Polycyclic aromatic hydrocarbons (PAHs) in the water column and sediment core of Deep Bay, South China

Yao-Wen Qiu [a,b,*], Gan Zhang [a], Guo-Qing Liu [a,c], Ling-Li Guo [a], Xiang-Dong Li [d], Onyx Wai [d]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China
[b] Key Laboratory of Tropic Marine Environmental Dynamics, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, PR China
[c] Institute of Nuclear Technology, College of Physics, Shenzhen University, Shenzhen 518060, PR China
[d] Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR, PR China

ARTICLE INFO

ABSTRACT

The levels of 15 polycyclic aromatic hydrocarbons (PAHs) were determined in seawater, suspended particulate matter (SPM), surface sediment and core sediment samples of Deep Bay, South China. The average concentrations Σ_{15}PAHs were 69.4 ± 24.7 ng l^{-1} in seawater, 429.1 ± 231.8 ng g^{-1} in SPM, and 353.8 ± 128.1 ng g^{-1} dry weight in surface sediment, respectively. Higher PAH concentrations were observed in SPM than in surface sediment. Temporal trend of PAH concentrations in core sediment generally increased from 1948 to 2004, with higher concentrations in top than in sub-surface, implying a stronger recent input of PAHs owing to the rapid economic development in Shenzhen. Compared with historical data, the PAH levels in surface sediment has increased, and this was further confirmed by the increasing trend of PAHs in the core sediment. Phenanthrene, fluoranthene and pyrene dominated in the PAH composition pattern profiles in the Bay. Compositional pattern analysis suggested that PAHs in the Deep Bay were derived from both pyrogenic and petrogenic sources, and diesel oil leakage, river runoff and air deposition may serve as important pathways for PAHs input to the Bay. Significant positive correlations between partition coefficient in surface sediment to that in water (K_{OC}) of PAH and their octanol/water partition coefficients (K_{OW}) were observed, suggesting that K_{OC} of PAHs in sediment/water of Deep Bay may be predicted by the corresponding K_{OW}.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), a class of ubiquitous contaminants with two or more fused aromatic rings, are mainly introduced into the environment via anthropogenic processes (Fulton et al., 1993; McGroddy and Farrington, 1995). Anthropogenic inputs of PAHs from oil spills, ship traffic, urban runoff, waste discharge, as well as atmospheric fallout of vehicle exhaust and industrial stack emission have caused significant accumulation of PAHs in the marine environment which is generally considered as the ultimate pool (Simpson et al., 1996; Seruto et al., 2005). PAHs, most of which are categorized as persistent organic pollutants (POPs), are of environmental significance due to their widespread distribution in the environment and potential toxicity to organisms. These contaminants are often hydrophobic and easily accumulated in organisms through food chains, and present potential threat to aquatic ecosystems and even to human health (Colborn et al., 1993).

The sorptive properties of PAHs are largely controlled by their hydrophobicity and by the particle organic carbon content. In the water column, PAH tend to associate with suspended particulate matter and are eventually deposited in sediments (Santschi et al., 2001). Since the deposition of sediments continues over time, sediments can act as geochronometers of the contaminant deposition in the environment as well as of general environmental change over time (Hites et al., 1977; Yamashita et al., 2000; Zhang et al., 2002; Luo et al., 2004; Kannan et al., 2005; Van Metre and Mahler, 2005). Studies concerning PAHs in water column and core sediments can lead to better understanding of PAHs cycles in top-to-bottom processes and their historical trend.

Deep Bay ($22°24'18''$ N–$22°32'12''$ N, $113°53'06''$ E–$114°02'30''$ E), located in the eastern Lingdingyang of Pearl River estuary, South China, is a natural, shallow estuarine bay with an average water depth of about 3 m, and a tidal range of about 1.4 m. It is 17.5 km long in SW–NE direction and 4–10 km in NW–SE direction (Fig. 1). There has been a rapid expansion of marine culture and industrial

* Corresponding author.
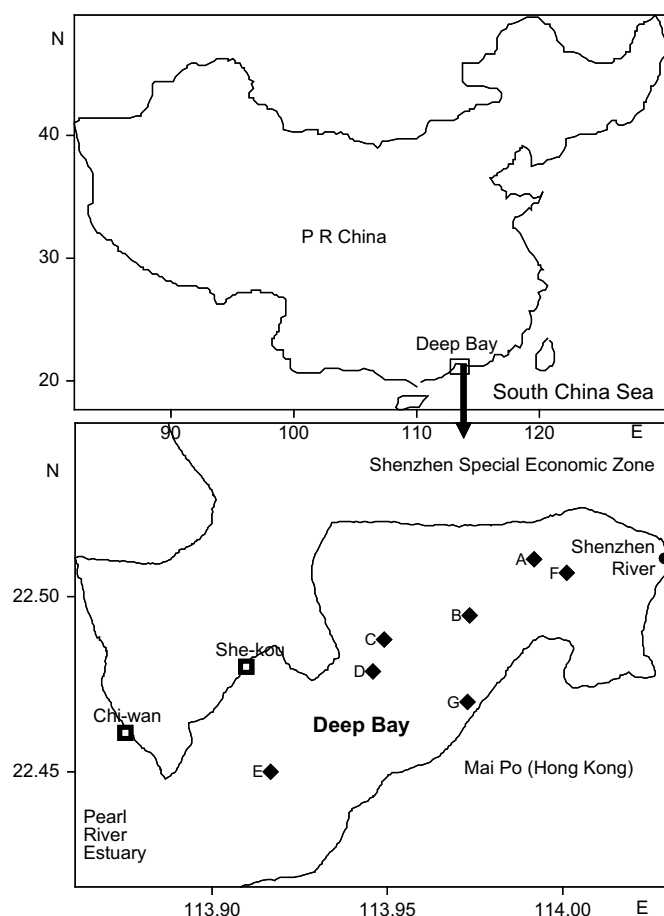E-mail address: yqiu@scsio.ac.cn (Y.-W. Qiu).

Fig. 1. Sampling locations in Deep Bay, South China.

et al., 1998). The present project aimed to study (1) distribution and sources of PAHs in seawater, suspended particulate matter (SPM) and surface sediments of Deep Bay; (2) temporal trend of PAHs in core sediment; (3) PAHs partitioning processes between water and sediment.

2. Materials and method

2.1. Collection of samples

Seawater, SPM, surface sediment and core sediment samples in seven sites (A, B, C, D, E, F and G) from Deep Bay, as shown in Fig. 1 and Table 1, were collected in February 2004. A stainless steel static gravity corer (8 cm i.d.) was employed to collect sediment which was sliced immediately at 1 cm intervals. In the meantime, 50 l surface water (0.3–0.5 m under water) and bottom water (0.5 m above sea floor) were collected by pump. Water samples were filtered in situ using Whatman GF/F filters (pore size diameter 0.7 μm) to separate SPM and dissolved seawater. The latter was filtered with XAD-4 to collect dissolved target compounds. The samples were stored in PTFE bags and frozen at −20 °C until required.

2.2. Sediment dating

The ^{210}Pb activities in sediment sub-samples were determined by analysis of the α-radioactivity of its decay product ^{210}Po, on the assumption that the two are in equilibrium. The Po was extracted, purified, and self-plated onto silver discs at 75–80 °C in 0.5 mol l^{-1} of HCl, with ^{209}Po (NIST, USA) used as yield monitor and tracer in quantification. Counting was conducted by computerised multi-channel α-spectrometry with gold-silicon surface barrier detectors. Supported ^{210}Po was obtained by indirectly determining the α-activity of the supporting parent ^{226}Ra, which was carried by co-precipitated BaSO$_4$. As the core did not reach the critical depth of excessive ^{210}Pb→0, only a Constant Initial ^{210}Pb Concentration (CIC) model was used, which assumes that dry mass entering the sediment pool has the same radioactivity concentration, to give an average sedimentation rate. Sedimentation age was calculated using a constant flux (CF) model (McCall et al., 1984), where $\lambda = 0.03114$ a^{-1}, $\xi = \int_0^m A(g)dg / \int_0^\infty A(g)dg$, and dg is the thickness of each sediment interval (g cm^{-2} a^{-1}).

$$t = -\lambda^{-1} \ln (1 - \xi)$$

Among the three cores (A, B, E) analysed for sediment dating, only core B was eventually selected to determine PAHs concentrations as core A and E showed a mixing depth of ca. 7 cm and ca. 11.5 cm, respectively. Fig. 2 presents the distribution of excessive ^{210}Pb activity in the core B, showing that the average sedimentation flux was 0.28 g cm^{-2} a^{-1}, with an apparent sedimentation rate of 0.69 cm a^{-1}.

activities in the area, with simultaneous developments in tourism and the construction of harbours and highways since China adopted the "Reform and Open" policy in 1978. The wetlands around Inner Deep Bay and Mai Po marshes have been very important to migratory birds for many decades. The 1500 hectares of wetlands around the area was designated as a Wetland of International Importance under the Ramsar Convention in 1995. However, the declining water quality in Deep Bay due to increasing pollution loads from Shenzhen River and Yuen Long/Kam Tin catchments are now exerting a serious threat to the aquatic environment at Mai Po and Inner Deep Bay. Recently, Liang et al. (1999) assessed the ecological risk of polychlorinated biphenyls (PCBs) in the Mai Po marshes nature reserve, and Tam et al. (2001) and Zhang et al. (2004) studied the contamination of PAHs in surface sediments of mangrove swamps in the bay. Limited data are available concerning PAHs in water column and core sediment in Deep Bay (Connell

Table 1
Sampling location, water depth and PAHs concentration in the water column of Deep Bay.

Location	Longitude	Latitude	Water depth	Surface water	Bottom water	Surface SPM	Bottom SPM	Surface sediment
	E	N	m	ng l^{-1}	ng l^{-1}	ng g^{-1}	ng g^{-1}	ng g^{-1}
A	113°59′30″	22°30′38″	2.0		72.1	380.8	298.3	408.4
B	113°58′24″	22°29′40″	2.6	111.7	95.3	336.2	360.3	236.8
C	113°56′56″	22°29′16″	5.0	78.1	84.6	370.3	431.0	358.2
D	113°56′45″	22°28′43″	5.0	60.6	82.2	447.4	244.4	330.3
E	113°55′00″	22°27′00″	6.0	40.9	55.3	1202.1	377.1	376.9
F	114°00′04″	22°30′24″	2.0	51.6	31.7	490.1	316.1	581.5
G	113°58′22″	22°28′11″	6.0	96.8	41.4	428.1	324.8	184.1