Author version of paper published as:
Herngren, Lars, Goonetilleke, Ashantha and Ayoko (2005)
Understanding heavy metal and suspended solids relationships in urban stormwater using simulated rainfall.
Journal of Environmental Management 78(2)): pp. 149-158

UNDERSTANDING HEAVY METAL AND SUSPENDED SOLIDS RELATIONSHIPS IN URBAN STORMWATER USING SIMULATED RAINFALL

Lars Herngren[*1], Ashantha Goonetilleke[1], Godwin A. Ayoko[2]

[1]School of Civil Engineering, [2]School of Physical and Chemical Sciences

Queensland University of Technology, GPO Box 2434, Brisbane QLD 4000, Australia

[*]Corresponding author

Email: l.herngren@qut.edu.au

Tel: +61(0)738642046

Fax: +61(0)738641515

Email contributing authors: a.goonetilleke@qut.edu.au, g.ayoko@qut.edu.au

ABSTRACT

Urban stormwater from simulated rainfall on three different landuses in Queensland State Australia (residential, industrial, commercial) were analysed for heavy metals and physico-chemical parameters such as Dissolved Organic Carbon (DOC) and Total Suspended Solids (TSS). Rainfall events were simulated using a specially designed rainfall simulator for paved surfaces. Event mean concentration samples were separated into five different particle sizes and analysed individually for eight metal elements (Zn, Fe, Cr, Cd, Cu, Al, Mn and Pb). Multivariate data analysis was carried out for the data thus generated. It was found that DOC and TSS influence the distribution of the metals in the different particle size classes. Zn was correlated with DOC at all three sites. Similarly, Pb, Fe and Al were correlated with TSS at all sites. The distribution of Cu was found to vary between the three sites, whilst Cd concentrations were too low to assess any relationships with other parameters. No correlation between Electrical Conductivity (EC), pH and heavy metals were found at the three sites. The identification of physico-chemical parameters influencing the process kinetics of heavy metals in urban stormwater will significantly enhance the efficiency of urban stormwater management systems.

KEYWORDS: Heavy metals; Rainfall simulation; Physico-chemical parameters; GAIA-analysis

1. INTRODUCTION

Stormwater runoff from urban areas contains significant loads of inorganic elements, particularly heavy metals (Davis et al., 2001). The presence of heavy metals in solution in urban runoff is of concern as they are most toxic due to enhanced bioavailability and potential to not degrade in the environment. Many heavy metals, especially Pb and Zn, have been recognized as traffic-related pollutants (Dong et al., 1984; Wilber and Hunter, 1979; Sansalone and Buchberger, 1997). However, specific sources of heavy metals in an urban area also include corrosion of buildings and their fittings, atmospheric deposition, transport and various industrial activities and intentional and accidental spills (Christensen and Guinn, 1979; Davis et al., 2001). Sources of heavy metals and their contribution to urban stormwater runoff is significantly dependant on the land use.

Furthermore, parameters such as dissolved organic carbon and pH can significantly enhance desorption of heavy metals from suspended solids. Tai (1991) noted that the ratio of trace metals released into the dissolved phase at pH 6 against pH 8.1 is about 180 for Zn, 45 for Pb and 25 for Fe. Similarly, dissolved organic carbon plays a major role in partitioning of metals between soluble and particulate fractions in stormwater (Hamilton et al., 1984). Consequently, interaction between dissolved organic carbon and heavy metals can result in complexation processes that concentrate the metals in the dissolved phase. The partitioning of heavy metals into different particle size classes in terms of their adsorption to particulates has major implications for urban water quality management. Current approaches adopted to mitigate the impacts of urban runoff on receiving waters include the use of structural and/or regulatory measures such as detention basins, gross pollutant traps and restrictive zoning.

However, for these measures to be effective, an in-depth understanding of the processes involved in urban runoff is essential. Therefore it is imperative to understand the relationships between heavy metals and important parameters such as particle size, pH and organic carbon content.

Most of the heavy metals in urban stormwater runoff are attached to suspended solids (Bodo, 1989; Dong et al., 1984). Furthermore, metal concentrations generally increase with decreasing particle size (Liebens, 2001; Ujevic et al., 2000). This is due to the relatively large surface area of fine sediments and their higher Cation Exchange Capacity (Dong et al., 1984). Since most metals have a greater affinity for smaller particle sizes, conventional pollutant abatement programs such as street sweeping which only pick up large particles have little effect in reducing toxic runoff levels, as fine suspended solids are readily transported in stormwater. In addition to the relationship between suspended solids and metals, parameters such as rainfall intensity and rainfall volume have been noted as important factors in influencing the export of heavy metals from an urban area (Sonzogni et al., 1980). Despite the strong affinity between heavy metals and suspended solids, the evaluation of the dissolved fraction of the heavy metal load is important as an indicator of bioavailability.

In this paper, multivariate statistical methods and rainfall simulation have been used to correlate heavy metal distribution among different suspended solids particle sizes in wash-off samples with a number of physico-chemical parameters such as pH and dissolved organic carbon. The suspended solids in the wash-off samples were separated into five different particle size classes in order to investigate the processes governing the affinity of heavy metals to different particle sizes. The use of an artificial rainfall simulator helps to eliminate significant constraints such as dependency on natural rainfall experienced by researchers undertaking rigorous research into urban stormwater quality. Additionally, the random nature of occurrence and characteristics of natural rainfall introduces further variables into a research arena where so little of the inherent processes are known. A specially designed rainfall simulator was used to generate artificial rainfall and to obtain pollutant wash-off samples from paved areas in three landuses. The wash-off samples collected from the paved areas were tested for a suite of heavy metals species (Zn, Pb, Cu, Cd, Cr, Fe, Al, Mn) considered common to urban areas. Due to the limitations in univariate statistical methods, multivariate analytical methods were employed to analyse the large database generated and to investigate the affinity between heavy metals and suspended solids particle sizes and relationships with a number of physico-chemical parameters.

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.

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 intact street surface. An early investigation of the households suggested that various chemicals were used as fertilizers or for other uses and therefore 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 and a furniture manufacturer. Compared to the residential site, the street surface was significantly degraded.

Research site 3 was a parking lot in a suburban shopping centre in the Gold Coast area. 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 could be embedded within the voids.

2.2 Rainfall simulation

A specially designed rainfall simulator was used to simulate rainfall events typical for South-East Queensland, Australia. The rainfall simulator consisted of an A-frame structure with three Veejet 80100 nozzles equally spaced on a rotating nozzle boom. Artificially created rainfall was preferred for data generation due to the limited rainfall events occurring in the area. The use of an artificial rainfall simulator helps to eliminate significant constraints experienced by researchers undertaking rigorous research into urban stormwater quality. It helps to overcome the significant constraints associated with depending on natural rainfall events. The random nature of occurrence and characteristics of natural rainfall introduces further variables into a research arena where so little of the inherent processes are known. Rainfall simulation enables the generation of large volumes of data over a relatively short period for probabilistically different rainfall events, at the researchers convenience. Care was taken to simulate rainfall characteristics as closely as possible, including drop velocities and uniformity of distribution (Loch et al., 2001). The runoff plot area was chosen so that maximum uniformity was achieved. The uniformity of distribution inside the plot area was measured to 95% of the total distribution according to the method developed by Christiansen (1942). The rainfall simulator was calibrated for four different rainfall intensities inherent to the region, for twelve Average Recurrence Intervals. Different intensities were achieved by changing the rotation interval of the nozzle boom.

Prior to any analysis, the collected wash-off samples were mixed in equal proportions. The pollutant concentrations in the mixed sample were as considered as representing the Event Mean Concentrations of pollutants for that specific rainfall event. Well-mixed portions of the EMC-samples were prepared according to Australian/New Zealand Standard (AS/NZS, 1998) and were then refrigerated until further analysis as discussed in detail in Section 2.5 below. Investigated rainfall intensities and durations are shown in Table 1. Due to insufficient water supply at the residential site, three events (65mm/hr, 20min. duration, 65mm/hr, 35min. duration and 65mm/hr, 65min. duration) could not be simulated. The simulation of one event (115mm/hr, 25 min. duration) failed at the industrial site. All the intensities and durations were successfully simulated at the commercial site.

2.3 Development of a rainfall quality profile

The rainfall quality profile for the study region was derived to ensure that similar chemical characteristics to natural rainfall were used in the rainfall simulations. Rain water samples were collected during a number of natural rainfall events in different locations around the study area and were tested for pH, Electrical Conductivity (EC) and Dissolved Organic Carbon (DOC). Mean values obtained were 6.40, 51.71 μS/cm and 8.81 mg/L for pH, EC and DOC respectively. These parameters were selected because of their ability to significantly influence the partitioning of heavy metals between dissolved and particulate fractions as discussed above. De-ionized water was spiked with sulphuric acid (for pH), common salt (for EC) and methanol (for DOC) to obtain the required chemical quality.

2.4 Experimental Design and Sample Collection

Four different runoff plots were selected at each site as replicates. They were all equally spaced from the median strip to the kerb at the industrial and residential site. At the commercial site, four parking spaces were chosen as runoff plots. The runoff plot at the commercial site was situated in the exact middle of the parking spaces. The spacing between each runoff plot was kept as small as possible without any interference occurring between the plots. Hence, the amount of pollutants on the surface was assumed to be the same at each individual plot at each site. Although past research has shown that a large fraction of the sediments is located near the kerb (Sartor and Boyd, 1972), the distribution pattern of heavy metals in different particle sizes was assumed to be the same throughout the width of the study surface. Hence the fractioning of heavy metals into different particle size classes was considered independent of the sediment mass collected.

A collecting trough was attached to the runoff plot. The trough was fabricated so that approximately 30L of runoff could be detained at any time during the events. However, runoff was collected continuously throughout the events to ensure no water would spill over the trough.

2.5 Laboratory analysis

Prior to any chemical analysis, the particle size distribution of the wash-off samples was determined using a Malvern Mastersizer Particle Size Analyzer. The Malvern Mastersizer uses a laser beam to record the scatter pattern from a field of particles and then an analytical procedure to determine the size of particles that created the scatter pattern. Based on the particle size distribution, the samples were separated into the following five size classes: >300μm (corresponds well to sands), 151-300μm (fine sands), 76-150μm (very fine sands and silt), 0.45-75μm (silt and clay). The smallest size class (<0.45μm) was defined as the dissolved fraction of the runoff samples and fractionated according to standard method 2540D (Eaton et al., 1999). Wet sieving was used to separate the particles into the different size classes chosen. The different size classes was then individually analysed for the water quality parameters listed in Table 2.

2.5.1 Heavy metal analysis

Each particle size class and the filtrate were analysed for eight metal species (Zn, Al, Fe, Mn, Cu, Cd, Cr, Pb) commonly found in urban areas (Makepeace et al., 1995). Particulate samples were digested for heavy metal analysis using a nitric acid digestion procedure as described by Eaton et al. (1999). 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). External standards were used in the analysis, as well as blanks and duplicate samples as a quality control measure. The duplicate samples and spiked samples had recoveries ranging from 80-116%. 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. The standards used were high purity standards bought from Choice Analytical P/L. For quality control, AccuTrace Reference Standard "Laboratory Performance Check Standard " ICP Multi-element StandardL-PCS-01-1 was used.

2.6 Data analysis

Chemometric multivariate approaches were used to analyse the data. These techniques are useful where large volumes of data can be processed in order to explore and understand relationships between variables (Kokot et al, 1998). In this work, GAIA was used with the aid of DecisionLab software (Visual Decision Inc., 1999). GAIA is a visualisation method which is a principal component biplot obtained from the data matrix. Detailed information on how to use GAIA has been well documented elsewhere (Khalil et al., 2004).

GAIA was used to evaluate the heavy metals in each particle size at each site. The parameters outlined in Table 2 were also included in the GAIA analysis to evaluate any correlations between heavy metals and the parameters chosen. The samples from the different sites were initially evaluated individually and were later compared to identify similar pollutant behaviour between the sites.

3. Results

Particle size analysis revealed that the majority of sediments collected at each site were below 76µm, independent of the landuse, rainfall intensity and duration, as shown in Figure 1. As can also be seen in Figure 1, the 0.45-75µm size class dominates in all the samples. Up to 85% of the particles belong to this size class. Only 22% of the particles are larger than 300µm. Similar results of particle size distribution in urban stormwater have been found by several other researchers. For example, Andral et al. (1999) found that up to 90% of the total particles were below 150µm. Furthermore, pollutant abatement techniques such as street sweeping have been found to only efficiently remove relatively large particles of the order of 250µm and above (Bender and Terstriep, 1984; Sutherland et al., 1998). Hence, particulates smaller than 150µm can be a serious concern in an urban environment.

In order to assess relationships between heavy metals and physico-chemical parameters, Principal Component Analysis (PCA) was used. GAIA was used as a visualisation tool for correlations between physico-chemical parameters and heavy metals. GAIA also revealed correlations between the heavy metals themselves and in which particle size and site they dominate. In the PCA-analysis, all the parameters were given the same weighting and preference function. The preference function was set to V-shape, which meant that a preference threshold P, representing the smallest deviation considered decisive was used in processing the data. P was set to the maximum concentration of each variable. Concentrations below the detection limit were set to half the detection limit value of the specific parameter (Guo et al., 2004).

The concentration range of each parameter at the sites is shown in Table 3.

The GAIA analysis consisted of a number of steps. Firstly, the wash-off samples were divided into categories based on rainfall intensity and duration of the event as shown in Table 4 below. Secondly, each particle size range was given a short name as outlined in Table 4. An increasing number in the categories mirrored a decrease in particle size. For example, the wash-off sample in category 2 given number 6 corresponded to the largest particle size class (>300μm) while number 10 corresponded to the smallest particle size class (<0.45μm). The samples from each site were then analysed individually. The initial analysis was on the water quality data from the residential site (45 samples x 15 parameters). Figure 2 shows the relationship between parameters, whilst Figure 3 shows relationships between parameters and the particle size classes. As can be seen in Figure 2, correlations occur between Total Dissolved Solids (TDS), Zn, Cu and Dissolved Organic Carbon (DOC) since variables in general agreement are oriented in the same direction in the GAIA plane. Figure 2 also reveals a relationship between Total Suspended Solids (TSS) and the metals Pb, Fe, Al and Mn. EC and pH has a negligible effect on the heavy metal concentration, whilst Cr is slightly correlated with the Total Organic Carbon (TOC). In Figure 3, the particle size classes are added to the GAIA visualisation. It can now be seen that three major particle size clusters occur with particles larger than 300μm, particles smaller than 0.45μm and particles between 0.45 and 150μm. Al, Fe, Pb and Mn are correlated with particles between 0.45 and 150μm. This is of serious concern since the particle size distribution analysis showed that the majority of particles in urban stormwater are between 0.45 and 150μm. Since most of the metals are correlated with smaller particle sizes, conventional cleaning programs would have little or no effect in reducing toxic runoff levels and fine suspended solids are readily transported in urban stormwater.

The correlation between Zn, Cu and DOC can have a significant impact on urban stormwater quality. This is of concern since DOC has been found to act as a solubility enhancer for heavy metals (Warren et al., 2003).

The industrial site (55x15) shows similar relationships between parameters. As can be seen in Figure 4, Zn is once again correlated with DOC. However, Cu shows a completely different behaviour at the industrial site and is highly correlated with TSS. A possible reason for this could be the release of Cu, which is bound to particulates from industrial emissions. Whilst this might be the main source of Cu at the industrial site, the major source of Cu at the residential site could be fungicides and pesticides which are commonly used in residential areas (Makepeace et al., 1995). However, the partitioning of Cu has been found to vary significantly. For example, Shinya et al. (2000) found Cu to be mainly particulate-bound while Bubb and Lester (1994) found Cu to be mainly in the dissolved phase of runoff, which confirms its highly location specific behaviour.

Fe, Al and Pb were once again highly correlated with TSS and were mainly found in particles below 150μm as shown in Figure 5. EC, pH and Inorganic Carbon (IC) has only a minor effect, if any, on the concentration and distribution of heavy metals. Cd concentrations were frequently below detection limit at both the residential and industrial site making it hard to assess any relationship Cd might have with other parameters.

The commercial site (60x15) shows fairly similar physico-chemical characteristics as the residential site. As can be seen in Figure 6, Cu and Zn are once again highly correlated with DOC and TDS. Similar to the residential site, Al, Fe, Pb and Cr all have strong relationships with TSS. However, as shown in Figure 7, the distribution of heavy metals in particle sizes above 0.45µm is more random at the commercial site than at the residential and industrial site, forming only one cluster. This could be due to the increased frequency of street cleaning at the commercial site. Furthermore, frequent vehicle traffic would also disperse fine particulates leaving a higher fraction of coarser particles on the road surface compared to the residential and industrial site. The relatively coarse texture of the road surface could also influence the distribution of heavy metals at the commercial site, indicating that heavy metals irreversibly bound to particles originating from vehicles or surface wear could be bound to larger particle sizes. Similarly, road surface wear at the commercial site would be higher compared to the other two sites due to the amount of cars stopping and starting at the parking lot. Similar to both the residential and industrial sites, pH and EC has no significant correlation with heavy metals at the commercial site.

4. Discussion

Even though pH and EC was found to have none or little impact on the distribution of heavy metals, the importance of these parameters should not be underestimated. The variance of these parameters in this research was low since water used for simulations was prepared with a standard pH and EC. EC and pH in natural rainfall could vary between the sites due to atmospheric pollution. Hence, the relationships between heavy metals and parameters such as rainfall pH and EC could also have a significant influence on urban stormwater quality at specific sites.

The relationships found between physico-chemical parameters in this research can be of crucial importance in managing urban stormwater quality. Relatively easy measurements of parameters such as TSS and DOC could act as indicators of the distribution of heavy metals in an urban area. The measurement of DOC could give important information on the possibility of Zn and Cu being available in the dissolved phase. Similarly, TSS would give a good indication of the distribution of metals such as Fe, Al and Pb. Preferably, TSS should be measured in several particle size classes in order to assess the availability of metals in each class. Specific urban water quality management strategies could then be based on simple physico-chemical tests such as pH, TSS and DOC. Furthermore, street cleaning programs should focus on removing particles below 150µm, since the majority of the pollutants are associated with this size class. The results also show that the majority of sediments transported in urban runoff are below 150µm.

5. Conclusions

An investigation was made in order to determine the importance of physico-chemical parameters in mitigating the effects urban stormwater impose on the environment. A rainfall simulator was successfully used to simulate a number of rainfall events for collecting runoff samples from three different landuse sites. It was found that the major fraction of particulates transported in urban stormwater was in the size class 0.45-75µm which was independent of the site characteristics. Five different size classes were analysed for a range of parameters including eight heavy metal species. Due to the large number of variables measured, multivariate methods were preferred over univariate methods in the data analysis. The use of Principal Component Analysis (PCA) revealed correlations and relationships between physico-chemical parameters and in which size class heavy metals dominate. Similarly, PCA also revealed possible sources of heavy metals at the three sites. For example, the correlation between Al and Fe at all three sites suggests that the main input of these metals to urban stormwater is governed by the soil characteristics. Hence the use of multivariate methods can significantly improve the understanding of processes governing urban water quality and thereby enhance the development of effective urban stormwater management measures at specific sites.

At all three sites (residential, industrial, commercial), Zn was correlated with DOC. Cu and DOC were correlated at the residential and commercial sites. However, Cu was correlated with TSS at the industrial site. Pb, Fe and Al were correlated with TSS at all three sites and the majority of these metals were found in the size range 0.45-75μm. It is postulated that DOC and TSS could serve as indicators of the distribution of these metals in urban stormwater. Consequently, parameters such as DOC and TSS, which are relatively easy to monitor, could be used as indicators of the distribution of metals such as Zn and Pb. Furthermore, DOC and TSS measurements could help determine the characteristics of urban stormwater quality management practises such as street sweeping and retention/detention ponds. However, further investigations need to be made of the role of pH and EC at individual sites since previous research found that these parameters to be important indicators as well. Similarly, further information on the chemical quality of rainwater at individual sites is important in terms of determining suitable stormwater quality management systems.

5. References

1. M.C. Andral, S. Roger, M. Montrejaud-Vignoles, L. Herremans, Particle size distribution and hydrodynamic characteristics of solid matter carried by runoff from motorways, Water Environment Research 71 (1999) 398-407.

2. AS/NZS, *Water quality – Sampling; Part 1: Guidance on the design of sampling programs, sampling techniques and the preservation and handling of samples*, Report AS/NZS 5667.1:1998, Australian/New Zealand Standard, (1998).

3. G.M. Bender, and M.L. Terstriep, Effectiveness of street sweeping in urban runoff pollution control, The Science of the Total Environment 33 (1984) 185-192.

4. B.A. Bodo, Heavy metals in water and suspended particulates from an urban basin impacting Lake Ontario, The Science of The Total Environment 87/88 (1989) 329-344.

5. J.M. Bubb, and J.N. Lester, Anthropogenic heavy metal inputs to lowland river systems, a case study The river Stour U.K, Water, Air and Soil pollution 78 (1994) 279-296.

6. E.R. Christensen, and V.P. Guinn, Zinc from automobile tires in urban runoff, Journal of the Environmental Engineering Division ASCE 105 (1979) 165-168.

7. J.P. Christiansen, *Irrigation by sprinkling*, Bulletin No 670, University of California Agricultural Experiment Station, USA (1942).

8. A.P. Davis, M. Shokouhian, S. Ni, Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources, Chemosphere 44 (2001) 997-1009.

9. A. Dong, G. Chesters, G.V. Simsiman, Metal composition of soil, sediments and urban dust and dirt samples from the Menomonee River watershed, Wisconsin, USA, Water, Air and Soil Pollution 22 (1984) 257-275.

10. A.D. Eaton, L.S. Clesceri, A.E. Greenberg, *Standard methods for the examination of water and wastewater. 20th edition*, American Public Health Association, American Waterworks Association, Water Environment Federation (1999).

11. H. Guo, T. Wang, P.K.K. Louie, Source apportionment of ambient non-methane hydrocarbons in Hong Kong: Application of a principal component analysis/absolute principal component scores (PCA/APCS) receptor model, Environmental Pollution 129 (2004) 489-498.

12. R.S. Hamilton, D.M. Revitt, R.S. Warren, Levels and physicochemical associations of Cd, Cu, Pb and Zn in road sediments, The Science of the Total Environment 33 (1984) 59-74.

13. W.A-S. Khalil, A. Goonetilleke, S. Kokot, S. Carroll, Use of chemometrics methods and multicriteria decision-making for site selection for sustainable on-site sewage effluent disposal, Analytica Chimica Acta 506 (2004) 41-56.

14. S. Kokot, M. Grigg, H. Panayiotuo, T. Dong Phuong, Data interpretation by some common chemometrics methods, Electroanalysis 10 (16) (1998).

15. J. Liebens, Heavy metal contamination of sediments in stormwater management systems: the effect of land use, particle size and age, Environmental Geology 41 (2001) 341-351.

16. R.J. Loch, R.G. Robotham, L. Zeller, N. Masterman, D.N. Orange, B.J. Bridge, G. Sheridan, J.J. Bourke, A multi-purpose rainfall simulator for field infiltration and erosion studies, Australian Journal of Soil Research 39 (2001) 599-610.

17. D.K. Makepeace, D.W. Smith, S.J. Stanley, Urban stormwater quality: Summary of contaminant data, Critical Reviews in Environmental Science and Technology 25 (1995) 93-139.

18. J.J. Sansalone, and S.G. Buchberger, Characterization of solid and metal element distributions in urban highway stormwater, Water Science and Technology 36 (1997) 155-160.

19. J.D. Sartor, and G.B. Boyd, *Water pollution aspects of street surface contaminants*, USEPA-R2-72-081, Washington DC (1972).

20. M. Shinya, T. Tsuchinaga, M. Kitano, Y. Yamada, M. Ishikawa, Characterization of heavy metals and polycyclic aromatic hydrocarbons in urban highway runoff, Water Science and Technology 42 (2000) 201-208.

21. W.C. Sonzogni, G. Chesters, D.R. Coote, D.N. Jeffs, J.C. Konrad, R.C. Ostry, J.K. Robinson, Pollution from land runoff, Environmental science and technology 14 (1980) 148-153.

22. R.A. Sutherland, S.L Jelen, G. Minton, High efficiency sweeping as an alternative to the use of wet vaults for stormwater treatment, In: James W. (Ed.), Advances in Modelling the Management of Stormwater Impacts, Vol. 5. Computational Hydraulics International, Guelph (1998), Canada, 179-190.

23. Y-L. Tai, Physical and Chemical Characterisation of street dust and dirt from urban area. Department of Civil Engineering, Pennsylvania State University, 93 (1991).

24. I. Ujevic, N. Odzak, A. Baric, Trace metal accumulation in different grain size fractions of the sediments from a semi-enclosed bay heavily contaminated by urban and industrial wastewaters, Water Research, 34 (2000) 3055-3061.

25. Visual Decision Inc., Getting Started Guide, DecisionLab 2000, Montreal, Quebec (1999), Canada.

26. N. Warren, I.J. Allan, J.E. Carter, W.A. House, A. Parker, Pesticides and other micro-organic contaminants in freshwater sedimentary environments – a review, Applied Geochemistry 18 (2003) 159-194.

27. W.G. Wilber, and J.V. Hunter, Distributions of metals in street sweepings, stormwater solids and urban aquatic sediments, Journal Water Pollution Control Federation 51 (1979) 2810-2822.

Figure 1 – Percentage of particles by volume in each size class of all samples from the three sites

Figure 2 – GAIA analysis for the residential site, showing correlations between parameters; (■) parameter; (●) pi (π), decision-making axis

Figure 3 – GAIA analysis for the residential site, showing correlations between parameters and their affinity with particle sizes; (■) parameter; (▲) wash-off samples; (●) pi (π), decision-making axis

Figure 4 - GAIA analysis for the industrial site, showing correlations between parameters; (■) parameter; (●) pi (π), decision-making axis

Figure 5 - GAIA analysis for the industrial site, showing correlations between parameters and their affinity with particle sizes; (■) parameter; (▲) wash-off samples; (●) pi (π), decision-making axis

Figure 6 - GAIA analysis for the commercial site, showing correlations between parameters; (■) parameter; (●) pi (π), decision-making axis

Figure 7 - GAIA analysis for the commercial site, showing correlations between parameters and their affinity with particle sizes; (■) parameter; (▲) wash-off samples; (●) pi (π), decision-making axis

Table 1

Rainfall intensities and durations simulated in this research

Intensity [$mmhr^{-1}$]	Duration [min]	ARI
65	20	1 year
65	35	2 year
65	65	10 year
86	10	1 year
86	20	2 year
86	40	10 year
115	5	1 year
115	10	2 year
115	25	10 year
133	7	2 year
133	13	5 year
133	17	10 year

Table 2

Water analysis

Parameter	Test method
pH	Measurement with combined pH/EC meter. Only total sample measured.
Electrical Conductivity (EC)	Measurement with combined pH/EC meter. Only total sample measured. Method 2520B as described by Eaton et al. (1999) was used.
Total Organic Carbon (TOC)	A Shimadzu TOC-5000A Total Organic Carbon analyser was used. Method 5310 was used as described by Eaton et al. (1999). Detection limit for the TOC analyser was 0.001 mg/L.
Inorganic Carbon (IC)	Same as above.
Dissolved Organic Carbon (DOC)	Same as above.
Total Suspended Solids (TSS)	Each size class was filtered through a 0.45μm glass-fibre filter and analysed for TSS concentration as described in Method 2540D (Eaton et al., 1999).
Total Dissolved Solids (TDS)	The filtrate from the TSS-measurement was used to determine TDS concentration according to Method 2540D (Eaton et al., 1999).
Heavy metals (Zn, Pb, Cr, Cd, Cu, Fe, Al, Mn)	The suite of eight heavy metal elements was analysed using Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) according to Methods 3030E and 3120B (Eaton et al., 1999). Lower limit of reporting for heavy metals was 0.001 mg/L.

Table 3

Concentration range and deviation from mean

Parameter	Range			Standard deviation		
	Res	Ind	Com	Res	Ind	Com
pH	6.7-7.3	6.5-6.8	6.6-7.7	0.2	0.1	0.3
EC [µS/cm]	102-130	287-665	27-57	10	135	9
TOC [ppm]	<0.001-4.0	<0.001-2.9	<0.001-3.9	1.0	0.6	0.8
IC [ppm]	<0.001-3.6	<0.001-1.8	<0.001-1.9	1.2	0.4	0.4
DOC [ppm]	<0.001-9.4	<0.001-9.1	<0.001-8.9	3.1	2.9	2.5
TSS [ppm]	0.5-76.3	2.1-86.0	10.3-49.5	14.8	16.7	9.2
TDS [ppm]	60.0-95.0	60.0-250.0	10.0-40.0	32.0	77.4	10.0
Zn [ppm]	<0.001-3.6	<0.001-0.5	<0.001-0.7	0.7	0.1	0.2
Cu [ppm]	<0.001-0.4	<0.001-0.04	<0.001-0.1	0.08	0.007	0.03
Pb [ppm]	<0.001-0.02	<0.001-0.03	<0.001-0.01	0.002	0.005	0.002
Al [ppm]	<0.001-0.6	<0.001-0.4	<0.001-0.3	0.2	0.09	0.05
Fe [ppm]	<0.001-0.7	<0.001-0.9	<0.001-0.7	0.2	0.2	0.1
Cd [ppm]	< 0.001-0.3	<0.001-0.001	<0.001	0.05	0.0002	<0.001
Cr [ppm]	<0.001-0.007	<0.001-0.02	<0.001-0.003	0.002	0.003	0.001
Mn [ppm]	<0.001-0.01	<0.001-0.02	<0.001-0.01	0.003	0.004	0.003

Res = Residential; Ind = Industrial; Com = Commercial;

Table 4

Description of the objects used in GAIA analysis and their associated short name (Increasing number in each category responds to a decrease in particle size range)

Category	Short name*	Rainfall intensity [mm/hr]	Rainfall duration [min]
1	1-5	86	10
2	6-10	86	20
3	11-15	86	40
4	16-20	115	5
5	21-25	115	10
6	26-30	133	7
7	31-35	133	13
8	36-40	133	17
9	41-45	65	20
10	46-50	65	35
11	51-55	65	65
12	56-60	115	25

* Increasing number in each category corresponds to a decrease in particle size range

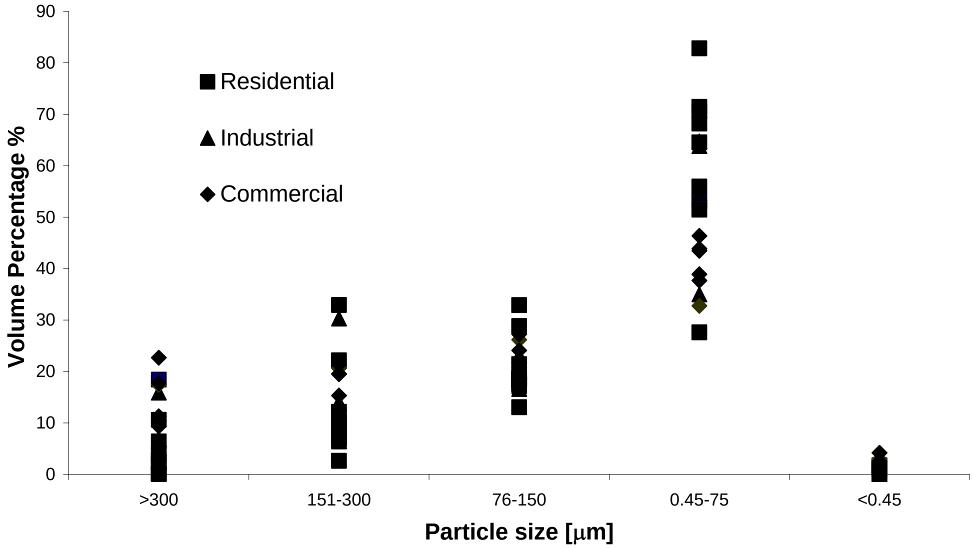

Figure 1 – Percentage of particles by volume in each size class of all samples from the three sites

Figure 2 – GAIA analysis for the residential site, showing correlations between parameters; (■) parameter; (●) pi (π), decision-making axis

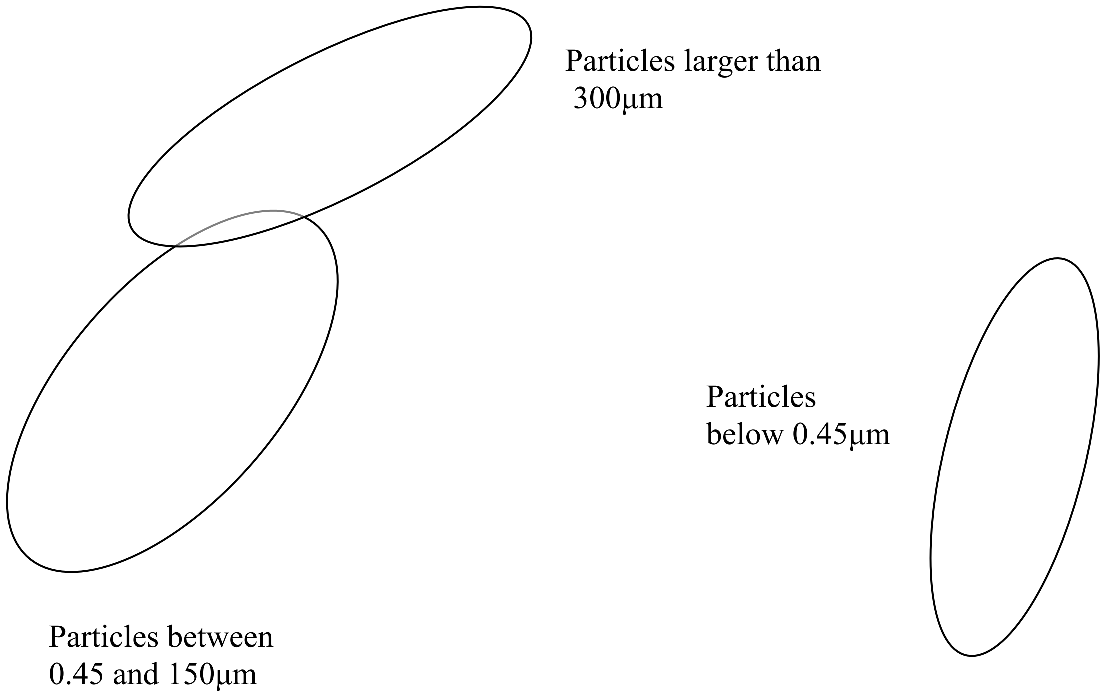

Figure 3 – GAIA analysis for the residential site, showing correlations between parameters and their affinity with particle sizes; (■) parameter; (▲) wash-off samples; (●) pi (π), decision-making axis

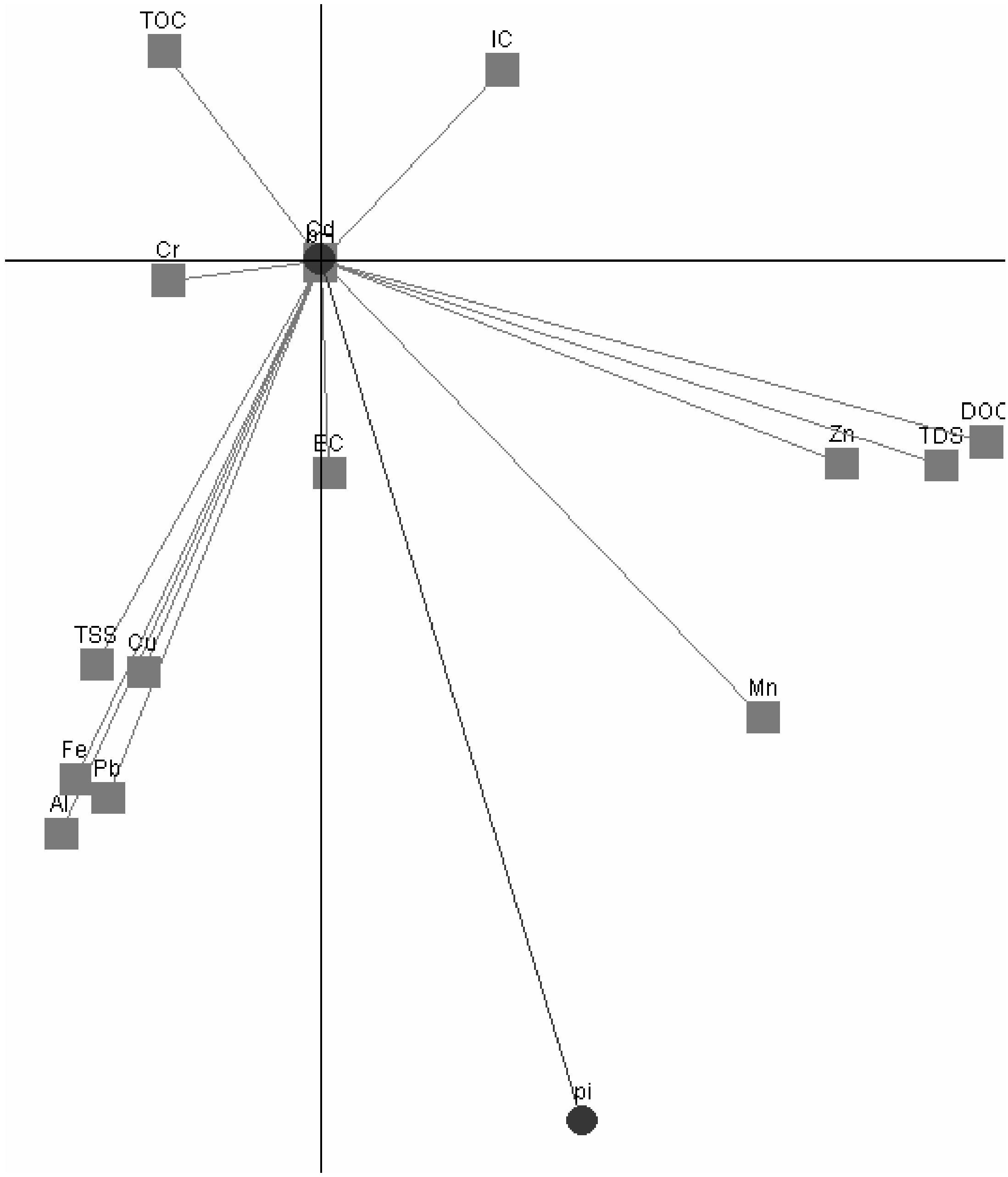

Figure 4 - GAIA analysis for the industrial site, showing correlations between parameters; (■) parameter; (●) pi (π), decision-making axis

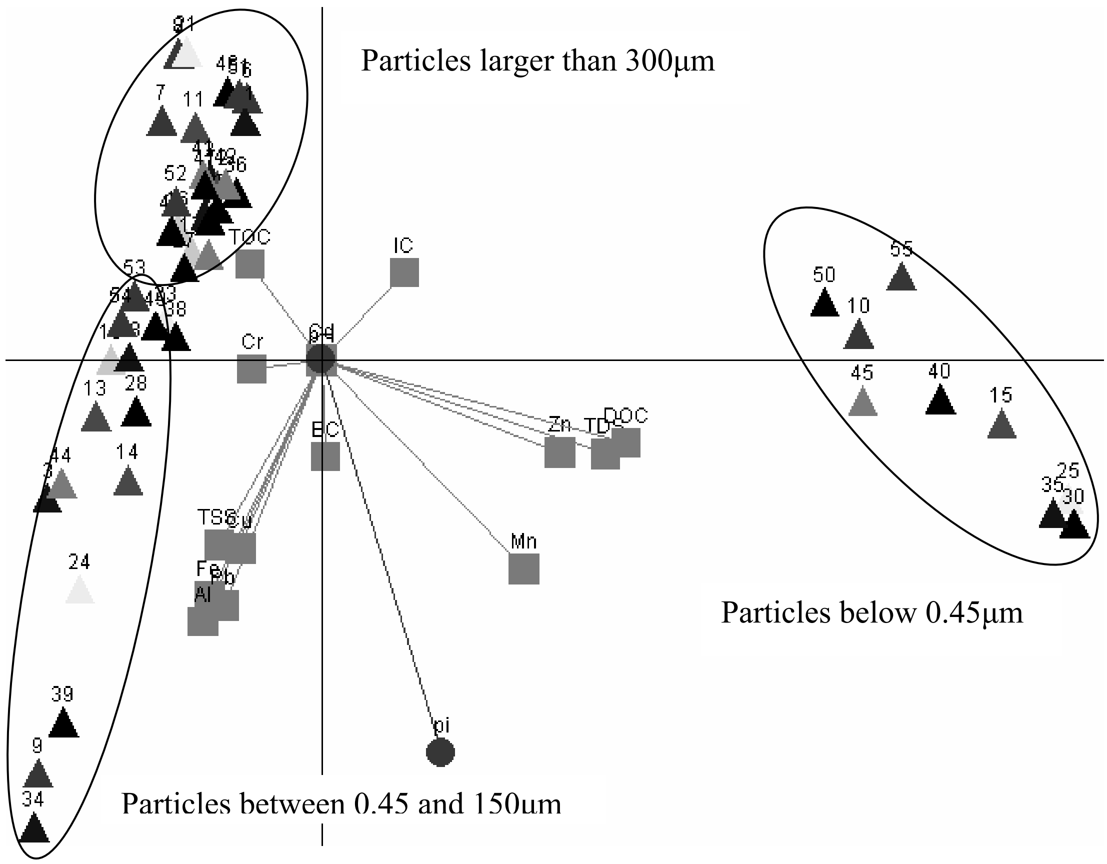

Figure 5 - GAIA analysis for the industrial site, showing correlations between parameters and their affinity with particle sizes; (■) parameter; (▲) wash-off samples; (●) pi (π), decision-making axis

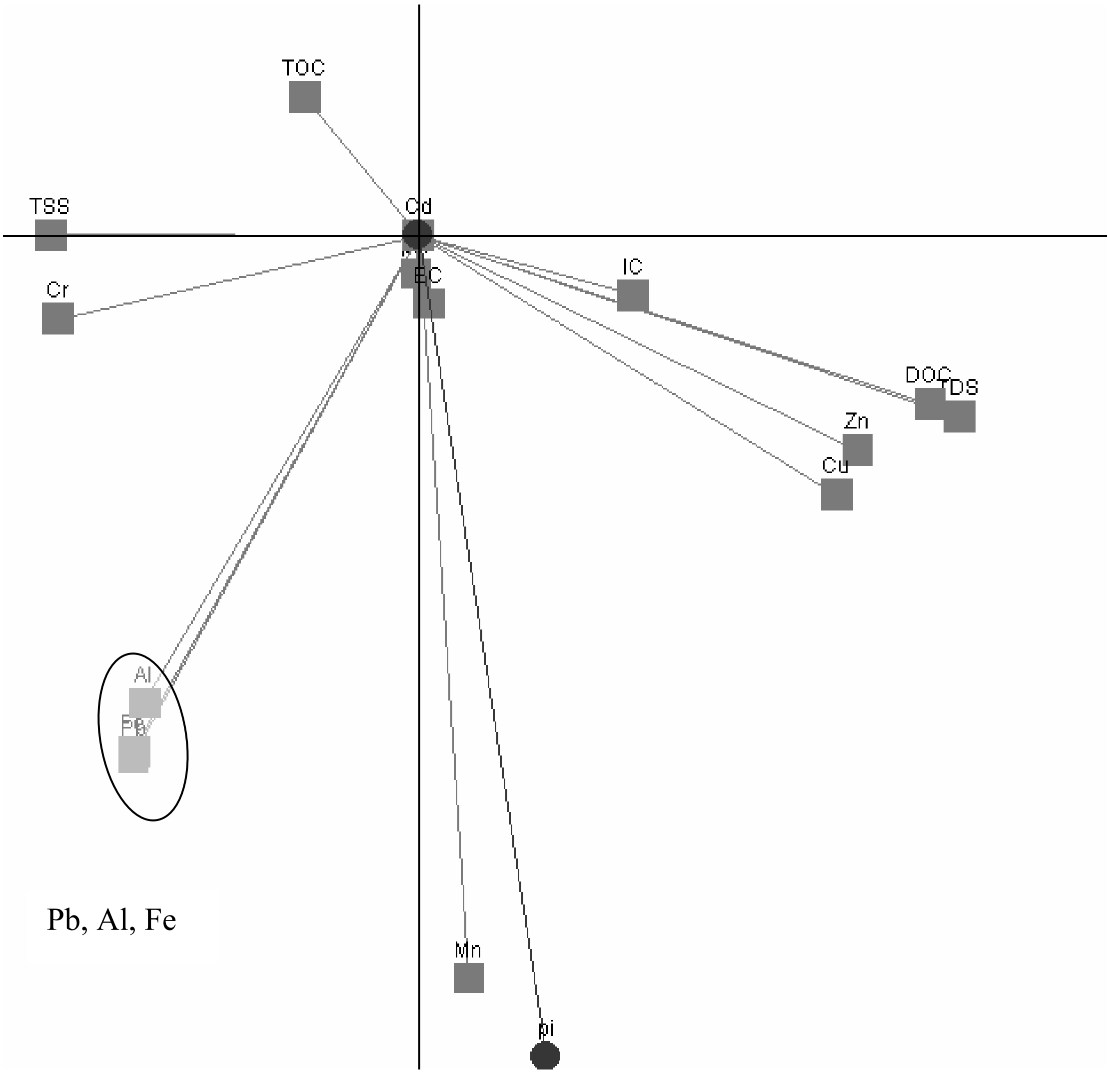

Figure 6 - GAIA analysis for the commercial site, showing correlations between parameters; (■) parameter; (●) pi (π), decision-making axis

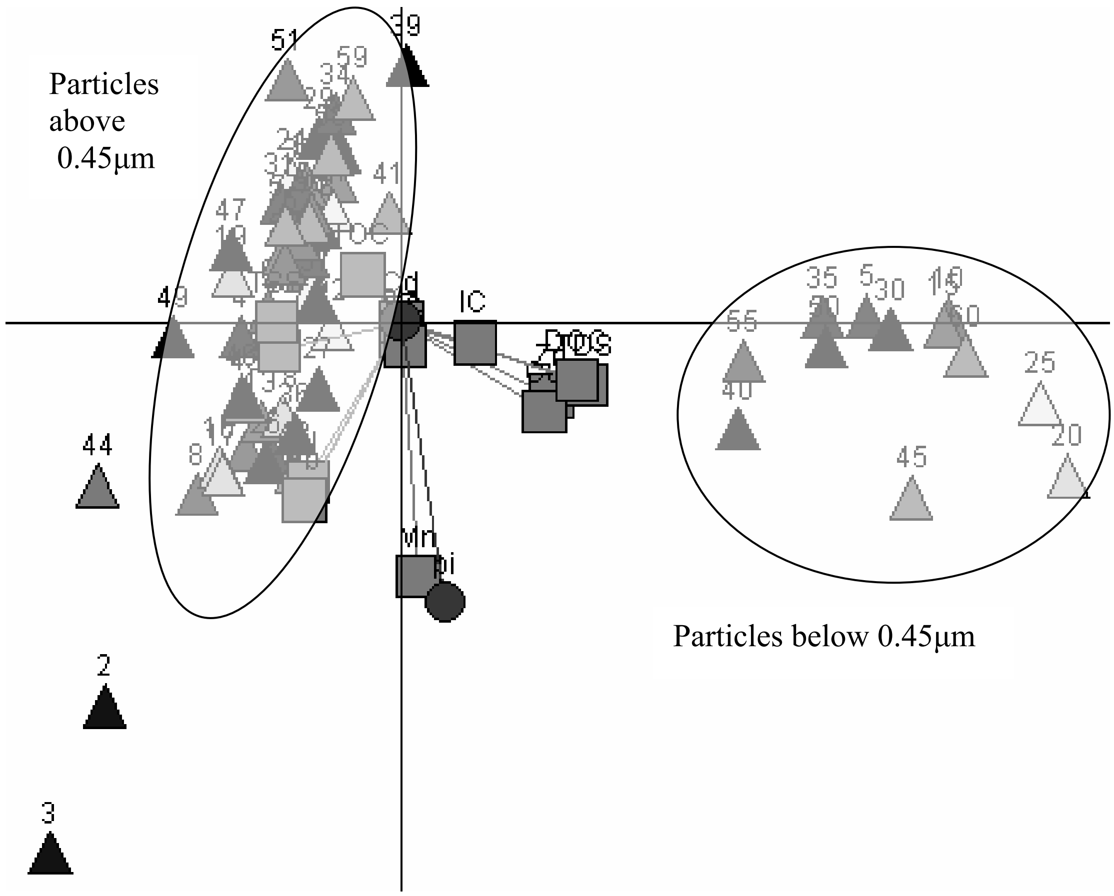

Figure 7 - GAIA analysis for the commercial site, showing correlations between parameters and their affinity with particle sizes; (■) parameter; (▲) wash-off samples; (●) pi (π), decision-making axis