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Analysis on the fractionation of heavy metals in a tree box filter treating urban runoff

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ABSTRACT

Nineteen storm events were monitored between July 2010 and September 2013 to determine the relative fractions of dissolved and particulate-bound heavy metal mass in runoff entering and exiting a tree box filter that was developed and constructed for the treatment of suspended solids and heavy metal constituents (Fe, Zn, Pb, Cr, Cu, Cd, Ni) in a parking lot runoff. Findings revealed that the system was capable of reducing the particulate-bound fraction of Ni, Cu, Zn and Cd; and the dissolved fraction of all the heavy metals. Majority of storm events favored the reduction of the predominately particulate-bound heavy metals such as Fe, Zn and Pb. TSS concentration was found to influence the generation and more likely the reduction of heavy metals in the tree box filter. The metal elements in the outflow were evidently dissolved with higher TSS concentration and particulate-bound with lower TSS concentration in the inflow. The fractionation of metals was found to be independent of the treated runoff rather by the incoming runoff particularly the concentration of particulate matters in it. The adsorption capacity of metals was ranked from greatest to least as follows: Fe > Zn ≈ Cd > Pb > Cu > Cr > Ni.

Keywords: Dissolved; Heavy metals; Particulate-bound; Urban runoff; Stormwater management; Tree box filter

1. Introduction

Urban stormwater runoff is recognized as a major source of heavy metals that pose a risk to the health of riverine and estuarine ecosystems in the catchment and should be targeted for remediation [1,2]. The heavy metal concentrations and loads in stormwater runoff depend on topography, vegetal covering, streets and highways sweeping, specific materials and components employed within the drainage area, as well as hydrometeorological effects such as rainfall intensity and extent [3]. The major sources of heavy metals arise from exhaust emissions, wear of vehicles tires and brakes, and degradation of asphalt road surfaces, use of de-icing compounds, atmospheric deposition, roof runoff, industrial activities, and resuspension of particulates from roads and exposed soils [1,4,5]. The fate of heavy metals transported by stormwater is controlled by salinity changes, physical mixing and dilution, flushing of the estuary, and chemical processes such as sorption, complexation, cation exchange and redox reactions [6].

The behavior of many metals in runoff depends on the metal-binding properties as well as the characteristics of both particulate and dissolved materials [7]. The degree of binding is a function of pH, average pavement residence time and the nature and quantity of solids present [5]. Particulate-bound heavy metals are typically associated with suspended particulates of stormwater and dependent upon flow capable of mobilizing particles from

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the road surface and drainage system. Dissolved heavy metals occur as free metal ions and have the potential for acute and long-term toxicity for aquatic life and a greater potential of affecting groundwater [8]. Particulate-bound heavy metals are likely to be deposited where stormwater channels discharge, whereas dissolved heavy metals may be trapped in interstitial water during sedimentation or remain in suspension and available for transport [9]. Thus, higher concentration of dissolved heavy metals may be present at the discharge point of stormwater channels (e.g., stormwater treatment systems, etc.). The fractionation of heavy metals between dissolved and particulate phases influenced by flow regime, pH, redox conditions, temperature, concentrations of particulates, etc. [4] has a major effect on the occurrence, transport, fate and biological effects of heavy metals in aquatic systems [10].

Although there are significant metal-dependent and study-dependent variability, a large fraction of the heavy metal load in roadway runoff are often associated with the suspended solids, that is, adsorbed to particles [11,12]. Given that a strong affinity between heavy metals and suspended solids exist [13], stormwater management practices are adopted to improve the runoff quality commonly targeting the removal of particulates from runoff by means of sedimentation [2,14–18]. Hence, toxicity and contaminant reductions by stormwater management practices are limited by the degree to which pollutants/toxicity associate with particles, and the efficiency to remove particles [2,19]. Knowledge of the partitioning kinetics and relative fractions of dissolved and particulate-bound mass delivered for treatment is of fundamental importance for on-site treatments where residence times on the urban surface or in the urban drainage system in the presence of entrained particulate matter are less than several hours [20]. This research was conducted to analyze the fractionation of heavy metals in the inflow and outflow of a tree box filter and determine its implications in the reduction of heavy metals from stormwater runoff in an impervious parking lot.

2. Materials and methods

2.1. Site location and design description of the tree-box filter

A tree box filter was developed to capture stormwater runoff from a 312 m^2 impervious parking lot located at Kongju National University campus grounds in Cheonan City, northeast of South Chungcheong Province, Korea (36°51′1.11″N, 127°9′0.23″E). On average, the site received approximately 1,350 mm of rainfall annually wherein 42% of that amount was captured as runoff by the tree box filter. The mean annual total suspended solids (TSS) on the site were between 29,400 and 38,700 kg/year. Heavy metal loadings of chromium (Cr), nickel (Ni), copper (Cu), cadmium (Cd) and lead (Pb) were typically less than 600 kg/year except for lead (Pb) (700–1,400 kg/year) and iron (Fe) (830–1,100 kg/year) indicative of sources from parking lot runoff.

Fig. 1 shows the location and schematic of the detailed components of the tree box filter. The underground system situated at the middle edge and lower end of the asphalt-paved parking was made of a pre-casted concrete 1.5 m long, 1 m wide at the top and 1.3 m deep. The tree box filter consists of (1) a sedimentation chamber that provides pretreatment of runoff; (2) filter media zone comprising of layers of woodchip, sand, and gravel for filtration/adsorption of pollutants that also provides temporary storage of runoff; (3) perforated drain pipes that infiltrates runoff to the surrounding soil for groundwater recharge, and (4) an outflow pipe to discharge the treated runoff in the sewer or for potential reuse. The surface area of the tree box filter is only 0.7% of the total catchment area that it drains. Together with the aggregates, that is, wood chip (10–20 mm), sand (2–5 mm) and gravel (20–30 mm) in the filter media bed which provide approximately 30% void space; the total effective storage capacity is 1.76 m^3, equivalent to 60% of the total volume of the tree box filter. Periodic inspection and maintenance were conducted typically after the summer season and mid-winter season that include sweeping of litters and large debris, replacement of geotextile fabric, removal of accumulated sediments at the

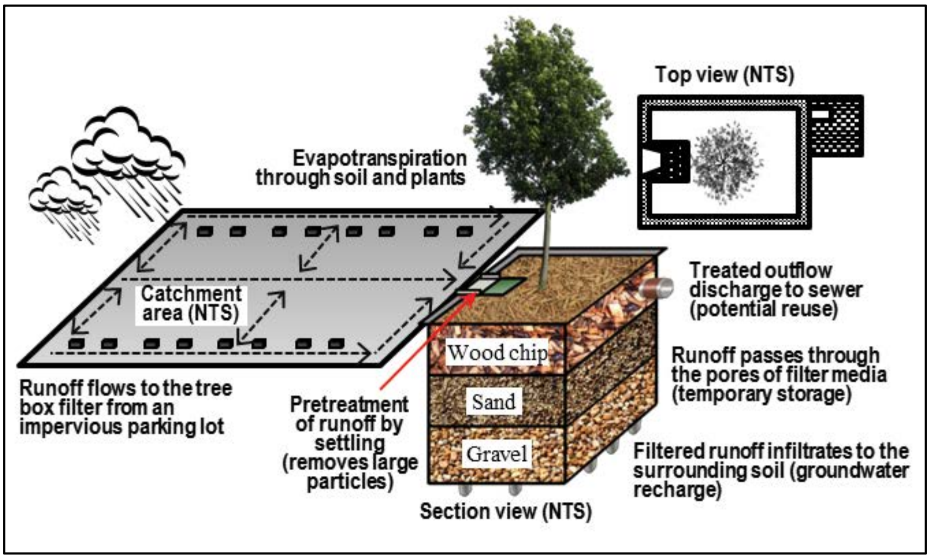

Fig. 1. Schematic diagram of the tree box filter.

pretreatment tank and cleaning of the facility area since the initial operation of the tree box filter in July 2010.

2.2. Data collection and analyses

Runoff samples were collected at the inflow and outflow units of the tree box filter during a total of 19 storm events monitored from July 2010 to September 2013. Ideally, six samples were collected by manual grab sampling at the initial hour, and more samples hourly thereafter until the cessation of runoff [18,21–23]. In low intensity and shorter storm events, the scheme was modified by adjusting the number of samples making it certain that the 'first flush' runoff was entirely collected [24]. Selected hydrologic and hydraulic data including event rainfall depth, rainfall and runoff duration, rainfall intensity, runoff volume, flow rate, etc. were obtained from the site during each storm event. TSS was analyzed by filtration of sample in a standard 1.2 μm glass fiber filters (Whatman GF/C) with the residue retained dried in an oven (SJ-201DL, Sejong Scientific Co., Korea) between 103°C and 105°C or until the weight is constant. Runoff samples for heavy metal analysis were solubilized with nitric and hydrochloric acids (total heavy metal constituents) or filtered in a 0.45 μm pore membrane filter (dissolved heavy metal constituents), prior to multi-element determination method by inductively coupled plasma-mass spectroscopy (ICPS-7510, Shimadzu Co., Japan). All analytical analyses performed were based on the standard methods for the examination of water and wastewater [25]. TSS and heavy metal (total and dissolved) concentrations of Cu, Pb, Fe, Ni, Zn, Cr and Cd were measured analytically at the laboratory following the standard methods for the examination of water and wastewater [25].

The inflow and outflow TSS and heavy metal loads were calculated by the summation of loadings during each storm event using the volume for that period (Eq. (1)).

$$M = \int_0^T C(t) \times Q(t)\, dt \approx \sum_0^{t=T} C(t) \times Q(\Delta t) \tag{1}$$

$$M_T = M_P + M_D \tag{2}$$

where M (mg) is the mass of a pollutant transported; $Q(t)$ (m^3) is the volume of runoff at time t; $C(t)$ (mg/L) is the concentration at time t. The limits of integration $t = 0$ and $t = T$ refer to the time associated with the initiation and cessation of runoff, respectively. Particulate-bound (M_P) heavy metal load was determined as the difference between the total (M_T) and dissolved (M_D) heavy metal load (Eq. (2)).

The fractionation of heavy metals into dissolved and particulate-bound was characterized by D/P mass fraction ratios or dissolved to particulate metal element mass ratios (Eq. (3)), and equilibrium distribution coefficient, K_D (Eq. (4)) for dilute solutions which expresses the ratio of metal element mass normalized to the dry mass of solids (particulates) to the metal element concentration in solution for a given volume of runoff [4].

$$\frac{D}{P} = \frac{M_D}{M_P} \tag{3}$$

where M_D (mg) is the dissolved metal element mass per unit volume of sample and M_P (mg) is the particulate-bound metal mass per unit volume of sample.

$$K_D = \frac{C_S}{C_D} \tag{4}$$

where K_D (L/kg) is the distribution coefficient between particulate-bound metal element mass and dissolved metal element concentration; C_S (mg/kg) is the particulate-bound metal element mass and C_D (mg/L) is the dissolved metal element concentration.

3. Results and discussion

3.1. Storm event characteristics and heavy metal loading

The total sampled rainfall from the 19 monitored storm events has a mean of only 6.6 mm and median of 3.5 mm signifying that most of the sampled events have low rainfall occurrence. The mean and median duration of rainfall and runoff were 3.1 and 2.8 h, and 1.9 and 1.2 h; respectively. The average runoff to rainfall duration ratio was 0.61 and in addition, it was taking more than an hour for the runoff to enter and exit the system even with the small storage capacity. The average flow rate was greater at the outflow than at the inflow as well as the peak flows but the coefficient of variation (CV) was 50%–60% greater at the inflow than at the outflow.

Fig. 2 shows the average mass loading of heavy metals fractionated into particulate and dissolved form in the inflow and outflow. Most metal elements including Cr, Pb, Cd and Ni existed in dissolved form in the inflow and outflow. Only Fe though not considered as a priority pollutant was predominately particulate-bound both in the inflow and outflow while Zn appeared to be particulate-bound in the inflow and dissolved in the outflow. Studies showed that metals such as Cu, Cr and Ni in runoff have higher solubility levels while Pb and Zn were primarily particulate-bound but there were also instances that such metals were proportionately partitioned between dissolved and particulate phases [4,19,26].

In outflow, the dissolved fraction was reduced for all the metal elements. The mass loading of particulate heavy metals was reduced by 30% to 73% for Ni, Cu, Zn and Cd; however, only the dissolved forms were reduced by 11% to 23% for these heavy metals. Export of particulate Cr, Pb and Fe were observed from the facility; however the dissolved forms were reduced between 11% and 37%. Typically, the removal of particulate heavy metal could be achieved through the attainment of a long residence time while removal of metals in dissolved phase necessitate employment of materials with large cation exchange capacity [2,27].

3.2. Mass fraction ratio (D/P)

The average D/P ratios of Cr, Fe, Ni, Cu, Zn, Cd and Pb in inflow were 2.21, 0.12, 2.18, 3.79, 1.22, 10.14 and 1.49; and in outflow were 1.80, 0.37, 2.19, 6.32, 4.74, 37.5 and 2.25. The proportion of storm events with $D/P < 1$ and $D/P > 1$ in the

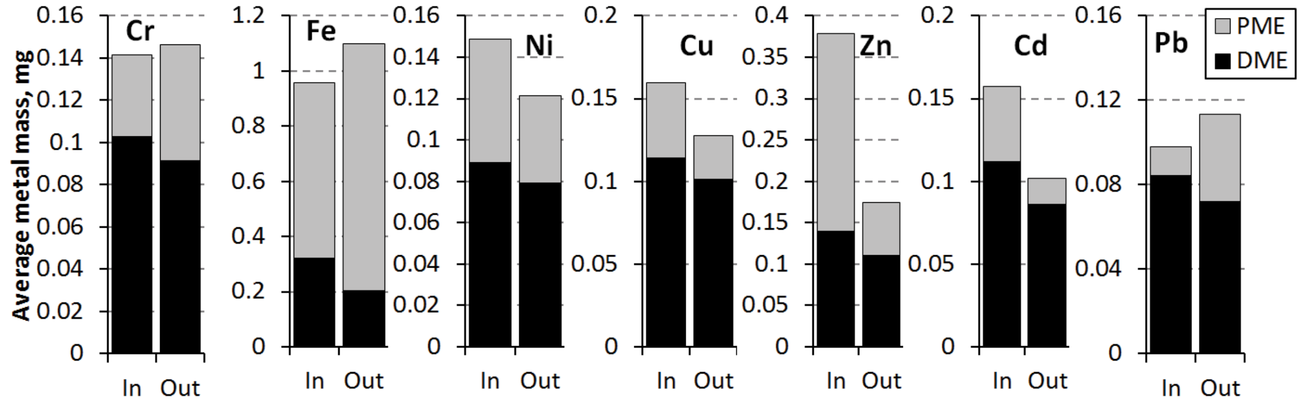

Fig. 2. Average mass loading of metal elements in inflow and outflow fractionated into particulate-bound (PME) and dissolved (DME) forms.

inflow and outflow of the tree box filter was investigated to determine the applicability of the tree box filter in reducing the particulate-bound and dissolved fraction of heavy metal element in runoff (Fig. 3). A D/P ratio greater than 1.0 indicates that the metal element is mainly in dissolved form indicating that enhancement of the sorption capacity of a stormwater treatment system would provide the greatest mass immobilization, while if less than 1.0 it is largely particulate-bound indicating filtration and sedimentation can be effective removal mechanisms [4]. Results revealed that Fe, Zn and Pb have $D/P < 1$ in almost 60%–90% of storm events in the inflow showing greater potential for reduction by the tree box filter that incorporate mainly filtration mechanism. On the other hand, about 64%–80% of storm events showed that Cr, Ni, Cu and Cd have higher dissolved fraction in the inflow. Apparently, majority of the storm events (70%–80%) produced higher fraction of dissolved metal element in the outflow which signifies that the system was more likely capable of reducing the particulate-bound fraction of metal elements based on the hydraulic condition on the site.

Analyses were carried out to investigate the possible reasons for the fractionation of heavy metals in the particulate and dissolved forms in the inflow and outflow of the tree box filter and it was found out that TSS concentration affects the mass fraction of metal elements. Fig. 4 shows the corresponding average TSS concentration for each heavy metal that resulted to particulate-bound (D/P < 1) and dissolved (D/P > 1) metal fractions in the inflow and outflow. Comparing the D/P at the inflow, it was found out that a higher TSS concentration (more than 120–175 ± 145 mg/L, except Cd) likely yield greater particulate-bound heavy metal. Nonetheless, predominately particulate-bound metals in nature such as Fe, Pb and Zn would have $D/P > 1$ at lower TSS concentration (~50 ± 43 mg/L). In general, the D/P ratio in the inflow did not differ significantly based on TSS concentration. But apparently, the inflow TSS concentration showed considerable influence on the metal D/P ratio in the outflow. As can be seen, the metal elements in the outflow were evidently dissolved with higher TSS concentration and particulate-bound with lower TSS concentration in the inflow implying that highly polluted runoff could also carry

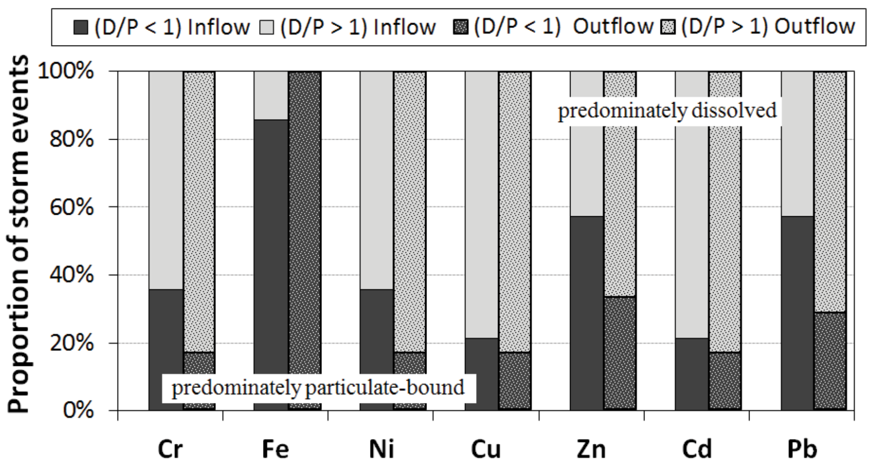

Fig. 3. Proportion of storm events with $D/P < 1$ (predominately particulate-bound) and $D/P > 1$ (predominately dissolved) at the inflow and outflow.

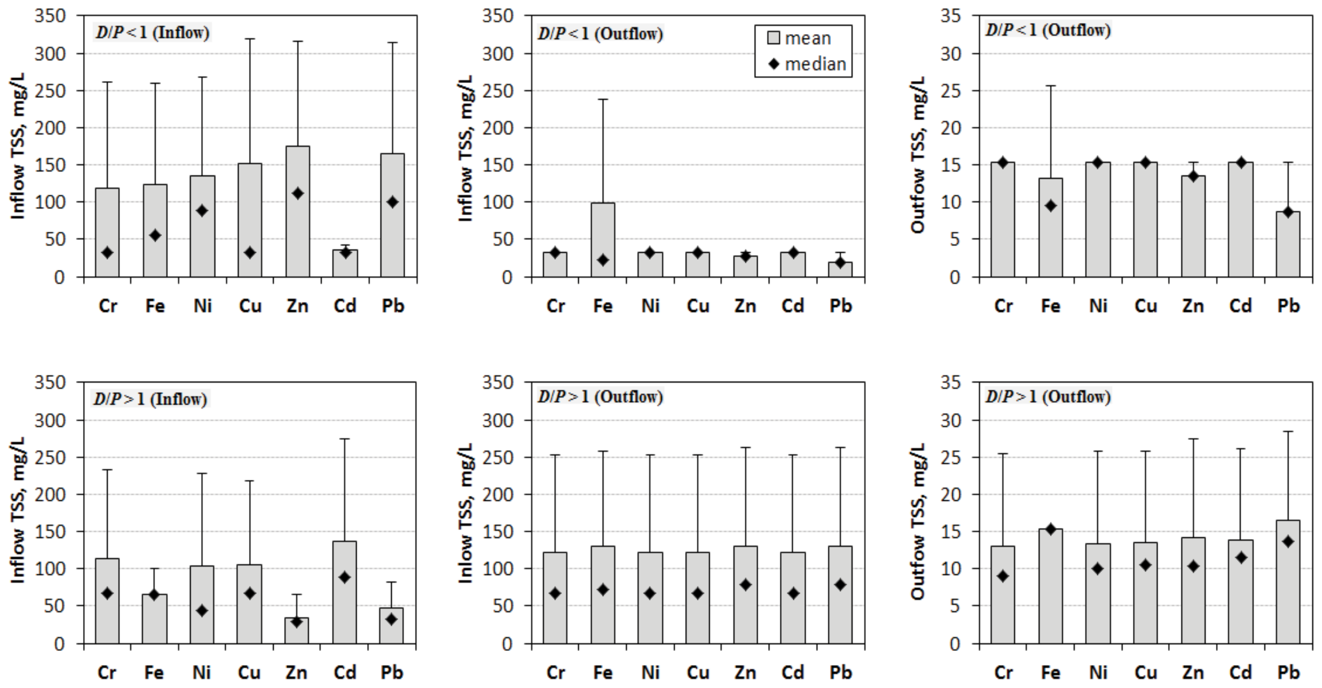

Fig. 4. Average (mean ± standard deviation and median) inflow and outflow TSS EMC for each heavy metal that correspond to various D/P criteria.

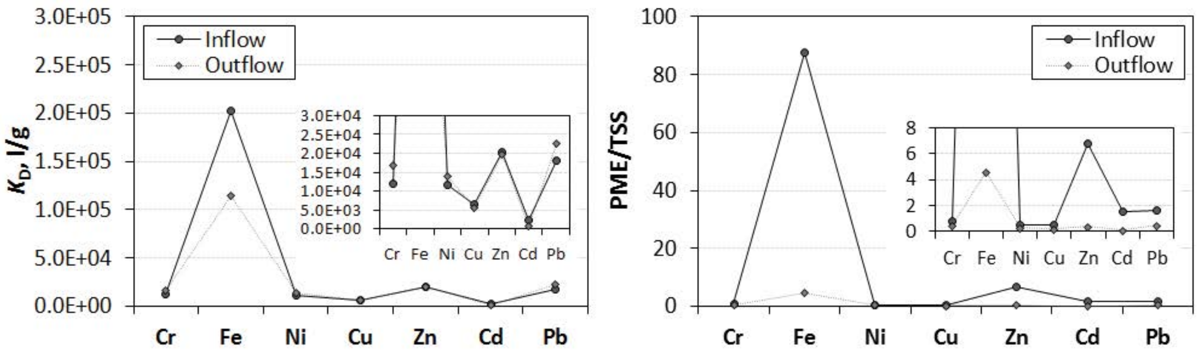

Fig. 5. Comparison of the distribution coefficient (K_D) and particulate-bound metal element mass (PME/TSS) in the inflow and outflow.

more heavy metals limiting the capacity of the tree box filter to reduce the metal fractions. Considering the outflow TSS concentration, no significant influence was observed with the D/P ratio of the metals in the outflow possibly due to the very low TSS levels (<15 mg/L). Based on the findings, the fractionation of metals was found to be independent of the treated runoff rather by the incoming runoff particularly the concentration of particulate matters in it.

3.3. Equilibrium distribution coefficient (K_D)

The average K_D for Cr, Fe, Ni, Cu, Zn, Cd and Pb in inflow was 1.2E + 04, 2.0E + 05, 1.2E + 04, 6.6E + 03, 2.0E + 04, 2.5E + 03 and 1.8E + 04; while 1.7E + 04, 1.1E + 05, 1.4E + 04, 5.7E + 03, 2.0E + 04, 7.9E + 02 and 2.2E + 04 in outflow (Fig. 5). In principle, higher K_D values indicate that the metal has been retained by the solid, that is, TSS through sorption reactions. On the contrary, lower K_D values signify that most metal remains in solution where it is available for transport. Among the heavy metals, the highest K_D values for both inflow and outflow were observed for Fe while low for metals such as Cd, Cu, Cr and Ni. K_D values were increased in the outflow by 19%–38% for Ni, Pb and Cr; while reduced for 14%, 44% and 68% for Cu, Fe and Cd, respectively. K_D values for Zn remain unchanged in the inflow and outflow. It can be seen that the trend in K_D was greatly influenced by the particulate-bound metal element mass (mg/kg of dry solids) or PME/TSS and highly comparable in the inflow than in the outflow. The main distinction observed was the reduction of particulate-bound metal element mass in outflow (all metals, inflow PME/TSS > outflow PME/TSS) and was highly evident in Fe > Zn ≈ Cd > Pb > Cu > Cr > Ni comparable with the results in the study of Rochford [26] wherein the partition of metals to the particulate phase was ranked in the order of Pb > Zn > Cu > As > Cr > Cd > Ni.

4. Conclusions and recommendations

Knowledge on the relative fractions of dissolved and particulate-bound heavy metal mass in runoff is important prior to designing a treatment system for stormwater management. Nevertheless, upon designing, the actual efficiency of stormwater treatment systems was not recognized and the systems often failed to function appropriately based on the desired requisites due to a number of factors such as hydraulic and hydrologic factors, environment and site condition, construction-related problems, etc. This research was conducted to investigate the actual applicability of a developed tree box filter employed to reduce particulate and toxic contaminants in runoff by physical and biological processes and determine the implications on the design of the system for its improvement.

Findings revealed that the system was highly capable of reducing the particulate-bound fraction of Ni, Cu, Zn and Cd; and the dissolved fraction of all the heavy metals. It was also found out that majority of the storm events produced higher dissolved fraction of Cr, Ni, Cu and Cd; but favored the reduction of the predominately particulate-bound Fe, Zn and Pb.

TSS concentration was found to influence the generation of particulate-bound heavy metals and more likely influence the reduction of heavy metals in the tree box filter. The metal elements in the outflow were evidently dissolved with higher TSS concentration and particulate-bound with lower TSS concentration in the inflow. On the other hand, no significant influence was observed considering the outflow TSS concentration implying that the fractionation of metals was found to be independent of the treated runoff rather by the incoming runoff particularly the concentration of particulate matters in it. The adsorption capacity of metals was ranked from greatest to least as follows: Fe > Zn ≈ Cd > Pb > Cu > Cr > Ni.

Acknowledgments

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Symbols

C_D	—	Particulate-bound metal element mass
C_S	—	Dissolved metal element concentration
$C(t)$	—	Concentration at time t
CV	—	Coefficient of variation
D/P	—	Mass fraction ratios or dissolved to particulate metal element mass ratios
K_D	—	Equilibrium distribution coefficient
M	—	Mass of a pollutant transported
M_D	—	Dissolved heavy metal load
M_P	—	Particulate-bound heavy metal load
M_T	—	Total heavy metal load
TSS	—	Total suspended solids
$Q(t)$	—	Volume of runoff at time t

References

[1] D.M. Revitt, R.S. Hamilton, R.S. Warren, The transport of heavy metals within a small urban catchment, Sci. Total Environ., 93 (1990) 359–373.

[2] V. Novotny, Water Quality: Diffuse Pollution and Watershed Management, 2nd ed., J. Wiley & Sons, New York, USA, 2003.

[3] A.P. Davis, M. Shokouhian, S. Ni. Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources, Chemosphere, 44 (2001) 997–1009.

[4] J.J. Sansalone, S.G. Buchberger, S.R. Al-Abed, Fractionation of heavy metals in pavement runoff, Sci. Total Environ., 189–190 (1996) 371–378.

[5] J.J. Sansalone, S.G. Buchberger, Partitioning and first flush of metals in urban roadway storm water, J. Environ. Eng., 123 (1997) 134–143.

[6] A. Turner, G.E. Millwatrd, A.J. Bale, A.W. Morris, Application of the K_D concept to the study of trace metal removal and desorption during estuarine mixing, Estuarine Coastal Shelf Sci., 36 (1993) 1–13.

[7] M.R. Wiesner, G.W. Characklis, D. Brejchova, Metals and Colloids in Urban Runoff, H.E. Allen, A.W. Garrison, G.W. Luther III, Eds., Metals in Surface Waters, Ann Arbor Press, Chelsea, MI, 1998, Chapter 2, pp. 23–36.

[8] R. Pitt, R. Field, M. Lalor, M. Brown, Urban stormwater toxic pollutants: assessment, sources, and treatability, Water Environ. Res., 67 (1995) 260–275.

[9] G.W. Characklis, M.R. Wiesner, Particles, metals and water quality in runoff from large urban watershed, J. Environ. Eng., 123 (1997) 753–759.

[10] Y. Ran, J.M. Fu, G.Y. Sheng, R. Beckett, B.T. Hart, Fractionation and composition of colloidal and suspended particulate materials in rivers, Chemosphere, 41 (2000) 33–43.

[11] D.W. Glenn, Heavy Metal Distribution for Aqueous and Solid Phases in Urban Runoff, Snowmelt and Soils, Ph.D. Thesis, Louisiana State University, Baton Rouge, Louisiana, USA, 2001.

[12] A. Florea, D. Busselberg, Occurrence, use and potential toxic effects of metal and metal compounds, Biometals, 19 (2006) 419–427.

[13] L. Herngren, A. Goonetilleke, G.A. Ayoko, Understanding heavy metal and suspended solids relationships in urban stormwater using simulated rainfall, J. Environ. Manage., 76 (2005) 149–158.

[14] J. Choi, F.K.F. Geronimo, M.C. Maniquiz-Redillas, M.J. Kang, L.H. Kim, Evaluation of a hybrid constructed wetland system for treating urban stormwater runoff, Desal. Wat. Treat., 53 (2015) 3104–3110.

[15] G. Mazer, D. Booth, K. Ewing, Limitations to vegetation establishment and growth in biofiltration swales, Ecol. Eng., 17 (2001) 429–443.

[16] G.R. Minton, Stormwater Treatment: Biological, Chemical, and Engineering Principles, Gary Minton, Seattle, Washington, USA, 2002.

[17] M.C. Maniquiz, S.Y. Lee, L.H. Kim, Long-term monitoring of infiltration trench for nonpoint source pollution control, Water Air Soil Pollut., 212 (2010) 13–26.

[18] M.C. Maniquiz, J.Y. Choi, S.Y. Lee, L.H. Kim, Performance comparison between infiltration and non-infiltration type of structural stormwater treatment systems, Water Sci. Technol., 66 (2012) 363–369.

[19] S.K. Pitcher, R.C.T. Slade, N.I. Ward, Heavy metal removal from motorway stormwater using zeolites, Sci. Total Environ., 334–335 (2004) 161–166.

[20] J.J. Sansalone, The Physical and Chemical Nature of Urban Stormwater Runoff Pollutants, R. Field, D. Sullivan, Eds., Wet-Weather Flow in the Urban Watershed: Technology and Management, CRC Press LLC, Florida, 2003, pp. 46–66.

[21] L.H. Kim, M. Kayhanian, K.D. Zoh, M.K. Stenstrom, Modeling of highway stormwater runoff, Sci. Total Environ., 348 (2005) 1–18.

[22] Y. Han, S.L. Lau, M. Kayhanian, M.K. Stenstrom, Characteristics of highway stormwater runoff, Water Environ. Res., 78 (2006) 2377–2388.
[23] M. Kayhanian, C. Suverkropp, A. Ruby, K. Tsay, Characterisation and prediction of highway runoff constituent event mean concentration, J. Environ. Manage., 85 (2007) 279–295.
[24] M.C. Maniquiz-Redillas, J.M.R. Mercado, L.H. Kim, Determination of the number of storm events representing the pollutant mean concentration in urban runoff, Desal. Wat. Treat., 51 (2013) 4002–4009.
[25] A.D. Eaton, L.S. Clesceri, A.E. Greenberg, M.A.H. Franson, Standard methods for the examination of water and wastewater, J. Am. Public Health Assoc., 1015 (2005) 49–51.
[26] L. Rochford, Stormwater Heavy Metal Loadings to Port Jackson Estuary, MS Thesis, University of Sydney, NSW, Australia, July 2008.
[27] H. Genc-Fuhrman, P.S. Mikkelsen, A. Ledin, Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater: experimental comparison of 11 different sorbents, Water Res., 41 (2007) 591–602.