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Dynamics of polycyclic aromatic hydrocarbons (PAHs) in water column of Pearl River estuary (China): Seasonal pattern, environmental fate and source implication

Lixia Niu[a,b,c], Huayang Cai[a,b,c,*], P.H.A.J.M. Van Gelder[d], Peizhen Luo[a,b,c], Feng Liu[a,b,c], Qingshu Yang[a,b,c]

[a] Institute of Estuarine and Coastal Research, School of Marine Sciences, Sun Yat-sen University, Guangzhou 510275, PR China
[b] Guangdong Provincial Engineering Research Center of Coasts, Islands and Reefs, Guangzhou 510275, PR China
[c] Guangdong Provincial Key Laboratory of Marine Resources and Coastal Engineering, Guangzhou 510006, PR China
[d] Section of Safety and Security Science, Delft University of Technology, 2628 BX Delft, The Netherlands

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ABSTRACT

Based on a monthly sampling effort in 2011, > 62 polycyclic aromatic hydrocarbons (PAHs) in different environmental phases were detected in the Pearl River estuary, China. The study aimed to investigate seasonal variation in PAH concentration and composition, potential risk source, depth profile and environmental correlation and to provide a non-deterministic insight into the PAH behavior. The total PAHs varied widely throughout the 12 months of the study period, ranging from 25.99 ng/l to 522.26 ng/l in seawater and from 7.37 μg/g to 167.44 μg/g in suspended sediment (SPM). The 16 Environmental Protection Agency (EPA) priority PAHs ranged from 12.70 ng/l to 160.15 ng/l in seawater and from 2.82 μg/g to 112.32 μg/g in SPM. Low molecular weight (LMW) PAHs (2- and 3-ring) were the most abundant, responsible for 81% in seawater and 73% in SPM. Moreover, it appeared that SPM and ambient water temperature were the determining factors controlling the transport and distribution of PAHs in the water column. A higher concentration of SPM contributed to a higher content of PAHs due to adsorption and low solubility. The PAHs were more significantly associated with particles than were dissolved in seawater. In addition, petroleum emissions, vehicle emissions, and wood combustion were considered a potential risk of PAHs via statistically-based methods of principal component analysis (PCA) and diagnostic ratios. The findings are useful for understanding the dynamics of estuarine PAHs, which exert significant influence on coastal ecosystems.

1. Introduction

Persistent organic pollutants (POPs) have raised increasing concern due to their environmental properties. Polycyclic aromatic hydrocarbons (PAHs), one ubiquitous group of POPs, have affected wildlife and threatened human health via the food chain, due to their carcinogenicity, toxicity, and mutagenicity (Wan et al., 2007; Yang et al., 2008; Liu et al., 2012; Moeckel et al., 2014; Boehm et al., 2016). More than 100 types of PAHs have been found in the environment, mainly originating from incomplete combustion and petroleum leakage (Zakaria et al., 2002; Mai et al., 2003; Lima et al., 2005; Tobiszewski and Namieśnik, 2012), and their existence in air (Harrison et al., 1996; Lang et al., 2008), water (Ruge et al., 2015; Yan et al., 2016), suspended particulate matter (Liu et al., 2017), soil (Cetin, 2016) and sediments (Kannan et al., 2005; Timoney and Lee, 2011; Gu et al., 2016).

Estuaries, which are river-ocean transitional zones, play an important role in transporting organic pollutants from land to sea and in discharging pollutants from river to open ocean (Mai et al., 2003; Yuan et al., 2015). Coastal ecosystems have suffered extensively due to excess input of PAHs, e.g. the riverine output of PAHs amounted to 367 tons (Wang et al., 2007) and atmospheric outflow was estimated to be 8092 tons each year (Lang et al., 2008). During these processes, environmental correlations of PAH dynamics serve as mutual functions, which can be explained by the cumulative effect of physical, chemical and biological properties (Yang et al., 2008; Timoney and Lee, 2011; Liu et al., 2014, 2017; Duran et al., 2016).

The Pearl River estuary (PRE), which is connected to the continental shelf of the northern South China Sea, is one of the most ecologically complicated zones in the world (Fig. 1). The estuarine system consists of three major tributaries (North River, East River and West River), and

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[*] Corresponding author. Institute of Estuarine and Coastal Research, School of Marine Sciences, Sun Yat-sen University, Guangzhou 510275, PR China.
E-mail address: caihy7@mail.sysu.edu.cn (H. Cai).

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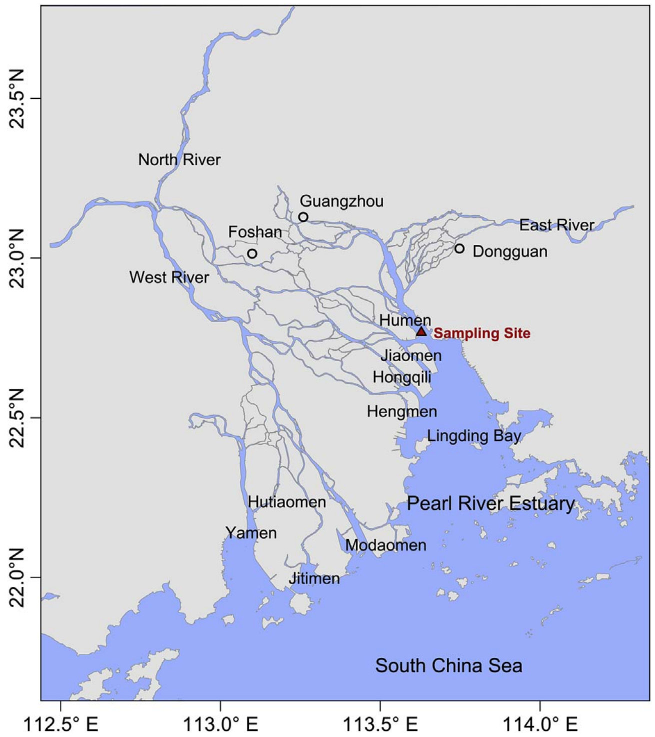

Fig. 1. Map of sampling site in the Humen estuary and adjacent coastal water.

has eight river outlets (Humen, Jiaomen, Hongqili, Hengmen, Hutiaomen, Jitimen, Yamen and Modaomen). The PRE has been characterized as a highly eutrophic zone, containing levels of inorganic and organic pollutants second only to the Bohai Sea, according to the State Oceanic Administration peoples republic of China (SOA; accessible through http://www.soa.gov.cn/zwgk/hygb/). In particular, the concentrations of several PAHs have been found to be over the threshold expected to cause adverse effects. The SCS is a potential receptor of PAHs and contributes notably to global pollution via air-water exchange. Studies have explored the distribution of PAHs in the PRE (Mai et al., 2003; Luo et al., 2008; Yuan et al., 2015; Liu et al., 2017) in terms of vertical profile (Yang et al., 2008), composition (Liu et al., 2014) and assignment of input sources (Wang et al., 2007; Liu et al., 2012). The riverine contribution of PAHs has been found to be significant (Wang et al., 2007; Yuan et al., 2015; Liu et al., 2017), but there have been limited discussion of the effects of hydrology and anthropogenic contamination. An understanding of how PAHs are dispersed is of central importance to estuarine ecosystems in the face of increasing pollutant loadings, particularly the seasonal variations as defined in the RRE (flood season, April-September; dry season, January-March, October-December). The objectives of this study were to: (i) investigate seasonal variation in PAH concentration, composition and depth profiles, (ii) present the environmental correlations of PAHs, and (iii) assign the potential risk sources of estuarine PAHs.

2. Material and methods

2.1. Field site

The Humen estuary is at the northern end of the PRE (Fig. 1). The sampling site is ca. 113°36.670′E and 22°48.622′N. Compared with the seven other river outlets, the Humen estuary is the most representative for investigating PAHs, which can be explained from three aspects. First, it is a tide-dominated channel, and the PAH behavior is complicated due to the strong interaction between runoff and tidal current. Second, it is the main passage for transporting pollutants from the cities of Guangzhou, Foshan and Dongguan. Third, it is a pool of the key processes for both the river networks (East River and North River) and the Lingdingyang Bay.

2.2. Sample collection and analysis

Water samples were extracted from five water layers (surface, 0.2*H*, 0.6*H*, 0.8*H* and bottom, where *H* represents total water depth during sampling time) each month in 2011 (January 19, February 19, March 20, April 20, May 19, June 17, July 16, August 14, September 14, October 22, November 11 and December 19) using traditional active sampling. The average water depth was ca. 11 m during sampling. The sampling site received a freshwater input both from the North River and the East River. However, the PAHs were attributed mainly to human contamination sources. Salinity, temperature and water depth were measured in situ with a Conductivity-temperature-depth/pressure (CTD) instrument (SBE 19 Plus). Water samples were filtered via a vermicular system with GF/D (3 μm pore) and GF/F (0.7 μm pore) glass fiber filters (Whatman International Ltd. UK) and precombusted at 450 °C for 4 h before use. Water samples were separated into particulate and dissolved phases. All samples were stored at −20 °C until lab analysis.

The analytical procedures used for the extraction and measurement of PAHs have been described in other studies (Zhou and Maskaoui, 2003; Yang et al., 2008; Men et al., 2009; Liu et al., 2014, 2017; Yan et al., 2016). All samples were analyzed for 62 PAH compounds and details are provided in the Supporting information (Table SI-1). Of these, the 16 priority PAHs designated by the U.S. Environmental Protection Agency (EPA) are naphthalene (Nap), acenaphthylene (Aye), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), benzo[a]anthracene (BaAn), chrysene (Chr), benzo[b]fluoranthene (BbFl), benzo[k]fluoranthene (BkFl), benzo[a]pyrene (BaPy), dibenzo[a,h]anthracene (DiAn), benzo [g,h,i]perylene (BePe) and indeno[123-cd]pyrene (InPy).

The extraction of particulate PAHs was performed with an extraction cell using accelerated solvent extractor (ASE) according to the EPA-3545A method, expressed in ng/l. The solid samples (10 g) were freeze-dried. The surrogate standards were added before extraction. The extraction solvent was Me_2CO:CH_2Cl_2 (v:v, 1:1). The solid samples were extracted for 10 min at 100 °C and 1500 psi. Subsequently, the extract was concentrated, the solvent was exchanged with n-hexane and the volume was further reduced to ca. 1 ml using a weak N_2 flow. The final extract was cleaned up and fractionated using a 1:2 Al_2O_3/SiO_2 gel glass.

The PAHs in the filtered water were extracted via solid phase extraction (SPE) according to the EPA-3535A method, expressed both in ng/l and μg/g. Each C_{18} cartridges (1 g, 6 ml; Sigma-Aldrich, St. Louis, MO, USA), was pre-cleaned with CH_2Cl_2 (20 ml) and EtOAc (5 ml). The analyte was eluted with Me_2CO (5 ml). The eluent was concentrated to 0.5 ml in a rotary evaporator and redissolved in 1 ml hexane prior to instrumental analysis.

2.3. Quality assessment/quality control

Analysis was performed using gas chromatography-mass spectrometry (GC-MS; Agilent, 6890, Agilent, 5973). Field blanks, laboratory blanks and replicate samples were analyzed along with the field samples. Concentrations of PAHs were corrected using the recovery from surrogate standards (e.g. naphthalene-d8, phenanthrene-d10, fluoranthene-d10, and pyrene-d10). The standard curves were determined using GC-MS with the standard concentration. The limit of detection (LOD), recovery (R′) and relative standard deviation (RSD) were used for method assessment, and the values are provided in the Supporting information (Table SI-1). The LOD for PAHs was 10 ng/g and blanks were below the LOD.