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DISTRIBUTION OF POLYCYCLIC MUSKS IN SURFACE SEDIMENTS FROM THE PEARL RIVER DELTA AND MACAO COASTAL REGION, SOUTH CHINA

XIANGYING ZENG, BIXIAN MAI, GUOYING SHENG, XIAOJUN LUO, WENLAN SHAO, TAICHENG AN, and JIAMO FU*
Guangdong Key Laboratory of Environment and Resources, State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, People's Republic of China

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Abstract—Polycyclic musks were measured in surface sediments collected from the Pearl River Delta and Macao coastal region, South China, to investigate contamination from domestic sewage. Three polycyclic musk compounds—4-acetyl-1,1-dimethyl-6-*tert*-butylindan, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(g)-2-benzopyran (HHCB), and 7-acetyl-1,1,3,4,4,6–hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN)—were detected in sediment samples. Two polycyclic musks, HHCB and AHTN, were dominant components in sediment, consistent with the use pattern of polycyclic musks by perfume industries in the Pearl River Delta region. The concentrations of total polycyclic musks ranged from 5.76 to 167 μg/kg. Because of the large amount of domestic sewage and industrial wastewater discharged from the city of Guangzhou, the highest concentration of polycyclic musks was found in sediments from the Zhujiang River. The significant positive correlation between the HHCB to AHTN ratios and the concentrations of polycyclic musks suggested that the HHCB to AHTN ratio could be used as a tracer for source discrimination and for the degree of degradation in the environment.

Keywords—Polycyclic musks Surface sediments Pearl River Delta Macao

INTRODUCTION

The Pearl River is the second-largest river in China and is located in southern China. It consists of a large number of tributaries, including the Zhujiang River, Beijiang River (North River), Dongjiang River (East River), and Xijiang River (West River), as well as other, smaller tributaries forming a complicated watershed named the Pearl River Delta (PRD). Zhujiang River runs across the city of Guangzhou, a highly urbanized and heavily populated city with approximately 6.6 million inhabitants, whereas the Dongjiang River drains across Dongguan, which is a newly developed city near Guangzhou. The Xijiang River runs across a less urbanized area with a smaller population. A detailed description of the PRD has been provided by Mai et al. [1].

The PRD has been subjected to increasing and more serious contamination as a result of rapid industrialization and urbanization during recent decades. A number of organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), have been detected in air, water, sediments, and human milk in this region [1–7].

Recently, concerns about the distribution of polycyclic musks, a group of synthetic chemicals, in the environment have been raised because of their persistence, bioaccumulation ability, and toxicity to aquatic organisms and humans [8–10]. They are widely used in perfumes, shampoos, soaps, and detergents, which mainly enter the domestic sewer and wastewater treatment plants after application and are released into the environment through effluent. Therefore, polycyclic musks have been used as anthropogenic markers to assess the impacts of domestic wastewater on the aquatic environment [11–13]. Because of their low solubility and high octanol–water partition coefficient (log $K_{OW} > 5$), polycyclic musks tend to adsorb to particulates in water and, subsequently, are deposited and accumulated in sediments. Sediments are the ultimate sinks and reservoirs of hydrophobic pollutants, so analyses of sediment samples are an important tool for assessing the impacts of anthropogenic activities on aquatic systems. Few data, however, are available regarding the concentrations and distributions of polycyclic musks in the environment of the PRD. The aim of the present study was to understand and assess the impact of increased anthropogenic activities on the aquatic environments of the PRD by determining the concentrations and distributions of polycyclic musks in surface sediments collected from the three major rivers in the PRD and Macao coastal region in the Pearl River Estuary.

MATERIALS AND METHODS

Materials and reagents

Six polycyclic musk standards—1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-4H-inden-4-one (DPMI; Cashmeran; purity, 90%), 4-acetyl-1,1-dimethyl-6-*tert*-butylindan (ADBI; Celestolide; purity, 98%), 6-acetyl-1,1,2,3,3,5-hexamethylindan (AHMI; Phantolide; purity, 94.5%), 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindan (ATII; Traseolide; purity, 90%), 7-acetyl-1,1,3,4,4,6–hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN; Tonalide; purity, 98%), and 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(g)-2-benzopyran (HHCB; Galaxolide; purity, 75%)—were purchased from LGC Promochem (Wesel, Germany). Hexamethylbenzene (purity, 99.5%) was acquired from laboratories of Ehrenstofer-Schäfer Bgm–Schlosser (Augsburg, Germany).

Analytical-grade dichloromethane (DCM) and *n*-hexane were redistilled in glass before use. Silica gel (80–100 mesh) and neutral alumina (100–200 mesh) were Soxhlet-extracted with DCM for 72 h, then activated at 180 and 250°C, respectively, for 12 h; deactivated with 3% redistilled water; and

* To whom correspondence may be addressed (fujm@gig.ac.cn).
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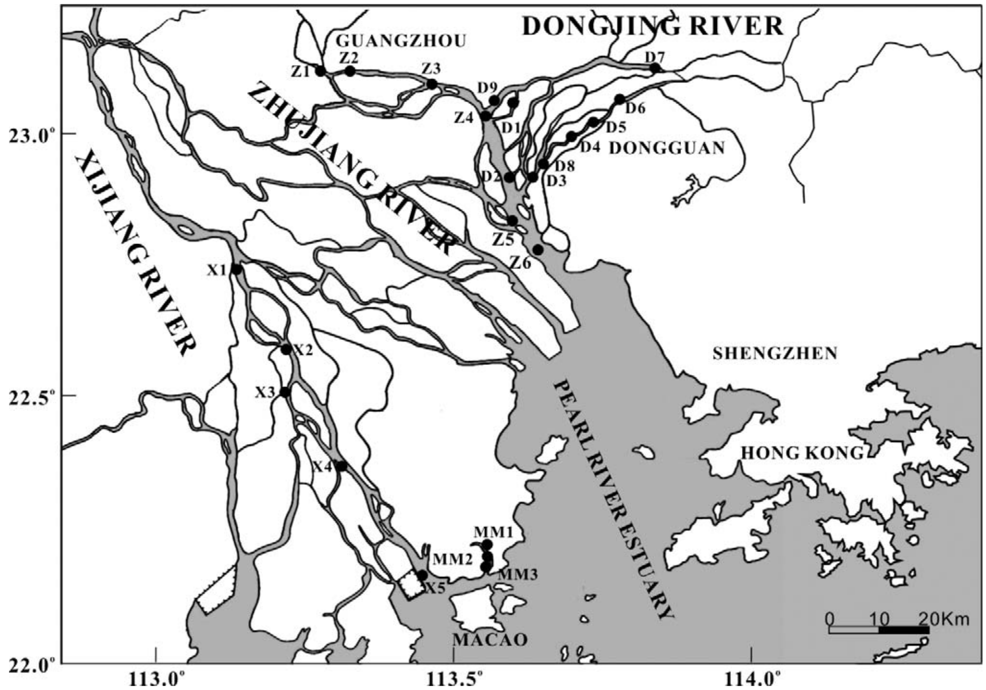

Fig. 1. Map showing sampling sites and surrounding area of the Pearl River Delta and Pearl River Estuary, China.

kept in *n*-hexane before use. Anhydrous sodium sulfate was baked at 450°C for 6 h.

Sample collection

Six sediments were collected from the Zhujiang River, of which three samples (Z1–Z3) were taken from the upper channel, running through the highly urbanized and densely populated city of Guangzhou, and three samples (Z4–Z6) were collected from the lower channel (Shiziyang River), which receives inflows from the Zhujiang and Dongjiang rivers. Nine sediments (D1–D9) were sampled from the Dongjiang River, which drains across Dongguan, a developing city near Guangzhou, and five sediments (X1–X5) were sampled from the Xijiang River, which runs through a rural area. Three samples (M1–M3) were collected from the coast of Macao, a known deposition zone in the PRD (Fig. 1) [14]. Sediments were collected during October and November of 2002 using a Van Veen stainless-steel grab. The top 5 cm of sediments was scooped using a precleaned, stainless-steel scoop into solvent-rinsed, aluminum containers and then transported on ice to the laboratory, where they were kept at −20°C until analysis.

Extraction and analysis

Sediment was freeze-dried, ground, and homogenized by sieving through a stainless-steel, 75-mesh (pore size, 0.5 mm) sieve and then stored in an amber glass bottle until extraction. Approximately 20 g of sediments were Soxhlet-extracted for 72 h with DCM. Activated copper granules were added to the extraction flasks during the extraction to remove elemental sulfur. The extracts were concentrated with a rotary evaporator to approximately 1 ml, solvent-exchanged to *n*-hexane, and finally, reduced to between approximately 0.5 and 1 ml. The concentrated extracts were cleaned and fractionated on a silica/alumina column (inner diameter, 10 mm). Three fractions were eluted with 20 ml of hexane, then with 70 ml of hexane:DCM (3:1), and finally, with 50 ml of DCM. The third fraction containing polycyclic musks was concentrated using a rotary evaporator and then further reduced to 0.5 ml under a gentle stream of nitrogen. A known quantity of hexamethylbenzene was added as an internal standard before gas chromatography–mass spectrometry.

Analyses were carried out on a HP6890 gas chromatograph equipped with a Platform II mass spectrometric detector and a HP-5 fused silica capillary column (length, 30 m; inner diameter, 0.25 mm; film thickness, 0.25 μm; Agilent Technologies, Little Falls, DE, USA). The polycyclic musks were identified and verified by comparing the retention times and mass spectra of samples with those of authentic standards. The chromatographic conditions as well as the procedure for qualification and quantification of polycyclic musks were the same as those detailed previously [15]. All concentrations were normalized to dry sediment weight. Nominal detection limits for individual polycyclic musk compounds ranged from 0.3 to 0.67 μg/kg.

Quality control and quality assurance

Method blanks (n = 3), spiked blanks (standards spiked into solvent, n = 3), and spiked matrix (standards spiked into 20 g of pre-extracted sediment, n = 3) were included in every batch of samples. None of the analytes was detected in two of the three blank samples, whereas HHCB and AHTN levels were at the limit of detection in the third sample. Recoveries of polycyclic musks ranged between 52 ± 2.88% to 82.3 ± 3.49% and from 56.5 ± 6.46% to 109 ± 0.35% for spiked blanks and spiked matrix, respectively, depending on the analytes (Table 1).

RESULTS AND DISCUSSION

The concentrations of polycyclic musks in sediments are listed in Table 2. Of the six target polycyclic musk compounds, HHCB and AHTN were detected in all samples, ADBI in 45% of samples, and DPMI, AHMI and ATII were below the detection limit in all samples.

The concentrations of total polycyclic musks ranged from 5.76 to 167 μg/kg. Generally, the concentrations of polycyclic

Table 1. Recoveries of polycyclic musks from spiked blanks and spiked matrix

	Spiked blanks		Spiked matrix	
Compounds[a]	Recoveries (%)	RSD[b] (%)	Recoveries (%)	RSD (%)
DPMI	51.96 ± 2.88	5.5	56.48 ± 6.46	11.4
ADBI	67.98 ± 6.34	9.3	62.84 ± 1.82	2.9
AHMI	72.36 ± 9.10	12.6	67.78 ± 2.32	3.4
ATII	72.02 ± 5.53	7.7	71.92 ± 2.12	2.9
HHCB	82.25 ± 3.49	4.2	108.75 ± 0.35	0.3
AHTN	78.69 ± 3.89	4.9	78.44 ± 1.78	2.2

[a] DPMI = 1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-4H-inden-4-one; ADBI = 4-acetyl-1,1-dimethyl-6-*tert*-butylindan; AHMI = 6-acetyl-1,1,2,3,3,5-hexamethylindan; ATII = 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindan; HHCB = 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(g)-2-benzopyran; AHTN = 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene.
[b] RSD = relative standard deviation.

musks followed the sequence Zhujiang River > Dongjing River ≥ Macao coast > Xijiang River. As expected, the sediments collected from Zhujiang River had the highest concentrations of polycyclic musks because of the large amounts of municipal sewage and industrial wastewater discharged from the city of Guangzhou. The concentrations of polycyclic musks also were high in samples collected from the coast of Macao. This was expected, because this coastal region receives effluents from Macao, which has a highly dense population, and fluvial suspended particles from the PRD water network, resulting from a southwestward coastal current (called the South China coastal current) originating from the counterclockwise Coriolis force in the Northern Hemisphere and the prevailing westward wind in the region of the PRD [14].

Levels of polycyclic musks in the Zhujiang River

Sediment from site Z1 had substantially higher concentrations of polycyclic musks (HHCB, 121 μg/kg; AHTN, 42.5 μg/kg) than sediment collected from other sampling sites. This sampling site is located in a typical urban area (Fangcun) of Guangzhou, with a population density of approximately 43,000 residents/km^2. One previous study suggested that domestic wastewater in the city of Guangzhou was either untreated or inadequately treated and directly discharged into the aquatic environment; this finding was based on the internal to external ratios of linear alkylbenzenes in the sediments collected from the Zhujiang River, a typical molecular marker of municipal wastewater (Luo XJ, Chen SJ, Ni HG, Yu M, Mai BX, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, Guangdong Province, China, unpublished data). Another related study indicated that effluents from an activated wastewater treatment plant at Guangdong contained relatively high levels of polycyclic musks (up to 2.22 μg/L; Zeng XY, Sheng GY, Gui HY, Chen DH, Shao WL, Fu JM, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, Guangdong Province, China, unpublished data). Therefore, the treated and untreated municipal sewage from domestic discharges was the likely source of polycyclic musks to the Zhujiang River. High concentrations of persistent organic pollutants (POPs), such as PAHs, organochlorine pesticides, PCBs, and PBDEs, also were observed in sediments collected at this location [1–7,16], reflecting the influence of anthropogenic activities on this aquatic environment. Considerably high concentrations of HHCB and AHTN were present in sediment collected from site Z3, a location proximate to the largest industrial zone of Guangzhou (Huangpu), where factories producing personal care products and cosmetic industries are situated. Apparently, in addition to the discharges

Table 2. Concentrations of polycyclic musks in sediment samples (μg/kg dry wt)

	Compounds[a]							
Samples	DPMI	ADBI	AHMI	ATII	HHCB	AHTN	Total	HHCB:AHTN
Z1	<0.3	3.94	<0.3	<0.67	121	42.5	167	2.84
Z2	<0.3	8.95	<0.3	<0.67	33.5	17.7	60.2	1.89
Z3	<0.3	3.16	<0.3	<0.67	58.5	25.7	87.4	2.28
Z4	<0.3	2.66	<0.3	<0.67	4.54	4.46	11.7	1.02
Z5	<0.3	2.53	<0.3	<0.67	3.29	3.62	9.44	0.91
Z6	<0.3	<0.3	<0.3	<0.67	3.51	3.76	7.27	0.94
D1	<0.3	<0.3	<0.3	<0.67	6.90	6.33	13.2	1.09
D2	<0.3	<0.3	<0.3	<0.67	12.9	6.73	19.6	1.92
D3	<0.3	2.57	<0.3	<0.67	11.7	6.21	20.5	1.89
D4	<0.3	2.61	<0.3	<0.67	48.6	11.2	62.5	4.33
D5	<0.3	<0.3	<0.3	<0.67	5.74	5.72	11.5	1.00
D6	<0.3	<0.3	<0.3	<0.67	13.1	8.77	21.9	1.50
D7	<0.3	<0.3	<0.3	<0.67	5.05	4.41	9.46	1.15
D8	<0.3	<0.3	<0.3	<0.67	3.57	3.51	7.08	1.02
D9	<0.3	4.32	<0.3	<0.67	9.75	9.16	23.2	1.06
X1	<0.3	<0.3	<0.3	<0.67	2.62	3.14	5.76	0.83
X2	<0.3	<0.3	<0.3	<0.67	2.94	3.92	6.86	0.75
X3	<0.3	<0.3	<0.3	<0.67	2.91	3.63	6.54	0.80
X4	<0.3	<0.3	<0.3	<0.67	3.24	3.63	6.87	0.89
X5	<0.3	<0.3	<0.3	<0.67	2.58	3.59	6.17	0.72
M1	<0.3	2.90	<0.3	<0.67	44.5	17.3	64.7	2.57
M2	<0.3	2.64	<0.3	<0.67	7.05	6.09	15.8	1.16
M3	<0.3	2.49	<0.3	<0.67	3.67	3.56	9.72	1.03

[a] DPMI = 1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-4H-inden-4-one; ADBI = 4-acetyl-1,1-dimethyl-6-*tert*-butylindan; AHMI = 6-acetyl-1,1,2,3,3,5-hexamethylindan; ATII = 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindan; HHCB = 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(g)-2-benzopyran; AHTN = 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene.

from domestic wastewater, the effluents from the treated and untreated industrial wastewater are potential sources of polycyclic musks at this site.

The concentrations of polycyclic musks in sediments decreased by approximately one order of magnitude from the upper channel in Guangzhou (Z1–Z3) to the lower channel (Shiziyang River; Z4–Z6). This may be attributed to the dilution of less contaminated water from the northern watershed of the Dongjiang River and the inflows of strong tide flushes from the Pearl River Estuary.

Polycyclic musks in the Dongjiang River

The concentrations of polycyclic musks in sediments collected from the Dongjiang River ranged from 7.08 to 62.5 μg/kg, with a mean value of 21.0 μg/kg, which was higher than those in sediments collected from the Shiziyang and Xijang rivers. Although reports from a water monitoring program in 1997 by Guangdong Environment Protection Bureau indicated that the Dongjiang River was the cleanest river in the PRD, with the lowest concentrations of biochemical oxygen demand and chemical oxygen demand [1], the relatively high levels of polycyclic musks, combined with the high concentration of other POPs (e.g., PBDEs and PAHs) [14,16] (Luo XJ, Mai BX, Chen SJ, Sheng GY, Fu JM, Zeng ED, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, Guangdong Province, China, unpublished data.) in surface sediments of this river signaled a substantial change in water quality as a result of the rapid economic growth and urbanization in the Dongguan region during the last decade. For example, Dongguan has become the world's largest manufacturing base for electronic/electrical products, with more than 6.4 millions inhabitants. The concentrations of polycyclic musks varied widely in samples from the Dongjiang River, suggesting that polycyclic musks probably are derived from local discharges, which agrees with the results for PBDEs in a previous study [16].

Polycyclic musks in the Xijiang River

Concentrations of polycyclic musks in sediments collected from the Xijiang River varied from 5.76 to 6.87 μg/kg, with an average concentration of 6.44 μg/kg (lower than those from other regions). Two explanations can be given. First, the watershed of the Xijiang River is less urbanized relative to the areas drained by the Zhujiang and Dongjiang rivers. Second, the high flows of the Xijiang River may reduce the magnitude of deposition for organic contaminants in the riverbed. The annual outflow of freshwater in the Xijiang River is estimated to be 8.84×10^{10} m^3/year, which is the highest among the rivers in the PRD [17]. Similar levels of polycyclic musks were found among different samples collected from the Xijiang River. The relatively constant and low concentrations within samples suggested that polycyclic musks in the Xijiang River are less likely to be from local sources of contamination. Atmospheric deposition via the gas and particulate phases is the most probable source of polycyclic musks to the Xijiang River, because previous investigations have shown that the Xijiang River is affected by atmospheric transport of contaminants from other industrialized and urbanized regions around the PRD [14,16].

Polycyclic musks in coastal sediments of Macao

Relatively high concentrations of polycyclic musks were found in samples from the Macao coastal region, with an average value of 30.1 μg/kg. This coincided with the results for POPs and suggested that this coastal region, situated at the southwestern part of the Pearl River Estuary, is an active area for deposition of organic pollutants from the PRD [14]. On the other hand, the Macao coast also receives discharges of local municipal sewage and industrial wastewater from the city of Macao, as indicated by the molecular marker coprostanol, which originates from domestic sewage [5].

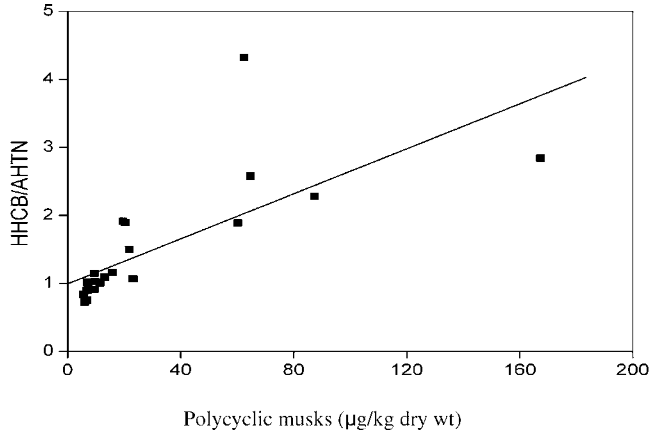

Fig. 2. Relationship between total concentrations of polycyclic musks and the 1,3,4,6,7,8- hexahydro-4,6,6,7,8,8- hexamethylcyclopenta(g)-2-benzopyran (HHCB) to 7-acetyl-1,1,3,4,4,6–hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN) ratios.

Implications of the HHCB to AHTN ratios

The HHCB to AHTN ratios in sewage sludge and effluents could be used to trace fragrance composition in the personal care products [18–21]. The HHCB to AHTN ratios in the sewage sludges collected from the wastewater treatment plants in Guangdong ranged between 3.4 and 7.6, with an average of 5.3, except for a sludge sample from a wastewater treatment plant for food processing activities, which had a HHCB to AHTN ratio of 1.5. The HHCB to AHTN ratios in sediment samples collected from the PRD ranged from 0.72 to 4.32, with an average of 1.46 (Table 1); these ratios were significantly lower than those in sewage sludge samples [15]. Similarly, lower average HHCB to AHTN ratios in sediments (~0.90) than in sewage sludges (~2.32) also were reported from an aquatic environment in Berlin (Germany) [22]. This phenomenon may be attributed to the fact that HHCB and AHTN underwent degradation in different manners after discharging into the aquatic environment.

A significant positive correlation ($r^2 = 0.73$, $p < 0.001$) between the HHCB to AHTN ratios and the concentrations of polycyclic musks was observed in sediments collected during the present study (Fig. 2). The sediments collected from locations near urban sources (e.g., Zhujiang and Dongjiang rivers) generally showed relatively high concentrations of polycyclic musks and ratios of HHCB to AHTN, whereas the samples collected from sites far from sources (e.g., Xijiang River) displayed lower values for both concentrations and ratios. The HHCB was reported to react quickly with HO radicals in the gas phase, resulting in an atmospheric lifetime of a few hours [23]. This suggested that HHCB is more active photolytically than AHTN, which results in much more photodegradation of HHCB during atmospheric transport. Therefore, the lower HHCB to AHTN ratio in Xijiang River results, in part, from the relatively higher photolysis rate of HHCB in the atmosphere. This finding indicated that the HHCB to AHTN ratio could be used as a tracer for the degree of degradation in addition to being used for source discriminators [24].

Comparison with published data

Levels of polycyclic musks in the PRD are close to those observed in sediments from the Lippe River (Germany; HHCB, <0.5–20 μg/kg; AHTN, 23–90 μg/kg) [22]. Fromme et al. [13] reported concentrations of polycyclic musks in river sediments from areas in Germany with different proportions of municipal sewage effluents. Up to 3.6 and 2.6 mg/kg of HHCB and AHTN, respectively, were found at contaminated sites. The HHCB and AHTN concentrations measured in the PRD are comparable with those measured in sediments collected from areas in Germany having low and moderate proportions of sewage effluents (HHCB, from less than the limit of detection to 520 μg/kg; AHTN, 20–610 μg/kg), but they are higher than the HHCB and AHTN concentrations detected in sediments from Lake Erie and Lake Ontario (both USA) [24].

Comparison with levels of other POPs detected in PRD sediments

During the last two decades, the population in the PRD has increased continuously, and this has been accompanied by rapidly developing industrialization and urbanization, creating increased demand and disposal of industrial waste and wastewater as well as large amounts of local municipal discharges. Many studies have focused on POPs contamination. These studies have revealed very serious pollution, with PAHs, PCBs, and PBDEs found in sediments collected from the PRD [1,3,16]. Kang et al. [3] measured high levels of PCBs in sediments from the Zhujiang River (48.3–486 μg/kg) and Macao (339 μg/kg) and relatively lower loads in sediments from the Xijiang River (11–13.6 μg/kg) and Shiziyang River (10–30.3 μg/kg). Sediments collected from the Zhujiang River and Macao showed very high levels of PAHs (1,434–10,811 and 9,220 μg/kg, respectively) [1,14,25]. The DDT was used on a large scale in agricultural practice, and its production and use in China was banned in 1983. During the last two decades, many agricultural lands have been developed for commercial use, resulting in contaminant transfer from agricultural land into aquatic environments through surface runoff. Sediments from the Zhujiang River have higher levels of DDTs (35.1–91.0 μg/kg) than those from the Xijiang and Shiziyang rivers (5.0–16.6 and 22.9–40.4 μg/kg, respectively) [17]. These sediments showed relatively lower levels of polycyclic musks compared with PAHs, PCBs, and DDTs under similar distribution characterization—that is, concentrations of these chemicals followed the same order (Zhujiang > Shiziyang > Xijiang). The PBDEs are widely used as flame retardants, which can be found in many commercial and household products. Dongguan is one of the main electrical manufacturing bases in the world and a main emission source of PBDEs in the PRD. Sediments collected around Dongguan (Dongjiang River) have the highest loads of PBDEs, with BDE 209 concentrations at 21.3 to 7340 μg/kg and total PBDE concentrations (except for BDE 209) at 26.3 to 3,580 μg/kg. Mean concentrations of BDE 209 and total PBDEs (except for BDE 209) followed the order Dongjiang > Zhujiang > Macao > Xijiang [16]. With the rapid development of electronic manufacture and population growth in this city, discharges of local municipal wastewater into the Dongjiang River, an obvious point source of emissions, was affirmed by relatively higher loads of polycyclic musks at sediments from site D4.

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