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Adsorption and mobility of metals in build-up on road surfaces

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Adsorption and mobility of metals in build-up solids on road surfaces

Abstract:

The study investigated the adsorption and bioavailability characteristics of traffic generated metals common to urban land uses, in road deposited solids particles. To validate the outcomes derived from the analysis of field samples, adsorption and desorption experiments were undertaken. The analysis of field samples revealed that metals are selectively adsorbed to different charge sites on solids. Zinc, copper, lead and nickel are adsorbed preferentially to oxides of manganese, iron and aluminium. Lead is adsorbed to organic matter through chemisorption. Cadmium and chromium form weak bonding through cation exchange with most of the particle sizes. Adsorption and desorption experiments revealed that at high metal concentrations, chromium, copper and lead form relatively strong bonds with solids particles while zinc is adsorbed through cation exchange with high likelihood of being released back into solution. Outcomes from this study provide specific guidance for the removal of metals from stormwater based on solids removal.

Key words: Desorption, Traffic generated metals, Stormwater quality, Stormwater pollutant processes

1. Introduction

The various anthropogenic activities common to the urban environment contribute a diversity of toxic pollutants including metals to stormwater runoff. Metals present in urban stormwater are transported primarily adsorbed to solids (Herngren et al., 2006). As a result, certain metal concentrations are much higher in solids compared to the soluble concentration (Lau and Stenstrom, 2005). However, metals adsorbed to solids can potentially desorb and become bioavailable by chemical changes in solution. Therefore, the toxicity and mobility of metals discharged to receiving water bodies are a challenging issue in stormwater management (Morrison et al., 1988). While treatment facilities are commonly designed to remove solids from stormwater, their effectiveness can be limited by the mobility of pollutants associated with solids particles.

The mobility and partition of metals between particulate and dissolved fractions in stormwater primarily depends on the adsorption mechanism with solids particles. However, detailed knowledge explaining how metals are attached to particles are limited (Lau and Stenstrom, 2005; Murakami et al., 2008). The mechanisms by which metals may be adsorbed to particles include cation exchange (outer-sphere complexation), chemisorption (inner-sphere surface complexation) and precipitation (Weber et al., 1991). These adsorption mechanism primarily depends on metal species and surface charge characteristics of solids particles (Weber et al., 1991).

Surface charge sites on solids include permanent charge sites (eg. isomorphic substitution of ions in the lattice structure of the minerals) and surface functional groups (pH dependent charge sites in organic matter, metal oxides and edge sites of clay minerals) (Weber et al., 1991; McBride, 1994). Presence of these sites primarily depends on the physical and chemical characteristics of particles (Bradl, 2004; Gunawardana et al., 2013).

The focus of this study was to characterise the metal adsorption behaviour of road deposited solids particles in order to develop an in-depth understanding of their retention and mobility and thereby, the bioavailability characteristics of particulate metals. The innovative approach adopted was underpinned by developing an in-depth understanding of the properties of solids

particles which influence the complex interactions between solids and metal elements. The correlations between metals adsorbed road deposited solids and the physical and chemical properties of these solids particles were evaluated in order to characterise the adsorption mechanisms. The study created fundamental knowledge in relation to metals adsorption by solids particles. The outcome of this study will provide guidance for mitigating metal pollution in receiving water bodies.

2. Materials and Methods

2.1 The Study Sites

The study sites were selected from the Gold Coast, which is one of Australia’s rapidly developing urban regions. The soils in the region constitute Dermosols (known as Red and Yellow Podzolic) and Kurosols which are mainly derived from the Neranleigh–Fernvale meta sediments and clayey sub-soils (Isbell, 1996). Variation in soil characteristics was considered as the main criteria in study site selection. Consequently, four suburbs with different soil profiles along a 12.5 km traverse were identified stretching from inland to the coastline along the Nerang River (Fig. 1). A total of sixteen road surfaces with varying levels of traffic densities and land uses were selected, representing four road sites from each suburb.

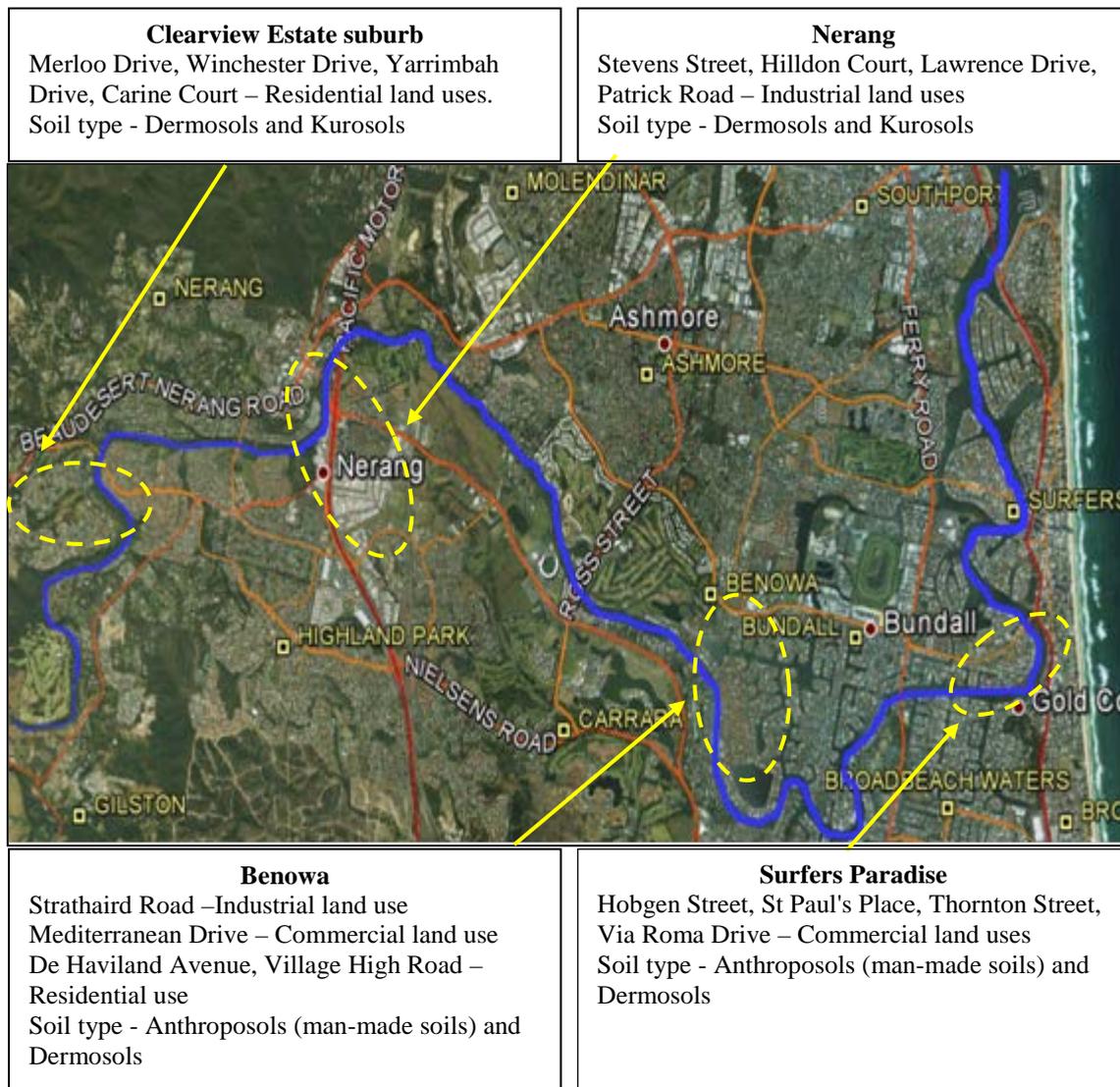


Fig. 1. Location of study sites

2.2 Build-Up Sample Collection

Pollutant build-up samples were collected using a dry and wet vacuuming system (with 90% collection efficiency) from 3 m² plots from each road surface (Gunawardana et al., 2012a). As pollutant build-up rate is rapid within the first seven to eight days and tend to asymptote to an almost constant value thereafter, two samples were collected from each site representing two different antecedent dry periods of less than and greater than eight days (Egodawatta and Goonetilleke, 2007).

2.3 Laboratory Analysis

The collected build-up samples were separated into particle size ranges; <75 µm, 75-150 µm, 150-300 µm and 300-425 µm by wet sieving and the particulates were analysed for the parameters listed in Table 1. These parameters are considered to be the most significant in influencing metal adsorption to particulates. The metal species selected for analysis (Fe, Al, Pb, Zn, Cd, Cr, Mn, Ni, Cu) are commonly present in the urban environment as identified in research literature (Herngren et al., 2006). Standard quality control procedures were followed to maintain accuracy and reliability of the laboratory analysis.

Table 1. Parameters and test methods

Parameter	Test method	Comments
Metals (Fe, Al, Pb, Zn, Cd, Cr, Mn, Ni, Cu)	ICP-MS, Method 200.8 (US EPA, 1994)	Nitric acid (HNO ₃) digestion
Mineralogy	X-ray diffraction (Brindley and Brown, 1984)	Powdered solid particles for mineralogy and orientated samples for clay minerals present in low proportions analysed using PANalytical X'Pert PRO Multi-purpose diffractometer
Specific surface area (EGME SSA)	Ethylene glycol monoethyl ether (EGME) (Carter et al., 1986)	EGME forms monolayer coverage, vacuumed under high pressure
Total organic carbon (TOC)	Method 5310C (APHA, 2005)	Shimadzu TOC-5000A Total Organic Carbon analyser
Exchangeable cations (Ca ²⁺ , Na ⁺ , Mg ²⁺ , K ⁺ and Al ³⁺)	Method 15A1 (Rayment and Higginson, 1992)	Effective cation exchange capacity (ECEC) calculated by the summation of Ca ²⁺ , Al ³⁺ , Mg ²⁺ , Na ⁺ and K ⁺

2.4 Batch adsorption and desorption experiments

In nature, only a fraction of the available adsorption sites in solid particles are occupied by heavy metals. Therefore, in order to validate the adsorption mechanisms identified in the preliminary analysis of field samples, it was necessary to undertake further studies with all of the adsorption sites being occupied by metal elements. For this purpose, single metal batch adsorption and desorption experiments were undertaken, providing particular attention to the

cation exchangeable heavy metal adsorption process, as it is considered to be the dominant mechanism of adsorption.

Among the nine metal elements analysed, 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 batch experiments as these originate primarily from anthropogenic sources such as tyre and pavement wear and vehicle emissions (Herngren et al., 2006). Due to the toxicity and abundance of these species compared to the other metal elements in the environment, understanding their mobility can contribute to environmental best practice particularly in urban areas. A total of six samples consisting of two samples per each size range were used. Since the 150-300 μm and 300-425 μm sizes indicated similarities in physical and chemical properties in the initial analysis undertaken (Gunawardana et al., 2012a; Gunawardana et al., 2013), these two particle size fractions were combined.

Based on an equilibrium time batch experiment (Kinetic study), the time necessary to reach equilibrium between metal solution and the solids was found to be 24 h (Gunawardana et al., 2013). The batch adsorption study was carried out for single metal adsorption (0.1 mM) of Zn, Cu, Pb and Cr at pH 6.5. Solids particles (1 g) were suspended in 40 mL of metal solution and stirred in a polyethylene test tube for 24 h with 0.1 M NaNO_3 as the supporting electrolyte to keep the ionic strength constant in the solution. The metal concentrations in the filtrate ($C_i \text{ mg L}^{-1}$) were quantified using ICP MS. Each test was performed in triplicate. To determine the migration of heavy metals from the solids surface to the solution, control samples were simultaneously run by agitating the solids (1 g) with deionised water at pH 6.5.

The total metal concentration adsorbed (q_T , mmol kg^{-1}) by the solids particles (adsorption capacity) at the end of the batch experiment was obtained using the equation given below.

$$q_T = q_b + \frac{V}{W} [C_o - C_i]$$

Where, q_T - equilibrium adsorption capacity (mg g^{-1}); C_o - initial metal concentration (mg L^{-1}); C_i - equilibrium metal concentration (mg L^{-1}); V - volume (L); w - weight of adsorbent (g). Background metal load (q_b , mg g^{-1}) in the samples had been measured previously.

Metal desorption from solid particles was carried out to study the amount of ion-exchangeable metals. Samples were centrifuged for 15 min at 1500 rpm and the suspension was removed (Young et al., 1987). The solids were washed with ethanol to remove the metal solution trapped, and oven dried at 40 $^\circ\text{C}$ 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 until a new equilibrium state was achieved between Mg^{2+} ions and the metal elements (24 h). The equilibrium solution was filtered through a 0.45 μm filter and analysed for the desorbed metal concentration ($C_{\text{ex}} \text{ mg L}^{-1}$).

The amount of metals adsorbed from solids by ion exchange ($q_{\text{ex}} \text{ mg g}^{-1}$) was determined using the following equation:

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

Where C_{ex} - desorbed metal concentration (mg L^{-1}); w - weight of adsorbent after desorption experiment (g).

2.5 Data Analysis

Analysis of the large data set generated with multiple variables required analytical approaches capable of clustering similar data together whilst identifying relationships between variables. In these circumstances, the application of multivariate analytical techniques has been found to be the most appropriate (Herngren et al., 2006; Settle et al., 2007). In this study, Principal Component Analysis (PCA) and multicriteria decision making method, PROMETHEE and GAIA were used.

PCA is a pattern recognition technique which transforms 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 that exhibit 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 orientation when plotted, whereas uncorrelated variables are orthogonal to each other. Detailed descriptions of PCA can be found elsewhere (Adams, 1995). Data pre-treatment is carried out to reduce 'noise' which interferes with the data analysis (Kokot et al., 1998). Accordingly, the data matrix was column centred and standardised (auto scaled).

PROMETHEE is a non-parametric method used to rank a number of actions based on performance criteria imposed on the data matrix. GAIA method consists of a PCA biplot, which is generated from a matrix formed by the decomposition of the PROMETHEE ranking. The GAIA biplot illustrates a distribution of objects, criteria vectors and decision axis π . An important difference between the application of GAIA and conventional PCA is, its ability to model scenarios based on the choice of individual preference functions for each criterion. The choice of such model specifications will be reflected in the distribution of the criteria vectors of the resulting biplot. This facilitates the testing of different experimental hypotheses, providing the user with options to test different scenarios. PROMETHEE and GAIA methods have been described in detail elsewhere (Keller et al., 1991). The DecisionLab 2000 software was used to perform PROMETHEE and GAIA.

3. Results and discussion

3.1 Physical and chemical parameters

Adsorption of metals to solids particles is primarily dependent on the physical and chemical characteristics of particles listed as in Table 2 (Weber et al., 1991). As evident in Table 2, total organic carbon (TOC), specific surface area (EGME SSA) and effective cation exchange capacity (ECEC) decrease with the increase in particle size. The X-ray diffraction (XRD) analysis showed that the solids particles mainly consists of crystalline quartz (SiO_2), albite ($\text{NaAlSi}_3\text{O}_8$), microcline (KAlSi_3O_8), chlorite ($\text{H}_8\text{Mg}_6\text{O}_{18}\text{Si}_4$) and muscovite ($\text{H}_2\text{KAl}_3(\text{SiO}_4)_3$). Additionally, a significant proportion of amorphous content was detected in all samples, which was identified as traffic related (Gunawardana et al., 2012b). At all the sites, quartz was the dominant mineral, especially in the larger particle size ranges.

3.2 Metal concentrations

It was important to investigate the available heavy metal content in different particle sizes of solids to determine adsorption behaviour. According to Table 3, which gives the mean and standard deviation of the nine metal elements per unit weight of total solids load (mg g^{-1}) for each particle size range, the average metal concentrations decrease with the increase in particle size while about one third of the overall concentration is associated with the particle size range $<75 \mu\text{m}$, with the exception of Cu and Zn. This highlights the fact that particle size has a significant influence on metal adsorption and fine particles have high adsorption

capacity compared to coarse particles. In the majority of the study sites, high Cu and Zn concentrations were associated with the particle size range 75-150 μm . The metal concentration was lowest in the 150-425 μm fraction at all sites, with the exception of Pb, which was highest in the 300-425 μm fraction at Surfers Paradise.

Table 2. Physical and chemical parameters of build-up solids

Parameter	Particle size (μm)			
	<75	75-150	150-300	300-425
EGME SSA ($\text{m}^2 \text{g}^{-1}$)	17.6	9.32	5	2.86
TOC (mg g^{-1})	2.95	0.66	0.57	0.44
ECEC ($\text{meq } 100\text{g}^{-1}$)	9.44	7.46	5.31	4.85
Amorp. (%)	40.6	29.1	18.2	19.1
Quartz (%)	32.7	44	68.4	67.5
Albite (%)	11.5	11.9	6.54	6.34
Microcline	4.83	6.23	2.5	2.65
Chlorite (%)	3.68	2.84	2.04	2.05
Muscovite (%)	6.48	5.51	2.08	2.07

3.3 Influence of physical and chemical properties on heavy metal adsorption

To understand the influence of solids properties on metal adsorption, PCA was carried out. Variables considered in the analysis were the nine metal elements, six mineralogical components and the parameters ECEC, EGME SSA and TOC. Objects represented the 32 samples collected. Particle sizes 150-300 μm and 300-425 μm were combined due to the similarity of their physical and chemical properties (Gunawardana et al., 2013). The resulting biplots for the three particle sizes are shown in Fig. 2.

3.3.1 <75 μm particles

According to Fig. 2(a), (b) and (c), Fe, Al and Mn (geogenic metal elements) are strongly correlated in the three particle sizes. These metals are typically present as metal oxides or hydroxides (surface functional groups) either as a coating on clay minerals or complex with organic matter which act as an adsorbent for other metals (Bradl 2004).

As evident in Fig. 2(a), Fe, Al and Mn show strong correlation with albite and a weak correlation with chlorite. As correlation of Fe, Al and Mn with clay forming minerals are stronger than the correlation with TOC, it can be concluded that a significant proportion of these metals are present as coatings on clay minerals in this particle size range. Strong correlations with Zn, Cu, Pb, Ni and Cr indicates preferential association of these metals with the oxides of Fe, Al and Mn. Similar preferences have also been noted by past researchers (Elliott et al., 1986). However, due to the weak correlation of Fe, Al and Mn with ECEC (Fig. 2(a)), it can be postulated that adsorption of Zn, Cu, Pb, Ni and Cr with the oxides of Fe, Al and Mn predominately occur due to mechanisms other than ion exchange. The reason for this behaviour is attributed to the fact that the metal oxides mainly contain surface functional groups, rather than a permanent charge sites. Therefore, it can be concluded that adsorption to metal oxides would mainly occur by chemisorption (Weber et al., 1991). Chemisorbed metal elements have a less likelihood of being bioavailable due to their strong bonds.

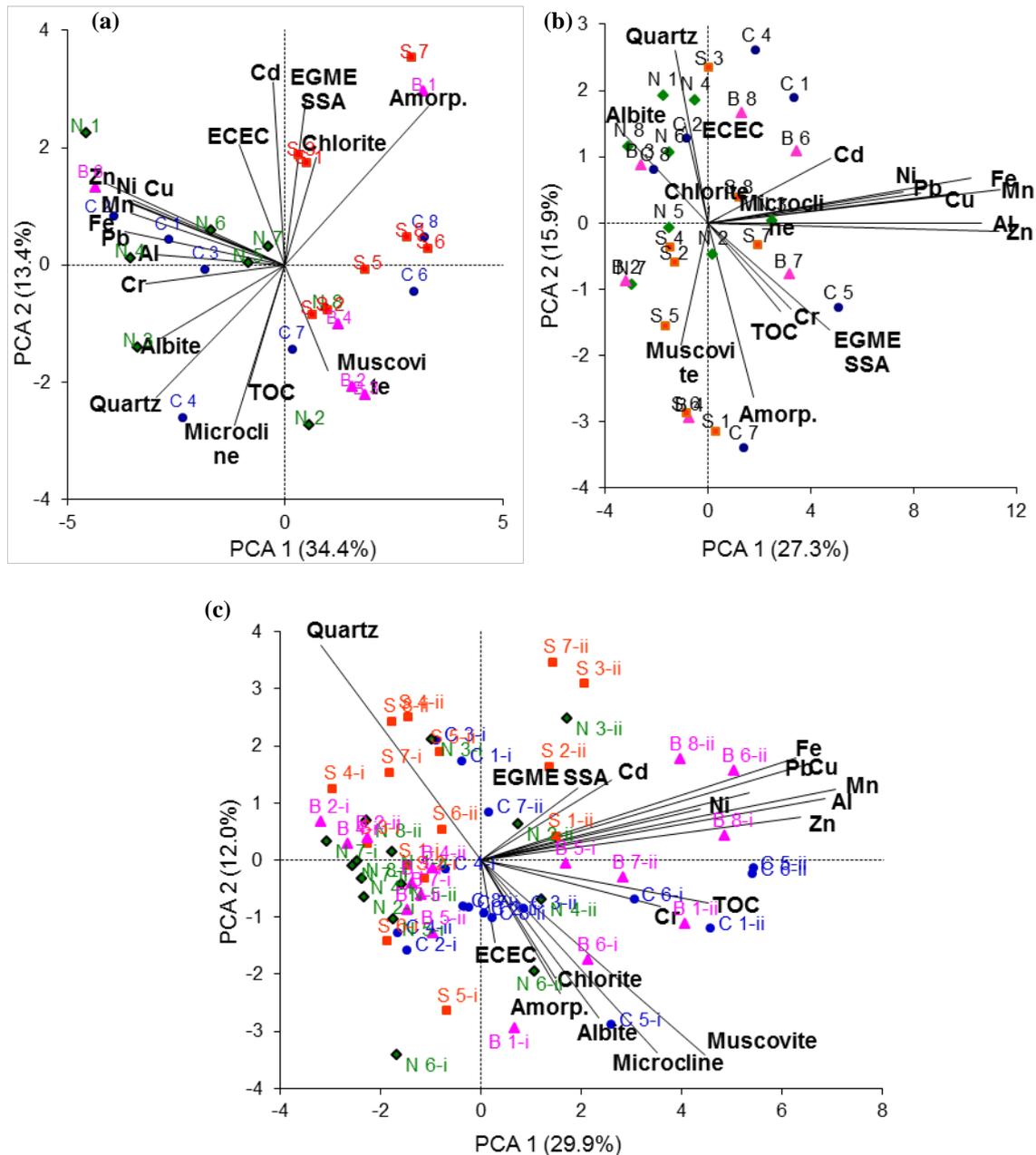


Fig. 2. PCA biplot obtained for particle size ranges: (a) <75 μm particles (b) 75-150 μm particles and (c) 150-425 μm particles

Note: C:Clearview Estate, N: Nerang, B: Benowa, S: Surfers Paradise; second character from 1-8 represents the sample number; i: 300–425 μm , ii: 150–300 μm

Similarly, Zn, Cu, Pb and Ni content show good correlation with albite and ECEC. However, considering the relatively strong correlation shown by the same metals with oxide forming metals, it can be postulated that adsorption to albite is a secondary form. Due to the presence of permanent charge sites in clay forming minerals, adsorption would occur primarily by ion exchange. This agrees with the findings of past researchers who have noted the cation exchangeable interaction of Zn, Cu, Pb and Ni in solids (Tiller and Hodgson, 1962). As evident in Fig. 2(a), TOC shows very weak correlation with the majority of the metals other than Pb and Cr. This suggests that organic matter in this particle size range is not in a form which is favourable for metal adsorption.

3.3.2 75-150 μm particles

Similar to the $<75 \mu\text{m}$ size range, Zn, Cu, Ni, Cd and Pb show strong correlation with Fe, Al and Mn (Fig. 2(b)). Since, Fe, Al and Mn show very weak or no correlation with ECEC, it was postulated that metal adsorption to Fe, Al and Mn oxides would occur by chemisorption.

As evident in Fig. 2(b), both TOC and EGME SSA are strongly correlated and show weak correlation with Pb, Zn, Cu and Cr. Therefore, the direct adsorption of metals to organic matter in this particle size range could be higher than in the case of the $<75 \mu\text{m}$ range. The adsorption to organic matter would occur by chemisorption due to the inverse correlation of TOC with ECEC.

Although, albite and chlorite are strongly correlated with ECEC, the majority of metals with the exception of Ni and Cr show very weak correlation with these minerals. Even though clay minerals have high capacity for cation exchange, in this particle size range metals adsorbed to clay minerals are considerably low. The majority of the metals in this particle size range show preference to be chemisorbed to solids particles. The possible reason for this behaviour is attributed to the preference for metals to bind with the strongest charge sites (Zhuang and Yu, 2002). Since the metal concentrations are relatively low compared to the $<75 \mu\text{m}$ particles, competition for charge sites would be relatively low.

3.3.3 150-425 μm particles

Once again, Zn Cu, Pb, Ni and Cd show strong correlation with the geogenic metal elements (Fig. 2c). Consequently, the primary form of Zn Cu, Pb, Ni and Cd adsorption would be with Fe, Al and Mn oxides. Due to the weak or no correlation of Fe, Al and Mn with ECEC, it can be postulated that adsorption would occur by chemisorption.

TOC is strongly correlated with all the metals rather than with clay minerals. Therefore, it can be concluded that the secondary form of Zn, Cu, Pb, Ni and Cd adsorption would be with organic matter. Metals adsorption to TOC would occur by chemisorption. Similar to the 75-150 μm particle size range, 150-425 μm particles have relatively low organic matter content (Table 2) compared to the finer particle sizes with metals showing a strong preference for TOC over clay minerals. This indicates that a predominant amount of organic matter is decomposed material compared to the finer particles.

3.4 Adsorption and desorption experiment

A batch adsorption experiment was carried out to validate the conclusions derived from the preliminary analysis. Results of the batch adsorption experiment revealed that higher metal concentrations were adsorbed to solids particles compared to the pre-existing metal concentration found in the field samples. On average, the adsorbed metals (q_{0-i}) as a percentage of total adsorbed metal concentration ($(q_{0-i}/q_T)\%$) were; 98% of the total Cr, 75% for Cu, 68% for Zn and 83% for Pb (Gunawardana et al., 2013). This indicates that road surface solids have a significantly high amount of vacant charge sites. In contrast, the percentage of desorbed metals with respect to adsorbed metal content was significantly low. On average, the percentage of total metals desorbed as a percentage of total adsorption was approximately 42.4% Zn, 8% Pb, 0.8% Cu and 0.1% Cr. Among the metal elements, Zn desorption was predominant compared to the other metals. This suggests that a relatively higher percentage of Zn would be in exchangeable form in solids particles. This is consistent with the conclusions by Benjamin and Leckie (1981), who noted that Zn is present in soils in predominantly water soluble or exchangeable form.

In order to investigate the influence of physical and chemical characteristics on metal adsorption, the data set was analysed using multivariate analytical techniques. Due to the limitations arising due to the limited number of samples, PROMETHEE and GAIA analyses were used to establish the relationships among adsorption and desorption processes.

Adsorbed (q_T) and desorbed (q_{ex}) metal concentrations were analysed together with the mineral components, TOC, ECEC and EGME SSA to identify the influence exerted by these parameters. Fe, Al and Mn were also included in the data matrix to explore the influence of these metal oxides on the adsorption process. The resulting GAIA biplots obtained for the four particle size ranges are shown in Fig. 3.

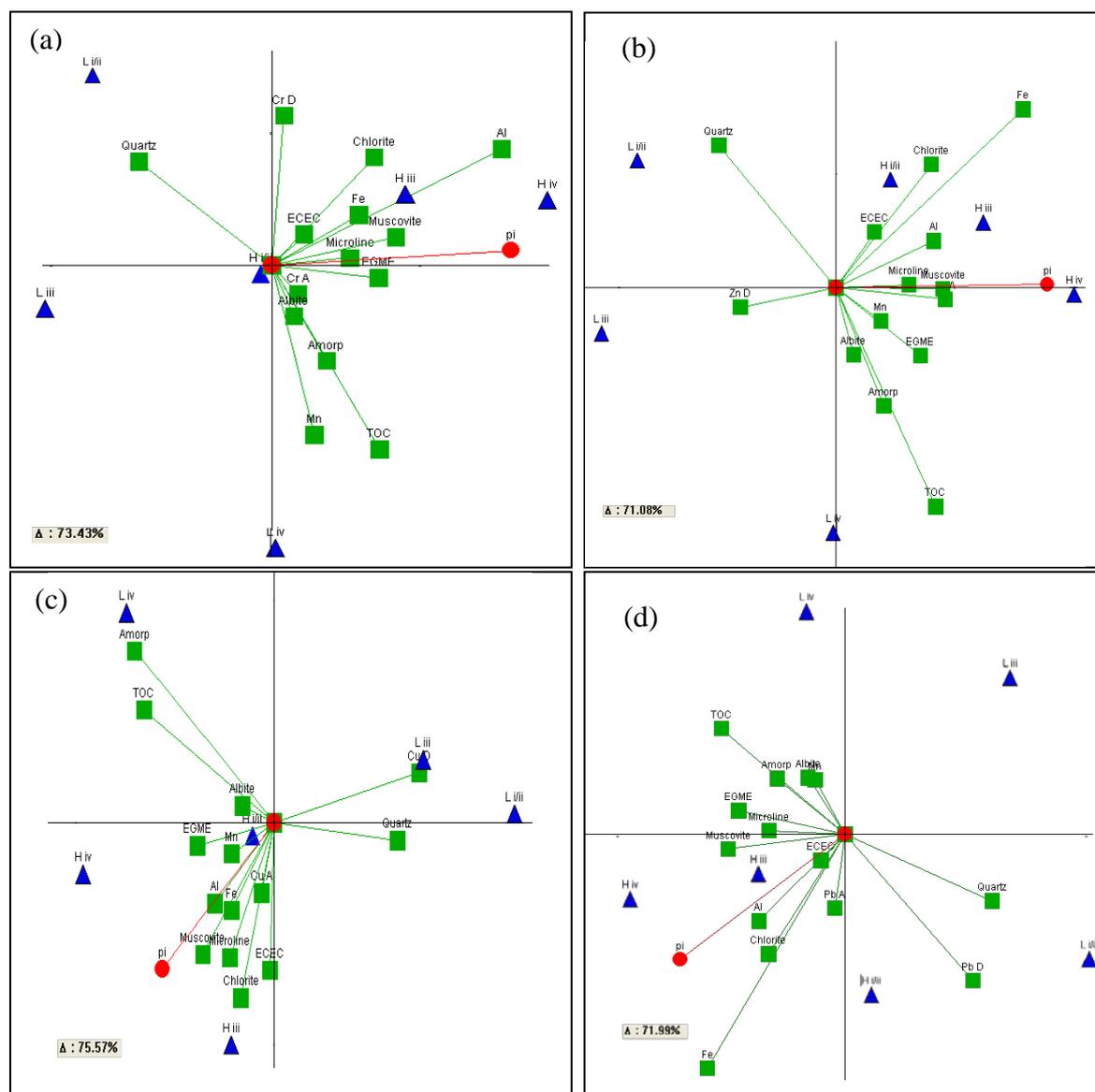


Fig. 3. GAIA biplot of (a) Cr adsorption and desorption (b) Zn adsorption and desorption (c) Cu adsorption and desorption (d) Pb adsorption and desorption

Note: Cr A: Cr adsorption, Cr D: Cr desorption, Cu A: Cu adsorption, Cu D: Cu desorption, Pb A: Pb adsorption, Pb D: Pb desorption, Zn A: Zinc adsorption, Zn D: Zinc desorption; H- highly favourable samples for adsorption, L- less favourable samples for adsorption; i/ii: Particle size 150-425 μm , iii: Particle size 75-150 μm , iv: Particle size <75 μm

3.4.1 Cr adsorption and desorption

As evident from Fig. 3(a), adsorbed Cr (Cr A) vector is strongly correlated with albite, amorphous, TOC, muscovite and EGME SSA vectors confirming the preference of Cr adsorption to organic matter, albite, amorphous content and muscovite. Due to very weak correlation of albite and TOC with ECEC, adsorption of Cr as exchangeable cations is minimal and it leads to the conclusion that Cr adsorption to albite and organic matter content is due to chemisorption. Chemisorption can occur in clay forming minerals at edge sites by donating electrons to metals (McBride, 1994). Additionally, Mn vector is projected in the same direction as Cr A, suggesting a strong correlation with Cr A, while Fe and Al vectors are projected orthogonal to Cr A. This suggests that an appreciable portion of Cr is also adsorbed to Mn oxide, but not with Fe and Al oxides.

Desorbed Cr (Cr D), ECEC, chlorite, muscovite, microcline and EGME SSA are strongly correlated to each other (Fig. 3a), suggesting that desorbed Cr had been attached to clay forming minerals of chlorite and muscovite (layer silicates). Since the experiment was designed only to desorb exchangeable cations, Cr bonding with clay forming minerals is evidently by cation exchange. Al and Fe oxide bound Cr would also be present in exchangeable form. Strong correlation of Cr D, ECEC, Fe and Al observed in Fig. 3(a) suggest that at high concentrations, Al and Fe oxide also adsorb Cr by cation exchange.

These outcomes confirmed that Cr adsorption to solids mainly occurs in non-exchangeable form. Although at low concentrations, Cr demonstrated cation exchangeable adsorption, in the presence of high Cr content in solution, the non-exchangeable form of adsorption with organic matter, albite and Mn oxide could also occur. Furthermore, the environmental impact of Cr bioavailability at the natural pH level of stormwater runoff would be very low. However, the metal content in the particulate fraction would be high as solids have high selectivity for Cr. Therefore, the removal of solids particles would mitigate Cr contamination of receiving waters.

3.4.2 Zn adsorption and desorption

As evident in Fig. 3(b), among clay forming minerals, the layer silicate minerals, muscovite and chlorite show strong correlation to Zn A than the framework silicate and albite (feldspar). The correlation of EGME SSA and muscovite indicates that there is strong influence exerted by the interlayer surface area of muscovite on adsorption. Therefore, it can be concluded that Zn is preferentially adsorbed to the interlayer surfaces of the clay minerals through cation exchange (Bradl, 2004; McBride, 1994). This confirms the findings in Section 3.3, which noted the preferential adsorption of Zn with clay minerals in all of the particle size ranges other than the 75-150 μm range. Furthermore, Fe and Al strongly correlate with ECEC indicating that at high metal concentrations, Zn adsorption to Fe and Al would occur through cation exchange, contrary to the findings in Section 3.3 which indicated chemisorption with metal oxides. It is hypothesised that at low concentrations metals are bound to the strongest adsorption sites, and at high concentrations, metals would also bind to the weaker adsorption sites (Spadini et al., 1994). Since surface adsorption sites consist of several distinct charge sites, at high concentration, Zn would have formed weak cation exchangeable bonds with surface charge sites (Benjamin and Leckie, 1981; Aualiitia and Pickering, 1986).

Although desorbed Zn (Zn D) represents the ion-exchangeable form, Zn D shows inverse correlation with ECEC. Possible reason for this would be the high adsorption of ion-exchangeable Zn (Zn A) in solid particles which results strong correlation of Zn A with ECEC. Past researchers have also shown that a significant amount of Zn adsorbed to clay

mineral surfaces is reversible, while the irreversible non-exchangeable form of Zn associated with edge sites is very low (Tiller and Hodgson, 1962). The study outcomes further revealed that a high amount of Zn adsorbed to clay forming minerals and metal oxides is subject to release due to weak bonds such as cation exchange, suggesting that the activation energy required for this process is low.

3.4.3 Cu adsorption and desorption

As evident in Fig. 3(c), Cu A is strongly correlated with Fe, Al and Mn vectors, ECEC, clay forming minerals and EGME SSA. The Fe, Al and Mn vectors are projected in the direction of the decision axis π_1 , with moderate lengths indicating the strong affinity of Cu A in the decreasing order of Fe, Al and Mn. However, clay minerals also show strong correlation with Cu A. Therefore, it can be concluded that Cu adsorption is dominated by metal oxides, followed by clay forming minerals. With the exception of the order of preference of Fe, Al and Mn oxides, this confirms the conclusions derived in Section 3.3.

Cu D is strongly correlated with quartz. Since quartz is an inert mineral, it can be hypothesised that the majority of desorbed Cu is present as precipitate or with weak electrostatic attachment to charged surfaces. Furthermore, Cu desorption is <2.6% of the total adsorbed Cu and, in most of the samples, desorption was less than 0.1%. Therefore, it can be concluded that a high amount of Cu is retained on the particles and adsorption would be by chemisorption. Accordingly, the bio-availability of this metal will be relatively very low.

3.4.4 Pb adsorption and desorption

Fig. 3(d) indicates that Pb A is strongly correlated with both Fe and Al, while inversely correlating with Mn. Fe being a long vector in the direction of the decision axis π_1 , it can be concluded that Fe exerts the dominant influence on Pb adsorption. Compared to the Fe, Al and Mn vector lengths, the ECEC vector length is low. Therefore, it can be concluded that the adsorption to oxides would be dominated by a non-exchangeable form. As metal oxides predominately create complexation with metal cations, the adsorption of Pb to metal oxides would occur by chemisorption. At relatively low concentrations (Section 3.3), Pb would be preferentially bound to organic matter, while at high concentrations metal oxides would be the preferred adsorbing site for Pb. This is attributed to the relatively limited organic matter content in the solids particles which would have been saturated by the excess Pb added during the batch adsorption experiment. Therefore, it can be concluded that due to the lack of primary preferential adsorbing sites for Pb in the solids particles, Pb had adsorbed to secondary sites. Similar observations were reported by Zhuang and Yu (2002) based on a study of Pb adsorption to metal oxides. Consequently, it can be concluded that preferential adsorption of Pb in the presence of limited organic matter content would follow the order of Fe oxide > Al oxide > clay forming minerals. This confirms the findings in Section 3.3 where, with the exception of organic matter, metal oxides provided the preferred adsorption sites for Pb.

In Fig. 3(d), Pb D shows inverse or no correlation with ECEC, TOC and clay forming minerals. Pb D is weakly correlated with chlorite, indicating the previous finding that clay bound Pb is present in exchangeable form. Additionally, Pb precipitation would have occurred during the adsorption process, as the formation of Pb hydroxides is common at pH 6.5 (Aualiitia and Pickering, 1986). Therefore, it can be concluded that precipitation would have been responsible for a portion of the Pb that had desorbed from solids during the desorption experiment.

4. Conclusions

The analyses undertaken provide an in-depth understanding of how metals are attached to solids particles at natural metal concentrations in the urban environment. Additionally, based on the adsorption and desorption experiments, the observed metal adsorption behaviour was further validated. The understanding developed relating to the adsorption processes assisted in identifying the mobility of metals in road deposited solids in urban areas. Based on the data analyses, the following conclusions were derived:

- Road deposited solids consist of distinct groups of charge sites influenced by mineralogical components, organic matter content, and Fe, Al and Mn oxides. Specific metal ions showed selectivity in adsorbing to different charge sites and the adsorption mechanism was found to be different for different charge sites.
- A significant fraction of metals are preferentially adsorbed to Fe, Al and Mn oxides by chemisorption.
- Metal adsorption to clay forming minerals occurs primarily by ion exchange, and the occurrence of chemisorption at edge sites of clay forming minerals is not significant.
- The primary mechanism in metal adsorption to organic matter is chemisorption, while cation exchange is the secondary mechanism.
- Zn, Cu, Pb and Ni in road deposited solids show similar adsorption characteristics. These metals have high affinity to Mn, Fe and Al oxides.
- Cd and Cr mostly undergo ion-exchangeable adsorption. These cations are associated with amorphous content, mineralogical components and organic matter. Pb is primarily found in association with organic matter content through chemisorption. The preferential association of Pb is in the order of organic matter > metal oxide > mineralogical components.
- At high concentrations, Cr, Cu and Pb are strongly bound to particles by chemisorption. In contrast, Zn undergoes cation-exchangeable form of adsorption which has a high likelihood of being subsequently released from the solid particles due to possible changes in environmental conditions. As such, Zn can exert a significant impact on receiving water quality. Therefore, for the removal of Zn, the removal of solid particles in a dry state is an effective mitigation measure. Due to low likelihood of desorption of particulate Cu, Pb and Cr from solids particles in stormwater runoff, solids removal using appropriate strategies is a possible mitigation option.

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