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Seasonal changes of polycyclic aromatic hydrocarbons in response to hydrology and anthropogenic activities in the Pearl River estuary, China

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ABSTRACT

The behaviours of PAHs (containing 2–6 aromatic rings) in the Pearl River estuary were examined each month in 2011. This study was designed to investigate the abundance of 16 priority PAHs and their response to the seasonal dynamics of anthropogenic activities and hydrological cycles. Monthly mean concentrations of $\sum_{16}$PAHs in water and suspended particulate matter (SPM) were 88.31 ng/L and 252.31 ng/L respectively, with higher concentrations in the wet season (April to September). Heavy precipitation in the wet season resulted in relatively increased PAH input via riverine discharges and atmospheric deposition. Seasonal variations in suspended sediment concentration (SSC), temperature and salinity have considerably affected the PAH phase association. Higher SSC in the wet season contributed to higher concentration of the PAHs in SPM, and higher temperature and lower salinity facilitated desorption from SPM. The PAH sources were largely attributed to vehicular emissions, coal combustion and coke ovens.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of ubiquitous contaminants in various environmental. The occurrence, transportation and fate of PAHs have attracted worldwide attention due to their carcinogenicity and mutagenicity (Williams, 1990; Witt, 2002; Li et al., 2010). PAHs are mainly derived from land sources and ultimately stored in the global oceans (Wang et al., 2007). Riverine runoff is one of the most important pathways of PAHs entering the oceans (Zhang et al., 2012).

As the transition areas between lands and oceans, estuaries play a critical role in the transportation and fate of PAHs (Liu et al., 2014a). Estuaries are affected both by riverine and oceanic dynamics and are sensitive to hydrological processes. River systems show seasonal variability with hydrological processes, resulting in seasonal variations in the organic matter (Ni et al., 2008; Gao et al., 2012). Wang et al. (2012) reported that the dominant input of terrestrial organic matter occurred during the high water discharge period in the Yellow and Yangtze Rivers. Estuarine environmental factors, like suspended sediment concentration (SSC), temperature and salinity, influence the distribution and partitioning of PAHs in the aquatic environment (Readman et al., 1984; Zhou et al., 1998; Tremblay et al., 2005). However, research on the response of PAH behaviours to the seasonal hydrological variations in estuarine environments remains poorly discussed.

PAH sources are mainly attributed to anthropogenic activities, such as pyrolytic and petrogenic sources (Zakaria et al., 2002; Zhang et al., 2012). Different anthropogenic sources and their contribution to the total PAHs lead to different types of PAH compound and composition (Yunker et al., 1996), which behave differently in the aquatic environment. Human activities also show seasonal patterns (Li et al., 2006). Although it is extremely important for aquatic ecosystems, few efforts have been paid to examine the impacts of human activities on the estuarine PAH behaviours.

The Pearl River ranks the second largest in China in terms of water discharge. High population density and rapid urbanization and industrialization in the Pearl River Delta (PRD) have resulted in abundant PAHs released into the Pearl River according to the record of the State Oceanic Administration People's Republic of China. Wang et al. (2007) reported that approximately 33.9 tons of $\sum_{15}$ PAHs (16 priority PAHs without Naphthalene) from the PRD are annually transported into the coastal ocean, 87% of which are delivered by riverine runoff. Although the occurrence, distribution, fluxes and fate of PAHs in the water column and surface sediments in the PRE have been widely documented (Mai et al., 2001; Luo et al., 2006; Li et al., 2014; Liu et al., 2014a), few studies have explored the seasonal impacts of hydrological processes and human activities on the behaviours of PAHs. In this work, a one-year field study on the variations in PAHs in the Pearl River estuary (PRE) was carried out each month in 2011. We examined the seasonal

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variations in the concentration, composition and sources of PAHs and their responses to hydrological cycles and human activities. The findings could help to explore the response of PAHs to climate change (i.e., precipitation), and are essential to assess the impact of human activities on the water quality.

2. Materials and methods

2.1. Study sites and sample collection

The Pearl River is mainly composed of three large tributaries (West River, North River and East River) and forms a complicated river network (Fig. 1). The Pearl River annually delivers 3360×10^8 m^3 of fresh water and 89×10^6 t of sediment load into the South China Sea via eight outlets (Humen, Jiaomen, Hongqili, Hengmen, Modaomen, Jitimen, Hutiaomen, and Yamen). The climate in the Pearl River basin is dominated by the monsoon and exhibits seasonal variability, and approximately 80% of the annual precipitation occurs in the wet season (April to September) (Zhao, 1990; Liu et al., 2014b). In this study, water samples were collected at the Humen river mouth of the PRE (around 113°36.670′E, 22°48.622′N) each month in 2011. Previous studies have detected the high contaminant levels of PAHs in water and surface sediment samples at this river mouth, and revealed that the Humen river mouth was an important pathway for transporting PAHs from the PRD to the Pearl River estuary (Mai et al., 2001; Liu et al., 2014a). No consideration was given to the PAHs in the surface sediments in this study.

The water samples were collected in the flood tide at five different layers, i.e., surface (0.5 m below the surface water), 0.2H, 0.6H, 0.8H and bottom (1.0 m above the riverbed), according to the specifications for oceanographic surveys in China (GB/T 12763-2007), using a stainless-steel submersible pump, where H is the total water depth. The average water depth is 10 m during the sampling time. The volume of water samples was 50 L at each layer, and the water samples were poured into 10 L brown glass bottles, cooled with ice, and then transported to the laboratory for further analysis. Meanwhile, salinity, temperature and water depth were measured with a conductivity-temperature-depth (CTD, SBE 19 Plus) in situ. Water samples for the SSC (i.e., SPM concentration) were firstly filtered through a 0.45 cellulose acetate filter. And the filters were dried at (40–50) °C and then were weighted in lab.

2.2. Sample extraction

The extraction procedure of PAHs in water and SPM has been described after Liu et al. (2014a), so only a short explanation was given here. The water samples were filtered by a vermicular system through GF/F (0.7 μm) glass fibre filters (Whatman International Ltd., Maidstone, England) that had been precombusted at 450 °C for 4 h before use. These samples were separated into aqueous and particulate phases. The filters were placed in pre-cleaned glass dishes, wrapped with aluminium foil, and stored in double layers of plastic bags at −20 °C until extraction. The blank water samples were also taken into account during each sampling event.

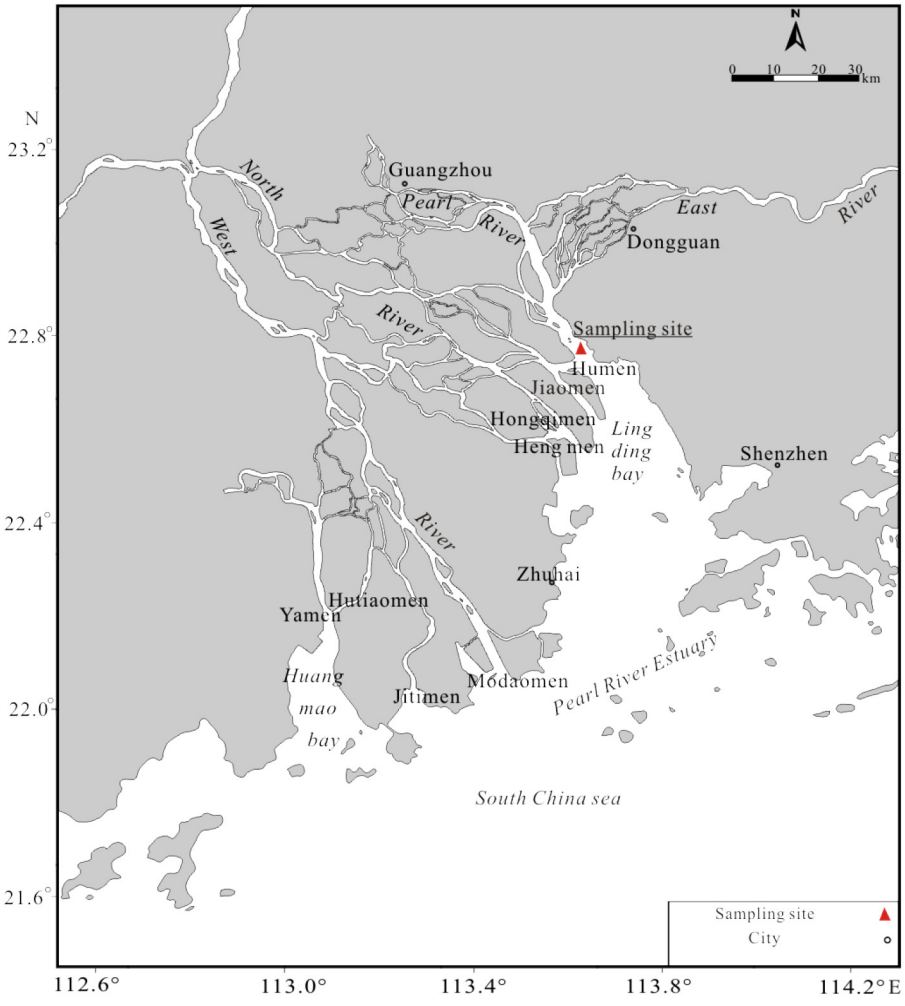

Fig. 1. Map of the Pearl River Estuary and the sampling site at the Humen outlet.