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Pollution status of polycyclic aromatic hydrocarbons in surface sediments from the Yangtze River Estuary and its adjacent coastal zone

Chenglong Wang [a, b], Xinqing Zou [a, b, *], Jianhua Gao [a, b], Yifei Zhao [a, b], Wenwen Yu [a, b, c], Yali Li [a, b], Qiaochu Song [a, b]

[a] School of Geographic and Oceanographic Sciences, Nanjing University, Nanjing 210093, China
[b] Key Laboratory of Coast and Island Development (Nanjing University), Ministry of Education, Nanjing 210093, China
[c] Marine Fisheries Research Institute of Jiangsu Province, Nantong 226007, China

HIGHLIGHTS

- PAHs are important indicators of anthropogenic activities on the environment.
- PAHs levels in the Yangtze River Estuary and adjacent coastal areas were studied.
- Kriging interpolation and PMF model used to study spatial distribution and sources.
- Anthropogenic activities were the main sources of PAHs in the study area.
- Distribution patterns influenced by factors like sediment size and hydrodynamics.

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are mainly produced by incomplete combustion and are used as indicators of anthropogenic activities on the environment. This study analyses the PAHs level in the Yangtze River Estuary (YRE), an important component of Yangtze River and a developed and populated region in China. Surface sediments were collected from 77 sites at the YRE and its adjacent coastal zone (IACZ) for a comprehensive study of PAHs. Kriging interpolation technology and Positive matrix factorization (PMF) model were applied to explore the spatial distribution and sources of PAHs. Concentrations of 16 PAHs (ΣPAHs) varied from 27.2 ng g^{-1} to 621.6 ng g^{-1} dry weight, with an average value of 158.2 ng g^{-1}. Spatially, ΣPAHs exhibited wide fluctuation and exhibited an increasing tendency from north to south. In addition, ΣPAHs exhibited a decreasing trend with increasing distance between the estuary and IACZ. The deposition flux of PAHs indicated that more than 107.8 t a^{-1} PAHs was deposited in the study area annually. The results of the PMF model revealed that anthropogenic activities were the main sources of PAHs in the study area. Vehicle emissions and marine engines were the most important sources and accounted for 40.9% of the pollution. Coal combustion, petrogenic sources, and wood combustion were other sources that contributed 23.9%, 23.6%, and 11.5%, respectively. The distribution patterns of PAHs in the YRE and IACZ were influenced by many complicated factors such as sediment grain size, hydrodynamics and so on.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are typical persistent organic pollutants that have attracted scientific and regulatory interests due to their toxic, carcinogenic, and mutagenic properties (Sverdrup et al., 2002; Qiao et al., 2006; Zhang and Tao, 2009). They mainly originate from anthropogenic activities such as incomplete combustion of fossil fuels, biomass burning, coke ovens, and exhaust emissions (Yunker et al., 2002; Simoneit, 2002). Natural processes such as oil seeps, forest fires, and organic matter

* Corresponding author. School of Geographic and Oceanographic Sciences, Nanjing University, Xianlin Avenue 163, Nanjing 210023, China.
E-mail address: zouxq@nju.edu.cn (X. Zou).

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diagenesis can also act as significant sources (Simoneit, 2002; Lima et al., 2005). PAHs are transported to marine ecosystems through direct and indirect pathways including atmospheric deposition and riverine inputs (Wang et al., 2007; Lin et al., 2013). Following release into the marine environment, most PAHs are easily adsorbed onto the surface of fine particles and are eventually deposited into the underlying sediments due to their high hydrophobicity and lipid solubility (Kim et al., 1999; Li et al., 2006, 2012). Therefore, marine environment, especially marginal sea is an important reservoir of PAHs.

Estuarine areas are important component of the river and the marginal sea, and serve as a transition zone between seawater and freshwater. Therefore, the hydrodynamic conditions and biodiversity are always complex in estuarine regions (Yu et al., 2015). River discharge and sedimentary processes influence the distribution and behavior of PAHs in estuarine-coastal environments (Lin et al., 2013). In addition, transport and storage of terrestrial organic materials in these zones, especially large-river delta-front estuaries, are significant due to interactions of several physical, chemical, and biological processes (Bianchi and Allison, 2009; Hung et al., 2011; Liu et al., 2012). Therefore, estuarine-coastal areas are important sinks of PAHs from the atmosphere and land. The Yangtze River Estuary (YRE), a typical estuary in the East China Sea (ECS), is one of the most prosperous regions in China and receives significant amounts of sediments and runoff from the river basin. Additionally, the YRE also acts as a conduit discharging large amount of organic pollutants including PAHs, which originate from intensive industrialization and urbanization in the basin, into the ECS. Therefore, more attention should be paid to the comprehensive study of the sources, compositions, distribution patterns, and environmental behavior of the PAHs in the YRE.

To date, several studies have investigated PAHs distribution in the YRE (Li et al., 2012; Lin et al., 2013; Yu et al., 2015), focusing on the sources, compositions, and distributions of PAHs. However, few studies have discussed influencing mechanisms such as hydrodynamic conditions and granularity effects (Lin et al., 2013). In addition, previous studies primarily focused on the Yangtze River subaqueous delta, and limited attention was paid to its adjacent coastal zones (IACZ). Fig. 1c highlights the demarcation of IACZ from the YRE, using a hypothetical line between the YRE and Hangzhou Bay. We called the north of this line as the YRE and the south of this line as IACZ. Numerous studies have demonstrated that transport of sediments from the Yangtze River to the ECS is controlled by tidal currents, shallow sea circulations, Changjiang estuarine circulations, and storm events (Gao et al., 2011; Milliman et al., 1984; Su and Wang, 1986). Under the influence of complex hydrodynamic conditions, a large amount of fine particles discharged by the river are transported southwards and formed two mud deposition centers: one outside the YRE and Hangzhou Bay named as the YRE mud area (YREMA) and the other along the Zhe-Min coast named as the Zhe-Min Coastal mud area (ZMCMA) (Qin et al., 1987; DeMaster et al., 1985; Liu et al., 2007) (Fig. 1b). Therefore, the distribution patterns of PAHs in these regions under the effect of ocean currents (e.g., the Yellow Sea Coast Current and the Taiwan Warm Current (TWWC)) and the reduction of river runoff will be distinct. In addition, other factors such as anthropogenic activities and granularity effect were also taken into account in this study to explore the behavior of PAHs in the YRE and IACZ.

This paper focuses on the concentration, composition, and distribution patterns of the PAHs in the YRE and IACZ. Spatial interpolation technology and the Positive Matrix Factorization (PMF) method were applied to quantify the distribution patterns and sources of PAHs based on 77 samples. The objectives of this study were: 1) to investigate the sources, composition, and spatial distribution of the PAHs in the YRE and IACZ; 2) to examine the role of granularity effect, hydrodynamic conditions, and anthropogenic activities on PAHs levels in the sediments.

2. Materials and methods

2.1. Study area and sample collection

The Yangtze River is the longest river (6300 km) in Asia, globally ranking fifth in water discharge levels and fourth in sediment loads, measuring at 920 $km^3\ a^{-1}$ and 480 million tons a^{-1}, respectively (Milliman and Syvitski, 1992; Yang et al., 2006). The Yangtze River Basin is one of the most prosperous regions in China hosting developed cities such as Chengdu, Chongqing, Wuhan, Hefei, Nanjing, Suzhou, Wuxi, and Shanghai. It is populated by 400 million inhabitants and has a drainage area of 1.8×10^6 km^2 accounting for nearly 20% of the mainland (Yang et al., 2006). Intensive industrialization and urbanization in the basin have resulted in large amounts of organic pollutants including PAHs being discharged into the river (Qi et al., 2014). The YRE, one of the most urbanized and industrialized regions, is a key shipping hub connecting inland and the ECS (Zhou et al., 2014). The YRE acts as a conduit, discharging large amount of sediments from the river basin into the estuary, forming a large-scale subaqueous delta and mud area (YREMA and ZMCMA) (Fig. 1b). Over half of these discharged sediments and PAHs are trapped in the YRE due to coastal currents (Liu et al., 2007; Li et al., 2012; Lin et al., 2013). Several studies have focused on the flux of PAHs discharged into the ECS. Wang et al. (2007) estimated that the annual flux of the 16 USEPA priority PAHs from the Yangtze River to the ECS was 232 t. Qi et al. (2014) estimated that more than 369 t PAHs were discharged into the ECS annually through the Yangtze River making it one of the largest contributors of PAHs to the western Pacific shore. Therefore, pollutant load of PAHs will pose an increasing burden to water security and health of the marine coastal ecosystem (He et al., 2011; Qi et al., 2014).

In this study, we focus on the YRE and IACZ which located at the north of ZMCMA as the study area. The study area was divided into 13 vertical sections and 77 compartments with sampling sites located in the center of each compartment. The sampling sties were uniformly distributed as highlighted in Fig. 1c. Surface sediment samples (at 0–2 cm depth) were collected from each site using stainless steel grab samplers, during December 2013. All samples were placed in pre-cleaned aluminum foil and stored at −20 °C prior to analysis.

2.2. PAHs analysis

A standard mixture solution consisting of 16 priority PAHs namely naphthane (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), anthracene (Ant), phenanthrene (Phe), benzo[*a*]anthracene (BaA), chrysene (Chr), fluoranthene (Flo), pyrene (Pyr), benzo[*a*]pyrene (BaP), dibenzo[a,h]anthracene (DahA), benzo[*b*]fluoracene (BbF), benzo[k]fluoracene (BkF), benzo[g,h,i]perylene (BghiP), and indeno[1,2,3-*cd*]pyrene (IcdP) was obtained from Supelco (Bellefonte, PA, USA) and used for external calibration. All solvents (dichloromethane, acetone, and n-hexane) used during the processing were HPLC grade (Tedia Co. Inc., USA). Analytical grade anhydrous sodium sulfate was activated at 450 °C for 5 h to remove impurities before use. Silica gel (100–200-mesh particle size; Qingdao Haiyang Chemical Co. Inc., Shandong, China) was extracted using acetone, dichloromethane, and n-hexane, and activated for approximately 16 h at 130 °C.

PAHs extraction was performed as described by Yim et al. (2014) and Wang et al. (2015). Sediments were freeze-dried and then sieved through an 80-mesh sieve. A 5 g surface sediment sample