



Monthly variation and vertical distribution of parent and alkyl polycyclic aromatic hydrocarbons in estuarine water column: Role of suspended particulate matter[☆]



Xiaowei Wang^a, Ke Yuan^{a, b}, Baowei Chen^a, Li Lin^b, Bensheng Huang^c,
Tiangang Luan^{a, b, *}

^a Guangdong Provincial Key Laboratory of Marine Resources and Coastal Engineering, School of Marine Science, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China

^b MOE Key Laboratory of Aquatic Product Safety, School of Life Sciences, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China

^c Guangdong Research Institute of Water Resources and Hydropower, Guangzhou 510610, People's Republic of China

ARTICLE INFO

Article history:

Received 13 April 2016

Received in revised form

1 June 2016

Accepted 8 June 2016

Available online 16 June 2016

Keywords:

Alkyl polycyclic aromatic hydrocarbons

Suspended particulate matter

Monthly variation

Vertical distribution

Pearl River Estuary

ABSTRACT

The distribution and interaction of parent and alkyl polycyclic aromatic hydrocarbons (EPA-34 PAHs) among the multiple phases were investigated in estuarine water column of Humen outlet over a 12-months period. The water column was divided into 5 vertical layers, and each layer included dissolved phase, large- and small-size suspended particular matter (SPM). Regarding to EPA-34 PAHs, alkyl homologues were abundant, especially in the dissolved phase and small-size SPM. Moreover, SPM contributed a large proportion of EPA-34 PAHs in the water column especially for the large-size SPM, which therefore play an important role for the transportation of these pollutants. The EPA-34 PAHs concentrations in water column during wet season were higher than those in the dry season due to the decreasing of K_D values which were affected by TSS and salinity obviously. Generally, the EPA-34 PAHs concentrations in the water column increased with the increasing of water depth, most of the highest concentrations of EPA-34 PAHs were found in the near-bottom layer due to the rapid sinking of large-size SPM and sediment resuspension. Additionally, during the ebb-flood tide period, the EPA-34 PAHs concentrations in different phases of the water column fluctuated oppositely based on the effects of hydrodynamic conditions.

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1. Introduction

As a transition region between the river and the ocean, estuary plays an important role in the migration and transformation of terrestrial pollutants to the ocean, and therefore is considered as the sink of terrestrial pollutants and the source of pollutants to the ocean (Jiang et al., 2013). In estuaries and the adjacent coastal ocean, suspended particular matter (SPM) has important influences on sedimentary, and ecological systems (Zhang et al., 2009; Leppard et al., 1998). SPM mainly derive from riverine input and/or disturbance and suspension of sediments, provides an important

link among the water column, bottom sediments and the food chain. Generally, organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) are considered to associate with SPM of the water column via diffusion and sorption, and riverine SPM is also the major carrier of elements and various pollutants in the aquatic environment (Debruyne and Sayler, 2009; Hu et al., 2011; Turner and Millward, 2002).

Traditional environmental assessments of PAHs are usually conducted on the 16 parent PAHs as prior control PAHs by the U.S. Environmental Protection Agency (EPA). Since 2003, the EPA recommends the measurement of EPA-34 PAHs (18 parent PAHs and 16 groups of prominent C1 to C4 alkyl PAH derivatives, where “C#” refers to the number of alkyl carbons attached to the PAH) based on the requirement of narcosis model (Hawthorne et al., 2006a). Alkylated PAHs are more thermodynamically unstable than their corresponding parent PAHs, and contribute approximately 60% and 99% of the total PAHs for pyrogenic and petrogenic sources,

[☆] This paper has been recommended for acceptance by Maria Cristina Fossi.

* Corresponding author. Guangdong Provincial Key Laboratory of Marine Resources and Coastal Engineering, School of Marine Science, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China.

E-mail address: cestlg@mail.sysu.edu.cn (T. Luan).

respectively (Hawthorne et al., 2006b; Zakaria et al., 2002). Due to the higher lipophilicity and levels in various environments, alkyl PAHs contributed a greater proportion of net toxicity than parent counterparts. Hawthorne et al. reported that alkyl PAHs contribute greater than 98% of the total PAH toxic units in diesel fuel and crude oil (Hawthorne et al., 2006b). when compared to the unsubstituted counterparts, alkyl PAHs has been proved to produce dioxin-like toxicity in fish embryos such as retene (7-isopropyl-1-methyl phenanthrene), the alkyl groups can alter their toxicity and provide an additional site for hydroxylation (Hodson et al., 2009). Moreover, alkyl PAHs could be converted into other more toxic compounds in the atmosphere such as nitro-PAHs (Dartnell et al., 2012). Therefore, alkyl PAHs pose a high risk to the public and wildlife.

The Pearl River is the second largest river in China, and the annual average discharge of the Pearl River Estuary (PRE) is $10,500 \text{ m}^3 \text{ s}^{-1}$ with approximately 20% occurring during the dry season and the rest in the wet season (Yin et al., 2001, 2004). The rapid economic development and urbanization in the Pearl River Delta in last several decades have resulted in significant pollution on the nearby environment. Many studies had been conducted in this region to reveal the spatial distribution, source, behavior, pollution flux about PAHs. It was reported that sediments were the main reservoir of parent PAHs in the PRE (Chen et al., 2006), and alkyl PAHs were also abundant in sediments of PRE according to our previous study (Yuan et al., 2015). In addition, the upstream riverine runoff of the Pearl River Delta and the flux of PAHs was estimated (Zhang et al., 2012), and riverine input had been proved to account up 87% of \sum_{15} PAHs in the PRE and northern South China Sea (SCS) (Wang et al., 2007). The water column in the PRE was highly stratified, especially during the wet season with a representative halocline (Dong et al., 2004). Indeed, monitoring data of the vertical distribution of PAHs in estuarine water column is still insufficient to allow fully understand the fate of parent PAHs and their alkyl homologues under the influences of hydrodynamic and tidal effects, especially in the SPM phase.

Therefore, the objectives of this study were to carry out a survey of the profiles and levels of EPA-34 PAHs contamination in Humen outlet based on a 12-month effort. The sampling plan was so designed as to allow the given of their monthly and vertical variation in different phases of water column (dissolved phase, large- and small-size SPM) and surface sediments. In addition, the interaction and distribution by the processes responsible for the tidal variation, fresh water discharge and precipitation were discussed as well as several environmental and chemical parameters including salinity, total suspended solid (TSS) and distribution coefficients (K_D) influencing the adsorption/desorption of the pollutants.

2. Material and methods

2.1. Field sampling

The Pearl River, the third largest river in the south of China, transports an average of $3.50 \times 10^{11} \text{ m}^3$ of freshwater into the South China Sea via eight major outlets. During the past three decades, the rapid economic development and urbanization in the Pearl River Delta have resulted in significant water pollution (Yuan et al., 2015). In this study, the sampling site ($22^\circ 48' 35.9'' \text{N}$, $113^\circ 36' 40.5'' \text{E}$) was located in the Humen outlet which was the largest one of the eight estuaries of the Pearl River (Fig. S1, Supplementary Material). Seawaters and sediments based on homogeneous distribution were collected monthly from the same sampling location during January 2011 and December 2011 in Humen outlet at the highest flood velocity of the spring tide except for August. In August, sea waters were collected twice during one

tidal cycle at the highest flood velocity and ebb velocity, respectively. Moreover, seawaters were collected from 5 different relative depths, i.e., surface layer (0.5 m), 0.2H, 0.6H, 0.8H and bottom layer (0.5 m from the bed) of the water column and approximate 50 L sea water samples were collected in 10 L precleaned amber glass bottles for each layer using a stainless submersible pump. Here H is the water depth of the sampling location and is approximate 10 m *in situ*. Seawaters were acidified immediately with 4 M HCl to $\text{pH} < 1$ to depress microbial growth and transferred to the laboratory within 2 h and stored at 4°C . Salinity of each seawater sample was recorded in the field and showed in Table S1 of Supplementary Material.

2.2. Sample preparation, analysis, and quality control/quality assurance

In the present study, the seawater samples were separated into dissolved phase, large- and small-size SPM by GF/D ($3 \mu\text{m}$) and GF/F ($0.7 \mu\text{m}$) glass fiber filters (Whatman International Ltd., Maidstone, England), respectively. The filters were precombusted at 450°C for 4 h before used. After filtration, the filters were then freeze-dried, placed in precleaned glass dishes and wrapped with aluminum foil, and stored at 20°C until extraction. The sediments were freeze-dried, homogenized, sieved (0.1 mm) and stored at 20°C until analyzed as well.

The sample pretreatment of 5 L filtered seawater that spiked with surrogate standards was conducted by solid phase extraction (SPE) according to EPA 3535A method. Sediments (10 g), large- and small-size SPM (loaded in the filters) were extracted by accelerated solvent extractor (ASE) according to EPA 3545A method. The instrumental analysis of EPA-34 PAHs concentrations in dissolved phase, large- and small-size SPM and sediments by GC-MS was performed based on the previous works by Hawthorne et al. (Hawthorne et al. 2005, 2006b). More details about the sample pretreatment and instrumental analysis methods were given in the Supplementary Material.

Most parent PAHs and their isotope-labeled analogues are available as pure standards, while few alkyl PAHs are available. The concentrations of those alkyl PAHs that are short of pure standards had to be estimated rather than measured in many cases. Moreover, a single group of highly alkylated PAH can have multiple alkylated isomers, even hundreds for C3 and C4 alkyl PAHs. Therefore, the calibration and quantitation of these compounds is increasingly complicated with the MS response varying significantly from isomer to isomer. In this study, we reference the methods to earlier work by Hawthorne et al. which reported the relative response factors (RRFs) for alkyl PAHs vs their related parent PAHs as being showed in Table S2 (Hawthorne et al., 2006b). The RRFs of alkyl PAHs for which no standards were available were estimated on the basis of the closest analogous alkyl PAH and these response factors were therefore used in all future analyses to estimate the alkyl-PAH concentrations in sediment/SPM and seawater samples.

TSS content was determined with gravimetric analysis. Particle loaded filters (GF/F) were dried at 60°C for 12 h and cooled in a desiccator. The weight difference before and after filtration of 1 L seawater was defined as TSS in this study and reported in Table S1 of the Supplementary Material. In addition, the data of monthly precipitation and fresh water discharge of PRE during 2011 were obtained from the Ministry of Water Resources of the People's Republic of China, and showed in Table S1 as well (Guo et al., 2011).

2.3. Data analysis

In the present study, the sums of the EPA-34 PAHs, EPA prior control 16 PAH compounds, alkyl PAHs and parent PAHs are defined

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