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Influence of organic matter in road deposited particulates in heavy metal accumulation and transport

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Abstract

The research study discussed in the paper investigated the influence of organic matter on heavy metal adsorption for different particle size ranges of build-up solids. Samples collected from road surfaces were assessed for organic matter content, mineral composition, particle size distribution and effective cation exchange capacity. It was found that the organic matter plays a key role in $>75\mu\text{m}$ particles in the adsorption of Zinc, Lead, Nickel and Copper, which are generated by traffic activities. Clay forming minerals and metal oxides of Iron, Aluminium and Manganese was found to be important for heavy metal adsorption to $<75\mu\text{m}$ particles. It was also found that heavy metals adsorbed to organic matter are strongly bound to particles and these metal ions will not be bio-available if the chemical quality of the media remains stable.

Keywords

Heavy metals, Metal adsorption, Organic matter, Solids, Stormwater pollution

1. INTRODUCTION

Solids are one of the most significant pollutants in stormwater runoff due to its physical presence and associated chemical pollutants (Shi et al. 2008; Goonetilleke et al. 2009). Among the associated pollutants, heavy metals are important due to their potential toxicity. The bio-availability of heavy metals in receiving waters depends on their chemical form or adsorption mechanisms. The common forms of adsorption of heavy metals to solids include chemisorption, ion exchange and precipitation (Weber et al. 1991; Bradl, 2004). The mechanisms of adsorption of heavy metals to solids depend on the composition of charge sites in solids (Weber et al. 1991).

It has been noted that the organic matter in solids play a key role in heavy metal adsorption to solids. However, the role of organic matter on heavy metal adsorption for different particle sizes is not widely understood. Furthermore, the decomposition of organic matter can cause changes in solids characteristics and increase the bio-availability of heavy metals. Therefore, an in-depth understanding of heavy metals adsorption at the solid-organic interface is important.

The organic matter present on road surfaces can be of anthropogenic origin, mainly derived from traffic related activities or natural organic matter, mainly derived from plant debris and surrounding soil in the form of residues of plant and animal products or decomposition by-products such as humus, fluvic acid and humic acid (McBride, 1994). As reported in research literature, the influence of various fractions of organic matter present in solids on metal adsorption would be different (Covelo et al. 2008). By-products of decomposition are comparatively more important in heavy metal adsorption than organic residue due to the presence of surface functional groups.

A primary aim of the research study discussed in the paper was to investigate the influence of organic matter on heavy metal adsorption to different particle sizes of road deposited solids. The specific emphasis was on traffic related heavy metals. For this purpose, characteristics including organic matter content, mineral composition, particle size distribution and solid surface charge characteristics of build-up solids were investigated.

2. MATERIALS AND METHODS

The study sites

Field investigations were conducted at Gold Coast, Southeast Queensland, which is one of Australia's rapidly developing regions. To ensure the collection of build-up samples with a range of different physical and chemical properties, a total of sixteen urban road surfaces with differing traffic characteristics, land use and surrounding soil characteristics were selected from four suburbs, as shown in Figure 1.

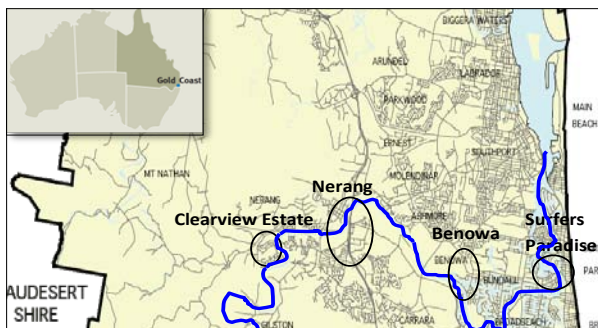


Figure 1 - Locations of study sites

Build-up sample collection

Pollutant build-up samples were collected using a dry and wet vacuuming system (with 90% efficiency) from 3m² plots from selected road surfaces (Gunawardana et al. 2010). Two separate samples were collected from each road surface representing two different antecedent dry periods having less than and greater than eight days. Egodawatta and Goonetilleke (2006) confirmed that pollutant build-up on road surfaces tend to asymptote to an almost constant value after seven days. The road surface texture depth was measured according to procedures specified in FHWA (2005).

Laboratory analysis

The collected build-up samples were separated into four particle size ranges; <75µm, 75-150µm, 150-300µm and 300-425µm by wet sieving and the separated particulates were analysed for physico-chemical parameters listed in Table 1. Standard quality control procedures were followed to maintain accuracy and reliability of the laboratory analysis.

Table 1 - Parameters and test methods

Parameter	Test method
Volumetric particle size distribution	Malvern Mastersizer S Particle Size Analyzer
Solids	Method 2540 D (APHA, 2005)
Total organic carbon (TOC)	Shimadzu TOC-5000A Total Organic Carbon analyser, Method 5310C (APHA, 2005)
Mineralogy	X-ray diffraction (Brindley and Brown, 1984)
Exchangeable cations (Ca ²⁺ , Na ⁺ , Mg ²⁺ , K ⁺ and Al ³⁺)	Method 15A1 (Rayment and Higginson, 1992), Ammonium chloride at pH 7
Heavy metals	ICP-MS, Method 200.8 (US EPA, 1994)

Data analysis

Principal Component Analysis (PCA), which is a multivariate analytical technique frequently applied in the analysis of environmental data (Adachi and Tainosho, 2005; Goonetilleke et al. 2009) was used to investigate the relationships among the large data set generated. Detailed descriptions

of PCA can be found elsewhere (for example Adams, 1995).

3. RESULTS AND DISCUSSION

Characteristics of build-up pollutants

The baseline data obtained from the field and laboratory analysis is given in Table 2.

Table 2 - Build-up pollutant load characteristics

Suburb	Land use	Road texture depth (mm)	Sampling event	Volumetric particle size distribution (%)					Average solids load (g/m ²)
				<75 μm	75-150 μm	150-300 μm	300-425 μm	>425 μm	
Clearview Estate	R	0.76-0.92	1	82.0	10.6	5.66	0.91	0.53	1.79
			2	48.1	9.15	11.2	8.38	23.2	0.81
Nerang	I	0.93-1.14	1	63.0	18.8	10.8	5.00	2.39	3.5
			2	45.4	15.3	11.3	10.2	17.8	7.03
Benowa	R, I, C	0.80-0.91	1	83.5	4.1	5.34	4.84	2.26	1.39
			2	71.9	9.77	7.87	4.88	5.55	0.78
Surfers Paradise	C	0.63-1.11	1	66.0	8.43	12.3	8.32	4.95	2.22
			2	47.0	18.5	16.3	6.07	12.2	1.79

Note: R: Residential, I: Industrial, C: Commercial

As evident in Table 2, more than 70% of the road deposited solids particles at all of the sites are finer than 150 μm . Particles <75 μm is the most dominant, accounting more than 50%, compared to other four particle sizes. The particle size distribution and build-up pollutant load (solids per unit area) illustrate the variability among the different suburbs. It is hypothesised that the relatively high average texture depth, nature of anthropogenic activities, traffic density and antecedent dry period would have influenced this variability (Egodawatta and Goonetilleke, 2006).

Organic carbon content in solids

The variation in solids properties for different particle sizes is shown in Figure 2. As evident in Figure 2 (a), organic carbon increases with the decrease in particle size. The differences in organic carbon for particle sizes 150-300 μm and 300-425 μm are insignificant indicating similarity in organic composition in coarser particles. Confirming previous research findings, the smallest particle size range always shows significantly high organic carbon content irrespective of location or land use (Herngren et al. 2006). This can be attributed to organic matter such as leaf litter with relatively lower structural strength being easily ground into fine particles by physical abrasion due to vehicular traffic (Sartor and Boyd, 1972). Additionally, an appreciable fraction of organic matter could be derived from particles released by vehicle tyre wear (Shi et al. 2008).

Contribution of a significant amount of organic matter from vegetation debris to road deposited solids can be confirmed by the presence of high organic carbon content in residential sites at Benowa and Clearview Estate. The smallest particle size range at Benowa shows significantly higher TOC content which is attributed to the presence of surrounding vegetation in the road sites. This suggests that the higher percentage of organic carbon content in street deposited solids can be mainly attributed to plant debris.

Clay forming minerals and effective cation exchange capacity (ECEC) of solids

As clay forming minerals have permanent charge sites (isomorphous substitutions) and edge sites on its surface, the presence of minerals increases the charge characteristics of solids (McBride, 1994). Accordingly, the data interpretation was undertaken based on the amount and type of minerals present in solids. Detected minerals in solids samples included quartz and clay forming minerals of albite, microcline, chlorite and muscovite. Among the detected minerals, clay forming minerals of albite and chlorite were used for the present analysis since these minerals were identified as surrogate parameters for other clay forming minerals (Gunawardana, 2011). As seen in Figure 2 (b) and (c), both albite and chlorite increase with the reduction in particle size indicating the importance of finer particle for heavy metal adsorption.

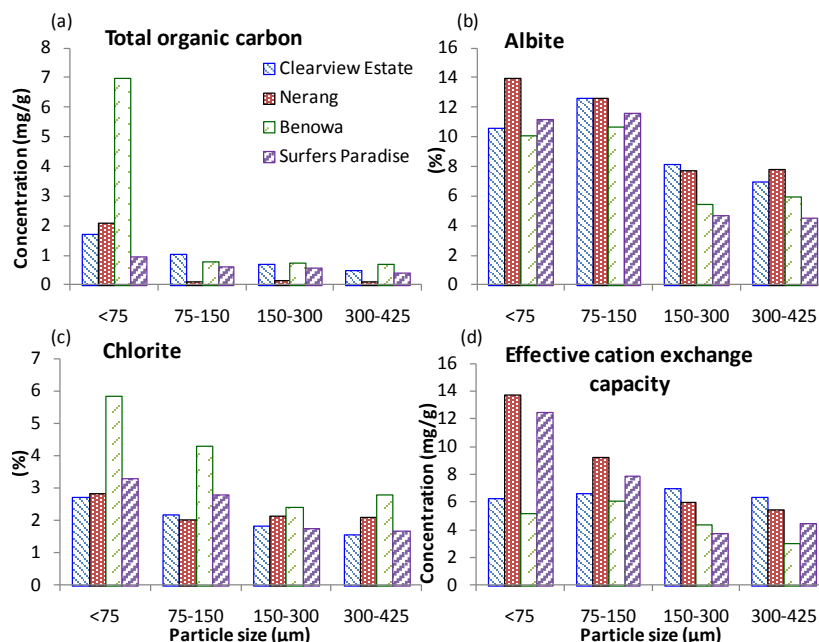


Figure 2 – Variation of solids properties with respect to particle size; (a) Total organic carbon, (b) Albite mineral, (c) Chlorite mineral and (d) Effective cation exchange capacity

Effective cation exchange capacity (ECEC) of solids represents the capacity for cation retention by solids particles. The sum of the exchangeable cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ and Al^{3+}) is referred to as ECEC (Evans and Scott 2007). To understand the variation of ECEC among the different particle sizes of road deposited solids in the four suburbs, the data values were separately analysed (Figure 2 (d)). As seen in Figure 2 (d), ECEC of the solids decreases with the increase in particle size. It appears that the ECEC variation with respect to particle size is compatible to the variation in TOC content and clay forming minerals. However, the contribution of TOC and mineralogical components to the ECEC of solids can be different. For example, the highest ECEC found in Nerang and Surfers Paradise samples implies that the highest contribution to ECEC would be from the clay forming mineral components in solids, due to the comparatively high mineral content compared to the TOC content in these study sites. This suggests that the mineralogical components have a higher influence on the ECEC rather than the organic matter content. The analysis indicated considerable variation in the influence exerted by TOC and clay forming minerals on ECEC of road deposited solids.

Heavy metal concentrations in solids

Nine heavy metal elements of Fe, Al, Mn, Zn, Cu, Pb, Ni, Cr and Cd were analysed for the four size ranges of collected build-up samples. As evident in Figure 3, the metal concentrations in solids particles decrease with the increase in particle size. It was found that the highest metal content is present in the <75μm particles. Furthermore, the data reveals that the heavy metal concentrations in

solids associated with the particle size range $<150\mu\text{m}$ is about 40% of the overall heavy metal concentration except for Cu and Zn. This highlights the fact that fine particles have a significant influence on the association of heavy metal with solids (Herngren et al. 2006). In the majority of the study sites, high Cu and Zn concentrations are associated with the particle size 75-150 μm .

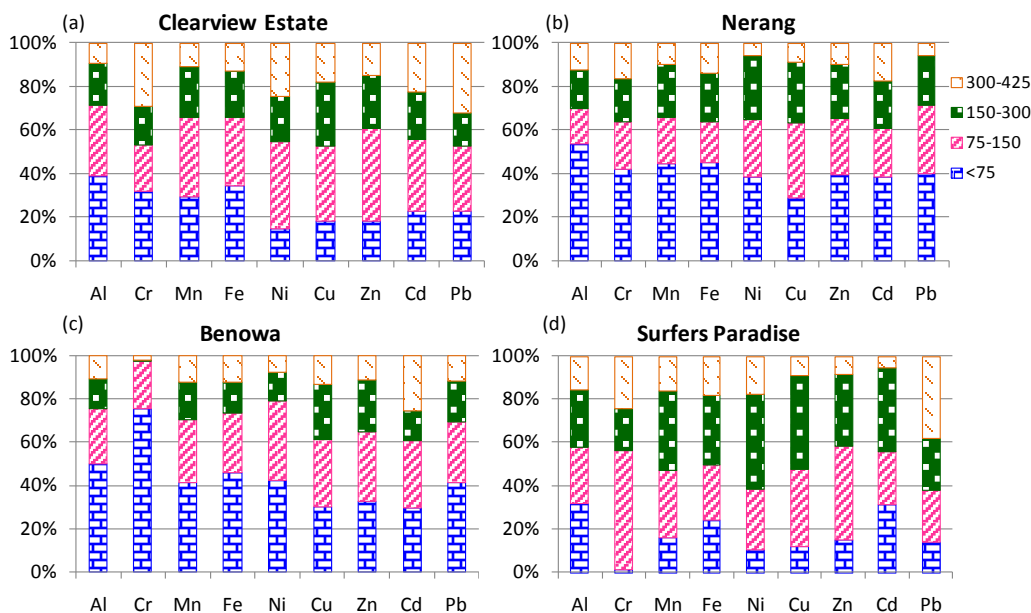


Figure 3 – Heavy metal concentrations in different particle sizes of solids; (a) Clearview Estate, (b) Nerang, (c) Benowa and (d) Surfers Paradise

Fe and Al are the most abundant metal element in solids particles. A significant amount of Fe and Al in road deposited solids can originate from soil sources (Herngren et al. 2006). Zn was the most abundant metal element other than Fe and Al in all of the particle sizes regardless of the study site. As noted in past research literature, Zn in road deposited solids primarily originate from traffic related activities and industrial processes (Adachi and Tainosho, 2005). Although, the concentrations of traffic related heavy metals in different particle sizes varied in different suburbs, for the majority of the study sites, metal concentrations decreased in the order of $\text{Zn} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Cr} > \text{Cd}$. Furthermore, the results indicate high variations in heavy metal concentrations among the road surfaces for the different land uses (Figure 3).

Heavy metal adsorption behaviour in different particle sizes

To understand the influence of solids properties on heavy metal adsorption, PCA was carried out for the four different particle sizes. Resulting PCA biplots are shown in Figure 4. As evident in Figure 4 (a), (b), (c) and (d), in all particle size ranges, metals of geochemical origin (Fe, Al and Mn) are strongly correlated to each other and form a cluster. Fe, Al and Mn in soil are typically present as metal oxides or hydroxides as a coating on clay minerals or complex with organic matter content and these metal oxides can absorb a significant proportion of other metal elements (McBride, 1994). According to Figure 4 ((a), (b), (c) and (d)), in all particle size ranges Zn, Cu, Pb and Ni show strong correlation with Fe, Al and Mn. As such, a significant proportion of these metals can be adsorbed to Fe, Al and Mn oxides. Due to the weak or no correlation of Fe, Al and Mn metal elements with ECEC, it can be postulated that the adsorption of Zn, Cu, Pb and Ni to metal oxides occurs by mechanism other than ion exchange. Heavy metals adsorption to metal oxides would mainly occur by chemisorption due to the presence of the surface functional groups rather than the permanent charge sites (Weber et al. 1991; McBride, 1994).

Correlations of heavy metals with organic matter and clay forming minerals are different in the four particle size ranges. In $<75\mu\text{m}$ particles, Zn, Cu, Pb and Ni content show a relatively good

correlation with albite (Figure 4 (a)). This suggests that a significant portion of these heavy metal elements are associated with albite. Due to the good correlation of ECEC and albite, it is postulated that albite would adsorb metal elements by ion exchange. However, in comparing 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 (Bradl, 2004).

Pb is the only metal element that shows correlation to TOC in <75µm size range. As evident in Figure 4 (a), TOC shows a very weak correlation with the rest of the heavy metal elements. This suggests that a higher fraction of TOC in this particle size range is not in a form which is favourable for metal adsorption. It leads to the conclusion that, though the higher amount of organic matter in these solids are mainly derived from plant debris, the majority of TOC in this particle size range is present primarily in the form of organic residue (non decayed fraction). This confirms that the nature of the organic matter is important in metal adsorption rather than its source or the amount (Krein and Schorer, 2000).

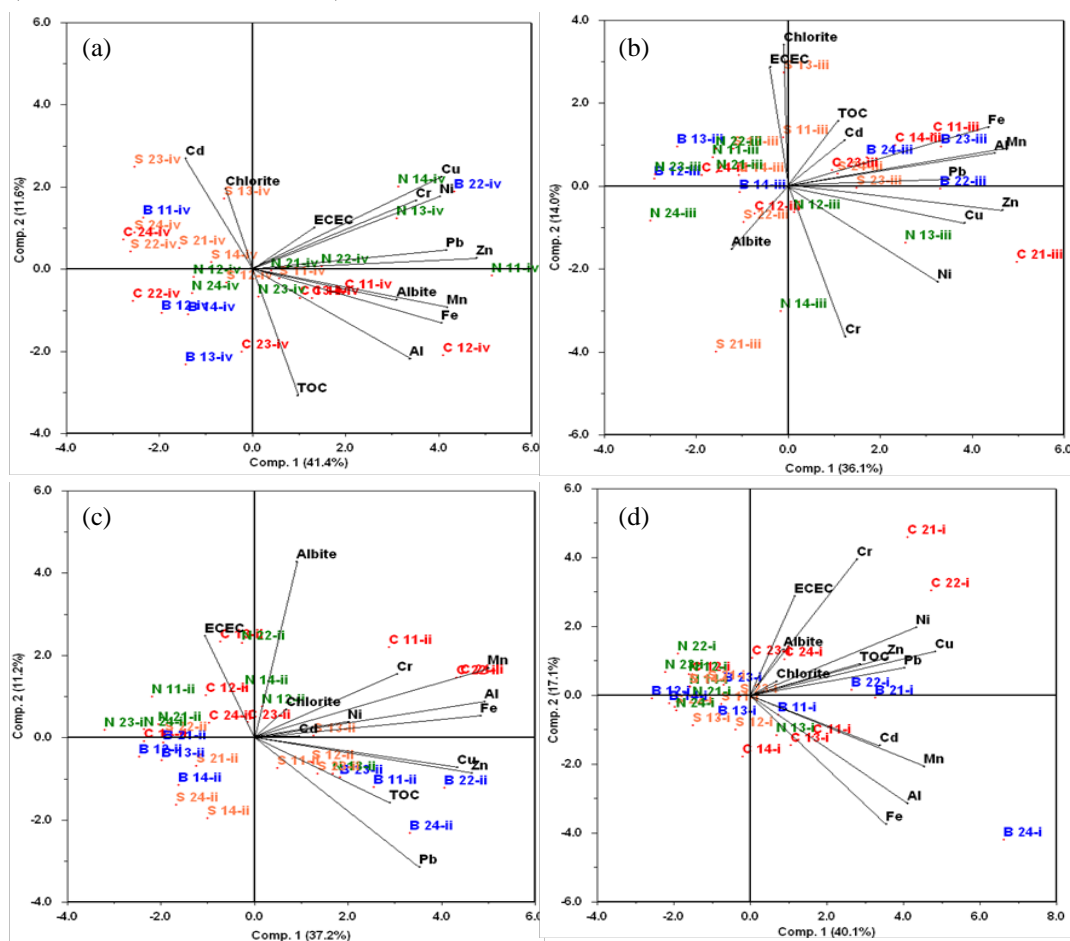


Figure 4 - PCA biplot of all sites for finer particle size ranges; (a) particles <75µm, (b) particles 75-150µm (c) particles 150-300µm and (d) particles smaller 300-425µm

Note: C: Clearview Estate, N: Nerang, B: Benowa, S: Surfers Paradise; Second character: from 1-4 represents the sample number

However, as evident in the 75-150µm particle size (Figure 4 (b)), TOC is correlated with Pb, Zn, Cu and Cr than with the clay forming minerals of albite and chlorite. Therefore, the direct adsorption of heavy metal elements to organic matter in 75-150µm particle size range can be higher than in the case of particles in the <75µm range. Adsorption to TOC would occur by chemisorption which forms strong bonds between heavy metal elements and solids particles. This conclusion is based on the negative correlation observed between TOC and ECEC in Figure 4 (b). However, this is not a

primary form of Pb, Zn, Cu and Cr adsorption, due to the weak correlation shown compared to correlations with metal oxides. Although chlorite is strongly correlated with ECEC, the majority of metal elements show a very weak correlation with chlorite, albite and ECEC in 75-150 μ m size range (Figure 4 (b)). The possible reason for this behaviour would be the high preference of heavy metal elements to bind with the strongest charge sites (Zhuang and Yu, 2002).

Correlations of solids properties and heavy metal elements in both 150-300 μ m and 300-425 μ m particles are similar, which suggest the similarity in heavy metal adsorption behaviour in both of the coarser particle sizes (See Figure 4 (c) and (d)). Here again, TOC is strongly correlated to all heavy metal elements. Therefore, it can be concluded that after metal oxides, Zn, Cu, Pb, Ni and Cd metal elements would preferentially adsorb to organic matter content. Similar to the 75-150 μ m particles, heavy metals adsorption to TOC would occur by chemisorption. Chemisorbed metal elements have a less likelihood of being bio-available due to their strong bonds.

Although, organic matter content in 150-300 μ m and 300-425 μ m particles size ranges is relatively low compared to the finer particle sizes, metal elements have a strong preference for TOC over clay forming minerals. Similarly 75-150 μ m particle size range show a high influence of TOC on heavy metals adsorption but not the <75 μ m particle size range. Therefore, it can be concluded that the particle size has an inverse relationship to the amount of decomposed organic matter content. Once again it confirms that rather than the amount of organic matter present, its composition or the nature of the organic matter would be the most important factor in relation to metal adsorption. A possible reason for such behaviour would be the association of decomposed by-products of fine organic residue with the mineral phase in coarse particles (Kahle et al. 2003). The characteristics of organic matter associated with different soils particles (clay, silt and sand) will vary with the types of minerals present or amorphous metal oxides content (crystalline minerals) (Laird et al. 1994).

4 CONCLUSIONS

The following important conclusions were derived from the research study:

- Organic matter content in road deposited particulates is relatively low with <75 μ m particles containing the highest organic matter content. The majority of organic matter content in the fine particle size range (<75 μ m) is present primarily in the form of organic residue while particles >75 μ m contain higher amount of decomposed organic compounds that are important in heavy metal adsorption to solids.
- Organic matter did not play a significant role in heavy metal adsorption by <75 μ m particles. Oxide of Iron, Aluminium and Manganese, and clay forming minerals was found to be important for heavy metal adsorption in this size range.
- Organic matter plays a key role in >75 μ m particles in the adsorption of traffic generated heavy metal elements of Zinc, Lead, Copper, and Nickel.
- Heavy metals adsorbed to organic matter are strongly bound to particles and these metal ions are not easily bio-available if the chemical quality of the media remains stable.
- Chemical composition or the nature of the organic matter is the most important in metal adsorption, rather than the amount of organic matter present in solids.

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