

Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy

Volume 11

Article 9

January 2010

Treatment Of Heavy Metals In Stormwater Runoff Using Wet Pond And Wetland Mesocosms

Swarna Muthukrishnan
U.S. EPA

Follow this and additional works at: <https://scholarworks.umass.edu/soilsproceedings>

Recommended Citation

Muthukrishnan, Swarna (2010) "Treatment Of Heavy Metals In Stormwater Runoff Using Wet Pond And Wetland Mesocosms," *Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy*: Vol. 11 , Article 9.
Available at: <https://scholarworks.umass.edu/soilsproceedings/vol11/iss1/9>

This Conference Proceeding is brought to you for free and open access by ScholarWorks@UMass Amherst. It has been accepted for inclusion in Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy by an authorized editor of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.

Chapter 8

TREATMENT OF HEAVY METALS IN STORMWATER RUNOFF USING WET POND AND WETLAND MESOCOSMS

Swarna Muthukrishnan

ORISE Postdoctoral Fellow, Urban Watershed Management Branch, Water Supply and Water Resources Division, National Risk Management Research Laboratory, Office of Research and Development, U.S. EPA, Edison, NJ 08837

Abstract: Urban stormwater runoff is being recognized as a major source of pollutants to receiving waters and a number of recent investigations have evaluated stormwater runoff quality and best management practices to minimize pollutant input to receiving waters. Particle-bound contaminants are widespread in the urban environment causing impairment to urban water bodies such as streams and lakes. Non-point sources significantly contribute to this impairment, which occur in a variety of urban media. Trace elements associated with stormwater runoff are one group of contaminants identified in urban aquatic sediments (Van Metre and Mahler, 2003). In the aquatic environment, heavy metals are distributed among water-soluble species, colloids, suspended matter and sedimentary phases; deposition-mobilization processes play an important role in influencing the concentration of metals in water and sediments (Filgueiras et al., 2004). The primary objectives of this research are to investigate the particulate association (20 to 0.4 μm) of heavy metals in stormwater runoff generated from parking lots and rooftops, to assess the removal of particulate-bound and soluble heavy metals by wet pond and cattail wetland mesocosms, and to examine any seasonal variability. The secondary objective is to study the solid-phase fractionation of these heavy metals in wetland sediments by selective sequential extraction procedures for a qualitative assessment of heavy metal bioavailability. Early studies investigated the relative removal of heavy metals in stormwater in different particulate size classes using structural best management practices. The following heavy metals were investigated: Aluminum (Al), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Lead (Pb), and Zinc (Zn). Preliminary results for the sampling events conducted in April and June 2005 are presented in this paper.

Key words: urban stormwater runoff, heavy metals, retention ponds, constructed wetlands, suspended particulates.

1. INTRODUCTION

Urban stormwater discharge during wet-weather flows is a major contributor to the pollution of many receiving waters (Lee et al., 2004; Nordeidet et al., 2004). Impervious surfaces have long been implicated in the decline of watershed integrity in urban and urbanizing areas (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. Heavy metals are of particular interest in stormwater runoff due to their toxicity, ubiquitousness, and to the fact that they do not degrade in the environment. The sources of heavy metals in urban stormwater runoff are numerous and the release of metals into the environment is governed by several complex mechanisms (Davis et al., 2001). Generally speaking, heavy metals are dominated by discharges from impervious areas such as highways, road surfaces, and roofs (Nelson and Booth, 2002; Van Metre and Mahler, 2003; Chang et al., 2004; Nordeidet et al., 2004). These 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 (Sansalone and Buchberger, 1997). This partition between the solid and aqueous phase has a major effect on the occurrence, transport, fate, and biological effects of heavy metals in aquatic systems (Ran et al., 2000). A significant portion of the heavy metals in stormwater is associated with suspended particulate materials that vary from coarse ($>75 \mu\text{m}$) and fine particulates (<75 to $1 \mu\text{m}$), to colloids ($<1 \mu\text{m}$) (Sansalone, 2003).

Research investigations on stormwater runoff increasingly focus on evaluating stormwater runoff quality and the effectiveness of adopting stormwater best management practices (BMPs) to minimize pollutant input to receiving waters. Most pollutants in urban runoff, including heavy metals, are in particulate form, or, are bound to particulates and tend to settle out of the water column and accumulate in sediments (Campbell, 1994). Sedimentation is believed to be the primary means by which vegetated control facilities and other BMPs improve runoff quality (Mazer et al., 2001). One widely adopted method is to treat a large volume of stormwater in a detention pond, as this allows the pollutants to separate out prior to its controlled release to a local water course. This helps to reduce the heavy metal load associated with particulate matter (Yousef et al., 1990; Hares and Ward, 1999; Pontier et al., 2001). Constructed ponds used as stormwater

treatment facilities aim at reducing the levels of suspended solids and heavy metals (Persson and Wittgren, 2003). The use of constructed wetlands to treat wastewater and other sources of water pollution is another valuable and appropriate technology to be used alone or in combination with other systems. The long-term efficiency and sustainability of these systems is critically dependent on an integrated understanding of their biological, chemical, and hydrological processes (Shutes, 2001). Heavy metals in stormwater can be removed by specially constructed wetlands and filtration systems; both natural and constructed wetlands have been used for the treatment of road runoff (Farm, 2002). Heavy metals such as Zn, Pb, and Cu showed a significant reduction in wetlands (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 (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 (Ellis et al., 1994; Mungur et al., 1995; Shutes et al., 1999; Shutes, 2001; Sriyaraj and Shutes, 2001).

Relatively little work has been done on the use of wetland BMPs for the treatment of heavy metals in stormwater runoff and the solid-speciation study of metals in wetland BMPs is lacking (Lim et al., 2001). Since metals are primarily removed due to suspended solids removal in stormwater BMPs, the geochemical partitioning of metals should be an important consideration for BMP selection (Lee et al., 2004). Information on the particulate association of heavy metals in stormwater is a fundamental requirement prior to using wetland and wet pond BMPs for treatability studies of heavy metals in stormwater runoff. Previous studies on the use of these structural BMPs for the treatment of heavy metals in stormwater have not focused on either the lower or upper practical size limit for the removal of particulate-bound heavy metals, and this investigation will address this growing research need. Sedimentation has been recognized as the principal process in the removal of heavy metals from stormwater in pond BMPs (Bavor et al., 2001), and in natural as well as constructed wetlands (Walker and Hurl, 2001). However, due to the presence of extensive vegetation, constructed wetlands may be more effective in removing both coarse and fine particulate-bound pollutants, possibly due to phytological uptake, sequestration processes, and vegetation-aided precipitation of coarse and

fine suspended solids (Bavor et al., 2001). Heavy metals accumulated in sediments have the potential to produce toxic effects in benthic invertebrates and aquatic microorganisms, both in wetlands (Wood and Shelley, 1999) as well as ponds (Karouna-Renier and Sparling, 2001). In order to evaluate the possible toxicity or risk of environmental pollution of heavy metals present in sediments, it is imperative to assess the types of association between heavy metals and the sediment solid phase. The geochemical forms of particulate heavy metals allow a qualitative assessment of metal lability/stability, metal bioavailability and toxicity, and ultimately the potential for environmental degradation of receiving water bodies; these properties are strongly related to the type of metal-particle binding as well as to the chemical nature of the binding particles (Garnaud et al., 1999). This is precisely the reason why chemical speciation of heavy metals in sediments by selective extraction procedures is important to evaluate their mobility and the potential for bioavailability (Gumgum and Ozturk, 2001; Jong and Parry, 2004). For the purposes of this investigation, sediments are defined as those mineral and organic materials situated beneath the aqueous layer of the cattail wetland mesocosm. The sequential chemical fractionation procedure recommended by the Standards, Measurements and Testing Programme (SM&T) (formerly known as the Bureau Commun de Reference, BCR) of the European Commission will be used in this project and will yield four "operationally" defined species: (i) Water soluble, exchangeable, and carbonate bound; (2) Fe-Mn oxide bound; (3) organic matter and sulfide bound; and, (4) residual (Davidson et al., 1994; Rauret et al., 1999).

1.1 Objectives

The proposed investigation has the following objectives:

- (1) Characterize the particulate association of select heavy metals (Cu, Zn, Pb, Cr, Fe, Al, and Mn) in stormwater runoff, between 20 and 0.4 μm , generated from parking lots and roof-runoff;
- (2) Evaluate the effects of two types of structural BMPs (cattail wetland and wet pond) on the removal of particulate-bound and soluble heavy metals from stormwater;
- (3) Examine if the distribution of heavy metals in stormwater particulates exhibits a seasonal variability, and determine the effects of BMP type, water column chemistry as well as season on the removal of dissolved and particulate heavy metals in BMP mesocosms.
- (4) Assess the chemical associations between heavy metals and wetland sediments by selective sequential chemical fractionation techniques

[BCR procedure, (Rauret et al., 1999)] and thereby predict heavy metal mobility and toxicity.

2. STUDY SITE AND EXPERIMENTAL DESIGN

The two environmental systems tested in this project are wet pond and cattail wetland BMP mesocosms for the treatment of particulate-associated heavy metals in stormwater. To perform this investigation, urban stormwater runoff generated from a parking lot and rooftop of a county college campus (9.75 acres) next to the U.S. EPA's Urban Watershed Research Facility (UWRf) in Edison, NJ, (Figure 1) were sampled and analyzed prior to, and after passing through two circular BMP mesocosms, designed and constructed at UWRf, Edison, NJ. The two mesocosms were of the same size and with two different BMP treatments: (i) constructed wetland, vegetated with cattails, and (ii) wet, retention pond.

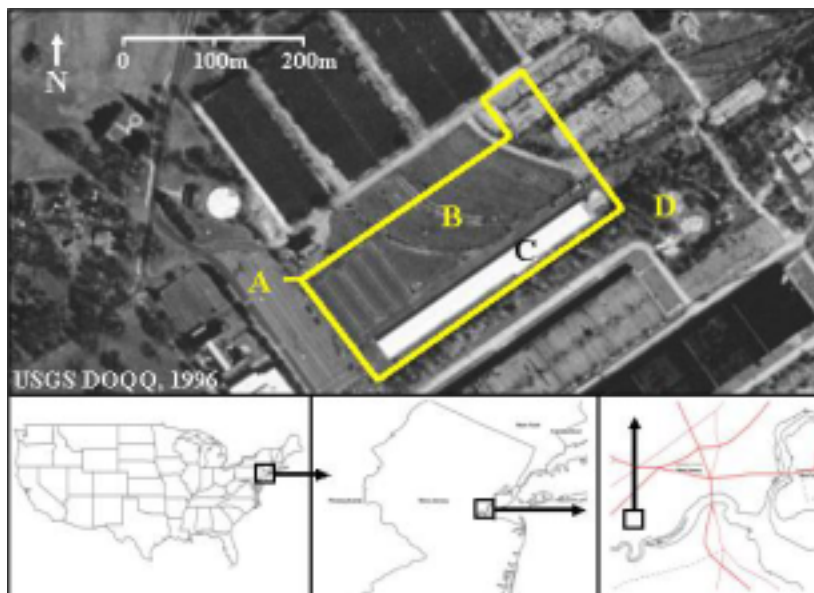


Figure 1. Map of study area, Edison, NJ. A – drainage area; B – location of the outfall

Stormwater runoff from the college campus was collected from an outfall near the UWRf and stored onsite. The stormwater was then routed to a smaller supply tank and then distributed to the two mesocosms by a “simulated” event, which is best described as follows: In a “simulated” event, adequate volume of gravity-fed stormwater was routed to each of the

two mesocosms. The detention time of a “simulated” event was 24 h conforming to general recommended detention time guidelines for stormwater BMPs. 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) out of which three stormwater sampling events (two events in spring and one event in summer 2005) have been completed to date. Wetland sediment was sampled prior to the stormwater sampling events and the results are awaited. Between storm event “simulations”, the mesocosms were operated under semi-continuous flow-through, regulated by a float valve connected to a tap water supply line (Nietch, 2002). Yellow Springs Instruments (YSI) data sondes were installed in the mesocosms and the control tank to monitor water quality parameters (pH, dissolved oxygen (DO), temperature, conductivity and oxidation-reduction potential (ORP) on a 12-min time step before, during, and after experimental events to assess the temporal variation and the dynamics of mesocosm-to-mesocosm water chemistry.

Stormwater from the outfall, storage tank, supply tank, and stormwater effluents from the retention pond, cattail wetland mesocosms, and one control tank were sampled using various techniques (flow-weighted, time-weighted, and grab) and analyzed during every storm sampling event. The addition of a control tank will help understand changes in stormwater chemistry in the mesocosms with time and also the relative differences in the heavy metals removal in the pond and wetland BMPs. In order to understand the particulate association of heavy metals, the samples were sequentially filtered through five different pore sizes - 20 μm , 10, 5, 1, and 0.4 μm using Millipore polycarbonate membrane filters. The unfiltered and the filtered samples were analyzed for major physico-chemical parameters: pH, ORP, total suspended solids (TSS), and total organic carbon, (TOC). The unfiltered samples were additionally analyzed for particle size distribution (PSD). Cations (Na, K, Ca, Mg) were analyzed in unfiltered samples and in samples filtered through 0.4 μm , while chloride and sulfate were determined in samples filtered through 0.4 μm . The seven heavy metals - Cu, Zn, Pb, Cr, Fe, Al, and Mn were analyzed in unfiltered and filtered stormwater samples and effluents from the two mesocosms and the control tank. Results from these analyses will help in evaluating the relative changes in particulate heavy metal distribution that occur in stormwater stored and routed through the wet pond and cattail mesocosms. Cleaning of samplers, sample containers, sampling, subsampling, and filtration of stormwater samples were done in accordance with U.S. EPA recommended procedures and UWRf standard operating procedures (SOP) developed for stormwater analysis. All the selected analytes in stormwater were

determined using Standard Methods (APHA, 1998) and U.S. EPA-approved/recommended techniques (U.S. EPA, 1983; 1985).

3. PRELIMINARY RESULTS AND DISCUSSION

3.1 Characterization of parking lot and roof runoff

The preliminary characterization of stormwater runoff from two sampling events conducted in spring 2005 showed that the pH of unfiltered stormwater was neutral (7.41) in the outfall (Table 1). With regard to the mesocosms, pH was a little higher (7.58) in retention pond effluent when compared to wetland (7.22). However, the redox potentials of the two systems were quite similar as seen from the unfiltered effluents (635.5 and 616.2 mV, respectively) and did not vary considerably from the outfall (672.1 mV). Organic carbon in runoff was mostly dissolved (TOC 18.67 and DOC 18.1 mg/l).

Table 1. Physicochemical characteristics of urban stormwater runoff

Sample	pH	Temp °C	ORP (mV)	TOC (mg/l)	DOC (mg/l)	SO42- (mg/l)	Cl- (mg/l)	Na (mg/l)	K (mg/l)	Mg (mg/l)	Ca (mg/l)
Outfall	7.41	22.6	672.1	25.4	22.1	30.5	335.3	152.7	3.47	7.26	48.1
Storage	7.19	20.1	646.7	18.4	17.5	22.6	232.6	103.8	2.42	5.29	34.9
Supply	7.47	20.5	600.7	18.4	16.9	22.8	229.3	105.8	2.47	5.33	35.3
Ret. (wet) pond	7.58	19.8	635.5	9.95	9.65	18.2	89.2	52.4	2.28	6.15	26.6
Wetland	7.22	20.6	616.2	12.6	12.3	21.7	141.4	81.1	3.38	7.76	34.9
Control	7.39	21.3	583.8	15.7	15.3	22.2	226.2	108.3	2.44	5.41	36.2

Results presented for pH, Temp., ORP, TOC, DOC, and anions are mean values for $n = 3$
 Results presented for cations are mean values for $n = 6$ (unfiltered $n = 3$; filtered $n = 3$)

3.2 Heavy metals partitioning in urban stormwater runoff

Heavy metals concentration in parking lot and roof runoff increased between the two events conducted in April and June, 2005, with a concomitant increase in TSS (Table 2), and this was more pronounced for Al (8-fold increase), Fe (7-fold increase) and Zn (6-fold increase) respectively (Figure 2). Most of the metals studied (Cu, Zn, Fe, Mn, and Al) were routinely detected in the runoff; Pb and Cr were detected sporadically, and especially in the second event. It was also seen from these events that both Al and Fe are particulate-bound and Mn remained dissolved ($< 0.4 \mu\text{m}$) in stormwater. Also, Cu and Zn were mostly soluble during the first event (71.9 % and 66.4 % soluble, respectively). However, during the second event, Cu and Zn were bound to particulates (83.7% and 82.6 % respectively) predominantly (Figure 3) compared to their soluble species. This was consistent with the observation of a 6-fold increase in TSS in the runoff during the second sampling event, i.e. it increased from 24.2 mg/l to 152.0 mg/l. The increase in TSS during June could be attributed to the rain event itself in that it was characterized by thunderstorms and heavy precipitation following a prolonged dry spell that resulted in a higher washing off of heavy metals and suspended solids in runoff. There was a wide variation in Zinc and TSS concentrations between outfall and the supply tank from where it was routed to the mesocosms. The relationships between the quantitative values for the various metals were investigated. Manganese exhibited reasonable associations with Cu ($r^2 = 0.665$, $P < 0.05$) and Zn ($r^2 = 0.792$, $P = 0.0175$) during the first event; Cu and Fe were strongly correlated ($r^2 = 0.955$, $P < 0.001$) during the second event (Figures 4, 5, 6). However, no significant relation was observed between TSS and heavy metals during the two events. Additional sampling and monitoring events will provide a better insight into these heavy metal associations in stormwater runoff.

Table 2. TSS and heavy metals concentrations in parking lot and roof runoff

Heavy Metal	Conc. (mg/l) - April'05	Conc. (mg/l) - June'05
Al _{tot}	0.405 (0.597)	3.06
Cr	NA	0.0115 (0.522)
Cu _{tot}	0.0157 (0.205)	0.041 (0.361)
Cu _{0.4}	0.0110 (0.241)	0.0063 (0.158)
Fe _{tot}	1.19 (0.375)	7.92 (0.366)
Fe _{0.4}	0.243 (0.021)	0.774 (0.022)
Mn _{tot}	0.311 (0.315)	0.739 (0.036)
Mn _{0.4}	0.317 (0.145)	0.533 (0.163)

Heavy Metal	Conc. (mg/l) - April'05	Conc. (mg/l) - June'05
Pb _{tot}	0.008*	0.0307 (0.391)
Zn _{tot}	0.043 (0.507)	0.258 (0.084)
Zn _{0.4}	0.030 (0.696)	0.044 (0.279)
TSS	24.2 (0.92)	152.0 (0.398)

Results presented are mean values for $n = 9$ (outfall, storage, and supply tanks);
 R.S.D values are given in parenthesis

tot – unfiltered sample

0.4 – sample filtered through 0.4 μm membrane filter

* possible analytical error

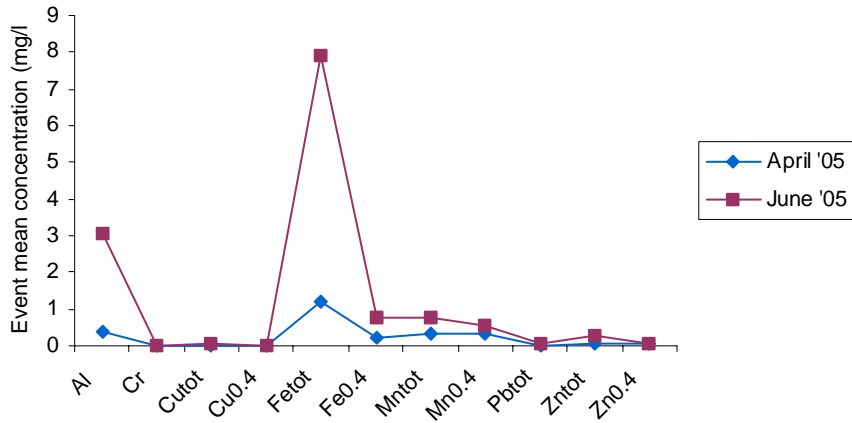


Figure 2. Heavy metal concentrations in stormwater runoff from roof and parking lot

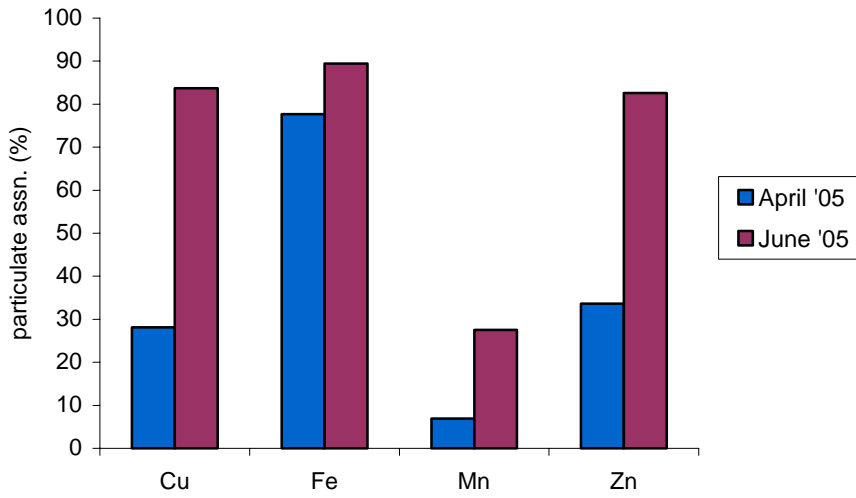


Figure 3. Particulate associations of heavy metals in urban stormwater runoff

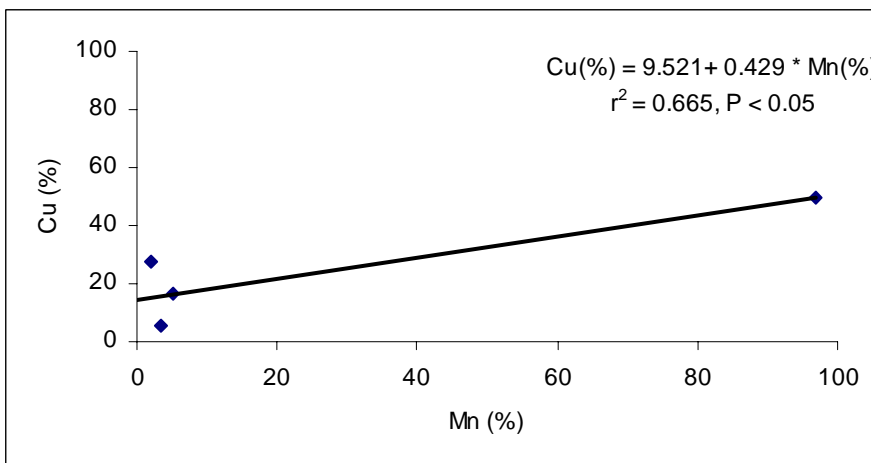


Figure 4. Cu vs. Mn in urban stormwater runoff

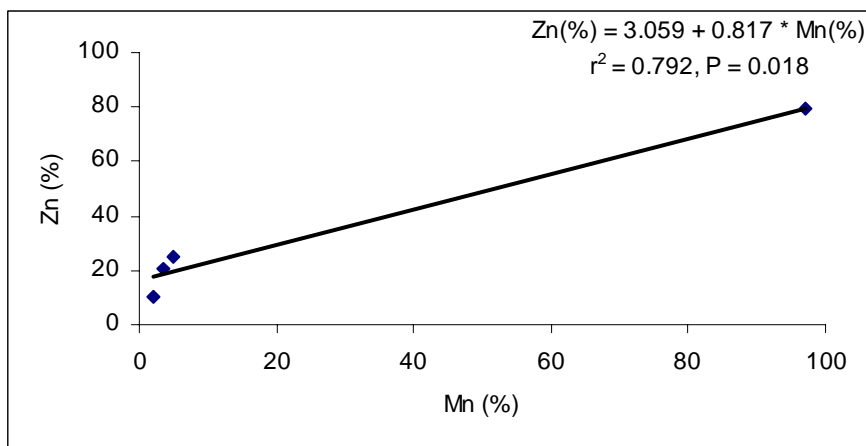


Figure 5. Zn vs. Mn in urban stormwater runoff

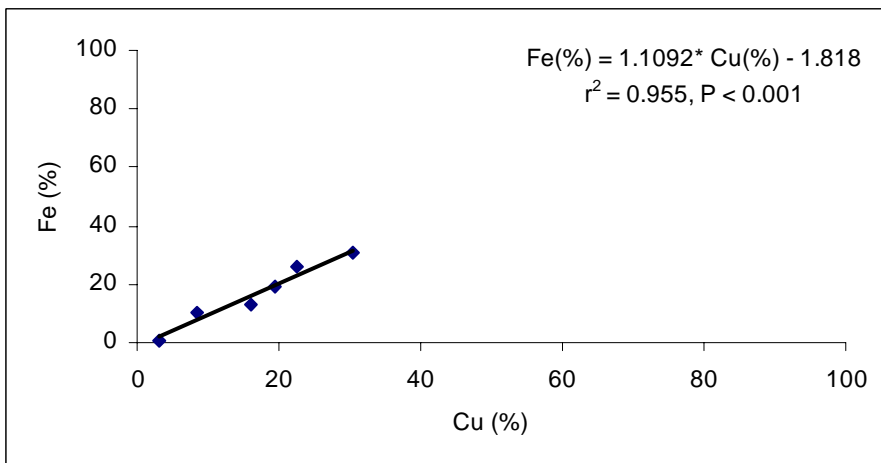


Figure 6. Fe vs. Cu in urban stormwater runoff

3.3 Changes in retention (wet) pond and wetland mesocosm chemistry during storm events

The various physico-chemical parameters measured *in situ* in the mesocosms and the control tank during the two spring sampling events are shown in Table 3. Changes in mesocosm chemistry observed using the YSI sondes in the two mesocosms (approx. 72 h) and in the control tank (approx. 48 h) are shown for the April sampling event in Figure 7. The temperature

increased between two sampling events and the wetland temperature was lower than the retention pond during both events. Wetland pH did not vary much between the events compared to the retention pond where the pH decreased by more than 1 unit in the second event. The lower values for these various parameters in the wetland could be attributed to several factors, the most important of these being the dead biomass resulting in a shallow water depth, and growing vegetation. The diurnal variations of these parameters in the two BMPs are shown for one sampling event (April '05) in Figures 8, 9, and 10. It is expected that results from the remaining sampling and monitoring events of these systems would lead to a better understanding of the chemistry in these BMPs during a storm event.

Table 3. YSI monitoring data in retention pond and wetland mesocosms

	April'05			June'05		
	Ret.pond	wetland	control	Ret.pond	wetland	control
Temp °C	14.7	12.4	14.4	26.4	23.3	25.7
pH	8.61	6.83	7.31	7.37	6.73	7.01
DO (mg/l)	0.12	5.39	8.16	3.78	4.28	3.93
Cond. (mS/cm)	0.281	0.431	0.613	0.511	0.662	0.970
ORP (mV)	329.2	531.6	243.3	341.2	153.5	367.8

Results presented are mean values of 72 h monitoring data.

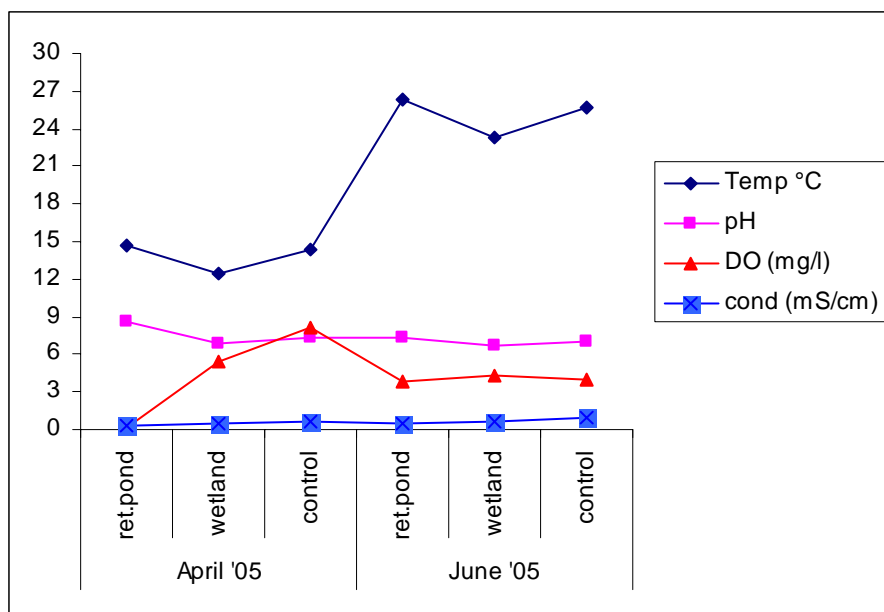


Figure 7. YSI monitoring in retention pond and wetland mesocosms

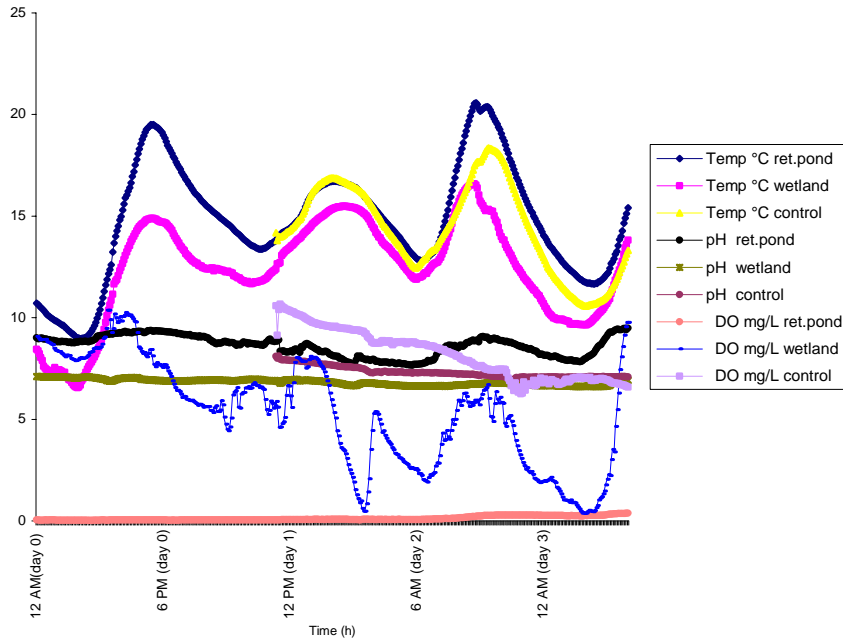


Figure 8. Variation in Temperature, pH, and DO in retention pond and wetland mesocosms

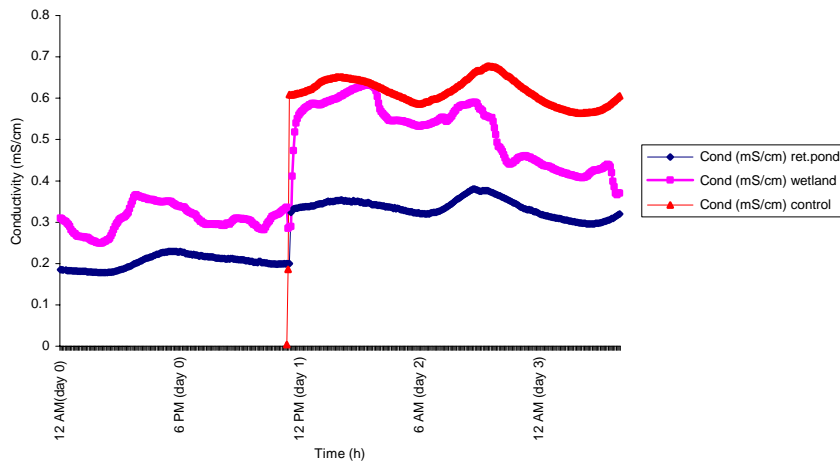


Figure 9. Variation in conductivity in retention pond and wetland mesocosms

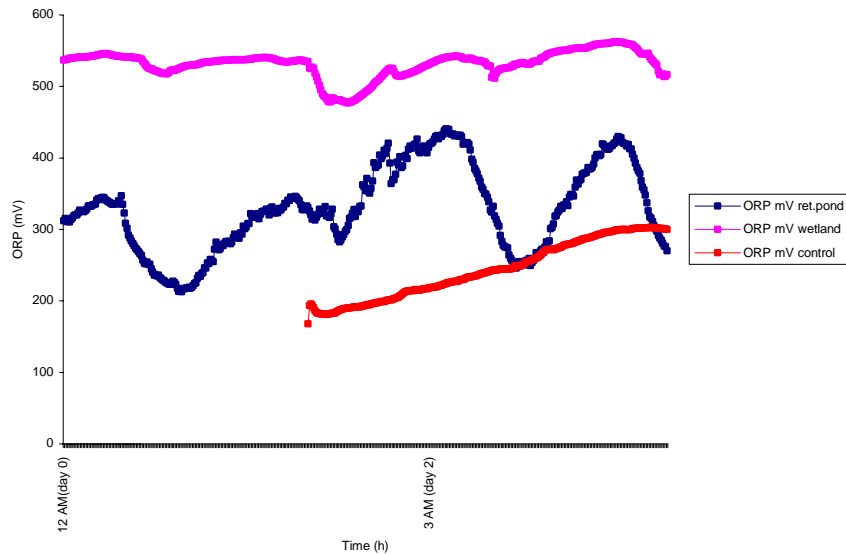


Figure 10. Variation in ORP in retention pond and wetland mesocosms

3.4 Heavy metals removal from stormwater runoff in retention (wet) pond and wetland BMP mesocosms

Preliminary results showed that Fe and Al were primarily particulate bound ($> 20 \mu\text{m}$); Mn was mostly in the soluble fraction ($< 0.4 \mu\text{m}$); and Cu and Zn were primarily associated with fine particulates ($1 - 10 \mu\text{m}$) as well as in the dissolved fraction ($< 0.4 \mu\text{m}$) in stormwater runoff. TSS increased during the June event and a size-partitioning study showed that there was a significant increase in fine particles $< 20 \mu\text{m}$ in runoff compared to the first event (Figure 11). The association of heavy metals with fine particulates ($10 - 5 \mu\text{m}$) increased in the second event (Figure 12). This clearly showed that the nature of the storm event, and the antecedent conditions, both of which are highly variable, largely influence the solids and heavy metals concentrations and the particulate associations of the latter in urban stormwater runoff. However, no discerning relationship between heavy metals and TSS loads could be determined from studying only two events that were highly variable.

The concentrations of heavy metals in the influent runoff and the composite effluents from the retention pond and wetland are shown in Figure 13. The effects of the two BMP mesocosms on heavy metals removal from urban stormwater runoff are shown in Table 4. Paired t-tests showed

that there was no significant in Cu loads in stormwater runoff between the two events. The attenuation of Cu concentrations was significant in both retention pond ($P = 0.013$) and 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 ICP 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. Al concentration 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 a 100% 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. As for Zn and Mn, no significant variation in runoff concentrations was seen between the two events was observed. While individual BMPs were seen to be effective in removing heavy metals from runoff, the two events were insufficient to suggest the effect of different BMP treatment; there were no significant statistical observations to verify if the two treatments differed significantly from each other in removing heavy metals from stormwater runoff. It is hoped that a much clearer insight on these could be gained with additional sampling events, which are underway.

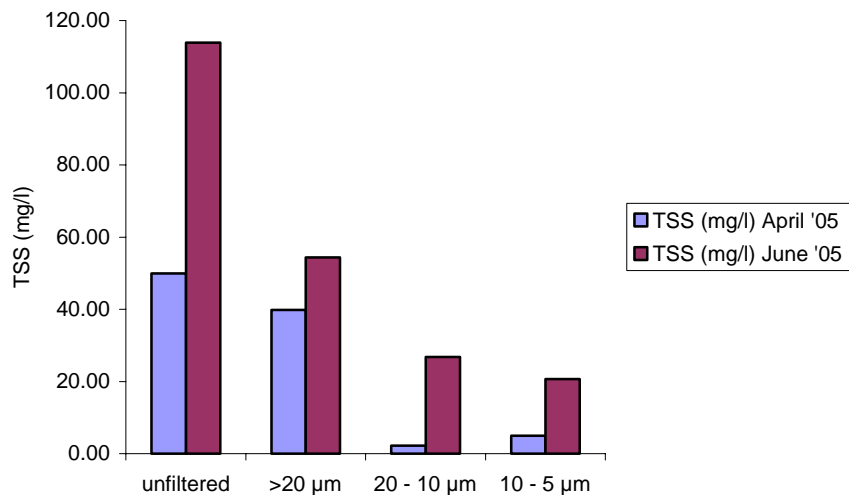


Figure 11. Variation in TSS in stormwater runoff

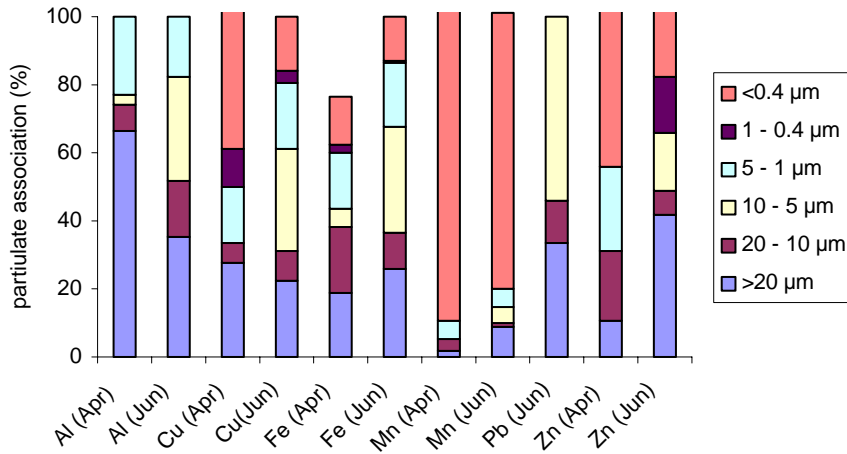


Figure 12. Size partitioning of heavy metals in urban stormwater runoff

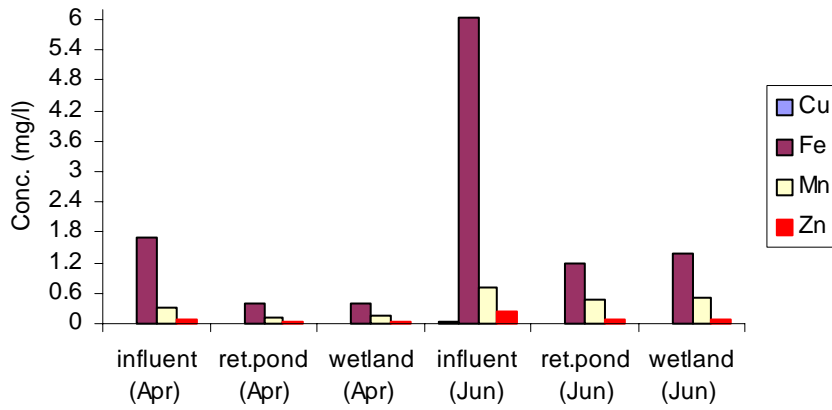


Figure 13. Concentrations of heavy metals in the influent (runoff) and mesocosm effluents

Table 4. Removal of heavy metals in stormwater runoff in retention pond and wetland mesocosms

	Influent (mg/l)	Retention Pond			Cattail wetland		
		Effluent conc. (mg/l)	Redn in conc. (mg/l) in	Redn. (%)	Effluent conc. (mg/l)	Redn in conc. (mg/l) in	Redn. (%)
April'05							
Al	0.684	0.113	0.571	83.5	NA	0.684	100.0
Cu	0.018	0.007	0.011	61.1	0.006	0.012	66.7
Fe	1.693	0.386	1.31	77.2	0.378	1.32	77.7
Mn	0.298	0.107	0.191	64.1	0.148	0.15	50.3
Zn	0.068	0.050	0.018	26.5	0.054	0.014	20.6
June'05							
Al	2.18	0.254	1.93	88.3	NA	2.18	100.0
Cu	0.031	0.006	0.025	80.6	0.005	0.026	83.9
Fe	6.06	1.38	4.68	77.2	1.08	4.98	82.2
Mn	0.726	0.469	0.257	35.4	0.526	0.200	27.5
Pb	0.024	NA	0.024	100.0	NA	0.024	100.0
Zn	0.233	0.073	0.16	68.7	0.069	0.164	70.4

Results presented are mean values for $n = 3$.

4. CONCLUSION

Structural BMPs such as retention ponds and cattail wetlands are effective in attenuating heavy metal loads in urban stormwater runoff and result in improving the quality of receiving waters. The overall efficiency and effectiveness of these systems largely depend on the proper design, monitoring practices, and maintenance of these systems. By conducting this heavy metals research under controlled meso-scales, these treatment methods can be better evaluated, and the various factors causing variability in these systems can be better understood. Heavy metal concentrations in stormwater and their associations with fine particulates (20 – 0.4 μm) are largely influenced by the nature of the storm event and antecedent conditions. Preliminary results from the mesocosm investigation conducted at UWRP, Edison, NJ clearly showed that Fe and Al are particulate-bound ($> 20 \mu\text{m}$), Mn remains soluble ($< 0.4 \mu\text{m}$), and Cu and Zn tend to associate with fine particulates (10 – 1 μm) and also remain dissolved in urban stormwater runoff. The spring sampling events showed that wetland and cattail BMP mesocosms are effective in attenuating Cu, Zn, Al and Fe in runoff. A greater understanding of the seasonal variability in heavy metals concentration in urban stormwater runoff is expected from the remaining

sampling events. From the entire investigation, notable differences are expected between the two BMP treatment types in the removal of heavy metals from urban stormwater runoff generated from roof and parking lot.

DISCLAIMER

Any opinions expressed in this paper are those of the author and do not, necessarily, reflect the official positions and policies of the U.S. EPA. Any mention of products or trade names does not constitute endorsement for use by the U.S. EPA.

ACKNOWLEDGEMENT

This research at the Urban Watershed Management Branch (UWMB) U.S. EPA, Edison, NJ, is supported by Oak Ridge Institute for Science Education (ORISE), and Office of Research and Development, U.S. EPA. I would like to thank UWMB for supporting this research and also wish to express my thanks to US Infrastructure Inc., the on-site contractor for sample collection and analyses under U.S. EPA contract EP-C-04-064. I also express my thanks to my coworkers at UWMB who reviewed this manuscript.

REFERENCES

- APHA (American Public Health Association), 1998, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC.
- Bannerman, R., Owens, D., Dodds, R., and Hornewer, N., 1993, Source of pollutants in Wisconsin stormwater, *Water Sci Technol.* 28(3-5): 241-259.
- Bavor, H. J., Davies, C. M., and Sakadevan, K., 2001, Stormwater treatment: do constructed wetlands yield improved pollutant management performance over a detention pond system? *Water Sci Technol.* 44(11-12): 565-570.
- Brattebo, B. O., and Booth, D. B., 2003, Long-term stormwater quantity and quality performance of permeable pavement systems, *Water Res.* 37(18): 4369-4376.
- Campbell, K. R., 1994, Concentrations of heavy metals associated with urban runoff in fish living in stormwater treatment ponds, *Arch. Environ. Contam. Toxicol.* 27: 352-356.
- Chang, M., McBroom, M. W., and Beasley, R. S., 2004, Roofing as a source of nonpoint water pollution, *J. Environ. Mgt.* 73(4): 307-315.
- Davidson, C. M., Thomas, R. P., McVey, S. E., Perala, R., Littlejohn, D., Ure, A. M., 1994, Evaluation of a sequential extraction procedure for the speciation of heavy metals in sediments, *Anal. Chim. Acta.* 291: 277-286.

- Davis, A. P., Shokouhian, M., and Ni, S., 2001, Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources, *Chemosphere*. 44(5): 997-1009.
- Ellis, J. B., Revitt, D. M., Shutes, R. B. E., and Langley, J. M., 1994, The performance of vegetated biofilters for highway runoff control, *Sci. Total Environ*. 146-147: 543-550.
- Farm, C., 2002, Evaluation of the accumulation of sediment and heavy metals in a storm-water detention pond. *Water Sci Technol*. 45: 105-112.
- Filgueiras, A. V., Lavilla, I., and Bendicho, C., 2004, Evaluation of distribution, mobility and binding behavior of heavy metals in surficial sediments of Louro River (Galicia, Spain) using chemometric analysis: a case study, *Sci. Tot. Environ*. 330(1-3): 115-129.
- Garnaud, S., Mouchel, J.-M., and Thevenot, D. R., 1999, Mobility evolution of particulate trace metals in urban runoff: From street deposits and road runoff to combined sewer deposits and catchment outlet, 8th ICUSD Proceedings, in: 8th International Conference on Urban Storm Drainage, Sydney, Australia, pp. 1511-1519.
- Gumgum, B., and Ozturk, G., 2001, Chemical speciation of heavy metals in the Tigris river sediment, *Chem. Speciat. Bioavail*. 13(1): 25-29.
- Hares, R. J., and Ward, N. I., 1999, Comparison of the heavy metal content of motorway stormwater following discharge into wet biofiltration and dry detention ponds along the London Orbital (M25) motorway, *Sci. Total Environ*. 235(1-3): 169-178.
- Jong, T., and Parry, D. L., 2004, Heavy metal speciation in solid-phase materials from a bacterial sulfate reducing bioreactor using sequential extraction procedure combined with acid volatile sulfide analysis, *J. Environ. Monit*. 6: 278-285.
- Karouna-Renier, N. K., and Sparling, D. W., 2001, Relationships between ambient geochemistry, watershed land-use and trace metal concentrations in aquatic invertebrates living in stormwater treatment ponds, *Environ. Pollut*. 112(2): 183-192.
- Lee, H., Lau, S.-L., Kayhanian, M., and Stenstrom, M. K., 2004, Seasonal first flush phenomenon of urban stormwater discharges, *Wat. Res*. 38(19): 4153-4163.
- Lim, P. E., Wong, T. F., and Lim, D. V., 2001, Oxygen demand, nitrogen and copper removal by free-water-surface and subsurface-flow constructed wetlands under tropical conditions, *Environ. Int*. 26(5-6): 425-431.
- Mazer, G., Booth, D., and Ewing, K., 2001, Limitations to vegetation establishment and growth in biofiltration swales, *Ecol. Eng*. 17(4): 429-443.
- Mungur, A. S., Shutes, R. B. E., Revitt, D. M., and House, M. A., 1995, An assessment of metal removal from highway runoff by a natural wetland, *Wat. Sci. Technol*. 32(3): 169-175.
- Nelson, E. J., and Booth, D. B., 2002, Sediment sources in an urbanizing, mixed land-use watershed, *J. Hydrol*. 264(1-4): 51-68.
- Nietch, C. T., 2002, Mechanistic evaluation of two popular stormwater BMPs: wet ponds and constructed wetlands, QAPP presented to Urban Watershed Management Branch, Water Supply and Water Resources Division, United States Environmental Protection Agency, Edison, NJ.
- Nordeidet, B., Nordeide, T., Astebol, S. O., and Hvitved-Jacobsen, T., 2004, Prioritising and planning of urban stormwater treatment in the Alna watercourse in Oslo, *Sci. Total Environ*. 334-335: 231-238.
- Persson, J., and Wittgren, H. B., 2003, How hydrological and hydraulic conditions affect performance of ponds, *Ecol.Eng*. 21(4-5): 259-269.
- Pontier, H., Williams, J. B., and May, E., 2001, Metals in combined conventional and vegetated road runoff control systems, *Wat. Sci. Technol*. 44(11-12): 607-614.

- Ran, Y., Fu, J. M., Sheng, G. Y., Beckett, R., and Hart, B. T., 2000, Fractionation and composition of colloidal and suspended particulate materials in rivers, *Chemosphere*. 41(1-2): 33-43.
- Rauret, G., Lopez-Sanchez, J. F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A. M., and Quevauviller, P., 1999, Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials, *J. Environ. Monit.* 1: 57-61.
- Sansalone, J. J., and Buchberger, S. G., 1997, Characterization of solid and metal element distributions in urban highway stormwater, *Wat. Sci. Technol.* 36(8-9): 155-160.
- Sansalone, J. J., 2003, The physical and chemical nature of urban stormwater runoff pollutants. in: *Wet-Weather Flow in the Urban Watershed: Technology and Management*, Field, R. and D. Sullivan, ed. Lewis Publishers, Boca Raton, FL, pp. 43-65.
- Shutes, R. B. E., Revitt, D. M., Lagerberg, I. M., and Barraud, V. C. E., 1999, The design of vegetative constructed wetlands for the treatment of highway runoff, *Sci. Total Environ.* 235(1-3): 189-197.
- Shutes, R. B. E., 2001, Artificial wetlands and water quality improvement, *Environ. Int.* 26(5-6): 441-447.
- Sriyaraj, K., and Shutes, R. B. E., 2001, An assessment of the impact of motorway runoff on a pond, wetland and stream, *Environ. Int.* 26(5-6): 433-439.
- U. S. EPA, 1983, *Methods for the Chemical Analysis of Water and Wastes*, EPA-600-4-79-020, United States Environmental Protection Agency, Washington, DC.
- U. S. EPA, 1995, *SW-846 Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods*, United States Environmental Protection Agency, Washington, DC.
- Van Metre, P. C. and Mahler, B. J., 2003, The contribution of particles washed from rooftops to contaminant loading to urban streams, *Chemosphere*. 52(10): 1727-1741.
- Walker, D. J., and Hurl, S., 2002, The reduction of heavy metals in a stormwater wetland, *Ecol. Eng.* 18: 407-414.
- Wood, T. S., and Shelley, M. L., 1999, A dynamic model of bioavailability of metals in constructed wetland sediments, *Ecol. Eng.* 12(231-252):
- Yousef, Y. A., Hvitved-Jacobsen, T., Harper, H. H., and Lin, L. Y., 1990, Heavy metal accumulation and transport through detention ponds receiving highway runoff, *Sci. Total Environ.* 93: 433-440