of abundance of the other metals in the wetland sediments were in the order Mn > Zn > Pb > Cu > Cr.

The spatial distribution of these heavy metals, observed from their “pseudo”total concentrations showed significant differences (P < 0.01 to P < 0.05) between samples collected near the inlet and outlet. Samples near the inlet exhibited higher concentrations as a result of particulate settling from the incoming runoff; and this varied significantly from samples collected near the outlet. Analysis of variance (ANOVA) and pair wise multiple comparison procedures (Tukey test) showed significant associations (P<0.001) between various metals in both the silt and sand fraction of the wetland sediments. However, Al and Fe did not exhibit any significant association with each other and so was the lack of any significant association between Mn and Zn in both types of samples (<63 µm as well as 63 to 2000 µm).

Table 5 - Concentrations ("Pseudo"total) of Heavy Metals in Wetland Sediments

Metal	<63 µm (mg/kg)	63-2000 µm (mg/kg)
Cr	53.9 ± 17.4	23.2 ± 4.8
Cu	129.9 ± 58.8	57.5 ± 23.6
Pb	282.0 ± 160.0	129.7 ± 53.3
Zn	731.8 ± 309.2	350.9 ± 217.8
Al	33677.1 ± 10938.7	8863.0 ± 2374.5
Fe	31584.9 ± 9559.7	14355 ± 3208.7
Mn	887.2 ± 378.0	387.1 ± 102.9

For the sake of simplicity, sequential extraction results for sediments <63 µm from the different depositional zones have been compiled together and are shown for Cu and Zn in Figures 5 and 6. The residual, non-reactive phase was the most dominant for metals like Al and Fe, while Mn was present primarily as soluble exchangeable species. Cu was largely present as the oxidizable organic matter/sulfide bound species. For Pb and Zn, the most abundant fraction was the reducible fraction characterized by an association with amorphous Fe and Mn oxides and hydroxides. The exchangeable and the easily available phase was the second most abundant fraction for Zn but was least dominant for other metals like Al, Fe, Pb, and Cr. The chemical fractionation of Zn and Cu was similar to other sediment speciation studies (Tsai et al., 2003, Pizarro et al, 2003) and was partially similar to Li et al. (2001).

Figure 5 – Speciation of Copper in Wetland Sediments (<63 µm)

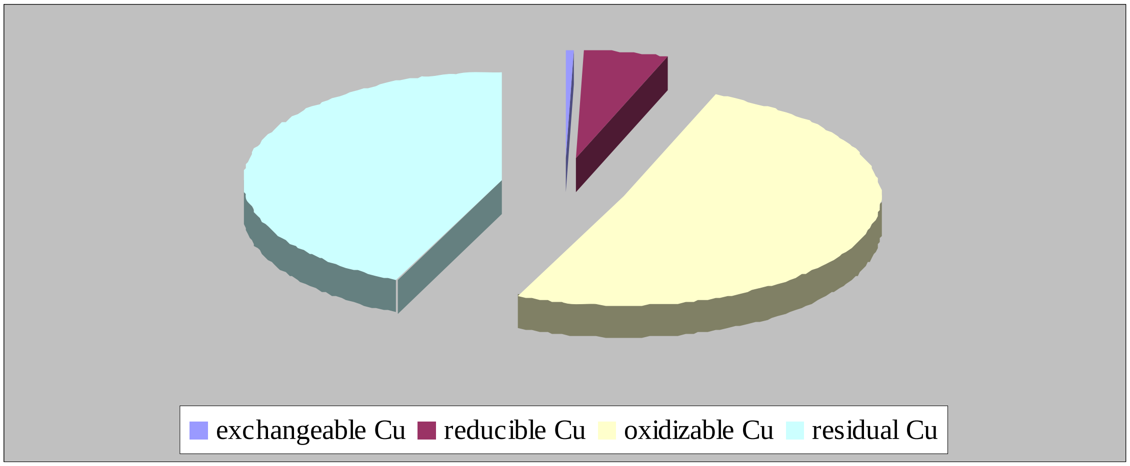
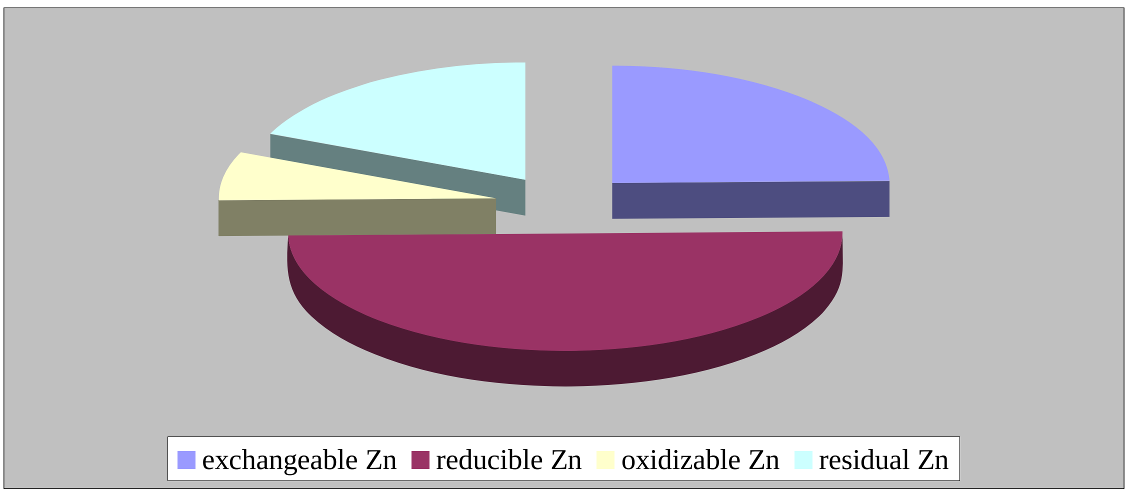


Figure 6 - Speciation of Zinc in Wetland Sediments (<63 µm)



The "pseudo"total concentration of Zinc in the finer particles <63 µm (median 570.8 mg/kg) appeared to exceed the consensus based probable effect concentration (PEC) of 459 mg/kg proposed for freshwater ecosystems (MacDonald et al., 2000). Additional speciation of Zn showed that the concentration of Zn in the most abundant (50%) reducible fraction was lower (367.6 mg/kg) than the proposed PEC, and thus may not be a potential toxicity threat to the biota in the wetland and downstream of the BMP. However, it remains to be seen if there is an elevation in Zn concentration from future runoff inputs and the resulting speciation has any ecological implications. Fifty percent of sediment Cu occurred as the oxidizable organic-bound species. The maximum concentration in this phase was 61.7 mg/kg, which was lower than the proposed PEC (149 mg/kg), and hence may not be potentially toxic.

CONCLUSIONS

The characterization of stormwater runoff is a critical requirement in order to evaluate the performance of BMPs such as ponds and wetlands in treating heavy metals and other pollutants in urban stormwater runoff. This study on runoff generated from roofs and a parking lot showed that antecedent conditions and storm characteristics influence TSS and heavy metal loads and their particulate associations in runoff. Heavy metal partitioning data showed that elements such as Fe and Al preferably exist in particulate phases >20 µm, while metals such as Cu and Zn exhibit highly varying associations with stormwater particulates. Preliminary results from the mesocosm experiments showed that structural BMPs such as retention ponds and cattail wetlands are effective in attenuating particulate-associated heavy metal loads, especially, Al, Cu, Pb, and Zn in urban stormwater runoff, and could potentially improve the water quality of receiving water bodies. Heavy metals removal in these BMPs is primarily governed by the settling of larger particles. The removal of dissolved metal species is quite low, possibly from the migration of soluble particles to hydraulically inactive regions in the pond or wetland. The different pollutant removal rates observed for the different events appeared to be significantly related to heavy metals partitioning in the solid phase. The role of vegetation in metals uptake was not clearly evident as metals removal did not vary significantly between the retention pond and the wetland. An initial speciation of accumulated wetland sediments showed that the exchangeable and easily-bioavailable fraction was not the dominant fraction for most of the metals studied. However, the high concentration of all these metals in the potentially mobile fraction (organic/sulfide-bound; amorphous Fe/Mn oxide-bound) should not be ignored. Heavy metals are less strongly-bound to these potentially mobile phases, and under changeable environmental conditions, may desorb from these fractions and become mobile and toxic to the biota. By conducting these experiments in a meso-scale under controlled conditions, the relative efficiencies of these BMPs can be better evaluated and the various factors influencing the removal of heavy metals can be better understood.

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