

Author version of paper published as:

Herngren, Lars, Goonetilleke, Ashantha and Ayoko, Godwin A (2006)

Analysis of heavy metals in road-deposited sediments. *Analytica Chimica Acta*, Vol. 571: pp. 270-278.

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## **ANALYSIS OF HEAVY METALS IN ROAD-DEPOSITED SEDIMENTS**

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### **ABSTRACT**

Road-deposited sediments were analysed for heavy metal concentrations at three different landuses (residential, industrial, commercial) in Queensland State, Australia. The sediments were collected using a domestic vacuum cleaner which was proven to be highly efficient in collecting sub-micron particles. Five particle sizes were analysed separately for eight heavy metal elements (Zn, Fe, Pb, Cd, Cu, Cr, Al and Mn). At all sites, the maximum concentration of the heavy metals occurred in the 0.45-75 $\mu$ m particle size range, which conventional street cleaning services do not remove efficiently. Multicriteria decision making methods (MCDM), PROMETHEE and GAIA, were employed in the data analysis. PROMETHEE, a non-parametric ranking analysis procedure, was used to rank the metal contents of the sediments sampled at each site. The most polluted site and particle size range were the industrial site and the 0.45-75 $\mu$ m range respectively. Although the industrial site displayed the highest metal concentrations, the highest heavy metal loading coincided with the highest sediment load, which occurred at the commercial site. GAIA, a special form of Principal Component Analysis, was applied to determine correlations between the heavy metals and particle size ranges and also to assess possible correlation with Total Organic Carbon (TOC). The GAIA-planes revealed that irrespective of the site, most of the heavy metals are adsorbed to sediments below 150 $\mu$ m. A weak correlation was found between Zn, Mn and TOC at the commercial site. This could lead to higher bioavailability of these metals through complexation reactions with the organic species in the sediments.

*KEYWORDS: Heavy metals; PROMETHEE and GAIA; urban water quality; chemometrics; MCDM methods*

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## 1. INTRODUCTION

The presence of pollutants such as heavy metals in road-deposited sediments play an important role in dictating urban stormwater quality [1]. During rainfall, pollutants from both natural and anthropogenic sources are transported into receiving waters, where they affect stormwater runoff quality markedly. Those from natural sources vary significantly within catchments and may include materials transported by water from surrounding soils, pollutants from dry and wet atmospheric deposition and biological materials from vegetation [2-3]. Significant quantities of particulate matter can also be attributed to anthropogenic sources such as industrial processes, vehicle emissions, and tyre and road surface wear [4-5]. Of these anthropogenic sources, particulates derived from automobiles and local soils have been identified as the dominant source of sediment accumulation on a paved surface in urban areas [6-7].

In addition to the load of such sediments, their size distribution plays a critical role in urban stormwater management plans. Therefore, in order to model stormwater runoff quality accurately and assess pollutant transport dynamics correctly [8], it is essential to have information on the magnitude of the sediment load, the particulate input from different sources and the particle size distribution. Larger particles are relatively easy to monitor and remove. On the other hand, when finer materials are incorporated into urban stormwater runoff, they have the ability to stay in suspension longer and are therefore transported a greater distance by urban runoff [9]. Furthermore, particles smaller than 50 $\mu\text{m}$  can be a significant component in runoff, contributing to as much as three quarters of the weight of total solids [10]. Bender and Terstriep [11] found that conventional street sweepers are only able to efficiently remove particles larger than 250 $\mu\text{m}$ . Though efficiencies have greatly improved over the last two decades, the removal of fine fractions is still an issue [12]. Hence, smaller particles remain behind after street sweeping and are incorporated into stormwater runoff.

In addition to the obvious water quality impairment caused by sediments such as high turbidity, sediments act as a mobile substrate for other pollutants such as heavy metals [13, 4]. In this regard, smaller particles are of more concern than larger particles because they have relatively high surface area, which facilitates the adsorption of pollutants [14-15]. Since anthropogenic sources contribute more to the smaller

particle sizes than natural sources [16], the adverse effects of such particles are more noticeable in urban areas where anthropogenic sources of water pollutants abound.

Wilber and Hunter [17] found a positive linear relationship between organic matter and heavy metals. Similarly, Hamilton et al. [18] showed that the organic fraction plays a major role in partitioning metals into different particle sizes. Several other researchers have reported that fine particulates contain higher organic carbon content than the coarse sediment [10, 19]. Therefore, the crucial role played by finer particulates in urban stormwater is further exacerbated by the high content of organic carbon present.

Given this background, this paper reports the results of a study of the importance of particle size in the accumulation heavy metals on road surfaces at three different landuse sites in the Gold Coast region, Queensland State, Australia where univariate and multivariate analytical methods were employed. PROMETHEE (Preference Ranking Organization METHod for Enrichment Evaluation) and GAIA (Graphical Analysis for Interactive Assistance) were the preferred multivariate methods, which are commonly used in chemometric studies. However, the use of these methods in an urban water quality study is quite novel. This paper highlights the significant advantages that can be obtained by using such methods in urban water quality investigations. The study also investigated the role of organic carbon content in the partitioning of heavy metals in sediments. The partitioning of heavy metals into different particle size fractions can have significant implications on urban stormwater management measures such as street sweeping and the use of retention/detention ponds. Additionally, the study is significant because an understanding of the relationships between heavy metals and particle size fractions with variables such as organic carbon could provide invaluable information for the development of appropriate management strategies to protect the water environment in urban areas.

## **2. MATERIALS AND METHODS**

### *2.1 Study area*

The research sites were located in the Gold Coast region just south of the Queensland State capital, Brisbane, Australia. Gold Coast region is a popular holiday destination

and has one of the highest population growth rates in the country. It has a subtropical climate with wet summers and dry winters and a varying topography covering both the south-eastern coastline of Australia and the hinterland.

Research site 1 was an access road (Millswyn Crescent) located in a typical suburban residential area (Residential A) with detached family houses with small gardens. The site was chosen due to its typical suburban characteristics. The road system is primarily used by the residents for access, which was reflected in the relatively satisfactory condition of the street surface. An early investigation of the households suggested that various chemicals were used as fertilizers or for other purposes. Therefore they could be incorporated into the wash-off from the area. It was also found that street sweepers operate in the area every six weeks, which may influence the availability of pollutants on the road surface at certain times.

Research site 2 (Stevens Street) was located in a light industrial area. The site was chosen because of the diversity of industries located along the road. Industries at the site include a sheet metal works, a boat painter, a furniture manufacturer and other small enterprises. The street surface condition compared to the residential site was significantly degraded.

Research site 3 was a parking lot in a major shopping centre. The shopping centre has 570 parking spaces and is considered to be one of the busiest in the region with 45 specialty retailers in the complex. The condition of the parking lot was found to be fair but with a coarse texture. The coarse texture suggested that large numbers of particles would be embedded within the voids.

## *2.2 Sample collection*

The collection of accumulated material on the road surfaces was carried out using a domestic vacuum cleaner. The vacuum cleaner had a water filtration system which significantly enhanced its efficiency in retaining fine particulates. Several previous studies have used vacuum cleaners to collect road deposited sediments [20-21]. However, the collection efficiency is usually hampered by the exhaust system on vacuum cleaners, which commonly release the collected sub-micron particles. This was prevented in the current study by the water filtration system.

In order to determine the collection efficiency of the vacuum cleaner, a known mix of particles with specific particle sizes was spread on a bitumen slab with an average texture depth of 467 $\mu$ m. This represents the medium texture of a standard road surface in Australia. The bitumen slab was then vacuumed four times and the quantity of particles collected was determined. The overall collection efficiency of the vacuum cleaner was found to be 91.0 ( $\pm$  0.5)%.

At each of the three research sites, a 3m<sup>2</sup> collection area was enclosed and the particulate matter collected from the enclosure, which was situated in the exact middle of the kerb and the median strip except for the commercial site where it was situated in the exact middle of a parking lot. Although past research has shown that a large fraction of the sediments is located near the kerb [4], the distribution pattern of heavy metals in different particle sizes was assumed to be the same throughout the width of the road.

The enclosed area was carefully vacuumed four times with the aid of a fine brush attached to the vacuum nozzle to ensure that as much solids as possible was collected. Bris et al. [20] found that brushing the surface to release particulates enhanced the collection efficiency significantly. Due to the water filtration system used by the vacuum cleaner, the collected material was suspended in de-ionized water and the suspended sediments were subsequently transferred into 1L polyethylene bottles before they were transported to the laboratory where any necessary pre-treatments were carried out. The samples were then refrigerated at 4°C until further analysis. Additional data on antecedent dry period was also collected for each site.

### *2.3 Laboratory analysis*

Prior to any chemical analysis, the particle size distribution of the sediments was determined using a Malvern Mastersizer S Particle Size Analyzer capable of analysing particles between 0.05 micron and 900 micron. The Malvern Mastersizer uses a laser to record the scattering pattern from a field of particles. It then uses an analytical procedure to determine the size of particles that created the scatter pattern. Electrical Conductivity (EC) and pH measurement were conducted on the collected

sample before it was separated into particle size classified sub-samples. Thus, the water samples were wet sieved using sieve sizes of: 300 $\mu\text{m}$ , 150 $\mu\text{m}$  and 75 $\mu\text{m}$  and the particles passing through the 75 $\mu\text{m}$  sieve was filtered using a 0.45 $\mu\text{m}$  nitrocellulose filter (Whatman). The filtrate was assumed to contain the dissolved fractions of the various pollutants. This procedure afforded five sub-samples for each water sample: >300 $\mu\text{m}$ , 151-300 $\mu\text{m}$ , 76-150 $\mu\text{m}$ , 0.45-75 $\mu\text{m}$  and <0.45 $\mu\text{m}$ . Organic carbon content, total solids and heavy metals analysis were then undertaken on the particles on each of the sub-samples.

Total Organic Carbon (TOC) content of the different particle sizes and dissolved organic carbon (DOC) content of the filtrate were measured using a Shimadzu TOC-5000A according to method 5310B in Standard Methods for the Examination of Water and Wastewater [22].

Each particle size fraction and the filtrate were analysed for eight metal species (Zn, Al, Fe, Mn, Cu, Cd, Cr, Pb). Particulate samples were digested for heavy metal analysis using the nitric acid digestion procedure described by Eaton et al. [22]. 50mL of de-ionized metal-free water and 5mL of nitric acid were combined in a 250 mL Erlenmeyer flask. The particulate sample was added to the solution and the extract was gently boiled until the volume of solution had evaporated down to 10mL. Nitric acid was then added (15mL) until the solution became clear, which indicated that the digestion was complete. The digested sample was then filtered through a 0.45 $\mu\text{m}$  filter to remove any leftover particles and kept under refrigeration until analysis. The filtrate sample was preserved using 1mL of nitric acid and analysed as a water sample.

The particulate extracts and the water sample were analysed using Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) (Perkin Elmer Elan 6100DRC). As part of quality control/quality assurance measures internal and external standards, duplicate samples as well as metal-free de-ionized water were used in the analysis. The recoveries of samples spiked with standards ranged from 80-116%, which is well within the acceptable recovery range of 75-120%. The lower limit of reporting was 0.005 mg/L for Al and Fe, and 0.001 mg/L for Zn, Pb, Cd, Cr, Cu and Mn.

#### 2.4 Data analysis

The relatively large amount of data generated in this research made it difficult to compare the sites and important particle sizes using univariate analysis only. This problem was overcome by using multi-variate approaches in order to explore and understand relationships between the objects and the variables [23]. The selected particle size ranges and sites were ranked with the help of multicriteria decision making (MCDM) methods. Different types of software can be used to help this decision making process. In this research, methods referred to as PROMETHEE and GAIA were used with the aid of DecisionLab software [24]. PROMETHEE is a non-parametric method, which ranks a number of objects or actions, in this case the sediment samples at different particle size ranges, on the basis of a range of variables or criteria (concentrations or loadings of heavy metals and Total Organic Carbon). GAIA is a visualisation method, which displays PROMETHEE results as simple principal component analysis biplots.

A number of modelling options have to be chosen before PROMETHEE and GAIA can be implemented on any raw data matrix. These options include the choice of an appropriate preference function and the weighting given to each variable. The preference function defines how one object is to be ranked relative to another and translates the deviation between the evaluations of two samples on a single parameter into a preference degree. The preference degree represents an increasing function of the deviation; hence smaller deviations will contribute to weaker degrees of preference and larger ones to stronger degrees of preference [24]. Six preference functions represented by specific shapes are available in the PROMETHEE method. Each shape is dependent on two thresholds, Q and P. Q is an indifference threshold representing the largest deviation that is considered negligible and the preference threshold P represents the smallest deviation that is considered as decisive. P cannot be smaller than Q. The Gaussian threshold S is a middle value that is only used with the Gaussian preference function. The six preference functions available in PROMETHEE [25] are represented in Table 1.

Preference flows are used to compare the samples with each other so that a positive preference flow ( $\Phi^+$ ) expresses the degree to which the sample is preferred over the

other samples while the negative flow ( $\Phi^-$ ) expresses the degree to which all the other samples are preferred to the specific sample. The net flow ( $\Phi$ ), which is the difference between the positive and negative flows is commonly used to rank objects in such a way that the larger the net flow of a sample, the higher the rank order of the sample relative to the other samples. PROMETHEE gives the user two options in displaying the results, either the partial ranking (PROMETHEE I) or complete ranking (PROMETHEE II).

GAIA, on the other hand, is a descriptive complement to the PROMETHEE methods, which makes use of the principles of Principal Component Analysis (PCA). The GAIA plane corresponds to the projection of PROMETHEE II results on the first two orthogonal principal components. Criteria or variables are then represented by axes or vectors, whose orientation and length illustrate the importance of the variables. Axes oriented in similar directions correspond to variables that are in general agreement and the length of the variable vector shows the amount of important deviations observed. Thus, a variable with a larger deviation will have a longer axis than a variable with a small deviation. Further information on how to use PROMETHEE and GAIA as well as the algorithms for these procedures have been documented elsewhere [25-26].

In this paper, PROMETHEE and GAIA were used to evaluate the heavy metals in each particle size. The TOC content was also included in the analysis in order to evaluate any relationship between organic carbon and the heavy metals. Hamilton et al. [18] found that the organic fraction can play a major role in the partitioning of metals in sediments. Therefore, multivariate data analysis was conducted on raw data matrices (15 x 9) containing the heavy metal and TOC data for each of the five particle sizes at each of the three sites.

### **3. Results and discussion**

#### **3.1 Distribution of the heavy metals**

Table 2 shows the amount of build-up collected in each of the five chosen particle size fractions. The largest amount of sediments collected in all size ranges was at the commercial site. It seems plausible that this is due to the large amount of vehicular traffic that passed through this site. Additionally, of all sites, the commercial site had

the shortest antecedent dry period (1 day) suggesting that sediments accumulated quickly after a rainfall event. The industrial site had the longest antecedent dry period (7 days) but the lowest amount of sediments were collected for the residential site, which had an antecedent dry period of 2 days. This is possibly due to the fact that the residential site had the lowest traffic volume. The importance of antecedent dry period in pollutant load has been widely discussed in past research [4, 27]. However, the degree of influence this parameter exerts on pollutant build-up is highly variable. For example, Hunter et al. [13] found that only 17% of the variance in pollutant load was attributable to variations in time since the last storm or cleaning event. Sartor and Boyd [4] found that the pollutant load increases with the antecedent dry period. However, small data sets and large data scatter make the form of the relationship hard to determine. The findings in this research further highlighted the uncertainty with regards to the importance of the antecedent dry period in pollutant build-up. This is particularly in the case of the commercial site where the sediment build-up load was the highest even after the shortest antecedent dry period. However, it is important that the sediment build-up is understood in the context of the landuse rather than purely in terms of the antecedent dry period.

A clear pattern in particle size distribution was apparent at all sites. The highest amount of particles collected was consistently in the 0.45-75 $\mu$ m size range followed by the 76-150 $\mu$ m size range. It was found that over 90% of the particles at each site were below 150 $\mu$ m. Similar results have been reported by Andral et al. [10] and this suggest that particulates below 150 $\mu$ m are of specific concern in urban areas. Since sediment removal techniques such as street sweeping only efficiently remove relatively large particles [11-12], the problems posed by sediment particles under 150 $\mu$ m size range are significant.

The particle volume distribution of the collected material at each site was also investigated. As can be seen in Figure 1, the residential and commercial sites had similar particle volume distribution while the industrial site had a higher volume of larger particles than the two other sites. The high volume of larger particles at the industrial site could be explained by the less frequent street cleaning practises in industrial areas compared to the commercial and residential areas [4]. Alternatively

this could be due to the dispersion of smaller sediments as a result of the heavy vehicle traffic operating in the industrial area.

The results of the heavy metal analysis from each site are shown in Table 3. Eight elements were tested in each particle size range and the highest concentrations were consistently found in the 0.45-75 $\mu\text{m}$  size range. This further strengthens the importance of removing fine particulates from road deposited sediments. The least detected heavy metal in this particle size range was Cd followed by Cr. With the exception of Fe at the commercial site, Zn was the most abundant element in the <0.45 $\mu\text{m}$  size range at all of the sites. This can be attributed to the relatively high TOC content in this size fraction at the three sites (Table 4). Similar correlations between TOC and Zn have been reported by several past researchers [28-29]. Such correlations highlight the importance of TOC in the dissolved phase of urban stormwater runoff. Although high TOC content was also found in the largest particle size range at all sites, the TOC content seemed to have a lesser effect on the heavy metal concentration in this size fraction. As noted in past research [14, 30], this could be due to the lower sorption capacity of larger sediments. Another reason could be the difference in the nature of the sediments, which depends on the source of the organic matter [19].

Fe and Al concentrations were usually the highest at all sites. Research has shown that soil dust can account for over 60% of the Al concentration [31], confirming that the deposition of eroded soil particles is an important pollutant source at all three sites. It is postulated that the primary source of Fe and Al would be the soil. It can also be seen in Table 3 that particles up to 75 $\mu\text{m}$  contribute more than half of the total concentrations of the heavy metals. However, the commercial site shows a fairly random distribution of heavy metals into the various size fractions. A possible explanation for the higher concentration of heavy metals in the larger particle size fractions at the commercial site could be the relatively heavier flow of traffic in this area. Furthermore, vehicle emissions give rise to soot-like particles, which may irreversibly trap compounds such as heavy metals [19].

The highest concentrations of Fe, Zn, Pb, Al, Cu, Cr and Mn occurred at the industrial site. However, the concentration of Cd found at the various sites is quite low and

hence it is difficult to draw firm conclusions from the distribution of this metal. Similar to this study, Sartor and Boyd [4] investigated the land use factor and found industrial areas to have the highest concentrations of heavy metals. In the current study, the relatively high concentrations of heavy metals at the industrial site reflected the variety of industries at the site. Al and Mn are signature elements for steel production but the presence of Zn, Fe and Pb would be due to heavy vehicle traffic [8, 32].

The means and the standard deviations (deviation from mean) of the concentrations of the heavy metals in Table 3, independent of particle size range, are shown in Table 5. Although the industrial area had the highest concentrations of seven of the eight heavy metals, it can be seen in Table 5 that the highest mean concentration of only four of the eight heavy metals occurred at this site. It is also evident from Table 5 that the standard deviations associated with the mean concentrations of the metals at the industrial site were higher than the corresponding figures at the residential and commercial sites. This suggests that irregular distribution of heavy metals occurred at the industrial site, which had a higher volume of larger particles (Figure 1) but poor distribution of heavy metals in the larger particle sizes. This again highlights the importance of removing smaller particles for mitigating heavy metal pollution in urban stormwater.

The total heavy metal loading in each particle size fraction is shown in Figure 2 while Table 6 shows the individual heavy metal loadings in each particle size fraction. As can be seen, the commercial site dominates the heavy metal loading. It is also evident that the 0.45-75 $\mu$ m particle size fraction has the highest loading of heavy metals at all sites. The higher loading at the commercial site compared to the other sites is due to the high amount of particles that were collected at the site. However, the industrial site show higher loadings of heavy metals in the largest size fraction (>300 $\mu$ m). This reflects the particle size distribution at the site, which showed a larger volume of larger particles than the two other sites.

### **3.2 PROMETHEE and GAIA analysis**

In order to assess the relationships between heavy metals and TOC and rank the sites and particle sizes on the basis of their metal loadings, PROMETHEE and GAIA

methods were used. GAIA was primarily used as a visualisation tool for examination of the correlations between TOC content and the heavy metals. It also revealed the correlations between the heavy metals themselves and indicated the particle size and site which they were associated with. PROMETHEE was used to determine the most detrimental particle size and at which site this occurred. The user is required by the PROMETHEE method to maximise or minimise each criterion, that is to declare whether the higher values of a variable (maximised) or lower one (minimised) are preferred. In this study, all the variables were “minimised” and given the same weighting. By minimising all parameters, particle sizes and sites with lower concentration of the heavy metals were preferred and using the same weighting no variable was favoured over the other. The preference function chosen for all variables was the V-shaped function and the threshold was set to the highest concentration of each variable, so that any variable value that is lower than this threshold is considered to be important in the analysis.

PROMETHEE ranked the sites and particle sizes from best to worst in terms of heavy metal pollution. As seen in Figure 3, the most polluted fraction was the 0.45-75 $\mu$ m fraction at the industrial site followed by the corresponding size fraction at the residential and commercial sites. Both the industrial and residential sites were ranked worse than the commercial site in the 0.45-75 $\mu$ m range. However, the commercial site had four out of its five particle size ranges ranked in the seven worst polluted objects. This indicates that a commercial site needs proper planning in urban stormwater management and that treatment of a large range of particles is necessary. This could be made by so called “treatment trains” where pre-treatment and secondary treatment will efficiently remove a large range of particles. In general, at all sites, sediments under 150 $\mu$ m were the most polluted size fraction based on their heavy metal content. Interestingly, the best ranked objects were the particle size ranges 151-300 $\mu$ m and 76-150 $\mu$ m at the industrial site. The major difference between the heavy metal loading in these particle sizes and the 0.45-75 $\mu$ m particle size range at the industrial site is likely reflecting fine industrial waste heavy metal particles deposited on the road. Larger waste particles are easier for industries to control at the source and are unlikely to be deposited on the road.

One of the advantages of using PROMETHEE and GAIA in this work was that PROMETHEE ranked the particle size fractions at each site while GAIA provided important information on correlations between the variables and particle size fractions. Another advantage of these MCDM methods is that GAIA incorporates a decision axis,  $\pi_i$ , which compliments the decision from the PROMETHEE ranking. When  $\pi_i$  is long, the most preferred objects are oriented in its direction and furthest from the point of interception of the principal component 1 and principal component 2 axes. With the “minimised” modelling option, variables which are associated with particular objects were displayed opposite those objects. Therefore, in order to facilitate the appreciation of the variables that correlated with a particular particle size fraction, the variables were modelled in GAIA analysis using the “maximised” option. Quadratic shapes represent the variables in the GAIA-analysis (heavy metals and TOC), while the size fractions of each site are represented by the numbers and different symbols given in Table 7.

79% of the total variance ( $\Delta$ ) of the data matrix was accounted for in the GAIA analysis, which indicates that more than three quarters of the available information was included in the GAIA analysis. As can be seen in Figure 4, with the exception of Cd, most of the heavy metals (Cluster A) showed a strong relationship with the particle size 0.45-75 $\mu\text{m}$  in all of the sites. Cd showed a somewhat different pattern possibly because its concentrations were low at all sites. It is also apparent from Figure 4 that the TOC content was independent of the heavy metal concentrations at any site but was correlated with two particle size fractions at the commercial site (Cluster B), <0.45 $\mu\text{m}$  and >300 $\mu\text{m}$ .

To explore the correlation between heavy metals and TOC content further, the GAIA-planes for each of the sites was examined separately. It is apparent from Figures 5, 6 and 7, that TOC content has a weak correlation with Zn and Mn at the commercial site (Cluster C) and a weak correlation with Pb, Fe, Al and Mn at the residential site, particularly in particles below 150 $\mu\text{m}$ . This could be due to the source, age or weathering of the organic matter in the sediments [19]. The lack of vegetation at the commercial site suggests that the organic matter at this site could be traffic related. Furthermore, since the commercial site had the highest TOC concentrations, sorption and desorption of pollutants such as Zn and Mn was more likely to occur at this site.

Such processes could have severe implications on urban stormwater management systems due to their potential to enhance the bioavailability of these heavy metals through complexation with organic carbon. The weak correlation between Pb, Fe, Al and Mn at the residential site was most probably influenced by the soil conditions since the TOC has a lesser effect on the remaining heavy metal elements at this site.

Another interesting observation in the GAIA-analysis is the behaviour of Cu. At both the commercial and residential site, Cu correlated with the particle size range 151-300 $\mu\text{m}$  as shown in Figure 5 and 6 respectively. This suggests that street cleaning efforts could potentially remove a relatively large percentage of the Cu concentrations at the commercial and residential sites.

#### **4. Conclusions**

Road-deposited sediments in urban areas contain high concentrations of heavy metals. The highest sediment load and heavy metal loading was at the commercial site. However, the highest concentrations of seven of the eight heavy metals investigated were found at the industrial site. Maximum heavy metal concentrations and loadings frequently occurred in the 0.45-75 $\mu\text{m}$  particle size fraction. This is of serious concern since conventional street cleaning practises are inefficient in removing particles smaller than 250 $\mu\text{m}$ . The 0.45-75 $\mu\text{m}$  particle size fraction also had the dominant sediment loading, especially at the residential and commercial sites which showed similar particle volume distributions. These findings highlight the importance of removing sediments below 75 $\mu\text{m}$  from paved surfaces in urban areas in order to safeguard water quality.

Previous research reports have postulated the importance of the antecedent dry period in influencing the amount of sediments and pollutants available. In this study, no correlation was found between antecedent dry period and sediment load. Rather, multivariate statistical analysis using PROMETHEE and GAIA elicited the correlations between heavy metals and TOC content, and provided ranking information on the loadings of heavy metals at different sites and the particle size fractions. PROMETHEE ranked the 0.45-75 $\mu\text{m}$  particle size fraction as the most polluted at each site. Through GAIA visualisation it was found that the TOC content could influence the partitioning of Zn and Mn, which occurred predominantly at the

commercial site. This influence could be due to several reasons such as age, source and weathering of the organic matter. Since the occurrence of metal-organic complexes in urban runoff could significantly enhance the toxicity of a metal, the relatively high content of TOC in the  $<0.45\mu\text{m}$  particle size range could lead to a higher concentration of Zn and Mn in this size fraction. This could in turn lead to higher complexation reactions of these heavy metals and increased bioavailability when they are discharged to receiving waters.

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Legend to Tables

**Table 1 – Preference functions in PROMETHEE**

**Table 2 – Build-up of sediments in each size fraction**

**Table 3 – Heavy metal concentrations in each size fraction**







**Table 4 – Organic carbon content of the samples**

**Table 5 – Mean concentrations of heavy metals (mgkg<sup>-1</sup>)**

**Table 6 – Heavy metal loading in each particle size fraction.**

**Table 7 – Short names and symbols used for each size fraction and site in the GAIA visualisation**

**Table 1 – Preference functions in PROMETHEE**

Function	Shape	Threshold
Usual		No threshold
U-shape		Q threshold
V-shape		P threshold
Level		Q and P thresholds
Linear		Q and P thresholds
Gaussian		S threshold

**Table 2 – Build-up of sediments in each size fraction**

Site	<0.45 $\mu\text{m}$ [mg]	0.45- 75 $\mu\text{m}$ [mg]	76- 150 $\mu\text{m}$ [mg]	151- 300 $\mu\text{m}$ [mg]	>300 $\mu\text{m}$ [mg]	Total [mg]
Residential	210 (8.6%)	1423 (58.1%)	570 (23.3%)	142 (5.8%)	104 (4.2%)	2449
Industrial	165 (2.4%)	4953 (72.0%)	1201 (17.5%)	393 (5.7%)	164 (2.4%)	6876
Commercial	1125 (7.1%)	8550 (53.8%)	4585 (28.9%)	1274 (8.0%)	348 (2.2%)	15882

**Table 3 – Heavy metal concentrations in each size fraction**

Particle size [µm]	Site	Fe [ppm]	Zn [ppm]	Al [ppm]	Pb [ppm]	Cu [ppm]	Cd [ppm]	Cr [ppm]	Mn [ppm]
<0.45	Res	0.01	0.39	0.01	nd	0.08	nd	nd	0.01
	Ind	nd	0.18	0.01	nd	0.01	nd	nd	0.02
	Com	0.96	0.83	0.07	0.01	0.12	0.003	nd	0.27
0.45-75	Res	14.00	1.80	8.80	0.04	0.56	0.002	0.02	0.23
	Ind	43.96	2.32	13.59	0.96	0.96	nd	0.06	0.51
	Com	16.78	0.42	5.51	0.34	0.26	0.002	0.03	0.22
76-150	Res	12.80	0.72	8.80	0.03	0.48	0.002	0.01	0.20
	Ind	2.16	0.11	0.63	0.04	0.04	nd	0.003	0.02
	Com	9.59	0.30	3.52	0.19	0.24	0.01	0.02	0.16
151-300	Res	3.48	0.29	2.64	0.01	0.68	0.001	0.01	0.06
	Ind	0.62	0.04	0.24	0.01	0.04	nd	0.002	0.01
	Com	4.72	0.11	1.76	0.09	0.53	nd	0.01	0.07
>300	Res	1.48	0.14	1.24	0.01	0.34	0.001	0.01	0.03
	Ind	1.36	0.08	0.46	0.02	0.04	nd	0.01	0.01
	Com	3.84	0.06	1.28	0.05	0.22	nd	0.01	0.06

nd = not detected, Res = Residential, Ind = Industrial, Com = Commercial

**Table 4 – Organic carbon content of the samples**

Particle size [µm]	Site	Organic carbon content [ppm]
<0.45	Res	4.26
	Ind	8.37
	Com	18.82
0.45-75	Res	0.00
	Ind	0.21
	Com	16.61
76-150	Res	4.16
	Ind	0.64
	Com	1.12
151-300	Res	4.00
	Ind	0.34
	Com	0.25
>300	Res	4.26
	Ind	11.06
	Com	23.99

**Table 5 – Mean concentrations of heavy metals (mgkg<sup>-1</sup>)**

Heavy metal	Residential		Industrial		Commercial	
	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
Fe	6.76	9.90	9.62	19.21	7.18	6.20
Zn	0.54	0.59	0.55	0.99	0.34	0.31
Al	5.33	7.35	2.99	5.93	2.43	2.12
Pb	0.02	0.03	0.21	0.42	0.14	0.13
Cu	0.59	0.48	0.22	0.42	0.28	0.15
Cd	0.002	0.001	0.00	0.00	0.002	0.003
Cr	0.01	0.01	0.02	0.03	0.01	0.01
Mn	0.11	0.16	0.12	0.22	0.16	0.09

**Table 6 – Heavy metal loading in each particle size fraction.**

Particle size [µm]	Site	Fe mg/km <sup>2</sup>	Zn mg/km <sup>2</sup>	Al mg/km <sup>2</sup>	Pb mg/km <sup>2</sup>	Cu mg/km <sup>2</sup>	Cd mg/km <sup>2</sup>	Cr mg/km <sup>2</sup>	Mn mg/km <sup>2</sup>
<0.45	Res	0.003	170	14.14	2.87	24.60	0.62	nd	55.34
	Ind	nd	0.24	0.01	0.003	0.009	nd	nd	0.03
	Com	200	0.14	0.003	nd	0.03	nd	nd	0.003
0.45-75	Res	1900	250	1200	6.08	77.42	0.22	2.54	31.52
	Ind	29000	1500	9000	630	630	nd	41.78	340
	Com	52000	1300	17000	1100	820	5.00	82.44	700
76-150	Res	180	10.27	130	0.49	6.85	0.03	0.20	2.85
	Ind	200	10.47	59.07	3.29	3.44	nd	0.25	2.09
	Com	4300	130	1600	86.64	110	3.54	6.86	72.20
151-300	Res	5.10	0.42	3.87	0.02	1.00	0.001	0.01	0.08
	Ind	26.54	1.69	10.34	0.41	1.72	nd	0.10	0.32
	Com	280	6.67	100	5.24	31.46	nd	0.48	4.29
>300	Res	0.28	0.025	0.23	0.001	0.06	nd	0.001	0.01
	Ind	19.50	1.15	6.66	0.28	0.62	nd	0.18	0.21
	Com	17.07	0.27	5.69	0.23	1.00	nd	0.03	0.25

**Table 7 – Short names and symbols used for each size fraction and site in the GAIA visualisation**

Short name	Symbol	Site	Particle size class
1	▼	Residential	>300µm
2	▼	Residential	151-300µm
3	▼	Residential	76-150µm
4	▼	Residential	0.45-75µm
5	▼	Residential	<0.45µm
6	●	Industrial	>300µm
7	●	Industrial	151-300µm
8	●	Industrial	76-150µm
9	●	Industrial	0.45-75µm
10	●	Industrial	<0.45µm
11	▲	Commercial	>300µm
12	▲	Commercial	151-300µm
13	▲	Commercial	76-150µm
14	▲	Commercial	0.45-75µm
15	▲	Commercial	<0.45µm

## **Legend to Figures**

Figure 1 – Particle volume distribution at each site

Figure 2 – Heavy metal loading in each particle size fraction

Figure 3 – PROMETHEE ranking of the sites and particle size fractions. (Samples were ranked from the most preferred on the extreme left hand side to the least preferred on the extreme right hand size.)

Figure 4 – GAIA analysis for all the sites ( $\Delta$  = Percentage variance explained = 79.2%)

Figure 5 – GAIA analysis for the commercial site ( $\Delta$  = 79.7%)

Figure 6– GAIA analysis for the residential site ( $\Delta$  = 93.7%)

Figure 7 – GAIA analysis for the industrial site ( $\Delta$  = 99.7%)

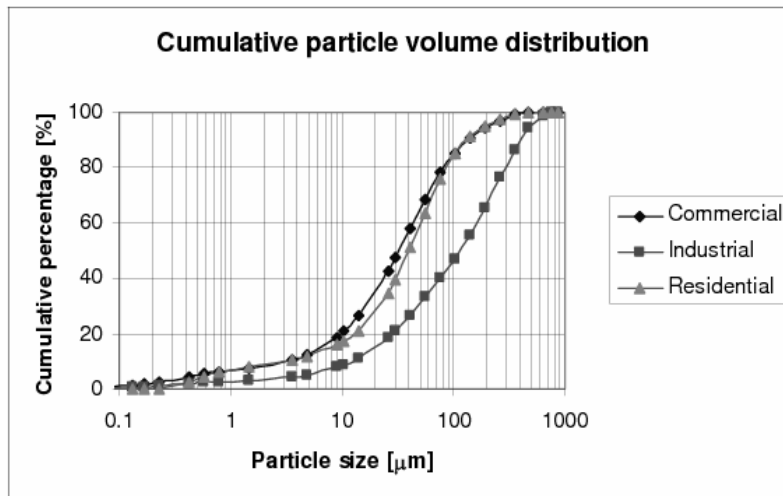


Figure 1

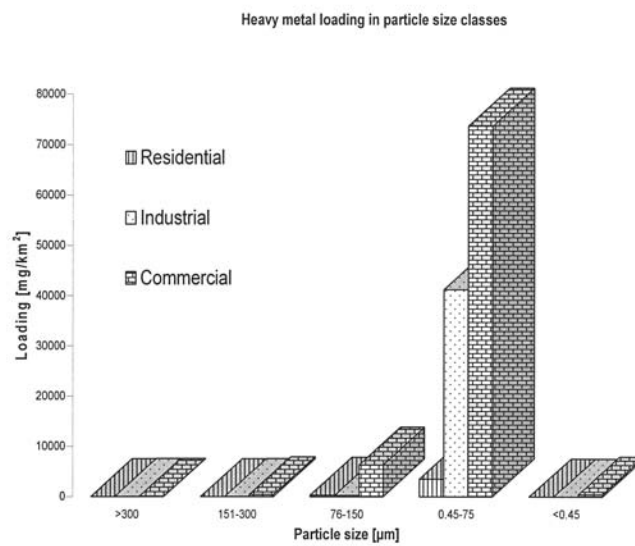


Figure 2

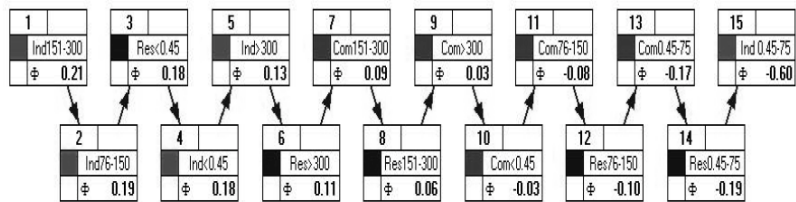


Figure 3

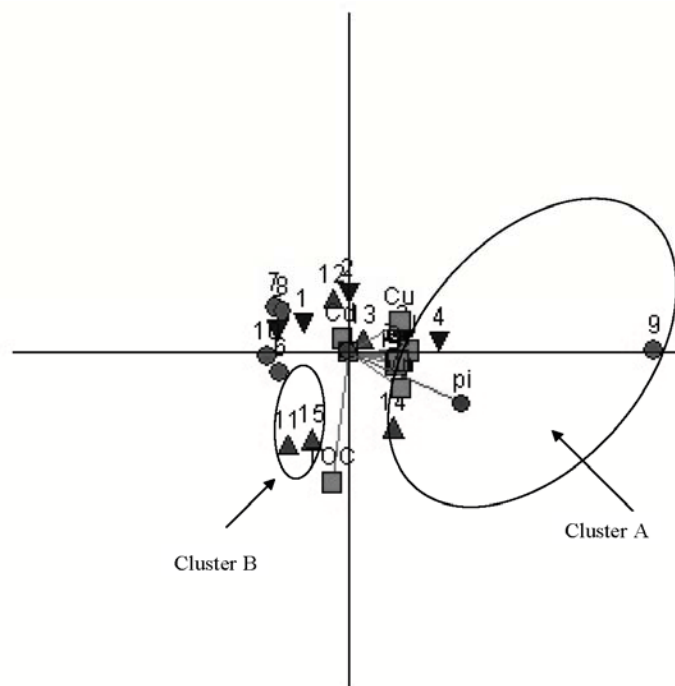


Figure 4

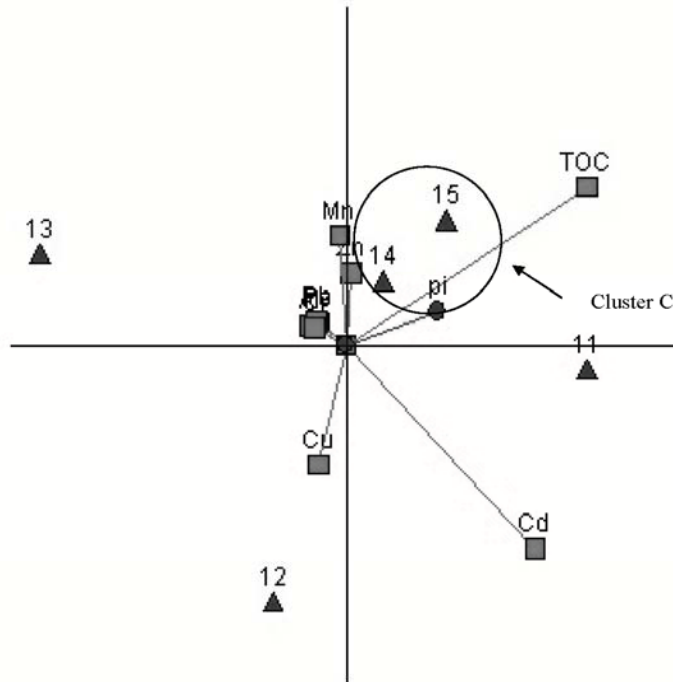


Figure 5

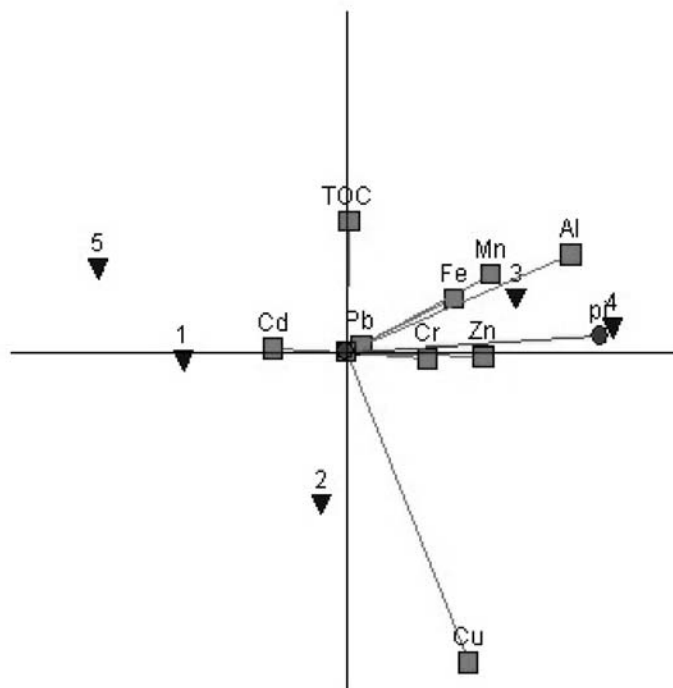


Figure 6

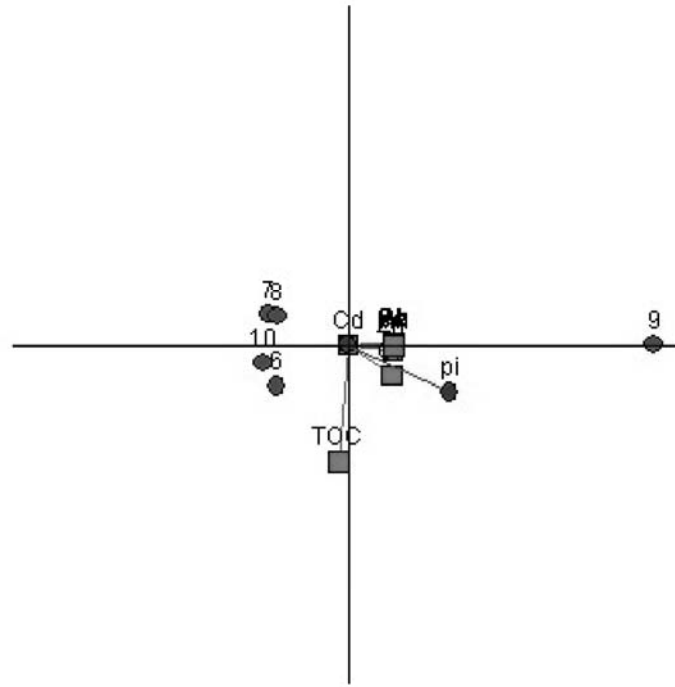


Figure 7