

## **Exploratory source identification of polycyclic aromatic hydrocarbons in urban stormwater**

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### **ABSTRACT**

Polycyclic aromatic hydrocarbons (PAHs) have been shown to possess mutagenic, immunotoxic and carcinogenic properties. Their presence in stormwater therefore poses real and potential adverse impacts on human and ecosystem health. Given the growing need to develop effective control measures and explore stormwater as a potential water source, it is critical to know the sources of stormwater pollutants; evaluate the characteristics of each source and estimate its contribution to a receptor site. PAH concentration data from a range of stormwater runoff events generated from residential, commercial and industrial land use areas were subjected to receptor-oriented models. Particle size of sediments has been shown to be an important factor in stormwater quality, with higher contaminant levels found in the finer fractions. Moreover, finer particles which make up a large fraction of road-deposited sediments are transported further, and are relatively more difficult to remove using conventional treatment measures such as gravity settling. Accordingly, the study focused on the 45-75  $\mu\text{m}$  fraction, and the results tentatively suggest that soot, and emissions from combustion sources, including vehicular exhaust are the main sources of PAHs in stormwater runoff. The implications of the observed correlation between the land use characteristics and the PAH source profiles for the development of mitigation measures are discussed.

### **1. INTRODUCTION**

The presence of pollutants in road-deposited sediments plays an important role in urban stormwater quality. During rainfall these pollutants are transported into receiving waters where they affect stormwater quality (Herngren et al. 2006). In the interests of appropriate stormwater management it is important to determine the nature and degree of contamination from such pollutants as well as the sources of the pollutants, which can be both natural and anthropogenic (Herngren et al. 2006). Anthropogenic sources contribute most to the smaller particle sizes and it has been reported that: (i) these fine particles contain higher organic content than coarser grains; and (ii) there exists a

linear relationship between organic matter and heavy metals (Herngren et al. 2006). Interest in finer particles also stems from the facts that they make up a large fraction of deposited sediments; they are transported further and are the most difficult to remove by regular street-sweeping equipment or gravity settling (Herngren et al. 2006).

Polycyclic aromatic hydrocarbons (PAHs), on the other hand, are products of incomplete combustion which have been shown to possess mutagenic, immunotoxic and carcinogenic properties (Wang et al. 2006). Their presence in road sediments therefore poses a real risk not only to human health through re-suspension, but also to the health of receiving waters. It is therefore important to examine the loading of such compounds on road sediments, especially in urban areas where fine dust can become airborne and inhaled, and are transported by stormwater runoff to receiving waters. Essentially, road sediments act as a mobile substrate in the transport of pollutants to receiving waters.

This paper employs multivariate techniques to investigate the interrelationships between particle size, PAH loading and various physico-chemical factors present in road sediments, with the view to investigating: (i) the sources of PAHs in road sediments; and (ii) the contribution of each source obtained at the receptor sites. To assess the influence of landuse, a selection of residential, commercial and industrial sites were used as study sites.

## **2. EXPERIMENTAL METHODS**

The study sites, sample collection methods, instrumental analysis procedures as well as the salient features of trends and patterns in the data were described earlier (Herngren et al, 2010). However, source identification and source apportionment of PAHs in the samples have previously received no quantitative attention. In the current work, we used Principal Component Analysis coupled with Absolute Principal Component Scores (PCA/APCS) to derive information on the sources of the PAHs and contributions of each source. Principal Component Analysis (PCA) reduces the dimensionality of a dataset; and enables patterns in the relationships of objects to objects, variables to variables and variables to objects to be assessed. However, it does not provide quantitative information on the contributions of pollutant sources because the factors obtained from PCA are not proportional to source contribution. To overcome this problem, receptor modelling can be undertaken by coupling PCA results with absolute principal component scores as described by Guo et al (Guo et al, 2004). Although PCA/APCS sometimes gives negative source contributions, it is a widely used receptor- model.

A data matrix that consisted of 159 samples and variables such as pH, inorganic carbon (IC), electrical conductivity (EC), total solid (TS), total suspended solid (TSS), naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benz(a)anthracene (BAA), chrysene (CHR), benzo(b)fluoranthene (BBF), benzo(a)pyrene (BAP), dibenzo(a, h)anthracene (DBA), benzo(g, h, i)perylene (BGP), benzo(k)fluoranthene (BKF), indeno(1, 2, 3-cd)pyrene (IND) in the finest particle fraction (45 -75  $\mu\text{m}$ ) of the road-deposited sediment was used for the PAC/APCS study.

### 3. RESULTS AND DISCUSSION

The initial PCA produced five factors. By examining the factor loadings closely, it was possible to identify the compositional profiles of the PAHs associated with each factor. Subsequent multiple linear regressions of the absolute principal component scores produced coefficients which were used to convert the absolute principal component scores into the mass concentrations for each source. A plot of the predicted mass versus the observed mass for all sources had a squared correlation coefficient ( $R^2$ ) of 0.9699. This linear relationship indicates that the resolved mass effectively modelled the PAH mass concentrations in the samples.

#### 3.1. Factor 1

Factor 1 (Fig. 2) exhibited elevated contributions of FLU, PHE and FLA and moderate contributions of ANT, ACY, BbF, CHR, BgP, NAP and BaA. FLU is a tracer for coke combustion, and BaA for natural gas combustion (Wang et al. 2006). This factor may therefore be taken as representing combustion sources.

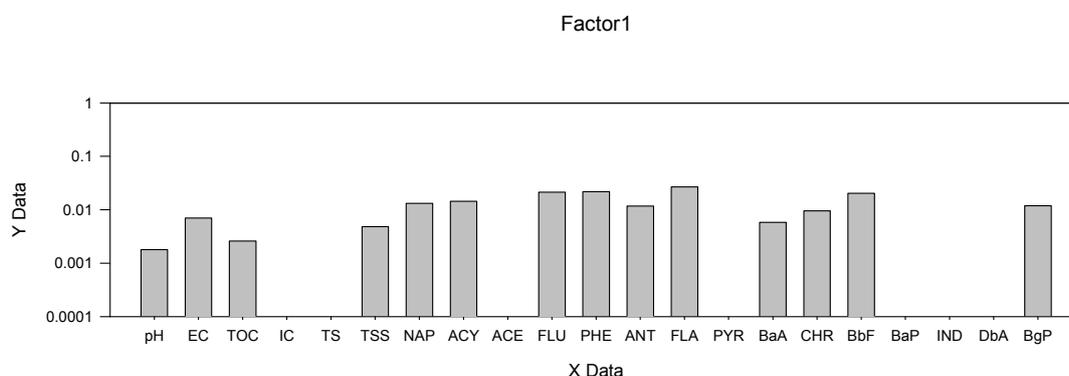


Fig. 1. Factor 1 for 45 – 75  $\mu\text{m}$  fraction, where X data represents the variables examined and Y data the relative mass contribution of the variables.

According to the contributions plot (Fig. 2), sites FA, FB, FD and FC, which are mainly commercial sites made the largest contributions to this factor. It can therefore be inferred that combustion is an important contributor of PAHs at the commercial sites.

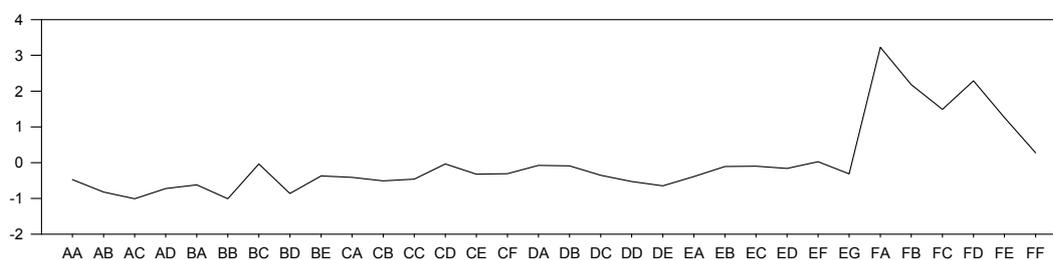


Fig. 2. Source contributions to Factor 1, where AA, AB etc are the sites and the y-axis represent the relative contributions.

### 3.2. Factor 2

Factor 2 (Fig. 3) shows elevated contributions from DbA, IND, PYR and ACE. DbA, IND and PYR has been associated with diesel emissions (Singh et al. 2007), so this factor may be attributed to diesel emissions.

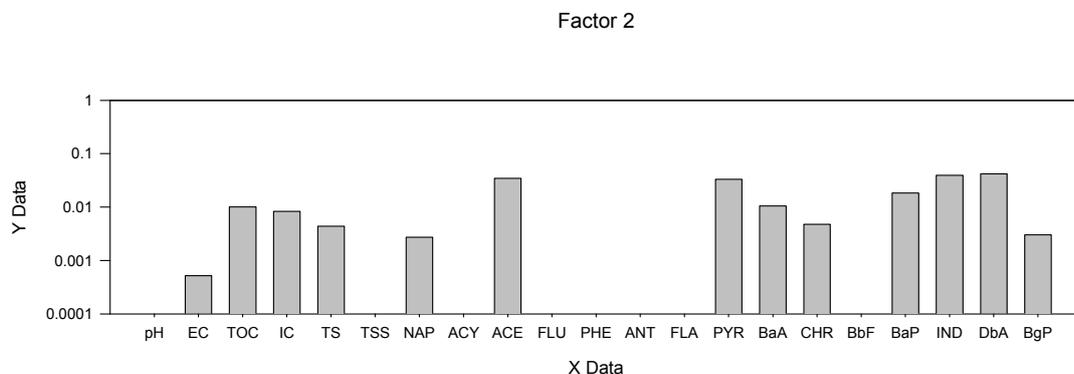


Fig. 3. Factor 2 for 45 – 75  $\mu\text{m}$  fraction, where X data represents the variables examined and Y data the relative mass contribution of the variables.

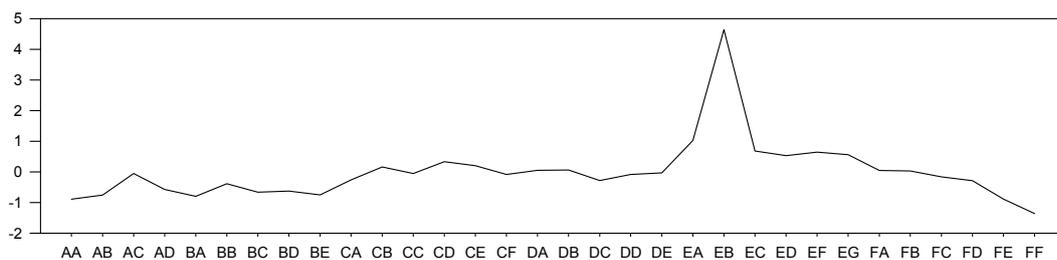


Fig. 4. Source contributions to Factor 2 where AA, AB etc are the sites and the y-axis represent the relative contributions.

The source contributions plot (Fig. 4) shows that the main contributor to Factor 2 is object EB, an object obtained from the commercial site.

### 3.3. Factor 3

Factor 3 (Fig.5) shows high IC and high pH. The associated PAHs are BaP and, to a lesser extent, BaA, PYR, DbA, IND and BgP. The PAHs are all associated with gasoline emissions (Singh et al. 2007) and given the presence of IC in this factor there appears to be appreciable contributions from soot .

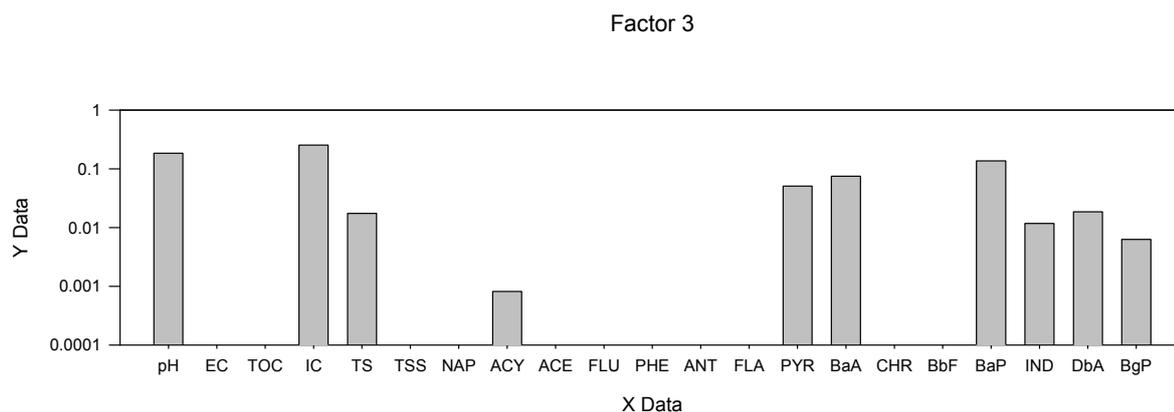


Fig. 5. Factor 3 for 45 – 75  $\mu\text{m}$  fraction, where X data represents the variables examined and Y data the relative mass contribution of the variables.

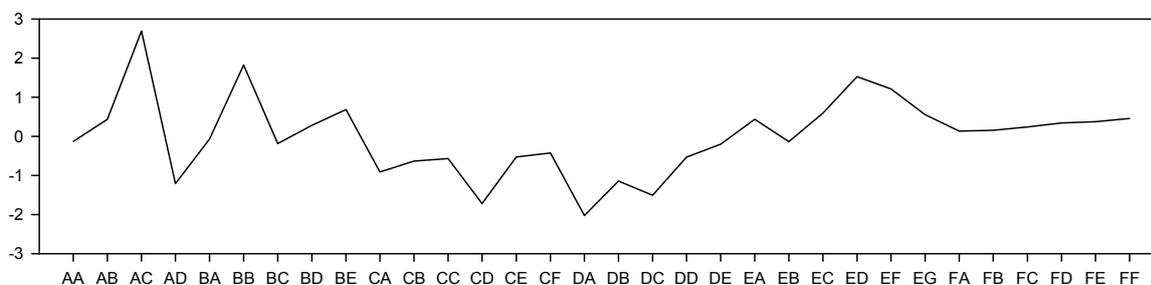


Fig. 6. Source contributions to Factor 3 where AA, AB etc are the sites and the y-axis represent the relative contributions.

The contributions plot (Fig. 6) shows that objects AB, BB, BE, and objects EA through FF contributed most to this factor. Objects AB, BB and BE were all obtained from the residential site, while EA to FF were obtained from the commercial site. This implies some considerable impact from gasoline contamination at the residential site for this particle size fraction.

### 3.4 Factor 4

Factor 4 (Fig. 7) exhibits high TS and ANT, with moderate contributions from BbF, BaP, IND, DbA, NAP and TSS. ANT, BbF, DbA, IND and BaP are associated with vehicular traffic emissions (Singh et al. 2007).

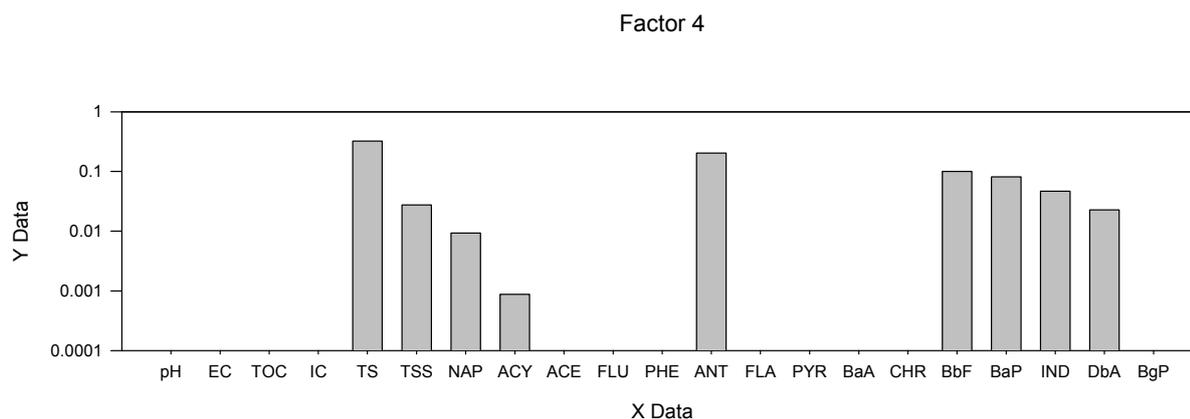


Fig. 7. Factor 4 for 45 – 75  $\mu\text{m}$  fraction, where X data represents the variables examined and Y data the relative mass contribution of the variables.

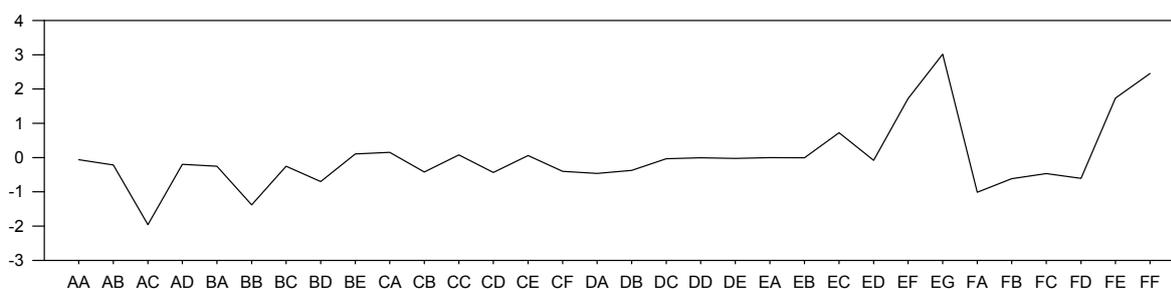


Fig. 8. Source contributions to Factor 4 where AA, AB etc are the sites and the y-axis represent the relative contributions.

The objects mainly contributing to Factor 4 are EF, EG, FE and FF). These objects are all from the commercial site. It seems reasonable to infer that the source is mainly vehicular emissions.

### 3.5. Factor 5

Factor 5 (Fig. 9) shows high TOC correlated with ANT, DbA and IND, with moderate contributions from FLU, PHE and TSS, and minor contributions from NAP and ACY. ANT is associated with combustion and DbA and IND indicate high vehicular emissions from cars and diesel engines (Singh et al. 2007), as is FLU and PHE.

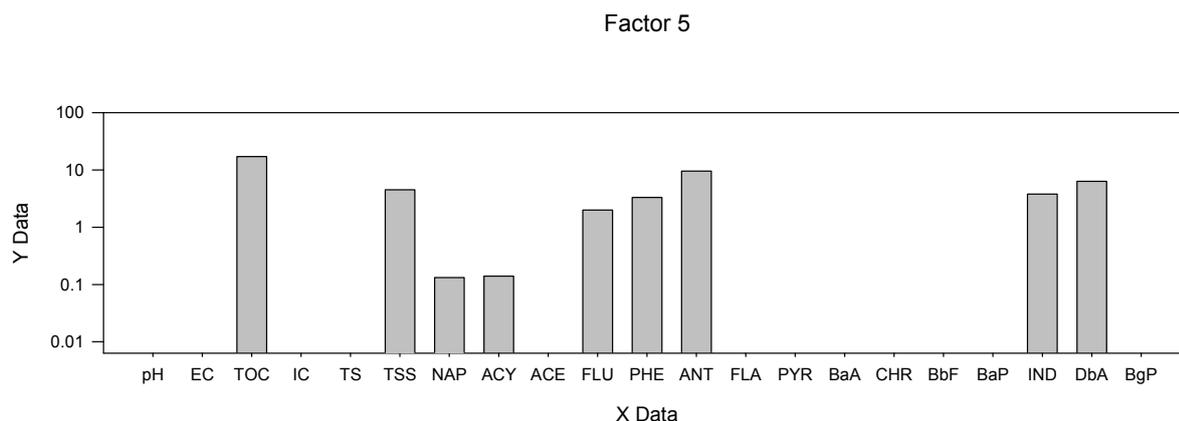


Fig. 9. Factor 5 for 45 – 75  $\mu\text{m}$ , where X data represents the variables examined and Y data the relative mass contribution of the variables.

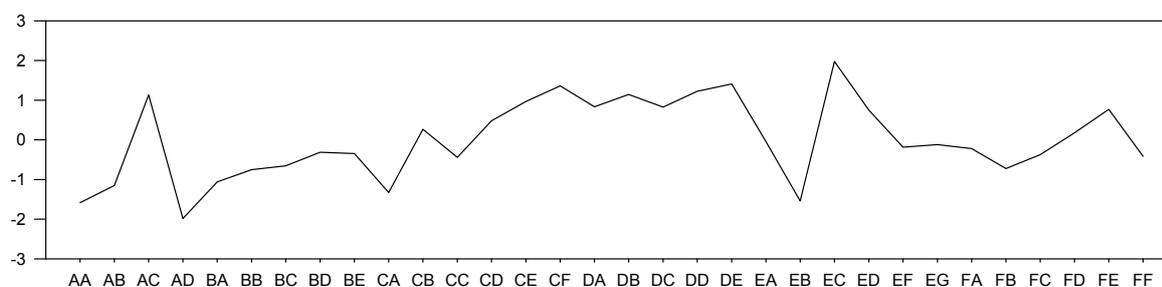


Fig. 10. Source contributions for Factor 5 where AA AB etc are the sites and the y-axis represent the relative contributions.

The bulk of the contributions to this source come from objects CA through DE, which are all samples obtained from the industrial site. Objects EC and FE (commercial site) make large individual contributions, as do object AC from the residential site. The consistent contributions from the industrial objects, though, indicate a considerable impact to this source from activities at industrial sites and it seems reasonable to infer that this source is mainly associated with heavy duty vehicular traffic.

#### 4. CONCLUSIONS

Various tentative sources of PAHs appear to be associated with 45- 75  $\mu\text{m}$  particle size fraction. Signatures for natural gas combustion, vehicular emissions, and soot feature in the various factors. This is not surprising, since the smaller particles appear to adsorb many different pollutants as result of the relatively high electrostatic charge volume to size ratios. In terms of the development of an urban stormwater management strategy, it would be important

to pay attention to the various sources of PAHs in urban environments in order to develop effective mitigation strategies to protect receiving waters.

## **5. REFERENCES**

- Guo, H., Wang, T., Louie, P.K.K. (2004) "Source apportionment of ambient non-methane hydrocarbons in Hong Kong: Application of a principal component analysis/absolute principal component scores (PCA/APCS) receptor model" *Environ. Pollut.*, **129**, 489-498.
- Herngren, L., Goonetilleke, A., Ayoko, G.A. (2006). Analysis of heavy metals in road-deposited sediments. *Anal. Chim. Acta*, 571, 270-278.
- Herngren, L., Goonetilleke, A., Ayoko, G.A. (2010). "Distribution of polycyclic aromatic hydrocarbons in urban stormwater in Queensland, Australia". *Environ. Pollut.* 158, 2848- 2856.
- Singh, K. P., A. Malik, et al. (2007). "Receptor Modeling for source apportionment of polycyclic aromatic hydrocarbons in urban atmosphere." *Environ. Monit. Assess.* 136, 183-196.
- Wang, Z., J. Chen, et al. (2006). "Polycyclic aromatic hydrocarbons in Dalian soils: distribution and toxicity assessment." *J. Environ. Monit.* 9, 199-204.