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Land-use dependent source apportionment of polycyclic aromatic hydrocarbons in urban watershed

Répartition des sources d'hydrocarbures aromatiques polycycliques en fonction de l'usage des sols dans un bassin versant

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RÉSUMÉ
Cette étude présente l'analyse des sources potentielles des hydrocarbures aromatiques polycycliques (HAP) dépendant de l'utilisation des sols dans les bassins versants urbains au moyen d'un modèle de récepteur de factorisation de matrice positive (FMP). Les échantillons de sédiments provenant des routes ont été prélevés dans des bassins versants urbains (surfaces routières imperméables) entourés de terrains utilisés de manière diverses dans la ville de Dresde, en Allemagne. Quatre types différents d'utilisation des sols ont été sélectionnés : centre commercial, autoroute, zone résiduelle et zone de campus. Les résultats indiquent que des facteurs de sources potentielles différents ont été identifiés sur les différentes utilisations de sols. Explicitement, quatre principales sources pour le centre commercial ont été provisoirement identifiées comme provenant des véhicules à essence (16.56%), de la combustion de la biomasse (23.12%), des véhicules diesel (20.78%) et de la combustion de bois (39.53%). Trois sources majeures pour l’autoroute ont été identifiées comme étant la combustion de bois (15.62%), les véhicules diesel (34.19%) et les véhicules à essence (50.19%). Deux sources majeures dans la zone résiduelle ont été identifiées comme provenant de la combustion de bois (32.69%) et des émissions des véhicules (67.31%). Les facteurs potentiels sur le campus ont été identifiés comme étant les émissions des véhicules (36.69%), les émissions d’un four à coke (13.88%) et la combustion de charbon (49.42%).

ABSTRACT
This study showcases the potential source analysis of land-use dependent polycyclic aromatic hydrocarbons (PAHs) on urban watershed by means of Positive Matrix Factorization (PMF) receptor model. The RDS samples were collected from urban watersheds (impervious road surfaces) with various surrounding land uses in the city of Dresden, Germany. Four different land-use types of commercial centre, highway, residual area and campus area were selected. Results show that different potential source contributors were identified at different land uses. Explicitly, four major contributors to the commercial centre were tentatively identified as gasoline-powered vehicle (16.56%), biomass burning (23.12%), diesel-powered vehicle (20.78%), and wood combustion (39.53%). Three major contributors to the highway were identified as wood combustion (15.62%), diesel-powered vehicle (34.19%), and gasoline-powered vehicle (50.19%). Two major contributors to the residual area were identified as wood combustion (32.69%) and vehicular emission (67.31%). The potential contributors to the campus area were identified as vehicular emission (36.69%), coke oven emission (13.88%), and coal combustion (49.42%).

KEYWORDS
Land use, PAHs, PMF, road-deposited sediment, source apportionment
INTRODUCTION

The deteriorated stormwater runoff has been regarded as a leading cause of nonpoint source pollutions. More recently, climate change induced extended periods of high-intensity rainfall and rapid urbanization induced changes of watershed hydrology boost the stormwater pollution loads due to the washing away of pollutants accumulated in urban watershed. In this regard, road-deposited sediment (RDS) which adsorbs non-particulate soluble and suspendable matters has been regarded as impervious surface pollutant and a major pollutant carrier (substrate) which flows into sewer systems or directly to receiving waters (Boonyatumanond et al. 2007). Therefore, the characteristics of RDS and its adsorbed pollutants should be well understood to appropriately mitigate stormwater pollutants.

Among these priority contaminants, polycyclic aromatic hydrocarbons (PAHs) are regarded as toxic, carcinogenic, mutagenic, teratogenic, and typical anthropogenic pollutants (Phillips 1983; Harrison et al. 1996; Zhang et al. 2015). Due to the significant risk to or via the aquatic environment, eight PAHs are included in the list of Priority Pollutants of the European Water Framework Directive (WFD) 2011/0429 (COD) and sixteen in the United States Environmental Protection Agency (EPA) Priority Pollutant List, with seven of them being potential carcinogens. Concerning this issue, the occurrences of PAHs have been studied in various matrices such as: atmospheric aerosols, soils, aquatic sediments and so on (Rogge et al. 1993; Harrison et al. 1996). However, comparatively less or no attention was paid to the source apportionment of PAHs in RDS with regard to the characteristics of different land-use types.

Positive matrix factorization (PMF) is a mathematical approach for quantifying the contribution of sources to samples based on the composition or fingerprints of the sources. Compared to other traditional receptor models, e.g. principal component analysis (PCA), PMF treats the fundamental receptor modelling equation as a least-squares problem and does not employ eigen-based analyses. The factor loadings and factor scores may be negative extracted by PCA receptor model, which makes the interpretation of the sources very difficult (Zhang et al. 2013). However, PMF rotates the matrices of factor loadings and scores with positive constraints, which makes factor axes less orthogonal and makes factor loadings and factor scores more interpretable. In addition, PMF takes uncertainty which encompasses errors of sampling and analytical into account. Therefore, PMF 5.0 receptor model released by EPA is recommend to use to make source apportionment results more robust and was employed in the present study (www.epa.gov, accessed October 2014).

The primary objective of this investigation was to provide data to reduce PAHs occurrence in aquatic environment by source tracking technique before they are introduced into the aquatic environment. The detailed focuses of the present study were to (i) investigate the impact of land use on the distribution of PAHs in RDS and (ii) identify the primary origins of PAHs regarding the different land-use types.

MATERIAL AND METHODS

Study Area

RDS samples were obtained from four traffic roads with bituminous pavement (asphalt) in the city of Dresden (51°02′55″ N, 13°44′29″ E) which is located in eastern Germany. The sampling sites with different surrounding land-use types are located along the urban-rural gradient, i.e. W site to Be site gradient. The major characteristics of the selected sampling sites are given in Table 1.

Sample collection

Sampling campaign was performed on July 2012. The largest portion of the sediments was assembled near roadside curb areas (Sartor & Boyd 1972). Therefore, all the enclosed sampling plots were situated next to the roadside curb areas. In terms of sample collection, the vacuum sweep with a water filtration system, also referred to as the wet vacuuming method, has been proven to be more efficient than dry vacuuming method in removing the fine materials within an impervious surface (Amato et al. 2010). Accordingly, a professional vacuum sweeper (Puzzi 100 Super, Kärcher) was employed in the current study for sample collection. The vacuum sweeper consists of an extraction pipe with a polyethylene brush (length, 230 mm) and a water spray (spray pressure, 1 bar) at the top of vacuum nozzle. The delivered sufficient pressure dislodged fine sediment particles without destroying the road.
surface. The power requirement was provided by a generator (Honda EU30i, Rated power COP, 2.6 kW).

Table 1. Characteristics of sampling sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Abbr.</th>
<th>Road class</th>
<th>Pavement quality</th>
<th>Lane number</th>
<th>Average daily traffic*</th>
<th>Heavy traffic %</th>
<th>Sample number</th>
<th>Vicinity land use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Walpurgis Str.</td>
<td>W</td>
<td>Main road</td>
<td>Good</td>
<td>4</td>
<td>12600</td>
<td>3-4</td>
<td>33</td>
<td>Commercial (city) centre</td>
</tr>
<tr>
<td>Bannewitz</td>
<td>Ba</td>
<td>Federal Highway</td>
<td>Average</td>
<td>2</td>
<td>15900</td>
<td>5</td>
<td>24</td>
<td>Highway area</td>
</tr>
<tr>
<td>Noethnitz (Rural area)</td>
<td>N</td>
<td>Secondary road</td>
<td>Good</td>
<td>2</td>
<td>50</td>
<td>&lt;1</td>
<td>20</td>
<td>Residual area</td>
</tr>
<tr>
<td>Berg Str.</td>
<td>Be</td>
<td>Secondary road</td>
<td>Average</td>
<td>1</td>
<td>10</td>
<td>&lt;1</td>
<td>52</td>
<td>Campus area</td>
</tr>
</tbody>
</table>

*The traffic loads were determined in one flow direction (www.dresden.de, accessed October 2014).

Laboratory analysis

A total of 129 RDS samples were texted for the total and individual sixteen PAHs, explicitly, Naphthalene (NAP), Acenaphthylene (ACY), Acenaphthene (ACE), Fluorene (FLU), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLUH), Pyrene (PYR), Benz(a)anthracene (BaA), Chrysene (CHR), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)pyrene (IDP), Dibenzo(a,h)anthracene (DBA), Benzo(g,h,i)perylene (BghiP). PAH compounds were firstly extracted from the RDS samples using solid-phase extraction method following German Norm DIN 38414-23 and DIN EN ISO 17993. Afterwards, the extracted solutions were further analysed for PAH compounds by using an ultra-high-performance liquid chromatography (Ultimate 3000, Dionex).

PMF receptor model

The PMF modelling approach was conducted using EPA PMF 5.0. A detailed discussion of the PMF model can be found in Paatero and Tapper (1993) and Norris et al. (2008). The fundamental equation of PMF is:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}$$

where $x_{ij}$ is the $j^{th}$ species concentration measured in the $i^{th}$ sample, $g_{ik}$ is the concentration in the $i^{th}$ sample from the $k^{th}$ source, $f_{kj}$ is the contribution of the $k^{th}$ source to the $j^{th}$ species and $e_{ij}$ is the residual for each sample/species.

PMF treats the fundamental receptor modelling equation as a least-squares problem by specifying an object function $Q$ of the residual matrix which is to be minimised. The function $Q$ value to be minimised is defined as:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left( x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj} \right)^2$$

where $u_{ij}$ is the uncertainty in the $x_{ij}$ measurement and is calculated by considering the method detection limit (MDL) for each species and the species-specific error fraction.

The equation-based uncertainty was used to calculate uncertainties required by PMF. More
explicatively, if the concentration is less than or equal to the MDL, the uncertainty \( (\text{Unc}) \) is calculated using the following equation (Polissar et al. 1998; Norris et al. 2008):

\[
\text{Unc} = \frac{5}{6} \times \text{MDL}
\]

If the concentration is greater than the MDL, the calculation is:

\[
\text{Unc} = \sqrt{(\text{Error Fraction} \times \text{concentration})^2 + (\text{MDL})^2}
\]

where, the Error Fraction indicates the percentage uncertainty in determination of the variable and normally estimated as the standard deviation of deuterated surrogates recoveries (Sofowote et al. 2008). More details regarding uncertainty setting and other technical usage of PMF can be found elsewhere (Norris et al. 2008).

RESULTS AND DISCUSSION
Source apportionment of PAHs

Percentage source contributions of individual PAHs to each specific source were firstly summarized in Table 2. The different sources were extracted at the different land-use types. The potential source contributions were identified primarily following the source fingerprints (tracers) reviewed from the reported literatures.

<table>
<thead>
<tr>
<th>Table 2. Percentage source contribution of individual PAHs to each specific source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sampling site</strong></td>
</tr>
<tr>
<td>Component</td>
</tr>
<tr>
<td>NAP</td>
</tr>
<tr>
<td>ACY</td>
</tr>
<tr>
<td>ACE</td>
</tr>
<tr>
<td>FLU</td>
</tr>
<tr>
<td>ANT</td>
</tr>
<tr>
<td>BaF</td>
</tr>
<tr>
<td>BaP</td>
</tr>
<tr>
<td>DBA</td>
</tr>
<tr>
<td>BgP</td>
</tr>
<tr>
<td>IDP</td>
</tr>
</tbody>
</table>

Furthermore, the fractional concentrations of PAH species and fractional percentage source contributions to each specific source were extracted by PMF and shown in Figure 1 - 4. The detailed source apportionments with regard to different land-use types were then discussed.

Source estimates of commercial centre

The sampling site W is a commercial city centre. As shown in Table 2, four potential sources (factors) were resolved by PMF for this land use. As shown in Figure 1, the first factor was predominantly weighted in the species concentrations of PYR, FLUH, BgP and BbF. According to the results from
Harrison et al. (1996), FLUH, PYR and especially BgP were suggested for the emissions from gasoline-powered vehicles. In addition, Guo et al. (2003) reported that BbF is indicative of gasoline engine emissions. This factor, therefore, was attributed to the gasoline-powered vehicle emissions.

The second factor was predominantly weighted by the high species concentrations of FLUH, PYR, PHE, CHR and BbF. According to the findings of Ravindra et al. (2008) and Yang et al. (2013), the high loadings of these species indicate low temperature pyrogenic process of biomass combustion. Therefore, biomass burning was identified as a potential source contributor to this factor.

The third factor was dominated by the high species concentrations of FLUH, PYR, PHE, BbF and CHR. Ravindra et al. (2008) reported that the high loadings of these species indicate the origin to be diesel-powered vehicles. Therefore, diesel-powered vehicle emission was identified as the major source for this factor.

The fourth factor was characterised with the dominant species contents of FLUH, PYR, PHE, and NAP. It is reported that PHE, FLUH and PYR are indicative of wood combustion (Khalili et al. 1995; Harrison et al. 1996). In addition, a majority of NAP releases result from the combustions of wood (HSDB 2013). Therefore, this factor was attributed to the wood combustion.

![Figure 1. Fractional source concentrations and percentage source contributions of individual PAH at site W](image)

**Source estimates of highway area**

The sampling site Ba is a highway area. As shown in Table 2, three potential sources (factors) were resolved by PMF for this land use. As shown in Figure 2, the first factor was characterised with the dominant species contents of PHE, NAP, FLUH, and PYR, which was consistent with the source of wood combustion (Khalili et al. 1995; Harrison et al. 1996).

The second factor was dominated by the high species concentrations of FLUH, PYR, PHE, CHR, and BbF, which was consistent with the source of diesel-powered vehicle emission (Ravindra et al. 2008).

The third factor was predominantly weighted in the species concentrations of PYR, FLUH, BgP and BbF, which was consistent with the source of gasoline-powered vehicle emissions (Harrison et al. 1996; Guo et al. 2003).
Source estimates of residual area

The sampling site N is a residual area. As shown in Table 2, two potential sources (factors) were resolved by PMF for this land use. As shown in Figure 3, the first factor was characterised with the dominant species contents of PHE, NAP, FLUH, and PYR, which was consistent with the source of wood combustion (Khalili et al. 1995; Harrison et al. 1996).

The second factor was heavily weighted by FLUH, PYR, PHE, and to a lesser extent by CHR and BbF. The dominance of CHY and BbF were suggested as a result of their origins being diesel-powered engine (compression ignition) exhausts. In addition, FLUH and PYR are also components of crude oil and fossil fuel. A portion of them was associated with their combustion (Kavouras et al. 2001). Consequently, this component was tentatively attributed to the vehicular emission (i.e., a combination of diesel and gasoline emissions).
Source estimates of campus area

The sampling site Be is a campus area. As shown in Table 2, three potential sources (factors) were resolved by PMF for this land use. As shown in Figure 3, the first factor was predominantly weighted in the species concentrations of FLUH, PHE, PYR, and to a lesser extent by CHR and BbF, which was consistent with the source of vehicular emission (Kavouras et al. 2001).

The second factor was predominantly weighted in the species concentrations of PHE, FLUH, PYR, and NAP. According to Lin et al. (2013), PHE, FLUH, and PYR were used as source fingerprints for the emission from coke ovens, and especially with the elevated level of NAP which reported as a predominant PAHs in the coke oven emissions. Therefore, the dominance of these species indicates that coke oven emissions were the main source of this factor.

The third factor was dominated by four-member ring PAHs of PYR, CHR, and BaA. According to Harrison et al. (1996), these compounds were considered to be strongly associated with coal combustion, especially when they appeared within a component as a group. Thus, this factor was representative of the coal combustion sources.

Model evaluation

To assess the accuracy of the PMF modelled results, as illustrated in Figure 5, the predicted $\Sigma_{16}$PAHs concentrations were compared with the measured concentrations for each land use with a confidence level of 95%.

For the regression equations, the slopes ranged from 0.9443 to 1.0267. The adjusted coefficient of determination $R^2$ which takes account of the phenomenon of the $R^2$ automatically and spuriously increasing when extra explanatory variables added was employed to assess the goodness-of-fit of the model resolutions. The adjusted $R^2$ values were from 0.9943 to 0.9999. The presented $R^2$ values were comparable with the data recorded by the other studies (Sofowote et al. 2008).
Figure 5. Fitting plot between modelled and measured Σ_{16}PAHs concentrations (μg/g).

Furthermore, as presented in Table 3, PMF model generated consistently lower modelled values of Σ_{16}PAHs concentrations than the measured concentrations for all land uses. Similar negative errors were obtained ranging from -2.1 to -8.3%, indicating underestimation of the concentrations in PMF model. The finding is consistent with previous studies concerning the underestimation of PMF modelling due to down-weighted outlying variables and the uncertainty estimated for each variable (Larsen & Baker 2003; Yang et al. 2013).

Table 3. Evaluation of total PAH modelled by PMF.

<table>
<thead>
<tr>
<th>Σ_{16}PAHs</th>
<th>W</th>
<th>Ba</th>
<th>N</th>
<th>Be</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modelled</td>
<td>55.024</td>
<td>18.078</td>
<td>24.089</td>
<td>15.936</td>
</tr>
<tr>
<td>%Error</td>
<td>-2.1</td>
<td>-8.3</td>
<td>-4.1</td>
<td>-3.4</td>
</tr>
</tbody>
</table>

CONCLUSION

This study focus on the land use dependent PAHs source apportionment in RDS by means of PMF receptor model. According to the PMF source apportionment, the primary contributors to PAHs contents in different land uses were identified. Generally, potential sources such as the emissions from gasoline- and diesel-powered engine vehicles, biomass, coal and wood combustions were identified as main sources for RDS associated PAHs which was consistent with source apportionments reported in various studies of atmospheric aerosols, soils, and aquatic sediments. The results reported herein could assist potential performance of stormwater best management practices in eliminating PAHs from urban watershed, and could be used for source-oriented mitigation of rainfall-induced urban runoff pollution.
LIST OF REFERENCES


