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The qualitative and quantitative source apportionments of polycyclic aromatic hydrocarbons in size dependent road deposited sediment

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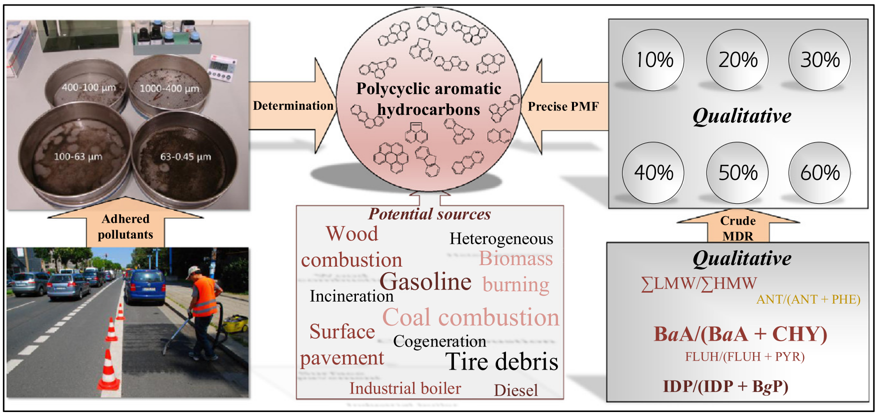
HIGHLIGHTS

- Increases of PAH contents were observed with decreasing size fractions in RDS.
- Low molecular weight PAHs were predominant PAHs in RDS.
- Regardless of size fraction, PAH crude sources were identified by the MDR approach.
- More refined PAH sources were identified by PMF model in size dependent RDS.
- Quantitative contributions of the identified sources were calculated by the MLR method.

GRAPHICAL ABSTRACT



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ABSTRACT

This study showcases the qualitative and quantitative source apportionments of size-dependent polycyclic aromatic hydrocarbons (PAHs) in road deposited sediment by means of molecular diagnostic ratio (MDR) and positive matrix factorisation (PMF) approaches. The MDR was initially used to narrow the PAH source candidates. PMF modelling was subsequently used to provide more precise source apportionment with the assistance of a multiple linear regression analysis. Through a combined qualitative and quantitative source apportionment, different potential source contributors were identified at different size fractions. Explicitly, three major contributors to sorption at the size fraction of 1000–400 µm were tentatively identified as incineration (26%), coal combustion (53%) and gasoline-powered vehicle (20%). Four major contributors to the size fraction of 400–100 µm were identified as gasoline-powered vehicle (25%), surface pavement (15%), diesel-powered vehicle (37%) and industrial boiler (24%). Four major contributors to the size fraction of 100–63 µm were identified as cogeneration emission (13%), diesel-powered vehicle (28%), tire debris (45%) and wood combustion (14%). The potential contributors in the size fraction 63–0.45 µm were identified as diesel-powered vehicle (21%), heterogeneous sources (41%) and biomass burning (38%). In addition, the highest $\sum_{16}$PAH concentration was found in the smallest size fraction of 63–0.45 µm, which is also where the highest BaPE and TEF values for potential risk assessment occurred.

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1. Introduction

An increased proportional area under impervious surface is the primary agent responsible for the catchment hydrologic changes associated with the urbanisation process (Shuster et al., 2005). The increases in impervious surface cause a decrease in the infiltration of stormwater and an increase in the production of surface runoff. The high volume and velocity of stormwater runoff could boost the pollution loads due to the washing away of road deposited sediment (RDS) and its associated pollutants of nutrients, pesticides, wear metals, organic pollutants, oil, grease and other toxics which are detrimental to aquatic life, wildlife, habitat, and human health (EPA, 2007). Therefore, the in-depth understanding of the RDS adsorbed pollutants and surface-based approaches which emphasise management at sources is significant to the context of stormwater pollution prevention and stormwater best management practices (BMPs) (Zhang et al., 2013a,b).

Among the RDS adsorbed contaminants, polycyclic aromatic hydrocarbons (PAHs), also known as polynuclear aromatic hydrocarbons (PNAs), are regarded as toxic, carcinogenic, mutagenic, and teratogenic pollutants (in Supporting Information, SI Table S1) (Phillips, 1983; IARC, 2005; ATSDR, 1995; EPA, 2013). Due to the significant risk, PAHs have been regarded as a major diffuse pollution to the aquatic environment via stormwater runoff (Aryal et al., 2011). Eight PAHs are included in the list of priority pollutants of the European Water Framework Directive (WFD) 2011/0429 (COD) (EU, 2012) and sixteen in the United States Environmental Protection Agency (EPA) priority pollutant list (EPA, 2014), with seven of them being potential carcinogens.

Specifically, PAHs are compounds containing typically two to eight benzene-member rings. Sources of PAHs can be both natural and anthropogenic. PAHs are ubiquitous in nature as a consequence of synthesis in terrestrial vegetation, microbial synthesis, volcanic activity forest and prairie fires, but quantities formed by these natural processes are small in comparison with those produced from anthropogenic sources. Anthropogenic activities are associated with the significant production of PAHs during pyrolysis of organic materials typical of some processes used in the iron and steel industry, heating and power generation, petroleum refining and so on, as well as the release of petroleum products. Moreover, PAH composition as a function of particle size fraction has been attributed to differential source inputs or partitioning among particle size fractions (Lee et al., 2005). Therefore, being able to identify and apportion the primary sources of PAHs, especially regarding different size fractions, is an initial and critical step towards stormwater management.

Several methods have been used to identify the potential sources of PAHs, e.g. molecular diagnostic ratio (MDR) (Raza et al., 2013; Tobiszewski and Namiesnik, 2012), hierarchical cluster analysis (HCA) (Boonyatumanond et al., 2007; Murakami et al., 2005), receptor models of principle component analysis (PCA), Unmix (Larsen and Baker, 2003a; Harrison et al., 1996; Reff et al., 2007), and positive matrix factorisation (PMF) (Anttila et al., 1995; Lee et al., 1999, 2003; Xie et al., 1999; Larsen and Baker, 2003b; Reinikainen et al., 2001; Du et al., 2008; Shao et al., 2014; Vaccaro et al., 2007; Bzdusek and Christensen, 2006; Bzdusek et al., 2005; Sofowote et al., 2008), which has been used in air quality and source apportionment studies, in water samples, more recently in soils, and aquatic sediments, etc. However, less attention has been paid to the source analysis of PAHs in size dependent RDS from the perspective of stormwater pollution. Therefore, in this study, MDR and PMF approaches were used to evaluate the potential sources of PAHs in the RDS samples.

MDR is one of the most common and widely used diagnostic tools to qualitatively identify the origin of PAHs in the environment due to the frequent and user-friendly application (Yunker et al., 2002; Katsoyiannis et al., 2011). In this study, the MDR approach was used to initially narrow the PAH source candidates and to conduct crude and qualitative source apportionments of PAHs. Subsequently, the PMF receptor model was employed to further provide refined and quantitative source apportionments.

PMF is a receptor modelling tool developed in the early 1990s (Paatero and Tapper, 1993, 1994). Compared to other traditional receptor models, e.g. 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 negatively extracted by the PCA receptor model, which makes interpretation of the sources very difficult (Zhang et al., 2013a). 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 (*Unc*), which encompasses errors of sampling and analysis into account. It allows each data point to be individually weighed, depending on the confidence in the measurement. Therefore, the PMF receptor model is recommended to make source apportionment results more robust (Norris et al., 2008a).

The primary objective of the present study was to provide qualitative and quantitative data to facilitate the source-oriented mitigation of PAHs in stormwater runoff by means of MDR and PMF source analysis approaches. To the best of the authors' knowledge, this is the first look at size-dependent PAH source apportionment in RDS by means of the PMF receptor model. The detailed focuses were to (i) determine the PAH contents in RDS samples with regard to the particle size distribution, (ii) assess the potential health risk posed by PAHs, and (iii) qualitatively and quantitatively identify the primary origins of PAHs.

2. Material and methods

2.1. Study area

RDS samples were obtained from six traffic roads with bituminous pavement (asphalt) in the city of Dresden (51°02′55″ N, 13°44′29″ E) which is located in the Saxony state, Germany. The six given sampling sites are located along the city centre–city border (CC–CB) gradient to afford the collected RDS samples to be more representative. The sampling site and land-use type maps are given in Fig. 1. The major characteristics of selected sampling sites are given in Table 1. The CC–CB gradient was categorised based on the concept of urbanisation. The urbanisation scale was primarily ranked according to the average daily traffic, which is suggested as a better proxy for stormwater runoff quality (Lau and Stenstrom, 2005), and the surrounding land-use type (Sartor and Boyd, 1972).

2.2. Sample collection

The sampling campaign was performed in July 2012. The sampling method was following the suggestions of Zhang and Krebs (2013). A vacuum sweeper (Puzzi 100 Super, Kärcher), with a water filtration system, was employed in the current study for sample collection, which has been proven to be more efficient in removing the fine materials within a typical pavement structure than mechanical broom sweepers and traditional domestic vacuum sweepers (Sartor and Boyd, 1972; Gunawardana et al., 2014). The power requirement was provided by a generator (Honda EU30i, rated power COP, 2.6 kW).

2.3. Sample fraction

To investigate the role of particle size, bulk RDS samples from each site were fractionated into sub-samples and wet-sieved using test stainless-steel sieves with mesh sizes of 1000 μm, 400 μm, 100 μm and 63 μm in sequence. The particles passing through the 63 μm sieve were filtered by a 0.45 μm cellulose nitrite filter. According to German Norm DIN EN ISO 14688-1, the sediments with grain size fraction of 1000–63 μm are classified as sand, while 63 μm is the boundary classification diameter of sand and silt. The grain size diameter of 0.45 μm is