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Spatial-temporal and multi-media variations of polycyclic aromatic hydrocarbons in a highly urbanized river from South China

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HIGHLIGHTS

- Monthly rainfall correlated with PAH levels in water and SPM but not in sediment.
- Mean sediment PAH concentrations decreased mainly due to the 4-ring PAH degradation.
- Water and SPM PAHs had similar sources which were different from that of sediment.
- Similarities of sediment PAHs vs. water/SPM PAHs decreased along the Maozhou River.
- Sediment PAHs were likely washed to lower reaches in the form of SPM by river water.

GRAPHICAL ABSTRACT

The GRAPHICAL ABSTRACT was from pictures we took of the Maozhou River when collecting samples.

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ABSTRACT

Comprehensive studies on polycyclic aromatic hydrocarbons (PAHs) within an urban river are urgently needed to carry out strategies to limit their contamination and dispersal. Here, we analyzed 16 PAH occurrences in water, suspended particulate matter (SPM), and sediment monthly for a year in the Maozhou River mainstream (Shenzhen, South China). Monthly rainfall positively correlated with both total PAH concentrations in filtered water (water PAHs) and SPM. Sediment PAH concentration increased from the river source to estuary. Compared to the earlier record, the sediment PAHs decreased at almost all sites due to the high-molecular-weight PAH (≥4 rings; especially the 4-ring PAH) degradation, except the estuary site that accumulated more low-molecular-weight PAHs (<4 rings). Results suggest that the water and SPM PAHs had similar and recent sources (e.g., rainfall and storm runoff) and actively exchanged with each other. The sediment PAHs had relatively different and complicated sources (fossil fuel combustion: 44.0%; oil pollution: 28.4%; biomass burning: 27.6%), and showed a long-term accumulation effect and increasingly weaker source-sink relation with both water and SPM PAHs from river source to estuary. This study highlights a disconnection in the source and migration mechanism between the water body (including water and SPM) and sediment PAHs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been causing widespread concern due to their ubiquitous nature and potentially adverse health effects on human and ecosystem (Jones et al., 1992; Modi et al.,

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2012; Shen et al., 2013). China contributed 106,000 metric tons of the atmospheric emission in 2007 for the 16 priority PAHs designated by the US Environmental Protection Agency (EPA), occupying ~21.0% of the global total amount (Shen et al., 2013). Although volcanic eruption, forest fire, and metabolism of plants and animals are known natural PAH sources, the 16 EPA-regulated PAHs are more closely related to anthropogenic production (Ma et al., 2013). Cities, supporting more than half of the earth's population (UN DESA, 2010), often have high-intensity anthropogenic activities and thus can be both PAH source and sink. Large amounts of PAHs accumulate in some urban rivers through urban surface runoff, soil percolation, pipe sewage, atmospheric deposition, etc. (Nagy et al., 2013; Sun et al., 2009). Because of their hydrophobicity and recalcitrance, PAHs from urban river water can be easily attached to various suspended particulate matter (SPM), and finally deposit in sediment (Patrolecco et al., 2010; Song et al., 2014). Also, water disturbance can resuspend sediment PAHs in the water and cause PAH desorption (J.L. Feng et al., 2007; Mitra et al., 1999; Mouhri et al., 2008; Ortega-Calvo and Gschwend, 2010). Moreover, river PAHs can migrate to foods through agricultural irrigation and industrial water consumption. Wang et al. (2007) estimated that 367 metric tons of 15 PAHs generated in China were transported into the sea via riverine outflow each year. During these processes, river PAHs can be bioaccumulated in the tissues of aquatic organisms, not only affecting the organisms' survival and reproduction (Incardona et al., 2014), but also endangering human health through the food chain (Ylitalo et al., 2012; Zhao et al., 2014). Therefore, it is of both theoretical and practical significance to study the urban river PAH pollution.

Significant advances have been made in understanding PAH occurrence and behavior in single or two media of rivers. For instance, studies have examined PAH occurrences (Doong and Lin, 2004; H.L. Zhang et al., 2013), distinguished various pyrolytic/petrogenic sources (Yu et al., 2015; Yunker et al., 2002), evaluated potential ecological or health risks (Hussain et al., 2015; Xu et al., 2007), and focused on specific processes related to river PAHs, such as sediment resuspension (J.L. Feng et al., 2007; Yang et al., 2008) and road runoff (Krein and Schorer, 2000). However, it remains difficult to offer a comprehensive spatial-temporal picture of river PAHs in the three media (water, SPM, and sediment). Also, the non-continuous sampling tends to aggrandize the uncertainty in estimating PAH flux and risk assessment. Several studies have reported PAH contents in the three media of rivers or lakes, and their relationships with particle organic carbon (OC) (Patrolecco et al., 2010), sample physicochemical parameter (Guo et al., 2007), site-specific sources (Ma et al., 2013), and season changes (dry/flooding season) (Sun et al., 2009). However, there is very limited information concerning spatial-temporal characteristics of PAH distribution and inter-media transport. Moreover, it is important and urgent to elucidate organic pollution patterns at an urban river basin scale for pollution control and environmental remediation.

Shenzhen represents a typical region of rapid urbanization and industrialization in the past 30 years in China (Zhang et al., 2014). The Maozhou River, the largest river in Shenzhen, had been seriously polluted these years (CCTV News, 2013). Recently, a comprehensive treatment project of water environment for Maozhou River with 15.2 billion RMB investment is carried out from February 2016 to the end of 2017 (Shenzhen Municipal Water Affairs Bureau, 2016). First-hand knowledge of environmental organic pollution status in this river is beneficial to guide the environmental remediation. Our research group collected 114 sediment samples of the river from December 2009 to January 2010, and found that concentrations of the total 16 PAHs ranging from 28 to7409 ng g^{-1} mainly came from both pyrolytic/petrogenic sources, and were in proportion with the built-up area density (Sun et al., 2012). In the present study, we chose five representative sites from the river source (S1), upstream (S2), midstream (S3), downstream (S4), and estuary (S5), and collected samples of water, SPM, and sediment monthly for one year from April 2012 to March 2013. This study focused on: 1) spatial-temporal differentiation and potential sources of target PAHs, and 2) multi-media PAH relationship within this river. The present study is expected to provide the basic data and decision support for the PAH-contamination control of this river and other urbanized rivers worldwide.

2. Materials and methods

2.1. Sample collection and analyses

The Maozhou River is the longest urban river with the largest basin area in Shenzhen, the fastest urbanizing city in China during last decades. It originates from the Yangtai Mountain within the city and flows westward into the Pearl River Estuary after flowing through the rapidly urbanized and industrialized region in northwest Shenzhen (Fig. 1). As a coastal city of south-central Guangdong Province, Shenzhen is located in the south of the Tropic of Cancer with latitude between 22.27°N and 22.52°N, and longitude between 113.46°E and 114.37°E. Shenzhen has a subtropical monsoon climate with mean annual temperature of 22.4 °C, annual rainfall of 1933.3 mm, annual hours of sunshine of 2120.5 h, and total amount of freshwater resources of 1.93 billion m^3 (Zhang et al., 2016). Shenzhen's rainy season and dry season are from April to September, and from October to March, respectively.

Five sampling sites were chosen along the Maozhou River mainstream including the river source (S1), upstream (S2), midstream (S3), downstream (S4), and estuary (S5) as shown in Fig. 1. From April 2012 to March 2013, the unfiltered water (containing SPM) and sediment were collected simultaneously at the five sites at the end of each month for 12 months continuously. All samples were placed into clean amber glass bottles or barrels, labeled well, and then stored at −4 °C refrigeration immediately after being transported back to our lab at a low temperature. Filtered water and SPM samples were separated using 0.3 μm membranes after thawing. All SPM and sediment samples were freeze-dried. The SPM contents in unfiltered water (in g-SPM L-$water^{-1}$) were recorded. A total of 180 samples were prepared (60 filtered water, 60 SPM, and 60 sediment samples) and analyzed for the 16 PAH concentrations, the detailed method of which is available in the Supplementary material.

The 16 studied PAH congeners are: naphthalene (NAP), acenaphthylene (AC), acenaphthene (ACE), fluorene (FL), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLU), pyrene (PYR), benzo[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno [1,2,3-*cd*]pyrene (IcdP), dibenzo[*a*,*h*]anthracene (DahA), and benzo[*g*,*h*,*i*]perylene (BghiP). The sum of these 16 PAHs is designated as Σ_{16}PAHs. The Σ_{16}PAHs concentrations in filtered water, in SPM, and in sediment were designated as "water Σ_{16}PAHs concentration" (in ng-PAH L-$water^{-1}$), "SPM Σ_{16}PAHs concentration" (in ng-PAH g-SPM^{-1}), and "sediment Σ_{16}PAHs concentration" (in ng-PAH g-$sediment^{-1}$) respectively. SPM is the suspended particulate solids in unfiltered water and serves as an important medium for PAH transportation in rivers (C.L. Feng et al., 2007). As the SPM content in river water could be site and season dependent, we calculated the SPM-associated Σ_{16}PAHs content per liter unfiltered water (ng-PAH L-$water^{-1}$; designated as "SPM-W Σ_{16}PAHs concentration"), which is the product of corresponding SPM Σ_{16}PAHs concentration (ng-PAH g-SPM^{-1}) and SPM content per liter unfiltered water (g-SPM L-$water^{-1}$).

2.2. Data analysis

2.2.1. Isomer ratios

The commonly used isomer ratios of ANT/(ANT + PHE), FLU/(FLU + PYR), BaA/(BaA + CHR), IcdP/(IcdP + BghiP) were selected to diagnose PAH sources (Budzinski et al., 1997; Yunker et al., 2002). The ANT/(ANT + PHE) <0.1 indicates mainly combustion source, while >0.1 is indicative of petroleum source (Budzinski et al., 1997). Yunker