Fractionation of heavy metals in runoff and discharge of a stormwater management system and its implications for treatment

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Abstract: A stormwater management system utilizing the mechanisms of sedimentation and filtration/infiltration was developed and constructed for the immobilization of suspended solids and heavy metal constituents (Fe, Zn, Pb, Cr, Cu, Cd, Ni) in runoff. Monitoring took place between May 2010 and November 2012 on a total of 24 storm events. This research on the fractionation of heavy metals in runoff and discharge of a stormwater system provided insight on the actual efficiency of the system and determined the implications for treatment of the particulate-bound and dissolved heavy metals in runoff. Results revealed that the partitioning of heavy metal load in runoff in either dissolved or particulate-bound were influenced by flow rate and total suspended solids load, and evident in high-intensity storm (rainfall-runoff event). On the other hand, the partitioning of heavy metal load discharge from the stormwater system was more apparent during the early period of discharge having higher variability in dissolved than particulate-bound heavy metal. Findings revealed that fractionation of heavy metals played an important role in the performance of the stormwater system; thus, must be considered in designing stormwater systems. For the stormwater system to be effective, it is recommended to design the system treating not only the early period of a storm (first flush criteria) rather until the peak part of the hydrograph (high flow rate where partitioning was greatest) from a load basis.

Key words: dissolved; heavy metals; particulate-bound; road runoff; stormwater management

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Introduction

In urban transportation landuses, significant quantities of heavy metal constituents are generated from traffic activities (e.g., tire wear, brake linings leakage of oil and lubricants), roadway maintenance operations (e.g., application of deicing compounds, pesticides and herbicides) and atmospheric deposition (Davis et al., 2001; Herngren et
al., 2006; Lau and Stenstrom, 2005; Sansalone and Buchberger, 1997). Once mobilized by storm flows, these heavy metals constituents are typically dynamically partitioned either as dissolved-dissociated in water or adsorbed onto fine sediments and particulate organic matter (Harrison and Wilson, 1985; Pitt et al., 1995). Particulate-bound heavy metals are generally associated with the non-filterable fraction of stormwater and dependent upon flow capable of mobilizing particles from the road surface and drainage system (Characklis and Wiesner, 1997; Sansalone et al., 1996). Whereas dissolved heavy metals have the potential for acute and long term toxicity for aquatic life and a greater potential of affecting groundwater (Hatje, 2003; Marsalek et al., 1999; Pitt et al., 1995).

Heavy metals in roadway runoff can adversely affect receiving waters by increasing toxicity in the water column and/or sediments, and bio-accumulating in the food chain. 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 (i.e. adsorbed to particles) (Florea and Busselberg, 2006; Glenn, 2001; Hatje, 2003). Thus, several best management practices (BMPs) for roadway stormwater management are designed to treat only the particulate fraction (Maniquiz et al., 2012; Minton, 2002). Hence, toxicity and contaminant reductions by BMPs are limited by the degree to which pollutants/toxicity associate with particles, and the efficiency with which BMPs remove particles. The efficiency of removal of metals could be correlated to the efficiency of removal of clay and silt fractions of the sediment and particulate organic carbon (suspended solids) parameters. However, only lead appears to be strongly associated with particulates; other toxic metals are typically found in both the dissolved and particulate phases (Novotny, 2003).

Knowledge of the partitioning kinetics and relative fractions of dissolved and particulate-bound mass delivered for treatment is of fundamental importance for on-site treatment of stormwater runoff. The partitioning reactions between the dissolved and particulate-bound fractions of heavy metals in stormwater runoff that include ion exchange, surface complexation and precipitation are nonlinearly reversible between the solid and soluble phase concentrations (Barry et al., 2000; Glenn, 2001; Stumm and Morgan, 1996). Studies revealed that adsorption or precipitation unit processes need consideration in treatment design and that knowledge of partitioning for a given set of residence time and stormwater chemistry parameters is also important for designing stormwater treatment systems (Genc-Fuhrman et al., 2007; Sansalone, 2003).
The objective of this research was to investigate the performance of stormwater treatment system in immobilizing heavy metals from runoff. Specific objective focuses on the identification of heavy metal elements fractioned into dissolved and particulate-bound at the runoff before it enters the system and at the discharge as it exited the system to determine the mobility of the metals and how well they were retarded in the system.

1 Materials and methods

1.1 Site and treatment system description

The eco-biofilter (EBF), a type of manufactured stormwater filtration/infiltration system was developed and constructed to capture and treat suspended solids, heavy metals and other constituents in runoff from an impervious road 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 1,400 mm of rainfall annually wherein 35% of that amount was captured as runoff by the EBF. The mean annual total suspended solids (TSS) loading rate on the site was between 76,000 and 140,000 kg/year. Heavy metal loadings of Cr, Ni, Cu, Cd, and Pb were typically less than 100 kg/year except for Zn (150 to 250 kg/year) and Fe (greater than 2000 kg/year).

Figure 1 shows the location and schematic of the detailed components of the EBF system. The underground system placed near the upper end of the asphalt-paved road was made of a pre-casted concrete 5 m long, 1 m wide at the top and 1.3 m deep with 2% top and bottom slope. The bed bottom and side perimeter were bordered by a 20 cm thick concrete. Runoff was conveyed to the EBF through a rectangular stainless steel open channel (300 × 20 × 23.5 cm) with 6% slope. The surface area of the EBF corresponds to only 1% of the 520 m² catchment area that it drains. The storage volume of the presettling basin designed to capture the initial first flush runoff volume is about 25% of the total volume of the EBF. Together with the aggregates, i.e., sand (2--5 mm), gravel (20--30 mm), wood chip (10--20 mm) in the filter media bed which provide approximately 30% void space, and an open effluent basin, the total effective storage capacity of the EBF summed up to 3.85 m³ and equivalent to 60% of the total volume of the system. Maintenance activities including routine inspections, sediment collection, few replacements and renovations were performed since the initial operation of the EBF in May, 2009.
1.2 Sampling and analysis

Monitoring was undertaken during 24 storm events between May 2010 and November 2012 to investigate the performance of the EBF system. Manual grab sampling was utilized at the runoff and discharge units of the EBF (see Fig. 1 for the sampling ports). The sampling scheme follows the typical sample collection method practiced similarly in most nonpoint source studies in Korea and globally (Kim et al., 2007; Maniquiz et al., 2010; Stenstrom and Kayhanian, 2005). At the runoff and discharge units, four samples were taken every 5 min for the first 15 min with the first sample collected as soon as runoff was evident, two samples after 30 min and 1 hr, and more samples hourly thereafter until a maximum of 12 samples. For most of the shorter events, the scheme was modified by adjusting the number of samples until the runoff flow ended (Maniquiz et al., 2013). Selected hydrologic and hydraulic data including event rainfall depth, rainfall and runoff duration, rainfall intensity, runoff flow rates, etc. were obtained from the site during each storm event. Runoff samples collected were analyzed for total suspended solids (TSS), and total (sum of the dissolved and the particulate-bound concentrations) and soluble or dissolved heavy metal (i.e., Cr, Cd, Pb, Zn, Ni, Cu and Fe) concentrations. 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 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 (APHA et al., 2005).

1.3 Calculations and statistical analysis

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

\[
M = \int_0^T C(t) \times Q(t) \, dt \approx \sum_{t=0}^{t=T} C(t) \times Q(\Delta t)
\]  

(1)
where, \( M \) (g) is the mass of a pollutant transported; \( C(t) \) (mg/L) is concentration at time \( t \) and \( Q(t) \) (m³) is the volume of runoff 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)) (Sansalone, 2003).

\[
M_T = M_p + M_D \tag{2}
\]

The dissolved to particulate metal element mass ratios or \( M_D/M_p \) ratios (mg/mg) were calculated for each heavy metal element. A \( M_D/M_p \) greater than 1.0 indicates that the metal element is mainly in dissolved form, while if less than 1.0 it is largely particulate-bound (Sansalone et al., 1996).

The partition (or distribution) coefficient, \( K_D \) is a factor related to the partitioning of a contaminant between the solid and aqueous phases and defined as the ratio of the quantity of the metal element mass normalized to the dry mass of solids (particulates) to the metal element concentration in solution for a given volume of runoff (Eq. (3)) (Sansalone et al., 1996).

\[
K_D = \frac{C_S}{C_D} \tag{3}
\]

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.

Statistical hypotheses were tested at 95% confidence level (\( \alpha = 0.05 \)), unless otherwise specified statistically different means that \( p \) value was less than 0.05. All the statistical analyses were performed using the OriginPro 7.5 SRO v7.5714 (B714) (OriginLab Corporation, Wellesley, MA, USA, 1991-2003) and SYSTAT 12 (SYSTAT Software, Inc. 2007) software packages.

2 Results
2.1 Characteristics of runoff and discharge

The water quality and quantity, and hydrologic and hydraulic characteristics of runoff and discharge are summarized in Table 1. Specifically, the runoff and discharge were characterized based on the TSS concentration since the system was designed to
reduce particulate matters primarily by sedimentation, filtration and infiltration mechanisms. Results showed that the TSS concentration in runoff was almost four-fold in magnitude higher than the TSS concentration discharged from the system. Nearly 30% of the monitored storm events showed no evident discharge from the system for particularly low intensity rainfall events (less than 1 mm/hr). It was observed that an apparent increase in TSS resulted to higher total heavy metal concentrations both in runoff and discharge regardless of certain hydrologic and hydraulic factors such as rainfall depth, flow rates and hydraulic retention time (HRT) signifying the unique tendency of heavy metals to sorbed into particulate matters (i.e., TSS). Studies showed that most of the heavy metals in urban runoff were attached and/or adsorbed largely onto particulates (Minton, 2002; Mishra and Singh, 2003; Sansalone et al., 1995), which will be individually and discriminately removed at different overland flow velocities; thus, making the prediction of metals more difficult on an event-to-event basis (Thomson et al., 1997). On the contrary, no direct relationship was observed between TSS and dissolved heavy metal elements indicating that sorption of dissolved metal elements to particulates were weakly occurring in the system; nonetheless, those high levels of dissolved heavy metals in the discharge were present in the lowest range of TSS concentration less than 50 mg/L. Based on studies in literature, it was stated that there is a relatively little time for heavy metal contact with TSS at the upper end of the watershed which makes most heavy metals to be predominantly dissolved for each event (Glenn, 2001; Sansalone, 2003). In addition, the short residence time and interfacial contact reduced the probability of solutes partitioning to solid matter (Glenn, 2001; Sansalone, 2003).

2.2 Fractionation of heavy metals

2.2.1 Particulate-bound and dissolved heavy metal load during a storm event

The temporal variation in partitioning of heavy metals for the highest intensity monitored storm event is shown in Fig. 2. It was observed that as the storm progressed, the fractionation of heavy metal load in runoff either dissolved or particulate-bound were influenced by both flow rate and TSS load. Particularly, during the peak period of the hydrograph signifying that the TSS (particulate matters) were considerably washed-off from the road surface and carried the heavy metals with it. It could be seen that during the beginning period of storm (i.e., initial hour) the partitioning between the dissolved and particulate-bound for all heavy metal elements was not very apparent since the flow rate and TSS load were almost at very low levels. Heavy metals such as
Cu, Cr, Ni, Cd and Pb showed the dominance of dissolved fraction during the initial low intensity flow. Sansalone et al. (1996) concluded that partitioning was dominated by the dissolved fraction of the heavy metal mass in the early portion of a rainfall and runoff event due to the location of source control BMPs wherein toward the upper end of the urban catchment, heavy metals can predominately partition toward the dissolved phase. Conversely, some heavy metals predominately in dissolved form such as Cu, Cr, Ni, and Cd slightly showed similar behavior with the flow rate and TSS load in their dissolved rather than their particulate-bound phase. At the nearly end of a high intensity storm event wherein dilution of runoff was expected, the dissolved and particulate-bound fractions of heavy metals also showed little or no significant difference. The findings suggest that the partitioning of heavy metals into particulate-bound and dissolved phases was likely during higher intensity storm flow events. Nonetheless, the distinct characteristics of heavy metal elements (i.e., existence in dissolved or particulate-bound) remain unchanged regardless of flow rate and TSS load. An analysis of the other storm events (plots not shown) revealed that majority of the storm events exhibited similar partitioning trend with the flow rate and TSS load; and more evident in the particulate-bound fraction. Partitioning could also vary significantly between hydrologic events and traffic patterns and other factors such as pH, alkalinity, residence time, and solids characteristics (Sansalone, 2003). For instance, in a longer duration storm event (after 6 hr), analysis of Sansalone and Buchberger (1997) revealed that Cu load was partitioned to particulate-bound fraction.

Unlike in the runoff, the partitioning of heavy metals in the discharge manifested rather a more distinct trend. The particulate-bound heavy metal load remained stable and in very low levels (i.e., 0.01 g, <1 g for Fe) for most heavy metal constituents except Pb which showed a slight increase in the early period of discharge but still become stable throughout the cessation of discharge. On the other hand, dissolved heavy metal load exhibited a highly variable trend at the discharge; yet, showed higher variability at the initial time of discharge.

### 2.2.2 Mass fraction ratio

The mass fraction ratio or $M_D/M_P$ ratio reveals the dominant mass fraction of a metal element. The average $M_D/M_P$ of heavy metals at runoff and discharge was shown in Table 2. Among the heavy metals, Fe though not considered as a priority pollutant was predominately particulate-bound both in the runoff and discharge. In runoff, Zn and Pb were the only heavy metals with significantly low $M_D/M_P$ indicating that the metals
existed largely in particulate-bound. On the other hand, Cd was apparently existed in dissolved form due to very high $M_D/M_P (=9.0)$. Heavy metals such as Cr, Ni and Cu have $M_D/M_P$ close to 1.0 which could be either in dissolved or particulate-bound depending on environmental conditions (e.g., rainfall intensity, TSS loadings, etc.). Similar studies revealed that in urban runoff, Cd exhibited a preference for the dissolved phase, whereas Pb was dominantly in the suspended phase (Morrison et al., 1984, Pitt, 1995).

At the discharge, it was noticeable that most of the $M_D/M_P$ exceeded 1.0 (except Fe) implying that the particulate-bound heavy metal was reduced, thus the fraction of the dissolved heavy metals was increased. Statistical analysis revealed that Pb was the only heavy metal with significantly different fraction between the runoff and discharge. Studies revealed that the only mechanisms available to remove nonvolatile heavy metal solutes from the water column in BMPs are partitioning of solids and then sedimentation; an increase in pH to promote precipitation; or through various biological uptake vectors. However, once heavy metals become part of settled sediments, the potential exists for the sediment in the benthic zone to become anaerobic, releasing the heavy metals and permitting advection and diffusion of the heavy metals back into the water column (Minton, 2002; Sansalone, 1995; Sun and Davis, 2007).

### 2.2.3 Partition coefficient

The proportion of dissolved to adsorbed portions of heavy metal constituents in water depends on its adsorption characteristics, typically the partition coefficient and the concentration of fine particles, primarily organic matter (Novotny, 2003). The average partition (or distribution) coefficient $K_D$ in runoff and discharge were provided in Table 3. The $K_D$ values obtained at the runoff and discharge were within the range of typical partitioning coefficients found in literature that was between $10^3$ and $10^5$ for organic compounds and heavy metals (Glenn, 2001; Novotny, 2003; Sansalone et al., 1996; Sansalone and Buchberger, 1997). Among the heavy metals, the highest $K_D$ value for both runoff and discharge was observed for Fe and lowest for Cd. In principle, higher $K_D$ values indicate that the metal has been retained by the solid (i.e., TSS) through sorption reactions. On the contrary, lower $K_D$ values signify that most metal remains in solution where it is available for transport. Each heavy metal showed varying $K_D$ values with higher variation in the runoff (100% to 430%) than in the discharge (110% to 330%) implying the different sorption behaviours among heavy metals. Based on statistical findings, it was revealed that predominately particulate-bound heavy metals
such as Fe, Zn, Pb and even Ni had significantly smaller $K_D$ values in the discharge. The $K_D$ values of Cd and Cu were lower in the runoff than at the discharge, while Cr appeared to remain unaffected at the discharge. The lower $K_D$ values also indicated that the heavy metals were already removed with particulates and the removal efficiency could be related to their biodegradability and volatilization. Novotny (2003) identified that higher partition coefficient was associated with lower suspended organic particles expressed as volatile suspended solids. In addition, it was revealed that the partition coefficient for metals reduced dramatically during winter due to the high salinity of urban runoff. As a result, the efficiency of BMPs that accumulate particulate metals fraction in the sediment was reduced, to the point that metals are leached from the sediments and the BMPs become a source rather than a sink of metals.

2.3 Load ratio of heavy metals

To investigate the relationship between runoff and discharge heavy metal load, the load ratio (i.e., ratio of the heavy metal discharge load to the runoff load) for dissolved ($\frac{DME_{DIS}}{DME_{RUN}}$) and particulate-bound ($\frac{PME_{DIS}}{PME_{RUN}}$) fractions was determined as shown in Fig. 3. Based on the results, it was found out that less particulate-bound heavy metals were discharged from the system with an average of 12%--30% relative to the runoff. Approximately 31% to 61% of dissolved heavy metal load in runoff was discharged from the system higher by 12% to 49% compared to particulate-bound heavy metals. Higher variations were observed for dissolved heavy metal load ratio with coefficient of variation (CV) ranging from 0.33 to 1.32. Only Ni had apparently high CV for particulate-bound heavy metal load ratio (CV = 0.6) while the rest of the metals have CVs less than 0.3. The rank of heavy metals from lowest particulate-bound load ratio was $\text{Fe} < \text{Cu} < \text{Pb} \approx \text{Cd} < \text{Zn} < \text{Cr} < \text{Ni}$, and dissolved load ratio was $\text{Cu} < \text{Cr} < \text{Cd} < \text{Pb} < \text{Ni} < \text{Zn} < \text{Fe}$. In a controlled bioretention systems utilizing soil, mulch, sand and plants, the percent removal trend by the media was $\text{Cd} > \text{Pb} > \text{Zn} > \text{Cu}$ based on the reduction percentage (Sun and Davis, 2007). Among the heavy metals, Fe, Zn and Pb have larger difference between dissolved and particulate-bound load ratios (25% to 49%) compared to Ni, Cr, Cu and Cd which was only between 12% and 17%. From the metal-complexing mechanisms, Fe oxyhydrates provide the strongest adsorption sites with the adsorption reactions which are strongly dependent on pH (Salomons and Forstner, 1984).

Correlation analyses revealed positive and some satisfactory relationships between the dissolved and particulate-bound heavy metals at runoff and discharge (Table 4).
Among the heavy metals, high and significant correlation only existed for Fe and Zn ($R^2 > 0.95$) in the runoff. Cd was found to be not correlated, while Pb was both highly correlated between the dissolved and particulate-bound phases. No significant correlation was observed for heavy metals at the discharge. Certain heavy metals were highly correlated between its dissolved and particulate-bound phases at the runoff including Cr, Cu and Ni but poorly correlated at the discharge.

3 Discussion

3.1 Implications for treatment of particulate-bound heavy metals

The developed stormwater system utilizes mechanisms of filtration and sedimentation, therefore promotes the removal of particulate matters such as TSS. The findings in this research implied that the relative reduction in TSS load resulted in appreciable reduction in particulate-bound heavy metals, especially during the peak period of a high intensity storm when sorption of particulate-bound heavy metals to TSS as well as partitioning was greatest. The treatment of particulate-bound heavy metals was found to be efficient since the initial (runoff) load was dropped down to very low levels after passing the treatment system. The stormwater system was found to perform efficiently in terms of reducing the dominant heavy metals (Zn, Pb and Fe), which appeared to be predominately particulate-bound due to their low $M_D/M_P$ in the runoff. Nonetheless, the increase in $M_D/M_P$ of other heavy metals after passing the stormwater system proved that their particulate-bound fraction was also possibly reduced due to partitioning and sorption that occurred in the system. Moreover, the higher $K_D$ values of Cu and Cd at the discharge indicated a more potential reduction of these heavy metals. The high correlation between dissolved and particulate-bound Pb load suggested that reduction in particulate-bound Pb load could perhaps reduce the dissolved fraction as well. However, the low correlation of other heavy metals indicated that reduction in particulate-bound could not merely reduce and treat the dissolved fraction.

3.2 Implications for treatment of dissolved heavy metals

The mechanisms of filtration and sedimentation utilized in the design of the stormwater system also played an important role in the reduction of the dissolved fraction of heavy metal. The research findings implied that the reduction of TSS was indirectly accounted for the reduction in dissolved heavy metals; however, the partitioning of heavy metals that initially occurred facilitated the sorption of dissolved fraction through sedimentation and filtration in the filter media. The treatment of
dissolved heavy metals was highly variable especially at the initial time of discharge signifying that HRT was an important factor since at the nearly end of discharge the dissolved heavy metal load was reduced; although still higher than the particulate-bound load. Overall, the stormwater system was not very efficient in the treatment of dissolved heavy metal load as manifested by the $M_D/M_P$ at the discharge. The discharge contains greater fraction of dissolved heavy metals that should be considered, and depending on the discharge limits additional treatment might be necessary. Among the heavy metals, only Cd was predominately dissolved although there was a possibility that Cr, Ni and Cu could have more dissolved fractions depending on environmental conditions. Nevertheless, Cu, Cr, Cd, Ni have lower dissolved load ratios compared to predominately particulate-bound, indicating that sorption occurred better for predominately dissolved heavy metals. Apparently, dissolved heavy metals may not be reduced by BMPs relying for settling only; other mechanisms, such as biodegradation, volatilization, and adsorption on additional organic matter must be considered.

4 Conclusions

Up until recently, many BMPs were designed employing sedimentation and filtration mechanisms to treat particulates and other constituents in runoff including heavy metals. The current research on the fractionation of heavy metals at the runoff and discharge of a stormwater treatment system provided insight on the actual efficiency of the system in the immobilization and reduction of heavy metals in runoff. The major findings were enumerated as follows: (1) The partitioning of heavy metal load in runoff in either dissolved or particulate-bound phases were influenced by both flow rate and TSS load, and evident in high-intensity storm (rainfall-runoff event). Yet, the distinct characteristics of heavy metal elements (i.e., existence in dissolved or particulate-bound) remain unchanged regardless of flow rate and TSS. (2) The partitioning of heavy metal load discharge from the stormwater system was more apparent during the early period of discharge having higher variability in dissolved than particulate-bound heavy metal. (3) After passing the treatment system, the geometric mean mass fraction ratio of heavy metals was increased (except Fe which was predominately particulate-bound) denoting a significant reduction in the particulate-bound heavy metals regardless of whether the heavy metal in runoff was predominately dissolved or particulate-bound. (4) Unlike in runoff where positive and some satisfactory correlations existed between the dissolved and particulate-bound, no significant correlation was found at the discharge.
It was therefore concluded that fractionation of heavy metals clearly played an important role in the performance of a stormwater treatment system. In designing stormwater system targeting heavy metals, it is recommended that the system should be capable of treating not only the early period of a storm (first flush criteria) rather from the initial runoff until the peak part of the hydrograph (high flow rate where partitioning was greatest) from a load basis. Research is underway to investigate the sorption capacity of the filter media to improve the reduction of the dissolved heavy metals as well as its design life, operation and maintenance considerations.

Acknowledgment

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References


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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 50-150</td>
<td>0.14</td>
<td>4.90</td>
<td>0.15</td>
<td>0.16</td>
<td>0.34</td>
<td>0.12</td>
<td>0.14</td>
<td>7.33</td>
<td>4.23</td>
<td>2.82</td>
<td>1.94</td>
<td>0.87</td>
<td>1.44</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.08)</td>
<td>(0.17)</td>
<td>(0.07)</td>
<td>(0.09)</td>
<td>(0.11)</td>
<td>(0.07)</td>
<td>(0.06)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 &gt;150</td>
<td>0.17</td>
<td>10.14</td>
<td>0.14</td>
<td>0.17</td>
<td>0.62</td>
<td>0.15</td>
<td>0.25</td>
<td>7.27</td>
<td>5.00</td>
<td>3.31</td>
<td>2.74</td>
<td>1.30</td>
<td>1.25</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.10)</td>
<td>(0.21)</td>
<td>(0.10)</td>
<td>(0.12)</td>
<td>(0.15)</td>
<td>(0.10)</td>
<td>(0.08)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>no discharge</td>
<td>4.71</td>
<td>2.50</td>
<td>3.07</td>
<td>1.14</td>
<td>-</td>
<td>0.32</td>
<td>-</td>
<td>0.27</td>
<td>-</td>
<td>0.82</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

N: number of storm events; ADD: antecedent dry day; HRT: hydraulic retention time; Values denote to total heavy metal event mean concentration and values in parentheses denote to heavy metal event mean concentration in dissolved form; refer to mean values
Table 2 Geometric mean mass fraction ratio of heavy metal constituents, $D/P$ as mg/mg

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Runoff</td>
<td>1.06</td>
<td>0.031</td>
<td>0.94</td>
<td>0.906</td>
<td>0.385</td>
<td>8.89</td>
<td>0.46</td>
</tr>
<tr>
<td>Discharge</td>
<td>3.1</td>
<td>0.1</td>
<td>2.1</td>
<td>2.5</td>
<td>1.1</td>
<td>16.9</td>
<td>1.4a</td>
</tr>
</tbody>
</table>

*statistically significant difference between runoff and discharge, $p = 0.0011$

Table 3 Geometric mean partition coefficient of heavy metal constituents, $K_D$ as l/g

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Runoff</td>
<td>2.7E+03</td>
<td>1.0E+05</td>
<td>3.0E+03</td>
<td>3.2E+03</td>
<td>8.0E+03</td>
<td>3.1E+02</td>
<td>6.9E+03</td>
</tr>
<tr>
<td>Discharge</td>
<td>2.7E+03</td>
<td>9.8E+04a</td>
<td>2.7E+03</td>
<td>4.0E+03</td>
<td>6.8E+03</td>
<td>4.9E+02</td>
<td>6.6E+03a</td>
</tr>
</tbody>
</table>

*statistically significant difference between runoff and discharge, $p < 0.001$

Table 4 Correlations ($R^2$) between dissolved and particulate-bound heavy metal load

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Runoff</td>
<td>0.87</td>
<td>0.95a</td>
<td>0.44</td>
<td>0.77</td>
<td>0.98a</td>
<td>0.01</td>
<td>0.87</td>
</tr>
<tr>
<td>Discharge</td>
<td>0.38</td>
<td>0.49</td>
<td>0.23</td>
<td>0.16</td>
<td>0.43</td>
<td>0.08</td>
<td>0.87</td>
</tr>
</tbody>
</table>

*statistically significant, $p < 0.001$
List of figures

Fig. 1 Site location and description of the stormwater treatment system.
Fig. 2 Dissolved and particulate-bound mass fraction of heavy metals, flow rate and TSS load at runoff and discharge during the course of a storm event on July 2, 2010 (rainfall depth = 29 mm, HRT = 1.28 hr).
Fig. 3 Average (mean±standard deviation) particulate-bound (PME) and dissolved (DME) load ratio ($N = 24$ storm events).