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Role of particle size and composition in metal adsorption by solids deposited on urban road surfaces

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Abstract:

Despite common knowledge that the metal content adsorbed by fine particles is relatively higher compared to coarser particles, the reasons for this phenomenon has gained little research attention. The research study discussed in the paper investigated the variations in metal content for different particle sizes of solids associated with pollutant build-up on urban road surfaces. Data analysis confirmed that parameters favourable for metal adsorption to solids such as specific surface area, organic carbon content, effective cation exchange capacity and clay forming minerals content decrease with the increase in particle size. Furthermore, the mineralogical composition of solids was found to be the governing factor influencing the specific surface area and effective cation exchange capacity. There is high quartz content in particles >150µm compared to particles <150µm. As particle size reduces below 150µm, the clay forming minerals content increases, providing favourable physical and chemical properties that influence adsorption.

Capsule: The mineralogical composition of solids is the governing factor influencing metal adsorption to solids in pollutant build-up on urban surfaces.

1.   Introduction

Build-up solids on urban road surfaces are a sink for potentially toxic pollutants such as metals generated by various anthropogenic activities common to the urban environment (Rogge et al., 1993; Goonetilleke et al., 2009). The significance of these pollutants on the health of receiving water bodies depends on the bioavailable fraction attached to solids which are available for wash-off by stormwater runoff (Sutherland and Tolosa, 2000). Therefore, in order to develop effective stormwater quality mitigation strategies, an in-depth understanding of the factors that influence metal adsorption to solids and the nature of the adsorption processes is essential.

Despite the common understanding that a comparatively high metal load is present in fine particles in pollutant build-up compared to coarser particles, there is paucity of scientific knowledge regarding the reasons for this behaviour (Sansalone and Kim, 2008). Research literature commonly states that the surface characteristics of solids influenced by their composition play a significant role in the adsorption and desorption processes of metals from a particle surface (Bradl, 2004; Gunawardana et al., 2013).

Considerable knowledge has been developed regarding the characteristics of individual substances common to build-up on road surfaces such as organic matter (Greenland and Hayes, 1981; Rogge et al., 1993), minerals (Roger et al., 1998), soil and tyre wear

particles (Adachi and Tainosho, 2004). Previous research studies have confirmed that road deposited solids contain a mix of these pollutants (Gunawardana et al., 2012a; Kreider et al., 2010). It is hypothesised that the diversity of physical and chemical properties exhibited by these pollutants is influenced by their sources of origin. Consequently, an in-depth understanding of the physical and chemical parameters of solids particles and their sources of origin are vital in order to assess the potential contribution of toxic pollutants adsorbed to road deposited solids particles.

The primary objective of the research study discussed in this paper was to identify the important factors which influence metal adsorption to different particle sizes of build-up solids. Accordingly, solids samples deposited on urban road surfaces with diverse mineralogy and anthropogenic origin were analysed for a range of key physical and chemical properties. The research study outcomes are expected to contribute to a greater understanding of the role of solids characteristics in metal adsorption and thereby to contribute to enhancing stormwater management practices which commonly target solids removal for stormwater quality improvement.

2.   Materials and methods

2.1   The Study Sites

The research study was carried out at Gold Coast, Southeast Queensland. Differences in solids characteristics were considered as the main criteria in the study site selection. Consequently, four suburbs with different soil profiles stretching from inland to the coastline along the Nerang River (Fig. 1) were identified as study areas from which specific road sites were selected as study sites.

Soils in the region are mainly derived from Neranleigh–Fernvale meta sediments and clayey sub-soils which vary between Dermosols (known as Red and Yellow Podzolic) and Kurosols (Noble, 1996; Isbell, 1996).The selected four suburbs; Clearview Estate, Nerang, Benowa and Surfers Paradise lie along a 12.5 km traverse with almost equal distance apart between each suburb. A total of sixteen road surfaces with varying levels of traffic density were selected, representing four road sites from each suburb and different land uses.

2.2   Sample Collection

2.2.1   Build-Up Sample Collection

Researchers have found that the wash-off process due to rainfall removes only a portion of the pollutants available on the surface (Sartor et al., 1972; Egodawatta et al., 2007). Consequently, an appreciable fraction of pollutants can remain on the road surface after a rain event. This suggests that pollutant wash-off do not necessarily provide a comprehensive representation of pollutants available on the road surface. Accordingly, in order to investigate the composition of solids present on an urban road surface, the research study focused on particulate pollutants present in build-up.

Pollutant build-up samples from each (road) study site were collected using a dry and

wet vacuuming system as described by Gunawardana et al. (2012b). Build-up samples were collected from four to six plots equally spaced between the median strip and the kerb or in the middle of parking spaces having an area of 3m^2 assuming uniform pollutant build-up across the surface. The plot area was initially vacuumed in a dry state using a vacuum cleaner (Delonghi Aqualand make) with a water filtration system. To enhance the collection efficiency of fine particles, the road surface was then moistened by spraying deionised water (using Swift 60L compact sprayer with pressure control) under a 2 bar pressure for 3 min. and the same vacuum system was re-used to collect the moistened sample. The collection methodology was tested under controlled field conditions and found to be 90% efficient in collecting and retaining particulates including fine particulates (Mahbub et al., 2010).

Altogether 32 build-up samples were collected, representing two separate samples from each road surface with different antecedent dry periods to account for changes in sample composition, particularly particle size. Previous research studies have found that pollutant accumulation at the initial period is rapid and tend to reach near equilibrium at around seven to nine dry days (Egodawatta et al., 2009; Ball et al., 1998). Consequently, sampling times were selected such that the antecedent dry period for one sampling episode was less than eight days and the other greater than eight days.

2.3   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. The metal species selected for analysis are commonly present in the urban environment as identified in research literature (e.g., Herngren et al., 2006). Standard quality control procedures were followed to maintain accuracy and reliability of the laboratory analysis. Precision and accuracy of metal analyses and the digestion procedure was monitored using internal standards, certified reference material and quality control blanks. Multi-element standards supplied by Accustandard® were used as calibration standards. Multi-element standards from Sigma-Aldrich® were used as the certified reference material. The percentage recovery was in the range of 85%-115%, which is within the specified limits.

2.4   Data Analysis

A large data matrix was developed based on the experimental data. Analysis of a large data set with multiple variables requires analytical approaches capable of clustering similar data together whilst identifying relationships between variables. Under these circumstances, the application of multivariate techniques, namely, Principal Component Analysis (PCA) has been found to be appropriate (Herngren et al., 2006).

The PCA technique describes the complete data matrix in a reduced number of principal components (PCs) by transforming the original variables to a new orthogonal set of PCs for describing the relationships among variables and samples. In PCA, objects that

exhibit similar variances 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.

In this study, data sets were pre-treated to reduce 'noise' which can interfere with the data analysis. Accordingly, the data matrix was column centred and standardised (auto scaled). This was done by subtracting the column mean from each cell value and dividing by the column standard deviation. This ensured equal significance of variables with a standard deviation of 1 (Kokot et al., 1998). Detailed description of PCA and data pre-treatment can be found elsewhere (e.g., Adams, 1995).

3.   Results and discussion

3.1   Relating particle size to metal adsorption

Initially, the particle size distribution of build-up pollutants based on site and land use was compared (Fig. 2). It was found that more than 70% of the road deposited solids particles at all of the sites are finer than 150µm, highlighting the importance of fine particles (<150µm) in build-up solids.

Total metal concentrations per unit weight of solids across the four particle size ranges, <75µm, 75-150µm, 150-300µm and 300-425µm are summarised in Table 2. The results show that other than for a few exceptions, the majority of the metal concentrations in solids particles decrease with the increase in particle size. About 60% of the overall metal concentration is associated with <150µm particle size range (except Cu) while <75µm particle size range account for 33% of the overall metal concentration with only about 40% of metal concentration being associated with coarser particle size range. This highlights the importance of fine particles in the adsorption of metals.

3.2   Physical characteristics of road deposited solids

3.2.1   Mineralogy

The X-ray diffraction analysis enabled the identification of the proportions of crystalline minerals as weight percentages of the mineralogical component for each particle size range (unit sample weight). The mineralogical variations of different particle sizes in the four suburbs are illustrated in Fig. 3. The major mineral components were, quartz (SiO_2), albite ($NaAlSi_3O_8$), microcline ($KAlSi_3O_8$), chlorite ($H_8Mg_6O_{18}Si_4$) and muscovite ($H_2Kal_3(SiO_4)_3$). Additionally, minor proportions of orthoclase, kaolinite and riebeckite which are clay minerals were also detected in a few samples. Also, most importantly, a significant proportion of amorphous content (an unidentified fraction) was detected in all the samples. Essentially, the solids contained minerals primarily originating from surrounding soils. Clay forming minerals of albite, microcline, chlorite and muscovite were present in small fractions in all the particle sizes while albite and microcline (feldspar) formed the highest fractions of clay forming minerals. The crystal

lattice structure and different isomorphous substitutions of these clay forming minerals increase the surface charge characteristics of the solids particles (Sparks, 2003). The clay forming minerals content increases with the decrease in particle size providing good binding capacity for fine particles.

As evident in Fig. 3, despite some differences, the mineralogical composition of specific particle sizes was essentially similar in all suburbs, independent of the sampling site. Furthermore, more than two thirds of the solids particles >150µm were made up of quartz, whilst the remainder consisted of amorphous content, albite, microcline, chlorite and muscovite. Amorphous content ranged from 4% to 36% in 150-300µm particles and 4% to 41% in 300-425µm particles. Likewise, proportions of other mineral components in the 150-300µm and 300-425µm particle sizes were also in similar ranges at all of the study sites independent of the land use. This is attributed to the fact that the structural strength of quartz is able to resist physical abrasion on road surfaces much better than the other mineral components and amorphous material (Sparks, 2003). Consequently, the coarser particles (>150µm) are dominated by quartz. Therefore, it is to be expected that 150-300µm and 300-425µm particle sizes would exhibit similar physical and chemical characteristics which in turn influence adsorption characteristics.

The amorphous content is the second largest component in all particle sizes. Interestingly, the amorphous content reduced with the increase in particle size, and was proportional to the increase in quartz content. This highlighted the need for the detailed identification of amorphous material. Based on a comparison of mineral content of surrounding soil and build-up solids, Gunawardana et al. (2012a) found that surrounding soil has amorphous content of about 10% while build-up solids has about 40% amorphous content. They found that build-up solids have on average about 30% of material that can be classified as amorphous, and this unidentified fraction is derived from non-soil material and mainly from vehicular sources. Apart from these, a minor portion of amorphous material can consist of clay minerals present in small fractions (Khalil et al., 2004). Thin film clay analysis was undertaken to detect their presence. Fig. 4 gives a sample of thin film X-ray diffraction patterns for a solid sample from Nerang. Fig. 4 show reflections of clay minerals of illite, semectite, kaolinite, chlorite and mixed layer illite-smectite. Illite, mica and chlorite minerals were present in all the samples and kaolinite and sepolite were present in a majority of the samples. The analysis revealed the presence of the crystalline form of the above clay minerals in the finer solids particles (<75µm) and this amorphous material has relatively greater charge characteristics due to the crystal lattice structure and with the degree of isomorphic substitution (Sparks, 2003).

3.2.2 Morphology

Morphological characterisation of the solids particles was undertaken using scanning electron microscopic images to investigate the extent of contribution by traffic related activities to the amorphous content. The results obtained are shown in Fig.5 (a), (b), (c) and (d). The images show that the solids contain a high proportion of elongated particles with an irregular surface. Additionally, elemental analysis (EDX) indicated the presence of traffic related metals, Fe, Cu, Zn, Ni and Pb in these particles. Similar morphology

and elemental composition of tyre wear particles have been reported in past literature (Adachi and Tainosho, 2004; Kreider et al., 2010). Therefore, it can be concluded that the build-up solids contain a high fraction of particles that are generated by traffic related activities.

3.2.3   Specific surface area (SSA)

Surface properties can substantially influence pollutant retention by increasing the opportunity for metal cations to interact with the solid particle surface (Eisma et al., 1981). The SSA values obtained using the EGME method which is a measure of the total surface area (Carter et al., 1986), were averaged based on the suburb in order to identify the variation at different mineralogical locations (Table 3). Relatively high standard deviation for SSA indicates the highly variable nature of solid particles in different locations primarily due to differences in contributing sources. Similar characteristics are evident for TOC and ECEC as shown in Table 3.

As evident in Table 3, SSA decreases with the increase in particle size. High quartz content detected in mineralogical analysis of coarse particles would have influenced the lower SSA values. Quartz, which is a three dimensional framework silicate mineral, has low surface area (Sparks 2003). Similarly, the SEM images revealed that particles >150µm have angular surfaces without much porous material, whilst fine particles exhibit irregular surfaces with high content of porous material (Fig. 5). It can be noted in Table 3 that the SSA of particles <75µm is four times larger than for the particle size range 300-425µm. However, SSA of road deposited particles is not consistent with organic matter content (Table 3). For example, <75µm particle size range at Benowa, which show high TOC content, do not show proportionally high SSA content. As reported by Gunawardana et al. (2012b), high SSA of fine particles would be influenced by material other than organic matter found in road deposited solids. This is confirmed by the mineralogical composition and morphology of fine solids particles as discussed above. As noted above, high clay forming minerals such as albite, microcline, chlorite and muscovite content increases with the reduction in particle size, which would have contributed to the high SSA in <75µm particles (refer to Fig. 3). Fineness and the interlayer crystal structural characteristics of these minerals contribute to the increase in SSA. For example, SSA of muscovite is 60-100m^2/g and chlorite 25-150m^2/g (Sparks, 2003).

Additionally, tyre wear particles present in amorphous material have complex shapes, morphology and high porosity (Milani et al., 2004; Gunawardana et al., 2012a). The significant presence of traffic related particles would have also contributed to high SSA. However, unlike clay minerals, tyre wear particles do not exhibit charge characteristics on its own (Gupta et al., 2012; Kreider et al., 2010). Relatively large SSA of road deposited solids is not indicative of high surface reactivity where metals are adsorbed over the entire particle. Therefore, in order to understand the influence of SSA on cation retention on solids surfaces, detailed investigation of the correlation of SSA with effective cation exchange capacity, amorphous content and organic matter content was needed.

3.3 Chemical characterisation of solids

3.3.1 Organic carbon

As evident in Table 3 which gives the average TOC values for the different particle sizes, organic carbon increases with the decrease in size. It is difficult to identify significant differences in particle sizes 150-300µm and 300-425µm. According to past research literature, the smallest particle size range always exhibits significantly high organic carbon content irrespective of study site location or land use (Herngren et al., 2006; Roger et al., 1998). As noted by Sartor and Boyd (1972), this could be attributed to organic matter such as leaf litter having a relatively lower structural strength and being easily ground to fine particles by physical abrasion by vehicles. Furthermore, an appreciable fraction of organic matter in road deposited particles could be derived from particles generated by tyre wear (Fergusson and Ryan, 1984; Rogge et al., 1993).

3.3.2 Effective cation exchange capacity (ECEC)

Effective cation exchange capacity (ECEC), which is the sum of the exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, Na^+ and Al^{3+}), is an important parameter of solids as it determines the capacity to retain metal ions (Sparks, 2003). ECEC can be primarily attributed to the clay mineral components and various forms of organic matter (Bortoluzzi et al., 2006). According to Table 3, it can be seen that ECEC decreases with the increase in particle size.

The variation of ECEC between suburbs does not show a consistent trend. This indicates that ECEC is influenced by several factors. Particle mineralogy and organic matter are two primary factors (Lin and Chen, 1998). However, the contribution to ECEC by SSA, TOC and mineralogical components could be different. For example, the highest ECEC in particles <150µm was recorded in Nerang and Surfers Paradise samples despite the fact that these samples had a predominantly sandy matrix (Fig. 3). This implies that the highest contribution would be from mineral components, amorphous content and SSA since the TOC content at these study sites are comparatively low. Benowa which had the highest TOC content shows low ECEC. This suggests that the presence of mineralogical components have a relatively higher influence on ECEC than the organic matter content.

The main reason could be that the clay fraction identified in these particles primarily consists of illite, illite-mica and smectite, which are minerals with interlayer surface areas (Sparks, 2003; Hepper et al., 2006). The cation exchange capacity of common clay minerals in solids samples are: smectite (45-160cmol (+)/kg); illite, muscovite and chlorite (10-40cmol (+)/kg); and kaolinite (0-15mol (+)/kg) (Sparks, 2003; Shaw, 1992). The presence of even relatively small fractions of these clay minerals will increase the ECEC (Morras, 1995). For example, smectite was present in all the samples from Nerang. Surfers Paradise samples contained illite, mica and kaolinite.

3.4 Relationship between physical and chemical properties of solids

It was difficult to investigate the possible relationships between different physical and chemical parameters on a one-on-one basis due to the involvement of a number of factors such as different land use and soil characteristics. Therefore, principal component analysis (PCA) was carried out to identify these relationships. Each particle size range was separately investigated to identify the correlations between physical and chemical parameters specific to each size range. The data matrix consisted of 32 objects (eight samples collected in two different sampling episodes from four road surfaces in each of the four different suburbs) and 9 variables (TOC, SSA, ECEC and the six mineralogical components). The resulting PCA biplots are given in Fig.6. The relatively low data variance explained by the first two principal components suggested the necessity of another form of analysis to confirm the interpretations derived from PCA. For this purpose a correlation matrix was used for confirmation of outcomes and presented as Supplementary Tables S1-S4.

In Fig. 6a, SSA shows strong correlation with ECEC in <75µm particles suggesting that the large SSA in this size range is associated with high exchangeable cation sites. In both <75µm and 75-150µm particle sizes, ECEC has a negative correlation with organic matter. In principle, organic matter content in the form of humus (decomposed fraction) should contain high cation exchange capacity than the clay minerals (Sparks, 2003). Therefore, it can be concluded that the organic matter in fine particle size ranges in road deposited solids provides only a low contribution to ECEC. Furthermore, the elevated level of clay forming minerals in solids is partly responsible for this behaviour by TOC. For example, microcline (feldspar) minerals and layered minerals of muscovite (mica) in solids samples contain permanent negative charges due to isomorphous substitution in its lattice structure (Filep, 1999; Sparks, 2003). This indicates that cation exchange capacity/clay ratio is the predominant parameter influencing the charge characteristics of solids rather than the organic matter content (Carroll et al., 2004).

Interestingly, in the coarser particles (>150µm) SSA, TOC and ECEC are strongly correlated with each other, whilst ECEC is weakly correlated with clay forming minerals (Fig. 6c and Fig. 6d). This implies that ECEC in this size range is influenced by the organic matter content rather than the mineral components. Low variance associated with ECEC in the >150µm size range indicates that these particles would contain low cation exchange capacity. Strong negative correlation between ECEC and quartz indicates that the high quartz content in coarser particle size range has significantly influenced the reduction in the charge characteristics.

Correlations among physical and chemical properties in both, 150-300µm and 300-425µm particles are similar, which suggest the similarity in metal adsorption behaviour (See Fig. 6c and Fig. 6d). This can be confirmed based on the values shown in the correlation matrix (Tables S3-S4 in Supplementary information), where quartz and amorphous show strong negative correlations of -0.880 and -0.903 for 150-300µm and 300-425µm particle size ranges respectively. This is due to the similar mineralogical percentages in these particle size ranges (Fig. 3). Therefore, this implies that the

physical and chemical parameters of solids are primarily governed by their mineralogical composition.

The dominant quartz content in the coarse particle size range has led to strong correlation between albite, microcline, chlorite and muscovite in Fig. 6c and Fig. 6d. This indicates that the influence of each of these clay forming mineral components on the physical and chemical properties would be similar and the coarse particle size range exhibits properties which are related to quartz.

For all particle size ranges, the amorphous content shows strong negative correlation or no correlation with other crystalline mineralogical components (Fig. 6, Tables S1-S4 in Supplementary information). This suggests that a significant portion of amorphous content is derived from material other than un-diffracted mineral components. In the particle sizes which had high amorphous content (<150µm), the amorphous material show strong correlation with SSA and no correlation with ECEC (Fig. 6a and Fig. 6b). This suggests that amorphous content is a material with large surface area, but with low charge characteristics on its surface. Therefore, it leads to the conclusion that the amorphous content does not favourably contribute to metal adsorption to solids by cation exchange.

3.5 Relationship between metals and physical and chemical properties of solids

PCA analysis was subsequently carried out combining all the collected build-up samples. Variables considered in the analysis were TOC, SSA, ECEC, the six mineralogical components and the nine metal elements. Objects represented the 128 samples collected as part of the research study (4 size classes x 32 field samples collected). As evident in Fig.7, quartz shows strong negative correlation with all the parameters, especially the amorphous content. Similarly, quartz is not correlated with all of the metals. This suggests that a predominant amount of quartz content present in solids could affect their behaviour due to its electrically neutral crystal lattice. According to Fig.7, mineralogical components show good affinity to metal elements. Among the metal elements, Fe, Al, Mn, Zn, and Cr have moderate correlation with albite.

Fig.7 also shows three clearly separated groups of objects constituting particle sizes <75µm, 75-150µm and 150-425µm. The finer particles comprising of <75µm and 75-150µm show two separate clusters with objects consisting of 150-300µm and 300-425µm sizes forming one cluster due to the similarity in their physical and chemical characteristics as discussed above. As evident in Fig. 7, objects of coarser particle size ranges (300-425µm and 150-300µm) show negative scores on PC1 while objects from <75µm particle size range show highest positive scores on PC1. The high negative loading on PC1 is associated to quartz while loading on PC1 is associated with SSA and amorphous content. Similarly, on PC2 the high positive and negative loadings are associated with quartz and amorphous content, respectively. Accordingly, it can be concluded that the separation of object groups into three particle size ranges in relation

to metals adsorption is primarily influenced by quartz and amorphous content. Therefore, the analysis confirmed that the particle composition of solids play a critical role in the adsorption of metals.

4   Conclusions

The following important conclusions were derived from the study:

- Road deposited solids consists of minerals derived from natural sources (quartz, albite, microcline, chlorite and muscovite) and a significant amount of material derived from traffic related activities (amorphous). Among these mineralogical components, clay forming minerals exert a significant influence on the effective cation exchange capacity and specific surface area, thereby enhancing metal adsorption to solids particles.

- Although, the traffic related particles have high SSA, they do not necessarily possess charged surfaces. As such, the amorphous content does not favourably contribute to the cation exchangeable form of metal adsorption to solids.

- Charge characteristics of <150µm particles is primarily contributed by the clay forming mineral content, whilst for >150µm particles, organic matter content exerts a strong influence. The influence exerted by organic matter to the charge characteristics in fine particles is dictated by the nature and source of supply.

- Due to the presence of different proportions of minerals and organic matter, <75µm and 75-150µm particles display different physical and chemical characteristics. However, the coarser particle sizes (150-300µm and 300-425µm) display similar physical and chemical characteristics due to consistently high quartz content.

- Therefore, it can be concluded that the majority of the physical and chemical parameters of solids are governed by the mineralogical composition. Consequently, the determination of solids characteristics would enhance the design of effective stormwater quality management strategies and for evaluating the impacts of stormwater pollution on urban receiving waters.

Supplementary information

The correlation matrices between the physical and chemical parameters for the particle size ranges of <75µm, 75-150µm, 150-300µm and 300-425µm are provided in the Supplementary information.

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Table 1 - Parameters and test methods

| Parameter	Test method	Comments
Volumetric particle size distribution		Malvern Mastersizer S Particle Size Analyzer
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 solids samples for mineralogy and orientated samples for clay minerals in low proportions analysed using PANalyticalX'Pert PRO Multi-purpose diffractometer
Morphology	Scanning electronic microscopic images (SEM)	Samples mounted on carbon tape attached to aluminium studs scanned using Quanta 3D FIB
Specific surface area (SSA)	Ethylene glycol monoethyl ether (EGME) (Carter et al., 1986)	EGME forms monolayer coverage vacuumed under high vacuum 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^+

Table 2 - Average metal concentration in solids of different particle sizes

| Particle size	Al	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb
μm									
					mg/g				
<75	5.18±3.07	0.01±0.00	0.14±0.08	7.98±5.98	0.01±0.01	0.09±0.02	0.25±0.16	0	0.05±0.05
75-150	3.11±2.21	0.01±0.01	0.13±0.01	5.37±5.00	0.01±0.01	0.14±0.11	0.32±0.30	0	0.05±0.03
150-300	2.13±1.58	0.00±0.00	0.10±0.06	4.18±2.55	0.01±0.01	0.13±0.10	0.23±0.19	0	0.03±0.01
300-425	1.29±1.05	0.01±0.01	0.05±0.04	2.79±1.97	0.00±0.00	0.05±0.05	0.11±0.14	0	0.03±0.02
Total	11.71	0.03	0.42	20.31	0.03	0.40	0.91	0	0.17

**Table 3 - Physical and chemical properties of different particle sizes of solids**

| Suburb	Particle size	SSA	TOC	ECEC
	µm	m^2/g	mg/g	meq/100 g
Clearview Estate	<75	14.3 $\pm$ 6.16	1.74 $\pm$ 0.92	6.30 $\pm$ 2.98
	75-150	8.83 $\pm$ 3.95	1.07 $\pm$ 0.66	6.66 $\pm$ 3.60
	150-300	4.22 $\pm$ 1.97	0.72 $\pm$ 0.31	6.98 $\pm$ 2.28
	300-425	3.21 $\pm$ 1.52	0.51 $\pm$ 0.35	6.36 $\pm$ 3.98
Nerang	<75	16.0 $\pm$ 5.41	2.13 $\pm$ 1.50	13.7 $\pm$ 7.01
	75-150	7.50 $\pm$ 2.77	0.14 $\pm$ 0.09	9.21 $\pm$ 4.81
	150-300	5.23 $\pm$ 1.93	0.17 $\pm$ 0.10	6.02 $\pm$ 3.00
	300-425	2.31 $\pm$ 1.61	0.14 $\pm$ 0.02	5.51 $\pm$ 2.56
Benowa	<75	17.6 $\pm$ 7.03	6.97 $\pm$ 5.39	5.22 $\pm$ 3.61
	75-150	7.39 $\pm$ 5.80	0.79 $\pm$ 0.38	6.09 $\pm$ 3.83
	150-300	3.52 $\pm$ 2.11	0.77 $\pm$ 0.42	4.44 $\pm$ 3.57
	300-425	3.21 $\pm$ 1.23	0.71 $\pm$ 0.45	3.06 $\pm$ 1.85
Surfers Paradise	<75	22.3 $\pm$ 3.41	0.96 $\pm$ 0.20	12.5 $\pm$ 6.19
	75-150	13.6 $\pm$ 6.63	0.65 $\pm$ 0.14	7.89 $\pm$ 3.29
	150-300	7.05 $\pm$ 4.55	0.62 $\pm$ 0.12	3.80 $\pm$ 1.63
	300-425	2.70 $\pm$ 1.06	0.42 $\pm$ 0.21	4.47 $\pm$ 2.63
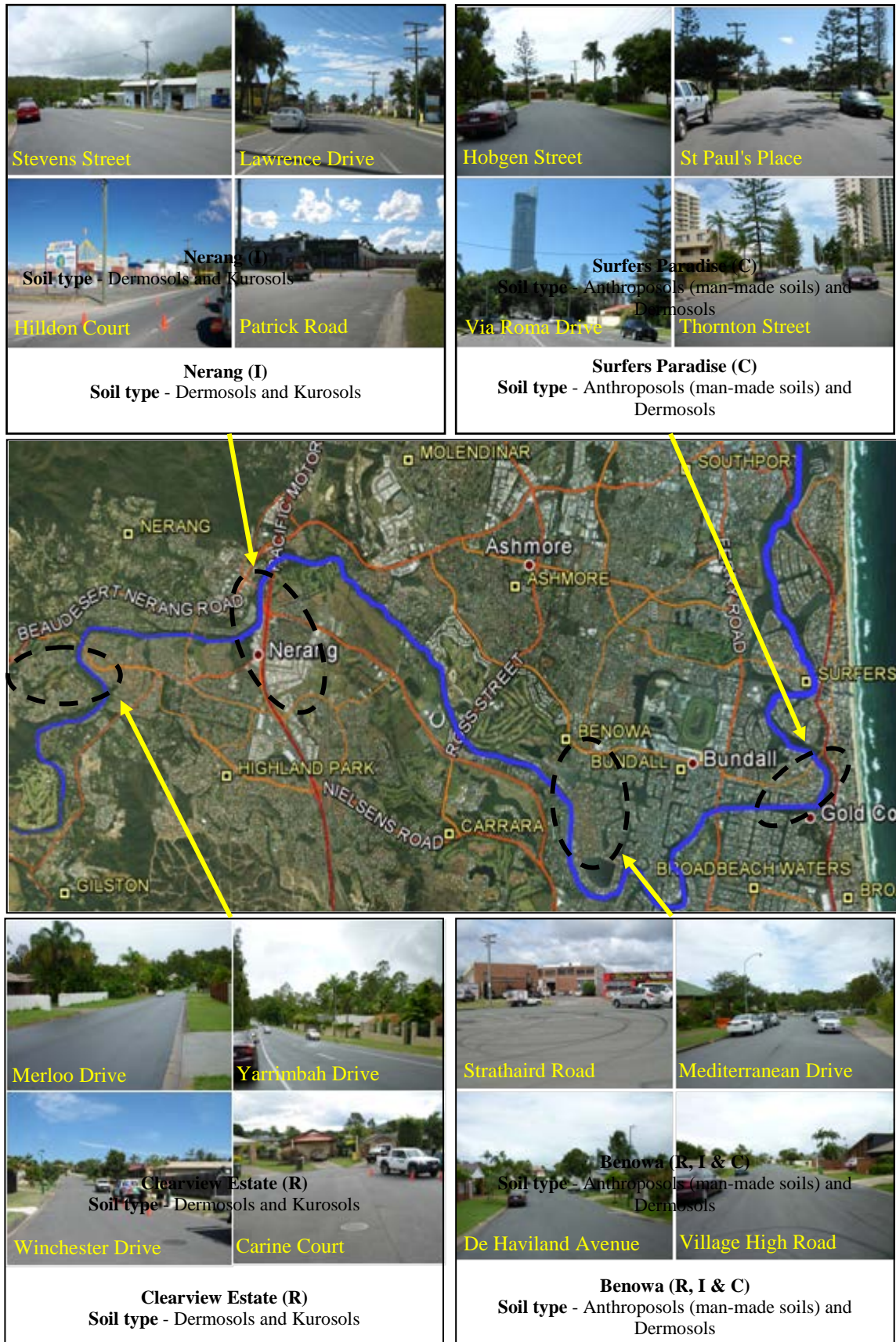
Fig. 1. Locations of study sites (Note: R- Residential, C- Commercial, I- Industrial)
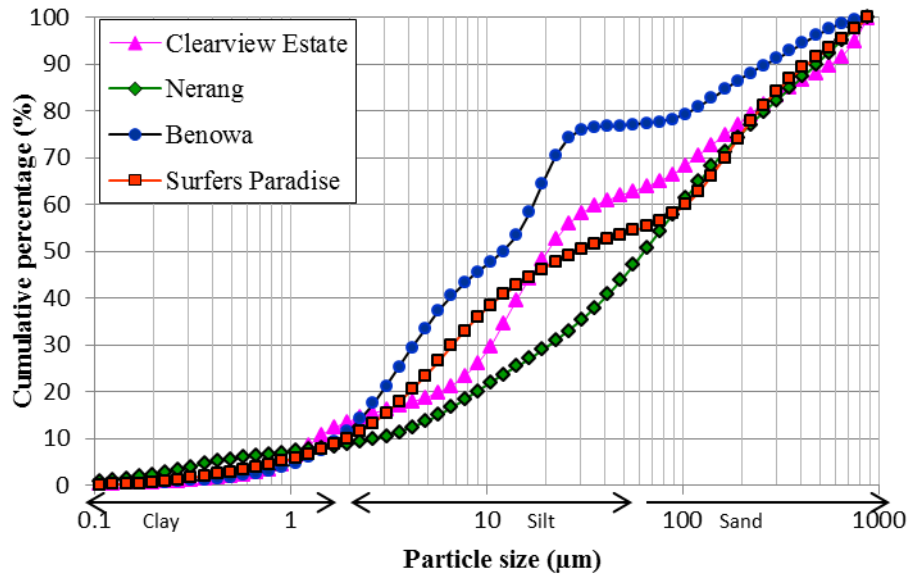
Fig. 2. Cumulative particle size distribution of solids build-up in each suburb
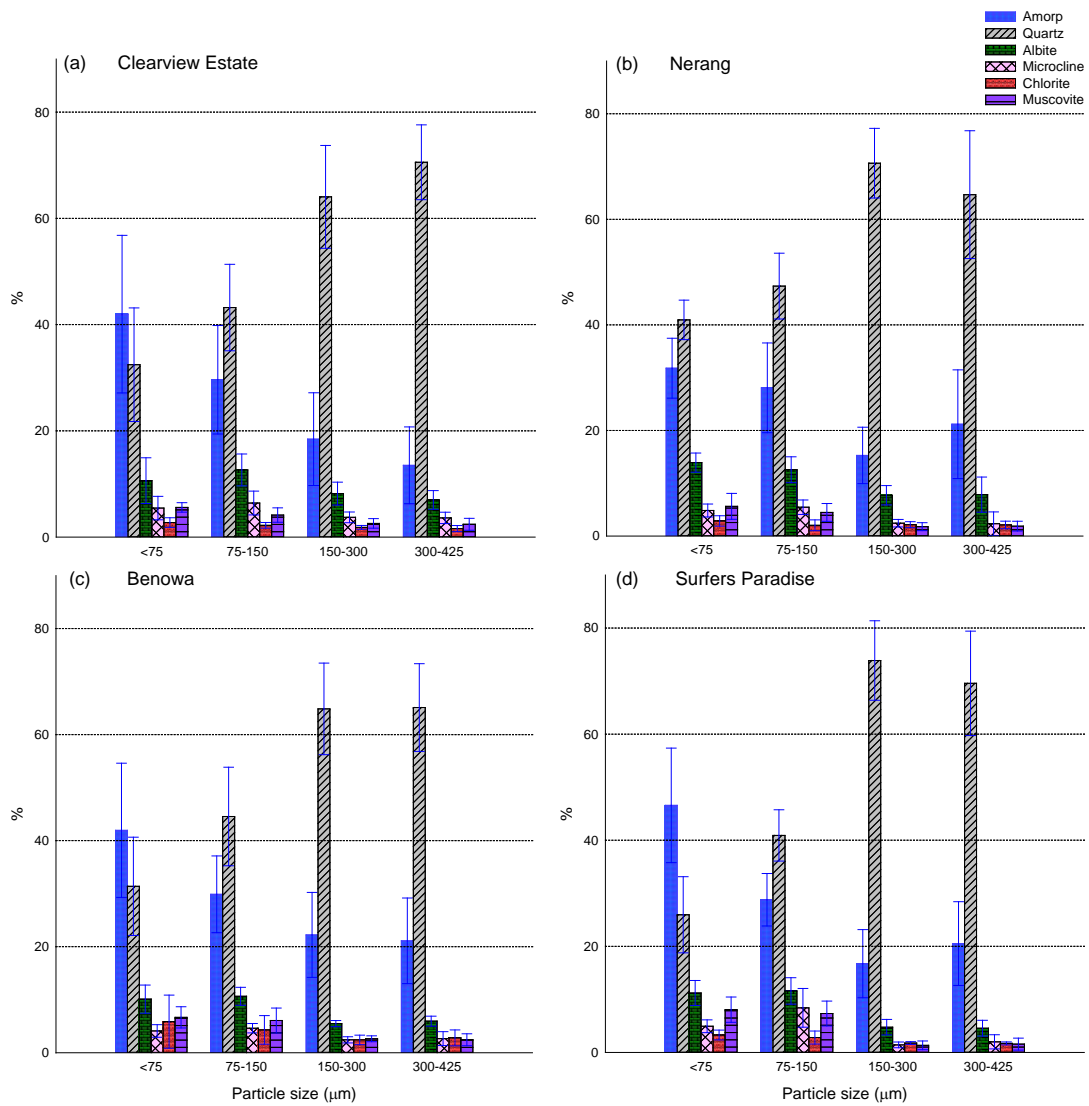
Fig. 3. Mineralogical variations in the four suburbs (a) Clearview Estate; (b) Nerang; (c) Surfers Paradise; and (d) Benowa
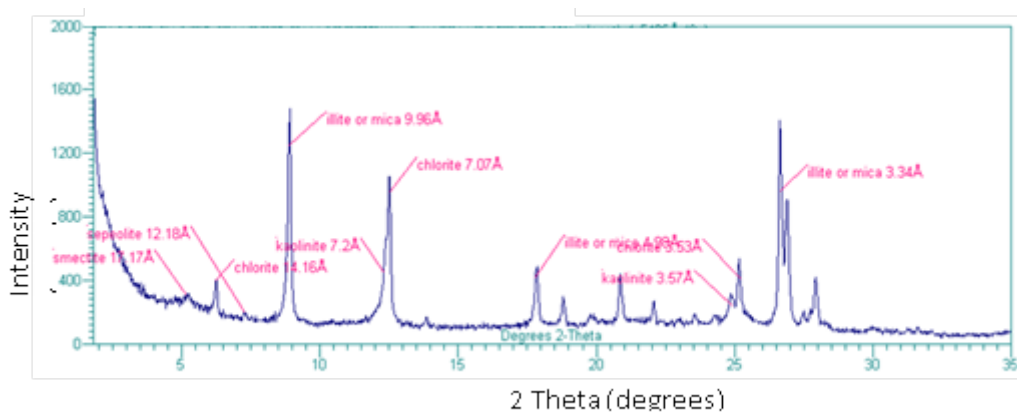
Fig. 4. Thin film X-ray diffraction patterns of solids collected at Nerang suburb
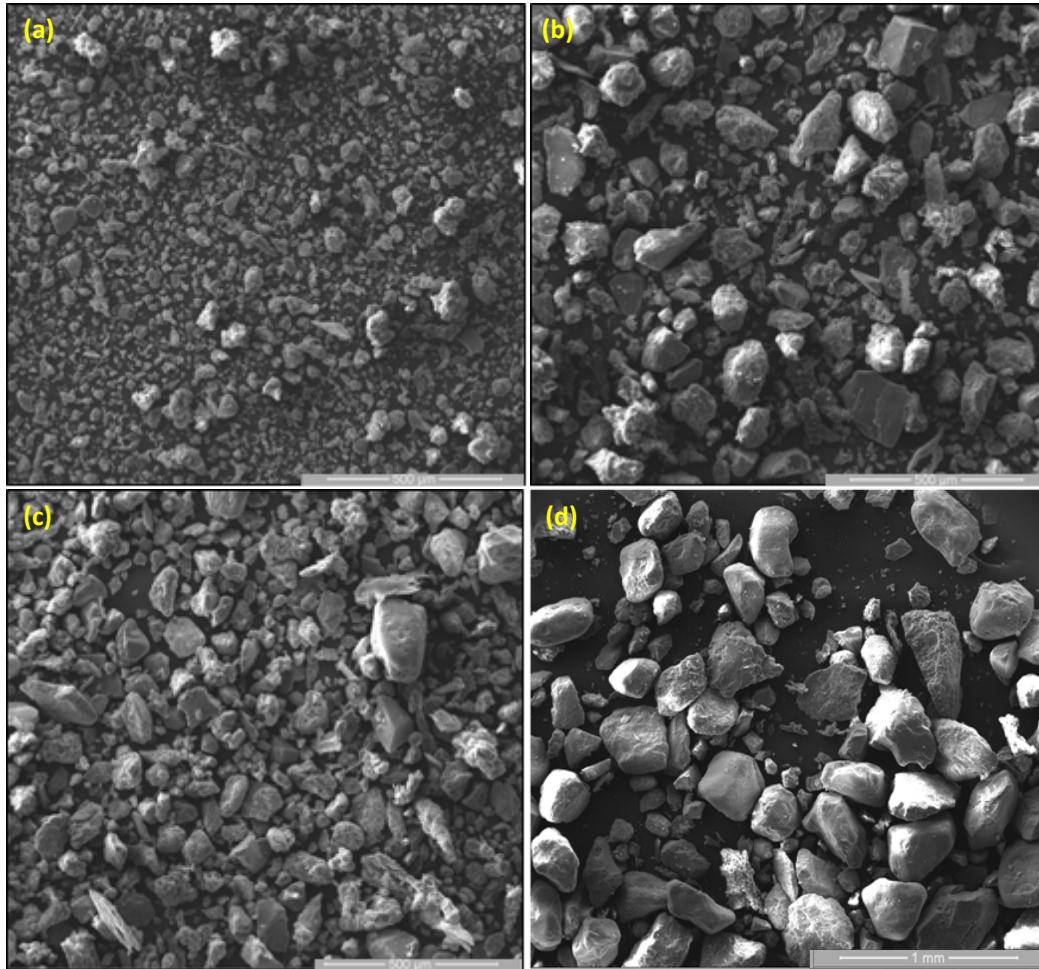
Fig. 5. Scanning electron microscope images of (a) particles <75µm; (b) particles 75-150µm; (c) particles 150-300µm; and (d) particles 300-425µm
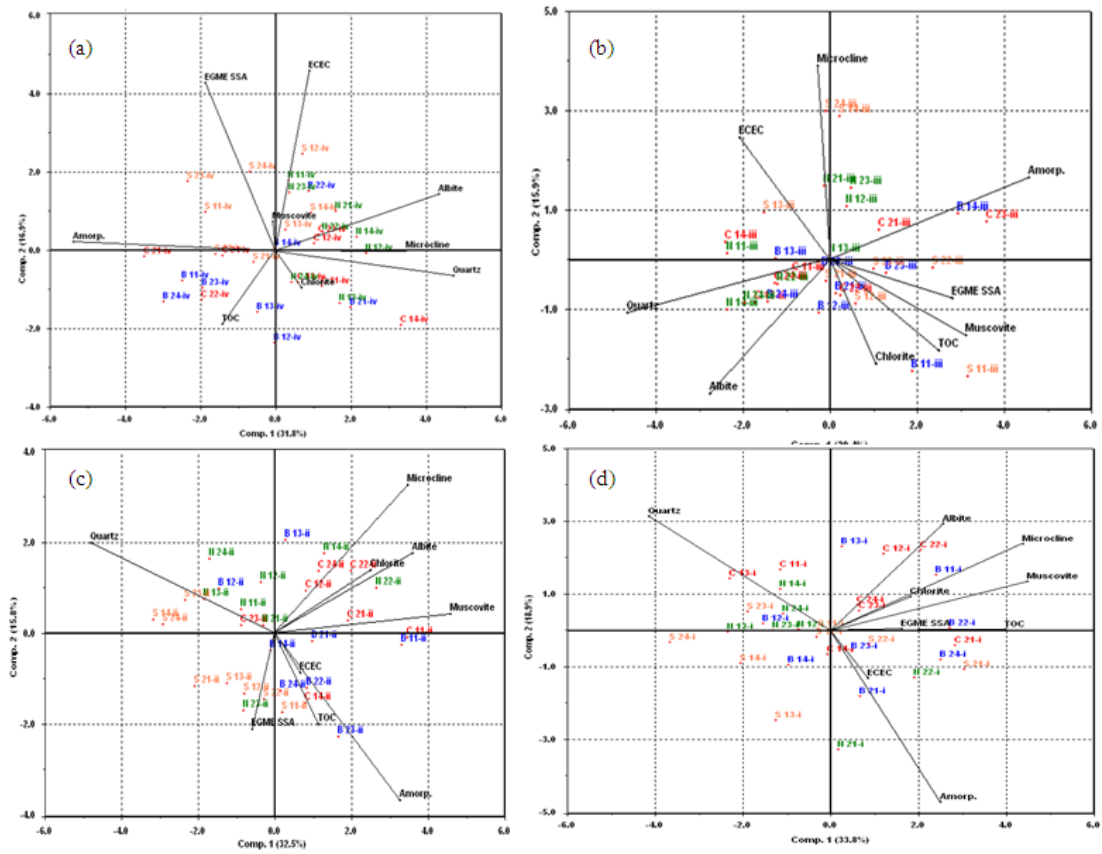
Fig. 6. PCA biplot of all sites for different particle size ranges; (a) particles <75µm; (b) particles 75-150µm; (c) particles 150-300µm; and (d) particles 300-425µm

Note: C: Clearview Estate, N: Nerang, B: Benowa, S: Surfers Paradise; Second character from 1-8 represents the sample number
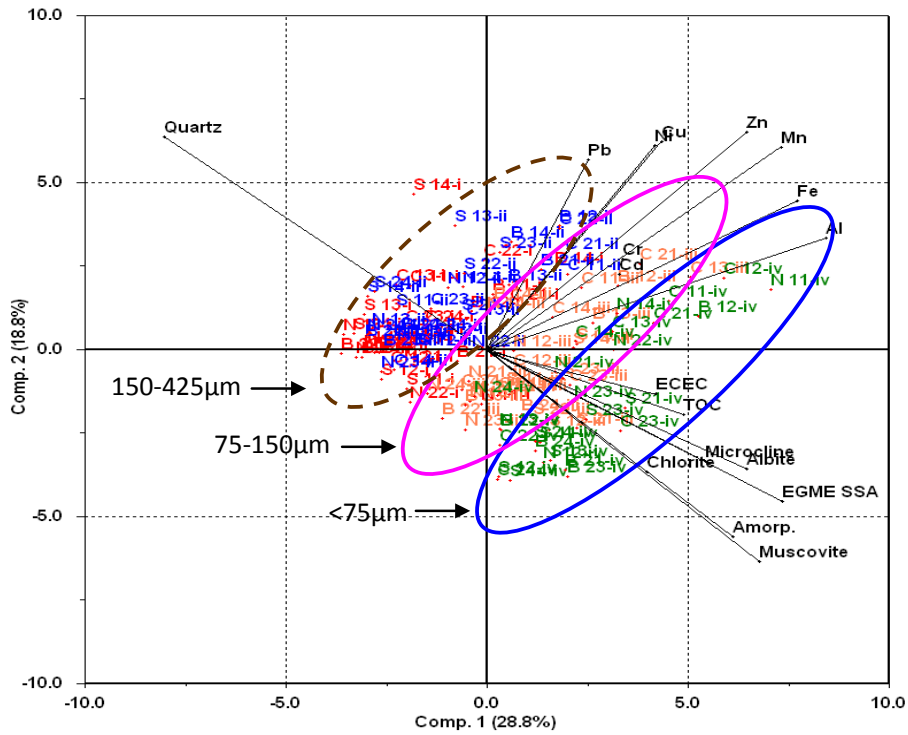
Fig. 7. PCA biplot of all particle size ranges

Note: C: Clearview Estate, N: Nerang, B: Benowa, S: Surfers Paradise; Second character from 1-4 represents the sample number; iv: <75µm, iii: 75-150µm, ii: 150-300µm, i; 300-425µm

Supplementary information

Role of particle size and composition in metal adsorption by solids deposited on

urban road surfaces

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Table S1: Correlation matrix between physical and chemical parameters for the <75µm particle size

	EGME SSA	TOC	ECEC	Amorp.	Quartz	Albite	Microcline	Chlorite	Muscovite
EGME SSA	1.000	-0.026	0.394	0.277	-0.366	-0.020	-0.170	0.043	0.202
TOC	-0.026	1.000	-0.201	0.130	-0.132	-0.132	-0.172	-0.012	0.174
ECEC	0.394	-0.201	1.000	-0.104	0.133	0.244	-0.007	-0.174	-0.106
Amorp.	0.277	0.130	-0.104	1.000	-0.887	-0.735	-0.502	-0.194	-0.049
Quartz	-0.366	-0.132	0.133	-0.887	1.000	0.462	0.303	-0.054	-0.177
Albite	-0.020	-0.132	0.244	-0.735	0.462	1.000	0.407	0.135	0.083
Microcline	-0.170	-0.172	-0.007	-0.502	0.303	0.407	1.000	0.026	0.247
Chlorite	0.043	-0.012	-0.174	-0.194	-0.054	0.135	0.026	1.000	-0.121
Muscovite	0.202	0.174	-0.106	-0.049	-0.177	0.083	0.247	-0.121	1.000

Table S2: Correlation matrix between physical and chemical parameters for the 75-150µm particle

	EGME SSA	TOC	ECEC	Amorp.	Quartz	Albite	Microcline	Chlorite	Muscovite
EGME SSA	1.000	0.168	-0.098	0.300	-0.363	0.004	-0.084	-0.081	0.328
TOC	0.168	1.000	-0.285	0.158	-0.132	-0.270	-0.096	0.162	0.242
ECEC	-0.098	-0.285	1.000	-0.228	0.185	0.001	0.206	-0.008	-0.149
Amorp.	0.300	0.158	-0.228	1.000	-0.852	-0.494	-0.081	-0.053	0.152
Quartz	-0.363	-0.132	0.185	-0.852	1.000	0.239	-0.081	-0.157	-0.395
Albite	0.004	-0.270	0.001	-0.494	0.239	1.000	-0.247	-0.067	-0.161
Microcline	-0.084	-0.096	0.206	-0.081	-0.081	-0.247	1.000	-0.129	-0.039
Chlorite	-0.081	0.162	-0.008	-0.053	-0.157	-0.067	-0.129	1.000	0.263
Muscovite	0.328	0.242	-0.149	0.152	-0.395	-0.161	-0.039	0.263	1.000

Table S3: Correlation matrix between physical and chemical parameters for the 150-300µm particle

	EGME SSA	TOC	ECEC	Amorp.	Quartz	Albite	Microcline	Chlorite	Muscovite
EGME SSA	1.000	0.156	0.047	-0.084	0.097	0.034	-0.325	-0.055	0.113
TOC	0.156	1.000	-0.147	0.145	-0.130	-0.102	0.054	0.014	0.307
ECEC	0.047	-0.147	1.000	0.074	-0.118	0.115	-0.155	0.153	0.091
Amorp.	-0.084	0.145	0.074	1.000	-0.880	0.093	0.013	0.038	0.287
Quartz	0.097	-0.130	-0.118	-0.880	1.000	-0.511	-0.347	-0.188	-0.569
Albite	0.034	-0.102	0.115	0.093	-0.511	1.000	0.507	0.149	0.452
Microcline	-0.325	0.054	-0.155	0.013	-0.347	0.507	1.000	0.200	0.540
Chlorite	-0.055	0.014	0.153	0.038	-0.188	0.149	0.200	1.000	0.524
Muscovite	0.113	0.307	0.091	0.287	-0.569	0.452	0.540	0.524	1.000

Table S4: Correlation matrix between physical and chemical parameters for the 300-425µm particle size range

	EGME SSA	TOC	ECEC	Amorp.	Quartz	Albite	Microcline	Chlorite	Muscovite
EGME SSA	1.000	0.107	-0.132	0.118	-0.180	0.053	0.259	0.026	0.141
TOC	0.107	1.000	0.163	0.223	-0.385	0.071	0.601	0.029	0.617
ECEC	-0.132	0.163	1.000	0.132	-0.126	-0.033	0.064	-0.041	0.068
Amorp.	0.118	0.223	0.132	1.000	-0.903	-0.154	-0.025	0.060	0.126
Quartz	-0.180	-0.385	-0.126	-0.903	1.000	-0.216	-0.324	-0.232	-0.426
Albite	0.053	0.071	-0.033	-0.154	-0.216	1.000	0.493	0.289	0.378
Microcline	0.259	0.601	0.064	-0.025	-0.324	0.493	1.000	0.225	0.702
Chlorite	0.026	0.029	-0.041	0.060	-0.232	0.289	0.225	1.000	0.168
Muscovite	0.141	0.617	0.068	0.126	-0.426	0.378	0.702	0.168	1.000