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Adsorption of heavy metals by road deposited solids

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Abstract: The research study discussed in the paper investigated the adsorption/desorption behaviour of heavy metals commonly deposited on urban road surfaces, namely, Zn, Cu, Cr and Pb for different particle size ranges of solids. The study outcomes, based on field studies and batch experiments confirmed that road deposited solids particles contain a significantly high amount of vacant charge sites with the potential to adsorb additional heavy metals. Kinetic study and adsorption experiments indicated that Cr is the most preferred metal element to associate with solids due to the relatively high electro negativity and high charge density of trivalent cation (Cr^{3+}). However, the relatively low availability of Cr in the urban road environment could influence this behaviour. Comparing total adsorbed metals present in solids particles, it was found that Zn has the highest capacity for adsorption to solids. Desorption experiments confirmed that a low concentration of Cu, Cr and Pb in solids was present in water-soluble and exchangeable form, whilst a significant fraction of adsorbed Zn has a high likelihood of being released back into solution. Among heavy metals, Zn is considered to be the most commonly available metal among road surface pollutants.

Keywords: Adsorption; Desorption; Heavy metals; Road deposited solids; Urban water quality; Water pollution

INTRODUCTION

Pollutants such as heavy metals attached to solids transported by stormwater play a significant role in the degradation of receiving water environments. It is widely known that road deposited solids contain a high heavy metal load (Herngren et al. 2005). Heavy metals in the aqueous phase create the most significant impact on waterway health (Dean et al. 2005). Additionally, depending on the adsorption mechanisms, desorption of heavy metals and consequent bioavailability can occur during physical processes such as wash-off, settlement and re-suspension and during the chemical degradation of solids over time in stormwater treatment devices (Dean et al. 2005). Leaching of heavy metals is an important issue in urban stormwater management (Morrison et al. 1988).

Adsorption occurs due to mechanisms such as cation exchange and chemisorption, which depends primarily on particulate physical and chemical composition. Characteristics of the heavy metals such as ion radii, valency and susceptibility to hydration also exert a significant influence on adsorption mechanisms. Cation exchange occurs as a result of electrostatic forces between cations and the permanent charge sites of the solids particles (clay minerals) (McBride 1994). Heavy metals which undergo cation exchange have the potential to desorb and become bioavailable due to their easily reversible bonds (Polcaro et al. 2003; Weber et al. 1991). Chemisorption occurs as a result of reaction between surface functional groups in solids and cations in the surrounding solution. It forms a strong bond between heavy metal elements and solids (Weber et al. 1991).

Based on in-depth research, this paper provides an in-depth understanding of the adsorption behaviour of heavy metals associated with road deposited solids. Correlation of heavy metal elements with physical and chemical properties of solids particles were used to characterise the adsorption behaviour. Consequently a series of batch adsorption/desorption experiments were carried out to validate the outcomes from the analysis of field samples. Four heavy metals, namely, Zn, Cu, Pb and Cr were investigated due to their predominance in road deposited solids. An in-depth understanding of adsorption processes provides essential information on the mobility and

bioavailability of heavy metals in urban stormwater runoff (Morrison et al. 1988). This in turn will contribute to strengthening strategies to mitigate the impacts on receiving water environments from stormwater pollutants.

MATERIALS AND METHODS

Study site selection and sampling

Based on the hypothesis that heavy metal adsorption depends on the mineral, physical and chemical properties of solids particles, road surfaces were selected as study sites to encompass variations in particle composition and pollutant concentrations. Consequently, samples were collected from 16 urban road surfaces in four suburbs, namely, Surface Paradise, Benowa, Nerang and Clearview Estate, with varying soil profiles from the inland to the coast, along the Nerang River in the Gold Coast region in Southeast Queensland, Australia (Figure 1). The study sites were located in different land uses with a range of traffic densities. Research literature has clearly identified the key role played by vehicular traffic in the road deposition of heavy metals (Mahbub et al. 2010).

Altogether 32 road deposited solids (pollutant build-up) samples were collected from the 16 road surfaces representing two different antecedent dry periods. This allowed consideration of the variations in the characteristics of build-up solids with the antecedent dry period (Egodawatta and Goonetilleke 2006). The solids samples were collected using a dry and wet vacuuming system (previously confirmed to have 90% collection efficiency) from 3 m² plots in the selected road surfaces (Gunawardana et al. 2012a).

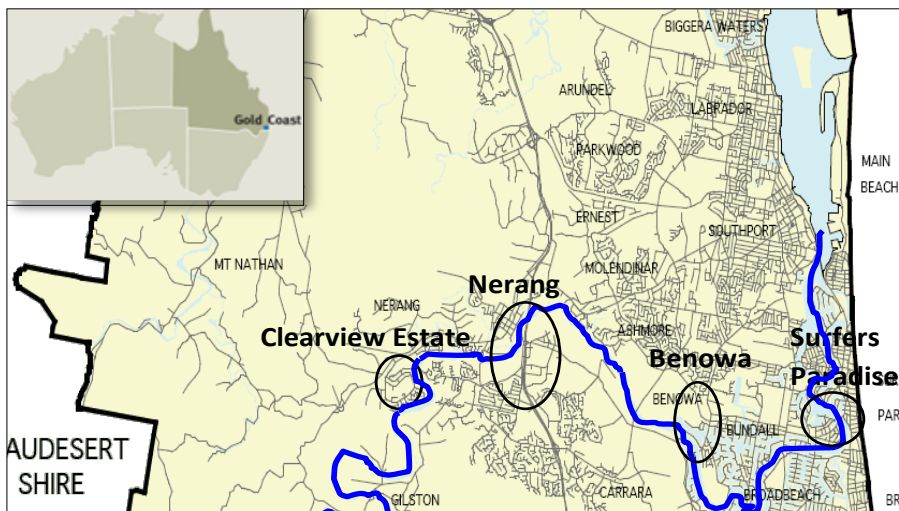


Figure 1 Locations of study sites

Sample preparation

The collected solids samples were separated into four particle size ranges; <75 μm , 75-150 μm , 150-300 μm , and 300-425 μm by wet sieving. Particles <75 μm contained settleable fine particles up to 1 μm size, which were extracted by gravity settling in an Imhoff Cone. Particles <1 μm size could be considered as the dissolved fraction in stormwater runoff. Each particle size range was separately analysed for specific surface area (SSA), total organic carbon (TOC), effective cation exchange capacity (ECEC), soil mineralogical constituents and metal species, namely, Fe, Al, Mn, Zn, Cu, Pb, Ni, Cr and Cd. The soil mineralogical constituents analysed were, quartz, albite, microcline, chlorite, muscovite and amorphous content.

Laboratory batch adsorption/desorption experiments

A series of batch adsorption/desorption experiments were carried out to validate the outcomes from the analysis of field samples. Among the nine metal species investigated, it was hypothesised that Al, Fe and Mn would mostly originate from soil sources (Gunawardana et al. 2012b). From the remaining metal elements, Zn, Cu, Pb and Cr were selected for the experiment because of their high occurrence in the urban environment compared to Ni and Cd. Based on the preliminary heavy metal analysis of field samples, three particle size ranges listed in Table 2 were selected for the batch study (as explained in the Results and Discussion in relation to Fig. 2). Two sets of solids samples were selected from each particle size range, which provided a good representation of the solids' physical and chemical properties. The average values obtained are given in Table 1.

Table 1 Average physical and chemical properties of solids particles used for the batch adsorption/desorption experiments

Particle size (μm)	SSA (m^2/g)	TOC (mg/g)	ECEC ($\text{meq}/100\text{g}$)	Amorp. (%)	Quartz (%)	Albite (%)	Microcline (%)	Chlorite (%)	Muscovite (%)
<75	18.8	0.86	4.89	37.1	37.8	12.5	4.00	2.75	5.95
75-150	9.50	0.25	15.0	19.6	53.6	12.5	6.00	2.80	5.55
150-425	3.79	0.25	7.495	20.7	63.6	8.7	2.10	2.90	2.20

Kinetic study

A kinetic study was carried out to determine the time required to reach equilibrium between the metal solution and solids (adsorbent). The experiments were undertaken using a homogeneous mixture of 10 g solids (oven dried at 50°C for 24 hours) containing equal proportions of each particle size range and equilibrated with Zn, Cu, Pb and Cr solutions (0.1 mmol/L), individually, under controlled temperature (20±0.1°C) and pH (6.5), with appropriate quality control measures. 5 mL of aqueous metal solution was collected at 2 hr intervals in the initial 6 hrs, then at 6 hr intervals up to 1½ days and, finally, at 12 hr intervals until the end of the 3 days. The samples collected were diluted with deionised water to 15 mL. The filtered samples were analysed according to US EPA Method 200.8 (US EPA 1994), using an ICP-MS. Based on the results (as discussed in the Results and Discussion), it was decided to maintain a 24 hour equilibrium time period for the metal adsorption experiment.

Adsorption experiment

Adsorption experiments were undertaken to investigate the total capacity available in solids particles to adsorb heavy metals. The equilibrium state batch adsorption study was carried out for single metal (0.1 mmol/L) adsorption in a homogeneous 1 g of solids sample. Each particle size was stirred in a polyethylene test tube for 24 hours, with 40 mL of metal solution and 0.1 M NaNO₃ as the supporting electrolyte to keep the ionic strength constant in the solution. The filtrate was acidified with HNO₃, and analysed according to US EPA Method 200.8 (US EPA 1994) for soluble metal ion concentration (C_i mg/L) using ICP-MS. Control samples and blanks were also tested as a standard QA procedure.

The amount of metal ions adsorbed (adsorption capacity) at equilibrium condition was obtained using the equation given below. Background metal load (q_b , mg/g) in the samples had been measured previously.

$$q_T = q_b + \frac{V}{w} [C_0 - C_i] \quad \text{Equation 1}$$

Where, q_T - equilibrium adsorption capacity (mg/g); C_0 - initial metal concentration (mg/L); C_i - equilibrium metal concentration (mg/L); V - volume (L); w - weight of adsorbent (g).

Desorption experiment (metal extraction)

Samples from the batch adsorption experiment were centrifuged for 15 min at 1500 rpm and the suspension was removed. The solids were washed with ethanol to remove any metal solution trapped in solids, and oven dried at 40°C to evaporate ethanol (Polcaro et al. 2003). The dried solids were treated with 40 mL of 0.5 M $\text{Mg}(\text{NO}_3)_2$ and stirred (24 hour) until a new equilibrium state was achieved between Mg^{2+} ions and the heavy metal elements, after adjusting for pH (6.5) with the addition of NaOH or HNO_3 . The equilibrium solution was filtered and analysed for the desorbed metal ion concentration (C_{ex} mg/L), using ICP-MS. Final solids weight was also measured to determine if there were any loss during the experiment.

The amount of heavy metals adsorbed to solids (q_{ex}) by ion exchange was determined as the amount of heavy metals released during the desorption experiment, using the following equation:

$$q_{\text{ex}} = \frac{C_{\text{ex}} V}{w} \quad \text{Equation 2}$$

Where q_{ex} – heavy metals adsorbed by ion exchange (mg/g); C_{ex} - desorbed metal ion concentration (mg/L); w - weight of adsorbent after desorption experiment (g).

Data analysis

Principal Component Analysis (PCA), which is a multivariate analytical technique frequently applied in the analysis of environmental data (Goonetilleke et al. 2009) was used to investigate the relationships among the large data set generated. The PCA technique is used to transform the original variables to a new orthogonal set of Principal Components (PCs) such that the first PC contains most of the data variance and the second PC contains the second largest variance and so on. Objects (in this case the four particle size fractions) that exhibited similar variances for the analysed variables have similar PCA scores forming a cluster when plotted on a biplot. Additionally, strongly correlated variables have the same magnitude and orientation of vectors when plotted, whereas vectors representing uncorrelated variables are orthogonal to each other. Detailed descriptions of PCA can be found elsewhere (Adams 1995; Massart et al. 1988).

RESULTS AND DISCUSSION

Analysis of field samples

To investigate the adsorption behaviour of heavy metals, PCA was undertaken for the four different particle size ranges as shown in Figure 2. A total of 128 samples (four size ranges \times 32 samples) derived as part of the research study represented the objects. Variables considered in the analysis were physical and chemical parameters including TOC, SSA, TSS, mineralogical constituents (quartz, albite, microcline, chlorite, muscovite and amorphous) and the nine heavy metal elements. The PCA analysis of the data matrix resulted in most of the data variance explained by the first three principal components according to the scree plot method (Cattell 1966). Figure 2(a) shows the PC 1 vs PC 2 biplot while Figure 2(b) shows the PC 1 vs PC 3 biplot.

As evident in Figure 2(a), finer particle size range of $< 75 \mu\text{m}$ and $75\text{--}150 \mu\text{m}$ show separate clusters, whereas the $150\text{--}300 \mu\text{m}$ and $300\text{--}425 \mu\text{m}$ clusters overlay on each other due to similarity in their physical and chemical characteristics. As such, for further study, $150\text{--}300 \mu\text{m}$ and $300\text{--}425 \mu\text{m}$ particle sizes were combined. In both Figure 2(a) and (b), metals of geochemical origin (Fe, Al

and Mn) are strongly correlated. Fe, Al and Mn in soil are typically present as an oxide or hydroxide coating on clay minerals or complex with organic matter and act as a binding agent for other metal elements (McBride 1994). In Figure 2(a) Zn, Cu, Pb and Ni are strongly correlated to the metals elements of geochemical origin, and are not correlated to ECEC. This suggests that the adsorption of Zn, Cu, Pb and Ni to metal oxide occur by mechanisms other than cation exchange.

Although Figure 2(a) shows no correlation of heavy metal elements with TOC, SSA, TSS and mineralogical constituents, in Figure 2(b), metal elements show good affinity to the mineralogical constituents. Among the metal elements, Zn has good correlation with albite and ECEC. This suggests that Zn is associated with albite due to cation exchange.

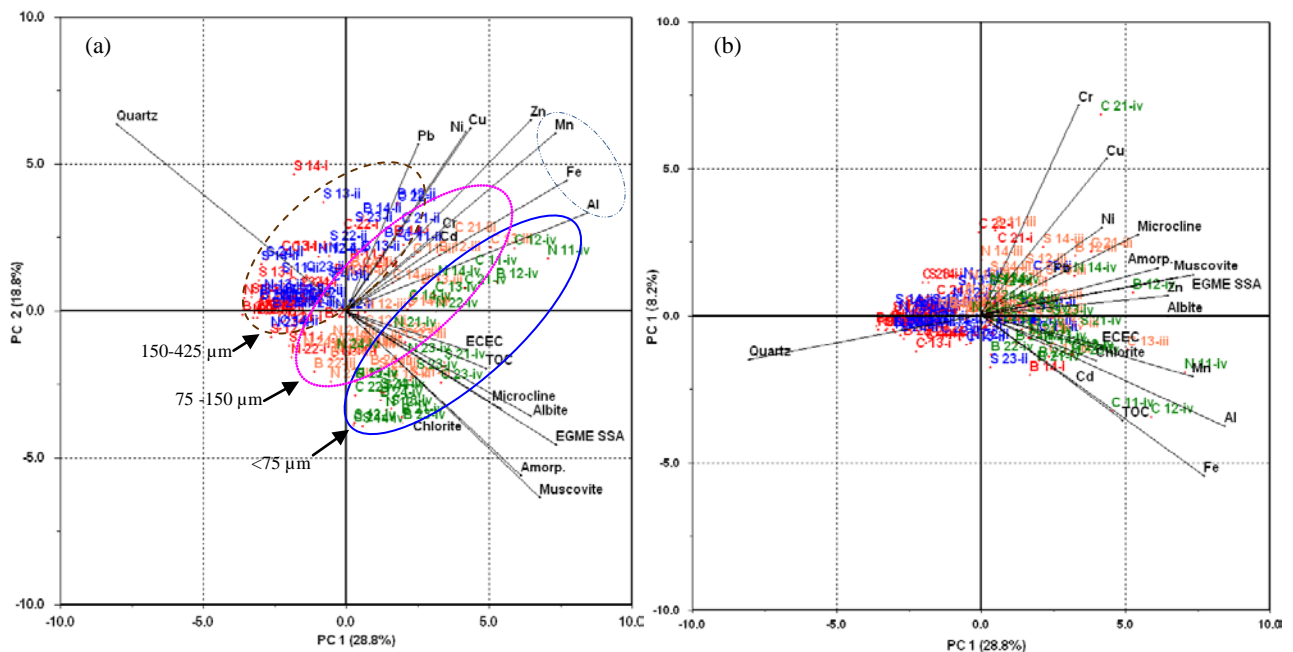


Figure 2 PCA biplot of all sites for finer particle size ranges: (a) PC 1 vs PC 2 biplot, (b) PC 1 vs PC 3 biplot; C: Clearview Estate, N: Nerang, B: Benowa, S: Surfers Paradise, 1 and 2 represents first and second sampling events; i: 300–425 μm, ii: 150–300 μm, iii: 75–150 μm, iv: < 75 μm

Based on the preliminary analysis, heavy metal adsorption characteristics at naturally occurring metal concentrations were identified. This analysis represented only the adsorption characteristics of heavy metals that were present at the site at the time of sample collection and as evident from the results of the adsorption experiments undertaken, represented the situation where only a part of the available adsorption sites in solids particles were occupied by heavy metals. Therefore, in order to develop an in-depth understanding of the heavy metal adsorption characteristics of solids particles, it was considered necessary to ensure that all of the adsorption sites are occupied by metal ions.

Analysis of laboratory experiments

Kinetic study

Results of the kinetic study carried out over a 3-day period shown in Figure 3 illustrate the variation in adsorbed metal concentrations (mmol/kg) with time. For all metals, the rate of adsorption is relatively rapid in the first 2-4 hours because of the high availability of adsorption sites in the solids particles. The maximum percentage adsorption was achieved within 24 hours, with all metal elements reaching an equilibrium state, confirming previous research studies (Elliot et al. 1986;

Polcaro et al. 2003). It was found that after a 24 hour period, more than 5% of the initial metal concentration remained in the supernatant confirming that there was sufficient metal solution available to achieve equilibrium with 0.1 mmol/L (of initial metal concentration).

Adsorption of heavy metals to road deposited solids

Considerably higher amount of metal content was adsorbed by the solids particles during the batch adsorption experiment compared to the pre-existing metal concentration (Table 2). On average, the $(q_{0-i} / q_T)\%$ values in Table 2 show that 98% Cr, 75% Cu, 68% Zn and 83% Pb were adsorbed to solids particles. This indicates that under natural conditions, road surface solids contain a significant amount of vacant charge sites. The adsorbed metal concentration with particle size confirms that adsorption decreases with the increase in particle size. This is attributed to the fact that relatively higher amount of adsorption sites are offered by fine particles when compared to coarse particles due to relatively high SSA, TOC and ECEC (Table 1).

Table 2 Adsorbed Cr, Cu, Zn and Pb concentrations (q_{0-i}), total adsorbed metal concentration (q_T) and adsorption as a percentage of total adsorbed metal concentration ($(q_{0-i} / q_T)\%$)

Particle size (μm)	Cr	Cu	Zn	Pb	Cr	Cu	Zn	Pb	Cr	Cu	Zn	Pb
	$(q_{0-i} / q_T)\%$				(q_{0-i}) mmol/kg				(q_T) mmol/kg			
<75	100	83.7	66.9	91.5	3.91	3.65	3.19	2.84	3.910	4.395	4.78	3.12
75-150	99.8	82.5	67.3	93.2	3.69	3.65	3.26	2.74	3.695	4.545	5.00	2.96
150-425	96.2	68.0	67.4	72.5	3.24	3.19	2.61	2.42	3.345	4.67	3.78	3.41

However, the differences in adsorbed metal concentrations for the three particle size ranges are comparatively low especially for particles <150 μm . This suggests that coarse particles have adsorbed metal ions, same as the fine particles. The low differences in metal concentrations for different particle sizes could be attributed to the high metal concentrations that were present in the metal solutions under the experimental conditions, which would have led to the creation of weak bonds with amorphous material and quartz. For example, as shown by past researchers, rubber (originating from tyre wear) can absorb metals under certain circumstances (Rowley et al. 1984)

Cr is the highest adsorbed metal element in most samples and, in the majority of samples, metal adsorption affinity (order of selectivity) increased in the order of $\text{Zn} < \text{Cu} < \text{Pb} < \text{Cr}$. This generally supports the selectivity found in the equilibrium state batch results shown in Figure 3. A similar selectivity sequence has been observed by past researchers in relation to soil samples for bivalent and trivalent cations (Aualiitia and Pickering 1986). This indicates that Cr is the most preferred metal element associated with road deposited solids. Cr^{3+} is a trivalent cation which has relatively high electro negativity and high charge density. This is attributed to be the primary reason for its high affinity to solids. However, the amount of Cr adsorption would vary, depending on its availability in the urban road environment.

Desorption of heavy metals in road deposited solids

The desorbed metal concentrations from solids particles are given in Table 3. According to Table 3, the percentages of desorbed heavy metals (amount of exchangeable or easily removable metal content) with respect to total adsorbed heavy metal content are significantly low. Particularly, desorbed Cr and Cu from solids samples are negligible. Among the metal elements, Zn desorption (50.5%) is predominantly high compared to Cr, Cu and Pb. This suggests that a higher percentage of Zn is present in exchangeable form in solids particles. Similar conclusions have been drawn by

Biddappad et al. (1981) who noted that Zn is present in soils in predominantly water soluble or exchangeable form.

As noted by Liu et al. (2009), the weak bonding of Zn compared to Cr and Cu is attributed to the electron configuration of Zn^{2+} [$3d^{10} 4s^0$] compared to Cr^{3+} [$3d^3 4s^0$] and Cu^{2+} [$3d^9 4s^0$]. According to the electron configuration, the outer orbital of Zn^{2+} is full [$3d^{10}$] and there is no empty orbital to form a strong bond with surface functional groups. However, for Cr^{3+} [$3d^3$] and Cu^{2+} [$3d^9$], the outer orbital has empty spaces (which can be filled up to [$3d^{10}$]). Transient metals (as identified in the Periodic Table) such as Zn, Cr and Cu with small ionic radii and empty orbital easily complex with surface functional groups (Gunawardana et al. 2012a). Therefore, Zn forms weak bonds with charge sites compared to the other transient metal elements. Zn being the highest available metal element in road deposited solids, its bioavailability can create a significant impact on receiving water environments. Therefore, providing effective measures for Zn removal is important for protecting receiving water environments.

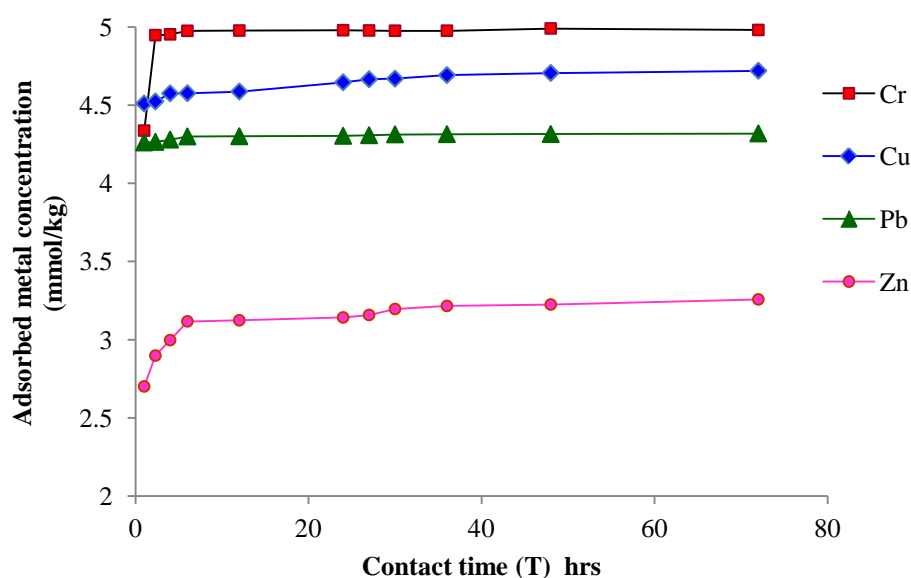


Figure 3 Variation in metal concentrations with time

Table 3 Desorbed Cr, Cu, Zn and Pb concentrations (q_{ex}) and desorption as a percentage of total adsorbed metal content ($(q_{ex}/q_T)\%$)

Particle size (μm)	Cr	Cu	Zn	Pb	Cr	Cu	Zn	Pb
	$(q_{ex}/q_T)\%$				(q_{ex}) mmol/kg			
<75	0.065	0.005	26.35	0.605	0.003	0.001	1.225	0.018
75-150	0.075	1.020	53.95	2.525	0.003	0.039	2.320	0.069
150-425	0.145	1.300	47.05	20.85	0.004	0.058	1.680	0.718

In contrast, the desorption process only removed <1.2% of adsorbed Pb, which suggested that a predominant fraction of Pb is associated with solids particles by much stronger bonding such as chemisorption. Also, Pb precipitation could also occur since its hydroxide formation is common at pH 7 (Markiewicz-Patkowska et al. 2005). Since throughout the experiment, as the pH was maintained at 6.5, precipitated Pb would have also contributed to the portion that desorbed from

solids. Hence, it can be concluded that the bioavailability of Pb in receiving water environments would be relatively low if conditions do not change.

Similarly, it can be concluded that, Cu and Cr is adsorbed to solids by chemisorption. This is based on the very low desorption of Cu (1.2%) and Cr (0.1%) from solids samples. This further suggests that at neutral pH levels, Cr and Cu mobility and bioavailability would be very low. Cr is a trivalent cation, which has a high electro negativity (hard acid) compared to the other metal elements. Therefore, Cr can compete with other metal elements for complexation sites and primarily forms strong bonds of chemisorption with solids particles (Gunawardana et al. 2012a). Cr association with solids particles through cation exchange is expected to be very low. This agrees with the findings of Covelo et al. (2007) who noted near-zero concentration of extractable Cr in batch adsorption studies using soil samples.

Furthermore, it was found that desorption increases with the increase in particle size (Table 3). For example, it can be seen that a high amount of Zn and Pb are desorbed from coarse particles (>75 μm) than from fine particle sizes. This is attributed to the creation of strong bonds between metal elements and fine particles (<75 μm) compared to the coarse particles due to the presence of a relatively higher internal surface area and preferred binding sites for chemisorption such as organic matter and metal oxides coating (Gunawardana et al. 2012a). Additionally, <75 μm particles contain clay minerals such as illite, mica and smectite (Gunawardana et al. 2012b). Heavy metal cations can be adsorbed to the interlayer surfaces of these clay minerals and would be more strongly adsorbed to the internal surfaces than the external surface area of the minerals (McBride 1994).

Consequently, it is more likely that at a high contamination level, heavy metals will be released more easily by the coarse particles rather than by the fine particles due to weak bonding with heavy metals (Rybicka et al. 1995). Therefore, the removal of solids particles >150 μm in dry state can help to mitigate heavy metal contamination of receiving waters. However, it should be noted that any changes in pH, ionic strength or dissolved organic carbon content in receiving waters could change the desorption processes observed for the metal elements investigated, for all particle sizes (Weber et al. 1991).

The adsorption mechanisms of Zn and Cr observed during the batch adsorption study and in the field samples were not consistent. This inconsistency in the adsorption mechanism could be attributed to the high amount of Zn and Cr adsorption to solids particles during the batch adsorption study. However, both Cu and Pb showed similar adsorption characteristics for field samples and laboratory study. This suggests that available metal concentration could lead to variations in the adsorption characteristics of metals.

CONCLUSIONS

In this study, heavy metal adsorption behaviour of road deposited solids particles were investigated using field samples and undertaking adsorption/desorption experiments. The following important conclusions were derived:

- Heavy metal elements are rapidly adsorbed to the vacant charge sites available in road deposited solids particles once they interact with the solids surfaces. This indicates that road deposited solids have a high amount of vacant charge sites available to adsorb metal ions. Therefore, it can be concluded that these solids may act as an adsorbent of any excess heavy metals present in stormwater treatment facilities.

- Zn is the heavy metal most susceptible to bioavailability due to relatively easy desorption from solids in stormwater runoff. This needs to be viewed in the context of Zn being a toxic metal which is commonly present in road deposited solids. As such, Zn can exert a significant impact on receiving water quality. Solids removal in a dry state and/or effective source control of Zn are possible mitigation options.
- Due to low likelihood of desorption of particulate Cu, Pb and Cr from coarse and fine particles in stormwater runoff, solids removal using appropriate strategies is a possible mitigation option.
- The adsorption capacity of coarse particles (>150 μm) is relatively low compared to fine particles and at high metal concentrations there is an appreciable potential for the release of adsorbed heavy metals from coarse particles. Thus, dry removal is feasible for reducing the potential for the bioavailability of heavy metal elements from coarse particles.

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