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Seasonal atmospheric deposition and air–sea gas exchange of polycyclic aromatic hydrocarbons over the Yangtze River Estuary, East China Sea: Implications for source–sink processes

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ABSTRACT

In this work, air samples and surface seawater samples covering four seasons from March 2014 to January 2015 were collected from a background receptor site in the YRE to explore the seasonal fluxes of air–sea gas exchange and dry and wet deposition of 15 polycyclic aromatic hydrocarbons (PAHs) and their source–sink processes at the air–sea interface. The average dry and wet deposition fluxes of 15 PAHs were estimated as 879 ± 1393 ng m^{-2} d^{-1} and 755 ± 545 ng m^{-2} d^{-1}, respectively. Gaseous PAH release from seawater to the atmosphere averaged 3114 ± 1999 ng m^{-2} d^{-1} in a year round. The air–sea gas exchange of PAHs was the dominant process at the air–sea interface in the YRE as the magnitude of volatilization flux of PAHs exceeded that of total dry and wet deposition. The gas PAH exchange flux was dominated by three-ring PAHs, with the highest value in summer and lowest in winter, indicating a marked seasonal variation owing to differences in Henry's law constants associated with temperature, as well as wind speed and gaseous-dissolved gradient among seasons. Based on the simplified mass balance estimation, a net 11 tons y^{-1} of PAHs (mainly three-ring PAHs) were volatilized from seawater to the atmosphere in a ~20,000 km^2 area in the YRE. Other than the year-round Yangtze River input and ocean ship emissions, the selective release of low-molecular-weight PAHs from bottom sediments in winter due to resuspension triggered by the East Asian winter monsoon is another potential source of PAHs. This work suggests that the source–sink processes of PAHs at the air–sea interface in the YRE play a crucial role in regional cycling of PAHs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), as ubiquitous semi-volatile organic pollutants (Brown et al., 1996; Li et al., 2009; Nizzetto et al., 2008), have a critical threat to the health of humans and ecosystems due to their toxic, carcinogenic and bio-accumulative effects in organisms (Cai et al., 2016; Cheng et al., 2013). Unlike some persistent organic pollutants (POPs), use of which is prohibited globally, ongoing release of PAHs from primary sources are typically well associated with anthropogenic activities, mainly including vehicle exhausts, coal and biomass combustion, and the emission of petroleum products (Kavouras et al., 2001; Park et al., 2001; Qin et al., 2013); therefore, the fate of PAHs is a matter of greater concern than other POPs (Nizzetto et al., 2008). China is a significant emitter of PAHs, releasing 25,300 tons of 16 PAHs (as identified by the United States Environmental Protection Agency, US EPA) in 2003 (Xu et al., 2006). Due to the rapid economic development and growth in energy consumption, the emission of PAHs in China shows an increasing trend (Guo et al., 2006; Hu et al., 2011).

The land-derived PAHs can be widely distributed into marine environments through several processes, inclusive of atmospheric deposition, gas exchange at the air–sea interface, riverine input and facility effluents (Arzayus et al., 2001; Cai et al., 2016; Tsapakis et al., 2006; Yunker et al., 2002). The marginal seas, prone to PAH inputs from the adjacent land could thus act as the sink of these outflowed PAHs (Baker and Eisenreich, 1990; Kim and Chae, 2016; Lin et al., 2011; Mulder et al., 2014). However, the bidirectional gas exchange of PAHs implies that PAHs can also be delivered to the atmosphere from the water column, provided that the dissolved PAHs are oversaturated as compared to upper atmospheric PAH burdens (Bamford et al., 1999; Chen et al., 2016; Gigliotti et al., 2002). The released PAHs from the

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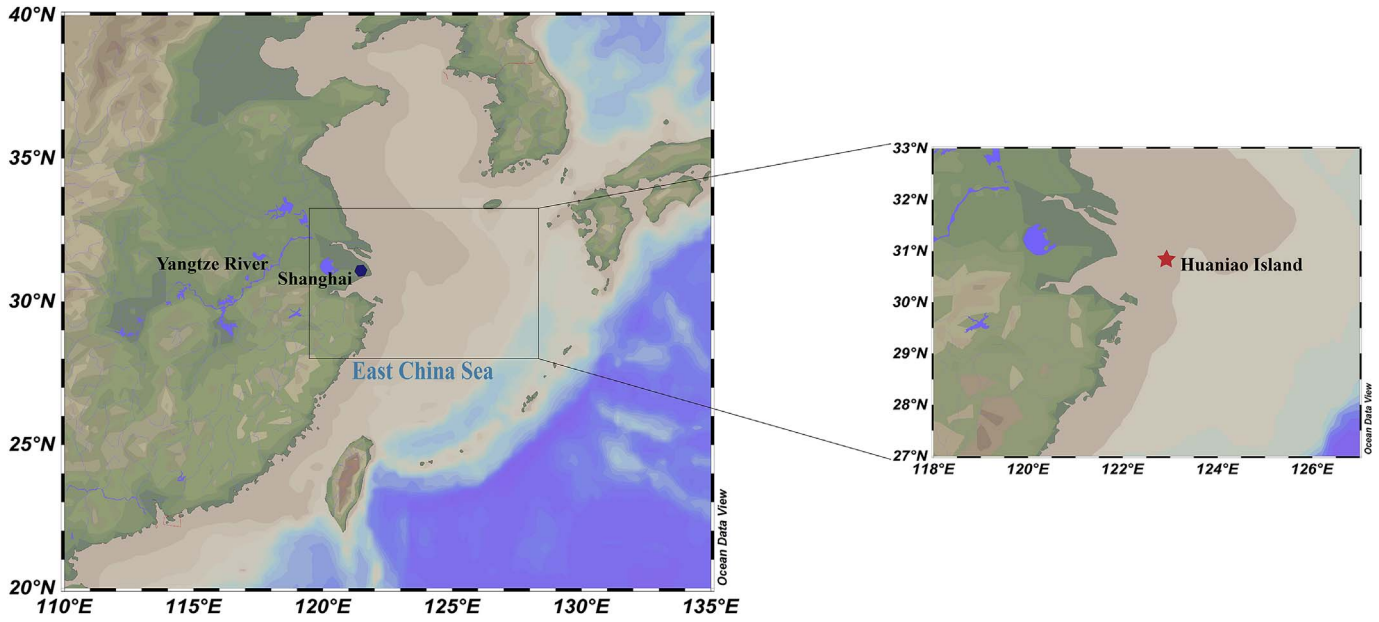

Fig. 1. Sampling site.

water column could then be atmospherically transported, and re-deposited in land areas (Fang et al., 2012). Therefore, a determination of the source–to–sink relationship of regional PAHs avails to reveal the biogeochemical cycling and dynamics of PAHs. However, the integrated air–sea gas exchange as well as dry and wet deposition of PAHs have been seldom touched in the East Asian marginal seas (Wu et al., 2017).

The Yangtze River Estuary (YRE), connected with the East China Sea (ECS) to the east (Fig. 1), is one of the world's largest and most prosperous estuaries, and is a home to over 15 million people (Feng et al., 2004). It accommodates more than 10% of the Chinese population and provides one-fifth of the national gross domestic product. The YRE is greatly influenced by the huge inputs from Yangtze River. As one of the largest rivers in the world, the Yangtze River drains an area of 1.94×10^6 km^2 and delivers 900 billion cubic meters of water, with 250 million tons of sediments and associated PAHs annually empting into the ECS through the YRE (Qi et al., 2014; Wang et al., 2007). Moreover, additional sources of PAHs in the marine environment of the ECS could be related to the long-range transport of continental air pollutants driven by the East Asian monsoon (Wang et al., 2014a; Zhang and Gao, 2007). It is reported that 8092 tons of PAHs are transported from mainland China to neighboring coastal areas annually, approximately 70% of which are retained within the offshore area (Lang et al., 2008). The ECS is greatly influenced by the Asian continental outflow under the westerly wind prevailing in winter and spring. As such, high levels of anthropogenic air pollutants or dust including PAHs from the Asian continent were transported across the ECS, with parts of which deposited to the ECS (Hsu et al., 2009). Conversely, the summer monsoon, which begins in late April, brings clean air masses originating from the west Pacific Ocean (Zhang et al., 2011). As one of the five main clusters in China, Yangtze River Delta port cluster in the YRE contains a large number of high-throughput ports. Concomitant with heavy marine traffic, high ship-based emissions generated could be a potentially local source of PAHs in the YRE and ECS. Recent surveys indicated that the PAH pollution in the YRE is more serious than that in other coastal areas of China. The concentrations of PAHs in YRE sediments were two-fold higher than those of the Yellow River Estuary (Hui et al., 2009). The total PAH concentrations in seawater of the ECS were higher than that in the South China Sea (Ren et al., 2010). Source analysis showed that the input from Yangtze River discharge was responsible for severe contamination in sediments, water and organisms in the YRE (Guo et al., 2007; Hung et al., 2014). Besides, the elevated concentrations of PAHs in seawater were due in part to the resuspension of sediments (Lin et al., 2013). PMF analysis showed that air–sea exchange represents 15.7% of the total atmospheric sources of particulate PAH over the ECS (Wang et al., 2014b). Most previous studies focused on the occurrence and concentrations of PAHs in the atmosphere, seawater, sediments, and zooplankton in the YRE and ECS on basis of cruise surveys, which usually processed within a few weeks. However, no study has estimated the seasonal air–sea gas exchange fluxes, as well as dry and wet deposition of PAHs in the YRE.

In this study, we collected 94 pairs of PAHs samples in ambient gas and aerosol phases at a receptor site Huaniao Island (HNI, 30.86°N, 122.67°E) in the YRE, covering four distinctive seasons when 20 surface seawater samples were also collected evenly. The objectives of the present study were to (1) estimate the seasonal dry and wet deposition fluxes and air–sea gas exchange flux of PAHs, (2) quantify the magnitude and direction of PAH exchange between air and sea compartments by integrating atmospheric deposition and air–sea gas exchange, and (3) establish the mass budget of PAHs at the air–sea interface in the YRE in a year round.

2. Materials and methods

2.1. Sampling site and sample collection

Ninety-four paired gas and particulate samples were collected at HNI in the YRE, ECS (Fig. 1). HNI is 66 km to the east of the Shanghai coast, and has an area of 3.28 km^2. It has fewer than 1000 inhabitants and no industrial activity. The sampling site was situated at the roof of a three-story building, at a height of about 50 m above the sea level. A sampler (Guangzhou Mingye Environmental Technology Company, Guangzhou, China) was used to collect ambient total suspended particulate (TSP) and gases simultaneously at a flow rate of 300 L/min for 23.5 h. The samples were collected evenly during four seasons: 27 March–18 April 2014 (spring, n = 23), 29 July–26 August 2014 (summer, n = 25), 16 October–10 November 2014 (autumn, n = 25) and 28 December 2014–18 January 2015 (winter, n = 21). The air mass first passed through a quartz filter (20 × 25 cm, 0.7 mm; Pall, Port Washington, NY) to gather particle-bound PAHs and then through a solvent-cleaned polyurethane foam (PUF) plug (length: 8.0 cm; diameter: 6.25 cm; density: 0.035 g cm^{-3}) to capture gaseous compounds. Prior to sampling, quartz filters were combusted at 450 °C for 4 h in a