Environmental Chemistry

Occurrence and Distribution of Organophosphorus Flame Retardants/Plasticizers and Synthetic Musks in Sediments From Source Water in the Pearl River Delta, China

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Abstract: The Pearl River (China) and its tributaries receive discharges of treated/untreated domestic sewage and industrial wastewater throughout the entire drainage basin. The river provides source water for many local inhabitants, and there is great concern over its pollution status. Fifteen sediment samples were collected from source water areas in the Pearl River Delta, and analyzed for the occurrence and distribution of 2 classes of emerging pollutants, organophosphorus flame retardants (OPs) and synthetic musks. In most sediments, 5 polycyclic musks and 2 nitro musks were detected, and galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta (g)-2-benzopyran [HHCB]) and tonalide (7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene [AHTN]) were the predominant components, with concentrations of 0.030 to 547 and 4.31 to 439 ng/g, respectively. Seven widely used OPs were found in most sediments, at varying total concentrations from 1.79 to 143 ng/g, with tris(2-butoxyethyl) phosphate (TBEOP), tris(2-chloro-isopropyl) phosphate (TCIPP), and triphenyl phosphate (TPHP) being the main components. The results indicated that industrial discharge and domestic sewage played important roles for synthetic musk and OP distribution in sediments in the study area. In general, higher levels of OPs and synthetic musks were found in Guangzhou, Foshan, and Dongguan, suggesting a significant impact from industrial discharges and the dense population of these regions. *Environ Toxicol Chem* 2018;37:975–982. © 2017 SETAC

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INTRODUCTION

In recent decades, polybrominated diphenyl ethers (PBDEs) have been widely used as flame retardants. Because of their ubiquitous presence in the environment, accumulation potential, and toxic effects, PBDEs have gradually been banned/restricted and replaced by alternative flame retardants. It is claimed that these alternatives (among which organophosphorus flame retardants or organophosphate esters [OPs] are the main components) are more environmentally friendly [1,2]. The OPs are a group of derivatives of phosphoric acid that exhibit excellent flame retardancy and flexibility, and they are widely used as flame retardants and/or plasticizers in a range of products, such as electronic/electric equipment, furniture and decorative materials, building materials, textiles,

and packing. With the ban/restriction on PBDEs, the production and application of OPs has increased sharply [1,3], resulting in elevated levels in the environment. However, several studies have demonstrated that chlorinated OPs have more adverse effects and are much more persistent than PBDEs [1,4]. In recent years, the occurrence, distribution, and toxicity of OPs has been a subject of increasing concern in the scientific community.

Synthetic musks are a group of artificial fragrance materials that for ethical and economic reasons are used as substitutes for natural musks. These compounds are widely used in daily household products such as detergents, cosmetics, shampoo, perfume, and food [5,6]. During the manufacturing process and after application, these compounds are discharged directly/indirectly into water bodies through wastewater [7,8]. In addition, because of their continuous discharge into the water bodies, synthetic musks are frequently detected at elevated levels in aquatic environments affected by domestic/industrial wastewater [9–11]. Many studies have demonstrated that synthetic musks exhibit a diverse range of effects on freshwater organisms and humans, and they are recognized as an emerging

class of pollutants [12,13]. Nitro musks have already been gradually phased out of the world perfume market because of their phototoxic, carcinogenic, and neurotoxic properties [7].

The Pearl River is the second largest river in China. It is located in southern China and also consists of the Zhujiang, Beijiang, Dongjiang, and Xijiang Rivers as well as a large number of smaller tributaries. The Pearl River Delta is located downstream of the Pearl River and connects the Pearl River Estuary and the South China Sea. It is one of the most developed areas of China, with a high level of urbanization. The Pearl River Delta contains the megacity of Guangzhou City, a well-known electrical/electronic manufacturing base in Dongguang City, and a manufacturing zone specializing in plastics, textiles, and personal protection products. Previous studies have shown that rapid economic development and urbanization have created high-risk regions in the Pearl River Delta in terms of contamination by polycyclic aromatic hydrocarbons, PBDEs, and polychlorinated biphenyls [14,15]. In addition, OPs and polycyclic musks are frequently detected in the sludge from domestic sewage and treated industrial wastewater in the region [16,17], suggesting potential high-risk regions with regard to OPs and synthetic musk concentrations.

As well as receiving a large amount of treated/untreated wastewater in its catchment, the Pearl River also acts as a drinking water source for the surrounding inhabitants. There is significant concern in the scientific community and local government about the occurrence and distribution of organic pollutants in drinking water sources (surface water and sediment) as well as the safety of the drinking water. Therefore, much attention has been given to pollution control and abatement in the Pearl River Delta [18]. In the present study, 15 sediment samples were collected from a water source area described in a related report [18], and analyzed for the occurrence and distribution of OPs and synthetic musks. A preliminary assessment was then made of their impact on the source water.

MATERIALS AND METHODS

Standards and reagents

Seven OP standards and 9 synthetic musks (including 6 polycyclic musks and 3 nitro musks) were chosen as target analytes (Supplemental Data, Table S1). The OPs were purchased from Sigma-Aldrich and the synthetic musks were purchased from LGC Promochem. Four deuterated compounds, d27-tributyl phosphate (TNBP; 98%), d15-triphenyl phosphate (TPHP; 98%), d12-tris-(2-chloroethyl) phosphate (TCEP; 98%), and d15-musk xylene (MX; 97.5%), were purchased from C/D/N Isotopes and used as surrogate standards. Hexamethylbenzene (99.5%) was obtained from the laboratories of Ehrenstofer-Schäfer Bgm-Schlosser and used as an internal standard.

All solvents used were of chromatographic grade. Methanol, acetone, acetonitrile, and n-hexane were purchased from Merck, and ethyl acetate was purchased from CNW Technologies. Oasis HLB Extraction Cartridges (200 mg, 6 mL) were purchased from Waters.

Sample collection

Nine cities are located in the Pearl River Delta: Guangzhou (study sites JC, YG, XC, YJS, and LWZ), Huizhou (study site HZh), Dongguan (study sites DG and YT), Shenzhen (study site SZYL), Foshan (study site FSH and ShD), Zhaoqing (study site ZhQ), Jiangmen (study site JM), Zhongshan (study site ZhZh), and Zhuhai study site ZHQS. As mentioned in the Introduction, the Pearl River consists of the Zhujiang, Dongjiang, Xijiang, and Beijiang Rivers and many tributaries. Specific sections of the Pearl River are protected as drinking water sources for local people. Fifteen locations, which are water sources for the 9 cities, were selected as study locations, which have been described in detail elsewhere [18]. Surface sediment (0–5 cm) was collected using a stainless-steel grab into an aluminum container, and then transported on ice to the laboratory. The sediment samples were kept in a refrigerator at −20 °C, freeze-dried, ground finely, homogenized via sieving through a stainless-steel sieve (80 mesh), and kept in amber bottles at 4 °C until extraction.

Sample analyses

Each freeze-dried sediment sample (∼5 g) was spiked with 50 ng of the surrogates (d27-TNBP, d12-TCEP, d15-TPHP, and d15-MX), and extracted with ultrasonic assistance using acetone and acetonitrile/water (25/75, v/v). The extract was concentrated, and solvents were exchanged for acetonitrile/water (1/99, v/v). The extracts were then subjected to solid phase extraction via an Oasis HLB cartridge (200 mg, 6 mL) for further enrichment and clean-up. The analytes were eluted using 4 + 4 mL ethyl acetate. The fraction was concentrated to near dryness under a gentle stream of N_2 and resolved again in n-hexane. An aliquot of 100 ng of internal standard hexamethylbenzene was added to the fraction before gas chromatography–mass spectrometry (GC–MS) analysis. The detailed procedures of sample extraction and clean-up are published elsewhere [19].

Identification and determination of OPs was performed using a GC-MS-QP 2010 (Shimadzu) in electron impact ionization mode, coupled with a TG-5MS column (30 m × 0.25 mm i.d. × 0.25-μm film; Thermo Fisher Scientific), with helium as the carrier gas at a flow rate of 1 mL/min. Determination and quantification of synthetic musks were conducted with a GC-MS-QP 2010 (Shimadzu) and a DB-5MS column (30 m × 0.25 mm i.d. × 0.25-μm film; J & W Scientific). Helium was applied as the carrier gas at 1 mL/min. The detailed analytical parameters have been reported previously [16,17].

Quality assurance and quality control

For quality assurance and quality control, method blanks ($n = 3$), spiked blanks ($n = 3$, i.e., spiked standards into solvent), and spiked matrix ($n = 3$, i.e., spiked standards into pre-extracted sediment) were analyzed alongside real samples. In addition, 3 sediment samples were chosen randomly in duplicate for verifying method reproducibility, with the average values used. Fifty nanogram OPs and 100 ng synthetic musks

were added to each spiked sample, and all samples were spiked with 50 ng of the surrogates.

The limits of detection (LODs) for specific target analytes, calculating as $3 \times (SD/S)$, where SD is the standard deviation of the response obtained from 7 replicate injections of target analytes at levels as low as possible, which was established using a dilution series of stock solution for each compound. The limits of quantification (LOQs) were defined as twice the maximum concentration measured in blanks for the 3 OPs (TCEP, tris-(2-chloropropyl) phosphate [TCIPP], and tris-(2-butoxyethyl) phosphate [TBEOP]), and galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta (g)-2-benzopyran [HHCB]). As for the other analytes not detected in blank samples, the LOQs were calculated as 2 times the LODs. In the present study, TCEP, TCIPP, and TBEOP were found at concentrations lower than 2 ng/g of 5 g sediment, and HHCB was found below the LOQ. The LODs and LOQs for the target analytes are listed in the Supplemental Data, Table S2.

Acceptable recovery rates were achieved for d27-TNBP, d12-TCEP, d15-TPHP, and d15-MX at $90 \pm 2.3\%$, $86 \pm 14\%$, $68 \pm 7.8\%$, and $97 \pm 4.7\%$, respectively. All the reported concentrations were background-subtracted and were not corrected with recovery rates.

RESULTS AND DISCUSSION

The results indicated that most of the target compounds were frequently detected in the study area. The levels and distribution of OPs and synthetic musks are listed in Tables 1 and 2, respectively.

Levels of OPs in sediments in the Pearl River Delta

As shown in Table 1, TCIPP and the 4 nonchlorinated OPs (TNBP, TBEOP, TPHP, and tritotyl phosphate [TMPP]) were detected in all samples; TCEP and tris-(1,3-dichloro-propyl) phosphate (TDCIPP) were found in 14 of the 15 sediment samples. Levels of TPHP, TBEOP, and TNBP were greater than those of the other OPs, with concentrations varying over LOQ to 70.5 ng/g (mean = 15.4 ng/g), 0.840 to 67.0 ng/g (mean = 10.2 ng/g), and LOQ to 32.2 ng/g (mean = 7.31 ng/g), respectively; levels of TMPP varied from LOQ to 1.78 ng/g (mean = 0.826 ng/g) in the study region. For the 3 chlorinated OPs, the TCEP and TDCIPP concentrations varied from LOQ to 11.3 ng/g (mean = 2.78 ng/g) and LOQ to 3.90 ng/g (mean = 1.41 ng/g), respectively, whereas higher levels of TCIPP than the other Cl-OPs were detected at all sampling sites, with concentrations varying from 0.259 to 24.7 ng/g (mean = 5.92 ng/g). Total sedimentary concentrations of OPs ($\sum 7$OPs) varied significantly from 1.79 to 143 ng/g in source water in the study area.

Until recently, only limited data about the sedimentary concentration of OPs were available (Supplemental Data, Table S3). The levels of OPs in the present study were similar to those found in Italy [20], Taiwan [21], and the Great Lakes (USA/Canada) [22], and were significantly lower than levels from European countries [23–25] and the United States [26], as well as from a sea-based waste disposal site in Japan [27]. With the restriction/ban on PBDEs, the United States, Japan, and several European countries have taken the lead in using OPs as alternative flame retardants. Their consumption has increased sharply, and therefore it is not surprising that higher levels of OPs have been reported in these countries [28]. In addition, such researches [23–27] focused on sediment from non-source water bodies, whereas the present study focused on source water. We speculate that the types of water function also played important roles in sedimentary OP levels, which might be verified by a related study carried out by Tan et al. [3], who found slightly higher levels of TCEP (not detected [ND]–58 ng/g), TCIPP (0.91–185 ng/g), TPHP (ND–253 ng/g), and TMPP (ND–11 ng/g) in sediment other than source water in the Pearl River Delta. The Chinese government has promulgated a series of laws and regulations for protection of drinking water sources, and the local government of Guangdong Province

TABLE 1: Occurrence and distribution of organophosphorus flame retardants in sediment source water in the Pearl River Delta[a]

Site location	TNBP	TBEOP	TPHP	TMPP	TCEP	TCIPP	TDCIPP	Total
YJS	3.84	4.67	33.8	1.03	3.28	9.68	1.51	57.8
YG	28.5	67.0	6.64	1.07	11.3	24.7	3.90	143
XC	32.2	37.8	7.31	0.741	5.46	7.19	2.78	93.5
JC	5.45	5.86	1.92	0.389	1.72	1.86	0.506	17.7
LWZ	LOQ	0.840	LOQ	LOQ	ND	0.952	ND	1.79
YT	1.60	1.14	0.334	LOQ	LOQ	0.803	LOQ	3.88
DG	8.46	7.73	12.9	0.477	2.16	8.15	1.44	41.3
FSH	6.39	3.79	56.6	0.707	1.00	2.09	0.873	71.5
ShD	0.917	1.03	70.5	0.957	1.32	20.7	0.219	95.6
ZHQS	2.49	15.6	7.99	1.78	3.06	6.54	2.44	39.9
SZYL	0.716	1.13	1.63	LOQ	1.21	3.09	1.29	9.07
JM	2.94	2.42	3.72	LOQ	1.98	0.895	0.299	12.3
ZhQ	2.54	1.41	0.925	LOQ	1.97	0.259	LOQ	7.10
ZhZh	3.63	1.53	5.37	0.280	0.918	0.830	0.245	12.8
HZh	2.62	1.21	6.47	LOQ	0.773	0.996	LOQ	12.1

[a]Data in ng/g.
ND = not detected; LOQ = below the limit of quantification; TNBP = Tributyl phosphate; TBEOP = Tris-(2-butoxyethyl) phosphate; TPHP = Triphenyl phosphate; TMPP = Tritotyl phosphate; TCEP = Tris-(2-chloroethyl) phosphate; TCIPP = Tris-(2-chloropropyl) phosphate; TDCIPP = Tris-(1, 3-dichloro-propyl) phosphate.

TABLE 2: Occurrence and distribution of synthetic musks in sediment source water in the Pearl River Delta[a]

Site location	DPMI	ADBI	AHMI	ATII	HHCB	AHTN	MK	MA	MX	Total
YJS	ND	0.164	0.101	ND	13.5	26.5	0.0616	ND	ND	40.3
YC	ND	3.51	0.759	ND	217	197	0.808	ND	0.270	419
XC	ND	6.41	1.34	ND	547	439	0.584	23.1	1.01	1018
JG	ND	LOQ	LOQ	ND	2.20	4.31	ND	ND	0.0550	6.62
LWZ	ND	ND	ND	ND	LOQ	7.57	ND	ND	ND	7.60
YT	ND	0.263	0.102	ND	4.11	20.7	0.0722	ND	0.083	25.3
DG	ND	0.554	0.232	ND	40.5	47.6	0.170	ND	ND	89.1
FSH	ND	0.778	0.181	ND	23.4	35.8	0.189	ND	0.246	60.6
ShD	ND	LOQ	0.065	ND	0.444	20.3	ND	ND	LOQ	20.8
ZHQS	ND	0.816	0.367	ND	199	193	0.169	ND	0.171	394
SZYL	ND	LOQ	0.072	ND	0.699	39.5	ND	ND	LOQ	40.3
JM	ND	0.206	0.119	ND	9.48	32.4	0.0770	ND	0.265	42.6
ZhQ	ND	0.227	0.157	ND	12.9	24.3	LOQ	ND	0.149	37.7
ZhZh	ND	0.406	0.110	ND	18.8	31.1	0.106	ND	0.119	50.6
HZh	ND	0.482	0.157	ND	46.0	37.6	0.127	ND	0.105	84.5

[a]Data in ng/g.
ND = not detected; LOQ = below the limit of quantification; 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; MX = 1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzne; MK = 4-tert-butyl-2,6-dimethyl-3,5-dinitroacetophenone; MA = 1-(tert-Butyl)-2-methoxy-4-methyl-3,5-dinitrobenzene.

has stringently managed contaminant-releasing and pollution abatement [18]. However, we note that the sedimentary OP concentrations found in the present study were much higher than those in source water sediment from Taihu Lake ($\sum$7OPs 3.38–14.25 ng/g) and Dahuofang Reservoir ($\sum$7OPs 1.11–7.14 ng/g) in China [29]. This might be because of the industrial emission of OPs in the Pearl River Delta from electronic/electrical equipment, furniture, and textile production facilities, as well as the large discharges of treated/untreated domestic sewage from the densely populated urban areas [16,30]. Because of their extensive usage, OPs have been found at high levels in different matrices in the Pearl River Delta, including sludge, sediment, indoor dust, and biota [3,16,30–32]. These results suggest severe regional OP pollution in the Pearl River Delta.

Levels of synthetic musks in sediments in the Pearl River Delta

It can be seen from Table 2 that 2 polycyclic musks, HHCB and tonalide (7-acetyl-1,1,3,4,4,6–hexamethyl-1,2,3,4-tetrahydronaphthalene [AHTN]), were found in all the sediment samples at concentrations in the range of LOQ to 547 ng/g (mean = 75.7 ng/g) and 4.31 to 439 ng/g (mean = 77.1 ng/g), respectively. These 2 chemicals were the predominant musks detected in the present study. Low levels of celestolide (4-acetyl-1,1-dimethyl-6-tert-butylindan [ADBI]; ND~6.41 ng/g) and phantolide (6-acetyl-1,1,2,3,3,5-hexamethylindan [AHMI]; ND~1.34 ng/g) were detected, whereas 1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-4H-inden-4-one and 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindan were not found in any samples, which suggested the limited application of these chemicals in the Pearl River Delta.

For the 3 nitro musks, musk ambrette (1-(tert-Butyl)-2-methoxy-4-methyl-3,5-dinitrobenzene [MA]) was only found in one location (XC, 23.1 ng/g), and trace amounts of MX (LOQ to 1.01 ng/g) and musk ketone (4-tert-butyl-2,6-dimethyl-3,

5-dinitroacetophenone [MK]; LOQ to 0.808 ng/g) were measured in 11 and 12 of the 15 samples, respectively. Because of their hazardous effects on ecological systems and humans, MA has been banned in cosmetic products in Europe, and MK and MX have been restricted in personal products and cosmetic products. They have gradually been replaced by polycyclic musks and macrocylic musks [7]. Consequently, in recent years, these nitro musks have been detected at low levels, with limited frequencies of detection in most studies (Supplemental Data, Table S3). In a related study, we analyzed the occurrence and distribution of synthetic musks in 18 sludge samples collected in the Pearl River Delta, and detected MK (ND–172.7 ng/g) and MX (ND–65.8 ng/g) in most of the samples; MA was found (<LOQ) in only one sludge [17]. These results might suggest their addition into inexpensive domestic and cosmetic products in the Pearl River Delta.

The levels of synthetic musks detected in the present study were similar to those reported in the United States [33], Japan [34], and the Haihe River draining through the Chinese city of Tianjin, which receives large amounts of wastewater [35], much higher than amounts found in Korea [36], Singapore [37], and several other rivers in China and the Pearl River Estuary [12,38] (Supplemental Data, Table S3).

Spatial distribution of OPs in the Pearl River Delta and their possible sources

Levels of $\sum$OPs (1.79–143 ng/g) varied significantly in the Pearl River Delta, and their spatial distribution is illustrated in Figure 1.

As indicated in Figure 1, higher levels of OPs were found in the central part of the Pearl River Delta (including Guangzhou, Foshan, Shunde, and Donguan) than in the surrounding area. The regional distribution of OPs was consistent with that of halogenated flame retardants, which might be ascribed to anthropogenic impacts, such as the high level of urbanization
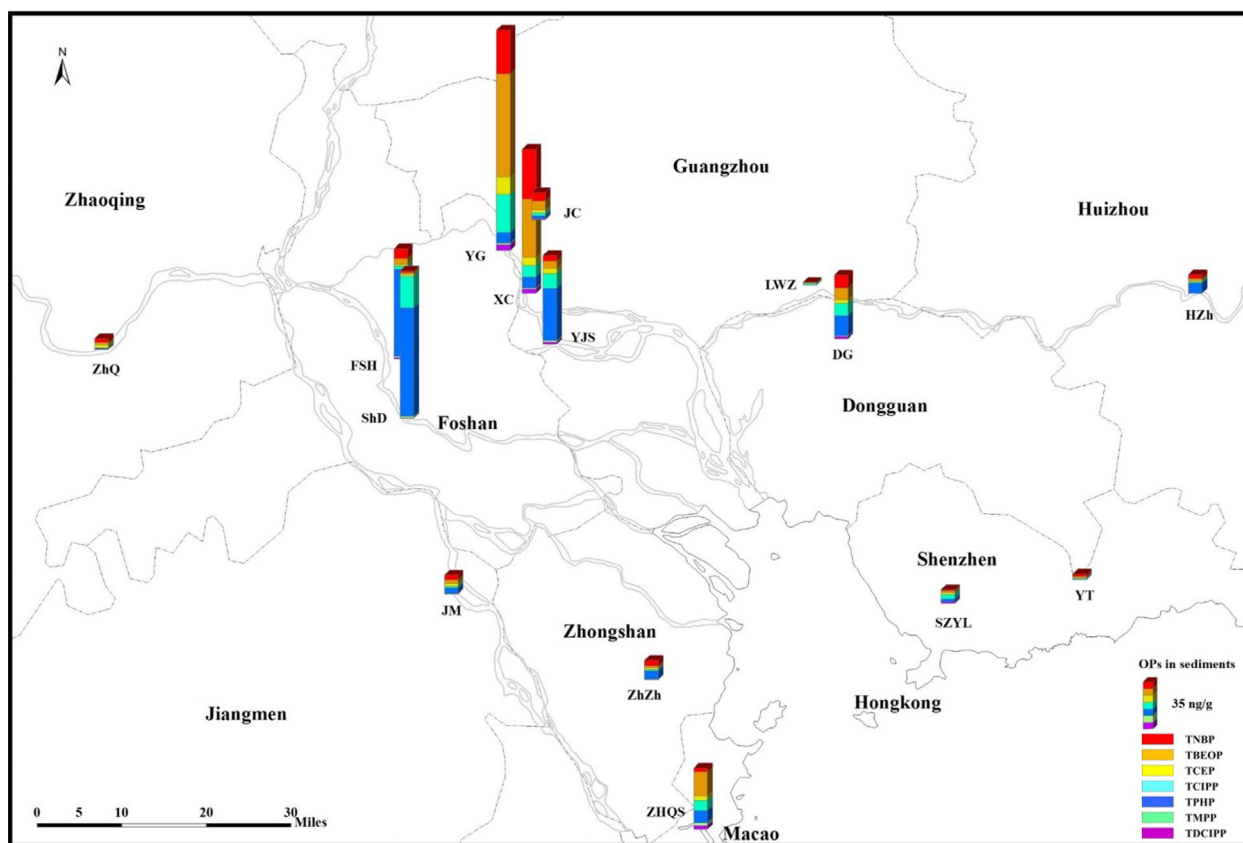
FIGURE 1: Occurrence and distribution of organophosphate esters in sediment in the Pearl River Delta. TNBP = tributyl phosphate; TBEOP = tris-(2-butoxyethyl) phosphate; TPHP = triphenyl phosphate; TMPP = tritotyl phosphate; TCEP = tris-(2-chloroethyl) phosphate; TCIPP = tris-(2-chloropropyl) phosphate; TDCIPP = tris-(1, 3-dichloro-propyl) phosphate.

with a dense population, and rapid economic development based on the extensive manufacturing industry [39]. The well-established electrical/electronic manufacturing base in Dongguan contributed most to the levels of flame retardants in soil, sediment, sludge, and biota [3,16,32,39].

In addition, we also found a different distribution pattern for individual OPs in the study area (Figure 1). For example, TPHP accounted for >70% of the ∑OPs from FSH and ShD, whereas TBEOP, which is an additive in wax, floor polish, and wallpapers, accounted for more than 30% of the total OPs in Guangzhou City, with the exception of the YJS sampling site. Our results indicated that domestic discharge from the densely populated Guangzhou City played an important role in the presence of TBEOP in sediment [16,29]. The flame retardant TCEP was an important additive to polyvinyl chloride products, textiles, and polyurethane foam, and so forth, and TCIPP was another widely used flame retardant in polyurethane foam [2]; because of their wide use, TCEP and TCIPP have been found at high levels in indoor environments, laundry wastewater, and effluent from wastewater treatment plants [40]. High levels of TCEP (11.3 ng/g) and TCIPP (24.7 ng/g) were found at the YG sampling site located in the Liuxi River, which receives water from the Shijing River upstream and runs through densely populated suburbs of Guangzhou City; large amounts of untreated domestic and industrial wastewater have been discharged into this river [41], acting as the main source of the OPs. Meanwhile,

high levels of TCIPP were found in the ShD (20.7 ng/g) sampling site located in Foshan City, where extensive electrical/electronic manufacture and furniture factories are located, acting as important emission sources of OPs and contributing the most to OPs in the environment. [16]. In general, TPHP is used as a flame retardant and plasticizer in electrical/electronic and wire production, and is readily degraded to diphenyl phosphate via hydrolysis and/or biotic processes [42]. The high sedimentary TPHP concentration suggested that TPHP was discharged into receiving water adjacent to the sampling sites. Because of the obvious adverse effect on aquatic organisms and its persistence in the environment, TCEP has gradually been replaced by its homolog TCIPP in developed countries [22,25]. It was found that TCIPP was more commonly detected than TCEP in most of the sampling sites in the Pearl River Delta, which is consistent with the worldwide trend in usage, although there is still some use of TCEP in the region. The results were similar to those for sludge [16].

Spatial distribution of synthetic musks in the Pearl River Delta and their possible sources

Levels of ∑9 musks (6.62–1018 ng/g) varied significantly in the Pearl River Delta, as indicated in Figure 2, with a very different spatial distribution from that of OPs (Figure 1). Generally, HHCB and AHTN are the main components
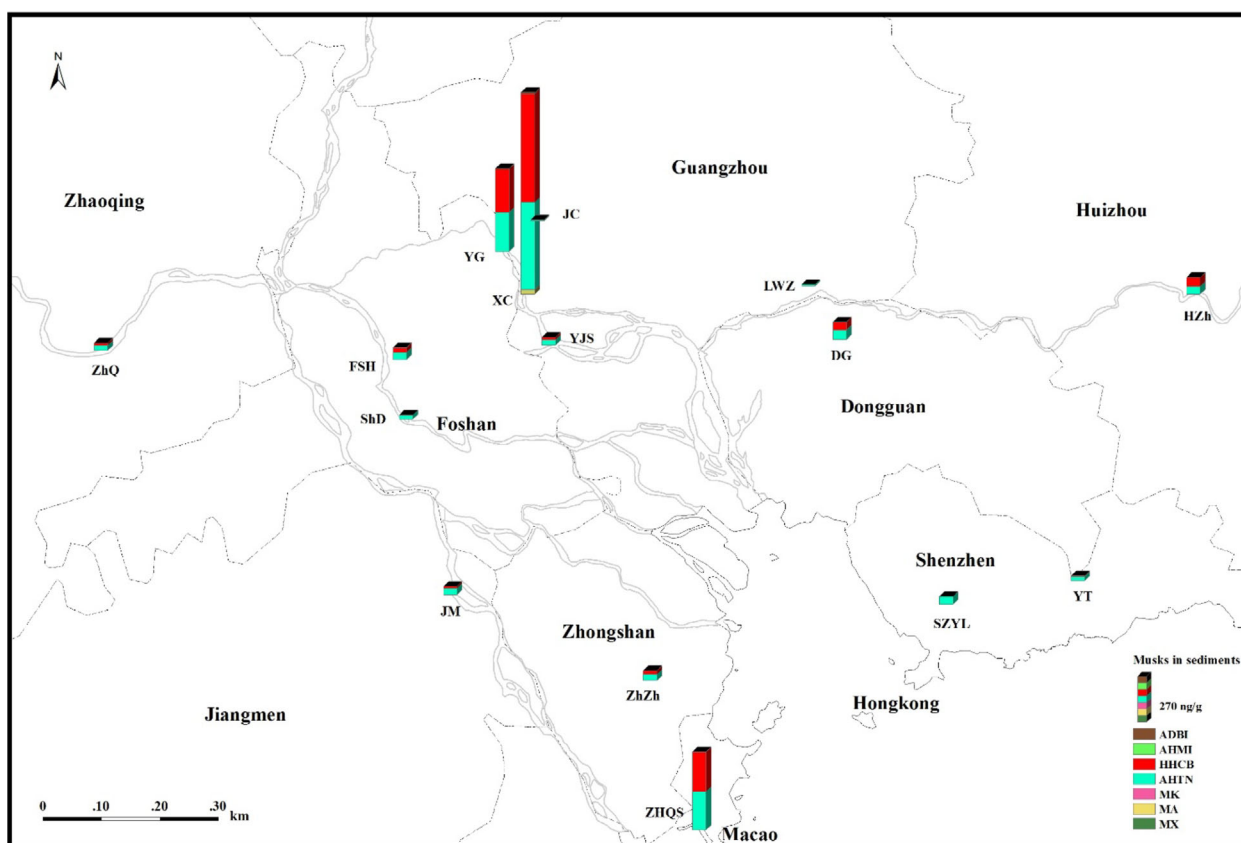
FIGURE 2: Occurrence and distribution of synthetic musks in sediment in the Pearl River Delta. DPMI = 1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-4H-inden-4-one; ADBI = 4-acetyl-1,1-dimethyl-6-tert-butylindan; AHMI = 6-acetyl-1,1,2,3,3,5-hexamethylindan; ATII = 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindan; 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; MX = 1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene; MK = 4-tert-butyl-2,6-dimethyl-3,5-dinitroacetophenone; MA = 1-(tert-Butyl)-2-methoxy-4-methyl-3,5-dinitrobenzene.

of synthetic musks used in household products, and both are frequently detected in domestic wastewater and aquatic environments impacted by domestic sewage. Consequently their presence in sediment can often be used to trace domestic sewage inputs into receiving waters [33,43]. The ubiquitous occurrence and distribution of synthetic musks in sediment in the present study reflected the impact of treated/untreated sewage from local inhabitants. However, significantly higher concentrations of synthetic musks were found in XC (1018 ng/g), followed by YG (419 ng/g) and ZHQS (394 ng/g), which might be related to the industrial wastewater discharge from factories producing cosmetic/personal products. The results were consistent with those found in sludge in the Pearl River Delta, where high levels of synthetic musks were found at the site locations: KFQ and KFQD in Guangzhou, and ZH in Zhuhai, at which industrial wastewater from cosmetic and personal products were treated [17].

In general, HHCB is a more frequently used fragrance than AHTN, resulting in higher levels of it in the environment [36,44]. On the other hand, HHCB is more readily biodegradable than AHTN, and AHTN is preferentially absorbed on particles, resulting in variation in the ratio of HHCB to AHTN during transportation in aquatic systems. Consequently, the HHCB to AHTN ratio could be used as an indicator of their different

patterns of application in specific regions, and as a tracer for their transportation and transformation/degradation in the aquatic environment after emission [35]. The HHCB to AHTN ratios in the present study ranged from 0.02 to 1.25, except for the YJS sampling site where HHCB was detected at the LOD, and differed from the ratios reported in the Hudson, Haihe, and Songhua Rivers [33,35,38], which might be related to their different modes of usage. It is notable that the ratios measured in the present study were also clearly different from those reported in our previous study [11]. In that study, we measured HHCB (2.62–121 ng/g) and AHTN (3.14–42.5 ng/g) in sediments from locations other than the source water area in this region, showing HHCB to AHTN ratios in the range of 0.72–4.32, and the ratios had a significant positive relation to total concentration of HHCB and AHTN, which could be used as a source discriminator and as a tracer of the distance from the emission source and the degree of transformation/degradation during transportation [11]. The obvious discrepancies in the HHCB to AHTN ratio were not related to their mode of usage and might be affected by their different environmental behaviors (such as volatilization, biotic/abiotic degradation, and sorption) during transportation after their introduction into the Pearl River. The smaller HHCB to AHTN ratio in the present study implies that the water source was shielded from direct domestic sewage inputs [11,12].

Based on the above discussion, it could be speculated that source water in the Pearl River Delta suffers to some degree from industrial manufacturing and limited domestic sewage discharges, even under the strict administrative regime of the local government. In the present study, water samples were not collected and analyzed for the target compounds used to assess the safety of drinking water. It is well known that TBEOP (1100 mg/L) and 2 chlorinated OPs, TCEP (7000 mg/L) and TCIPP (1200 mg/L), have rather high water solubilities [29], and it was therefore assumed that these compounds were distributed mainly in the water phase. The chlorinated OPs and MX are very persistent in the environment and are resistant to traditional drinking water treatment technologies [7,45], suggesting an exposure pathway to the human body via drinking water. Further studies should be conducted to determine the occurrence and distribution of these compounds in source water and drinking water in the Pearl River Delta, and to undertake a safety assessment of drinking water ingestion in humans.

CONCLUSIONS

Fifteen sediment samples were collected from source water areas of the Pearl River Delta, and analyzed for the occurrence and distribution of 2 classes of emerging pollutants, OPs and synthetic musks. The results indicated that OPs were ubiquitously distributed in source water sediment, with the concentration of $\sum$OPs varying significantly in a range of 1.79 to 143 ng/g, with TPHP, TBEOP, TNBP, and TCIPP being the main components. Four polycyclic musks (ADBI, AHMI, HHCB, and AHTN) and 2 nitro musks (MX and MK) were frequently detected in samples, with HHCB and AHTN being the dominant compounds. The total concentration of synthetic musks varied substantially from 6.62 to 1018 ng/g. It was also found that OPs and synthetic musks had a different spatial distribution, suggesting different emission sources. The results indicated that domestic sewage and industrial wastewater also played important roles in the occurrence of these compounds in source water sediment in the Pearl River Delta. Further monitoring of their presence in source water and drinking water should be undertaken, and an assessment should be conducted of the exposure of local inhabitants via drinking water.

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