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Polybrominated diphenyl ethers and organochlorine pesticides in sewage sludge of wastewater treatment plants in China

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Abstract

The concentrations of chemicals in sewage sludge from wastewater treatment plants (WWTPs) may relate to their levels of use and environmental pollution in the region. In this work, sludge samples were collected from 31 WWTPs in 26 cities in China and analyzed for polybrominated diphenyl ethers (PBDEs) and organochlorine pesticides (OCPs). The concentrations of ∑PBDE (sum of congeners 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, and 183) ranged from 6.2 to 57 ng/g (dw). The concentration of decabromodiphenyl ether (BDE-209) ranged from below limit of detection (LOD) to 1109 ng/g (dw) (with a median of 27 ng/g (dw)), and averaged 55% (median 69%) of the total PBDEs. These levels are about 10–100 times lower than those found in Europe and North America. PBDE levels in sludge were not found to depend on the location and capacity of the WWTPs. Concentrations of hexachlorocyclohexanes (HCHs), dichlorodiphenyltrichloroethane (DDTs) and its major degradation products, and hexachlorobenzene (HCB) ranged from below detection limit to 167 ng/g (dw), 11 to 1065 ng/g (dw), and 7.5 to 319 ng/g (dw), respectively. The major DDT degradation products were *p,p′*-DDE and *p,p′*-DDD. The major hexachlorocyclohexane (HCH) isomer in sludge is β-HCH, reflecting its higher affinity to solids and resistance to degradation than other isomers.

Keywords: Polybrominated diphenyl ethers; Sewage sludge; Organochlorine pesticides; Wastewater treatment plants

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants in plastics, electronic equipment, printed circuit boards, textiles, etc. (WHO, 1994). The global demand for PBDEs increased rapidly since the 1970s, and was estimated at 70 000 tonnes in 2001 worldwide (Hites, 2004). In China, the production of technical decabromodiphenyl ether (DeBDE) in 1995 was less than 2000 tonnes (Liu et al., 2005). It increased to about 13 500 tonnes/a in 2001 (Xia et al., 2005). No production of other PBDEs is documented.

It is highly likely that some components of consumer goods containing PBDEs, such as polyurethane foam in upholstered furniture, enter sewers after being discarded and fragmented. In addition, discharge of PBDEs into the sewer can occur during their manufacturing and incorporation into the host polymers and products.

Organochlorine pesticides (OCPs) were used in large quantities in China from the 1950s to the 1980s. During this period, the production of HCHs and DDTs was about 8×10^5 tonnes and 4×10^6 tonnes, respectively (Liu, 2004). The usage of OCPs was banned in 1983 in China, but a recent study showed that their residues in many

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environmental matrices were still higher than those in many other countries (Chen et al., 2005).

OCPs enter the environment mainly through non-point sources such as agricultural runoff and vaporization following their field application. In wastewater treatment plants (WWTPs), significant portion of PBDEs and OCPs in the influent may survive the water treatment and accumulate in the sludge generated from the activated sludge and other processes due to their hydrophobicity and potentially slow degradation kinetics. Therefore, sewage sludge can be one of the major sources of these environmental pollutants when it is landfilled or land-applied (Hale et al., 2003). In addition, their levels in sewage sludge can be indicative of the regional release of these compounds. Since the early 1990s, high levels of PBDEs in sludge samples have been reported from Europe and North America (Nylund et al., 1992; Hale et al., 2001; North, 2004) but few from Asian countries and none from China.

This study investigates the status of PBDEs and OCPs in sewage sludge of WWTPs in China. The objectives are to reveal the general range of concentrations and compare it with those reported in other parts of the world, to examine potential geographic distributions within China, and to identify important influencing factors. A comprehensive study of PBDEs like this work is urgently needed because data on PBDEs in environmental matrices in China are very scarce. Information on environmental PBDEs in China is restricted to a limited number of reports (Jaward et al., 2005; Mai et al., 2005; Wang et al., 2005; Chen et al., 2006).

2. Materials and methods

2.1. Sampling sites and samples collection

From February to June 2005, a total 31 sewage sludge samples were collected from 26 cities in China. Locations of the cities are shown in Fig. 1. These cities included most of the Chinese provinces and most of the sampling sites are the capital cities. The sewage samples (about 2000 g wet weight each sample) were collected by the WWTP staffs and then were packed in aluminum foil and sealed in Ziplock bags, and directly express-delivered to the laboratory where they were stored in a freezer at −20 °C until analysis. A survey form was associated with each sample, documenting information regarding the treatment capacity of and population served by the plant, sources of the sewage (domestic, industrial, or combined), type of sludge treatment and drying operation, and point of sample collection in the sludge treatment process.

Fig. 1. Map of sampling locations.

2.2. Chemical analysis

2.2.1. Materials, standards, and regents

All solvents were pesticide residue grade and were purchased from Fisher (Hampton, NH). Silica gel (0.063–0.100 mm) was obtained from Merck (Whitehouse Station, NJ). PBDE reference materials (EO5103, including BDEs-17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, and 209) were purchased from Cambridge Isotope Laboratories (Andover, MA). Injection standard solution ^{13}C-labeled PCBs (1668A-IS) and surrogate standard solution of ^{13}C-labeled PBDEs (BDEs-47, 99, 153, BDE-LCS) were obtained from Wellington Laboratories (Guelph, Canada). A small amount of DeBDE technical mixture DE-83R (purity >97%) was obtained from a distributor of the Greats Lake Chemical Corp (West Lafayette, IN) and used as the calibration standard for BDE-209. A mixed OCP standard solution including α-, β-, γ-, δ-HCH, *p*,*p*′-DDT, *o*,*p*′-DDT, *p*,*p*′-DDE, *p*,*p*′-DDD, and HCB was purchased from National Research Center for Certified Reference Materials of China and diluted to the desired concentrations.

2.2.2. Samples pretreatment

PBDE congeners were analyzed following the method described previously with modifications (Liu et al., 2006). Sewage sludge samples were freeze-dried and homogenized by sieving through a stainless steel 75-mesh (0.5 mm) sieve. An aliquot of 3 g of sample was spiked with the ^{13}C-labeled surrogate standards (BDE-LCS) and extracted in a Soxhlet extractor for 24 h using dichloromethane and hexane (1:1; 150 ml). After extraction, about 15 g of acidic silica (30%, w/w) was added to the extract to remove lipid. Then the extract was filtered through approximately 5 g of anhydrous sodium sulfate. Two gram of activated copper powder was added to the extract to remove elemental sulfur. The extract was rotary-evaporated to about 2 ml and then cleaned up by passing through a multi-layered silica gel column containing, from bottom to top, 1 g of activated silica gel, 4 g of basic silica gel (1.2%, w/w), 1 g of activated silica gel, 8 g of acid silica gel (30%, w/w), 1 g of activated silica gel, 2 g of $AgNO_3$ silica gel (10%, w/w) and 4 g anhydrous sodium sulfate. The column was pre-cleaned by passing 100 ml hexane prior to the transfer of the sample extracts. After the sample was loaded, PBDE congeners were eluted with 70 ml hexane followed by 70 ml dichloro-

methane and hexane (1:1). The eluant was then concentrated to 2 ml on the rotary evaporator. Its volume was further reduced with a gentle nitrogen flow and the solvent was changed to 20 μl nonane in a minivial. Then, ^{13}C-PCB-138 (1668A-IS) was added and the vial mixed by vortexing prior to GC injection.

For OCPs, the sample pretreatment was modified from the method of Tanabe et al. (2000). Before extraction, 100 μl of *n*-hexane containing 0.2 μg/ml internal standard PCB-209 was added to 1 g freeze-dried samples, which was then ultrasonically extracted using dichloromethane and hexane (1:1; 60 ml) for 60 min. Lipids were removed by acid silica gel and sulfur was removed by activated copper powder. The extracts were cleaned up by passing through a Florisil column (containing 6 g activated Florisil), and the column was eluted with 60 ml 4:1 *n*-hexane:dichloromethane. Then the eluant was concentrated, the solvent was exchanged into hexane, and the solution volume was adjusted to 0.5 ml with a gentle nitrogen flow.

Total organic carbon (TOC) of sewage sludge was analyzed by the $KMnO_4$ titration method (Wu and Zhao, 1998).

2.2.3. Instrumental analysis

The quantification of tri-through hepta-BDEs was performed on an Agilent 6890 gas chromatograph coupled with a high-resolution mass spectrometer (HRMS) (Waters Micromass, Manchester, UK) using an electron impact (EI) ion source. HRMS was operated in SIM mode with resolution >10 000. Exactly 1 μl of concentrated extract was injected with a CTC PAL autosampler in splitless mode into a HP-5 (30 m × 250 μm i.d. × 0.1 μm film thickness) capillary column. Helium was the carrier gas at a constant flow rate of 1.2 ml/min. The initial oven temperature was 90 °C, which was held for 2 min. It was increased to 210 °C at 25 °C/min, held for 1 min, then increased to 275 °C at 10 °C/min and held for 10 min and finally ramped to 330 °C at 25 °C/min and held for 10 min. The target PBDE congeners included BDEs-17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, and 183. Quantification was carried out with the internal calibration standard method. Peaks were quantified only if the signal-to-noise exceeded 3. Quantitative analyses of BDE-209 was performed on an Agilent Model 6890 GC coupled with a Model 5975 MS with an electron impact (EI) ion source. Exactly 2 μl of concentrated extract was injected into a DB-5MS (15 m × 250 μm i.d. × 0.1 μm film thickness) capillary column. Helium was used as carrier gas at a constant flow rate of 1.2 ml/min. Initial oven temperature was 90 °C, which was held for 1 min. It was then increased to 340 °C at 20 °C/min and held for 2 min. The MS was operated in selected ion monitoring (SIM) mode. Quantification was performed by external standard calibration on an Agilent ChemStation. A quadratic calibration equation ($R^2 = 0.99$) was obtained and used for quantification of BDE-209. All PBDE congeners were monitored at the molecular ion clusters $[M]^+$ and $[M+2]^+$.

For OCPs, samples were quantified on a Hewlett-Packard 6890 GC with a DB-5 column (30 m × 0.25 mm i.d., phase film 0.25 μm) and an electron capture detector (ECD). Nitrogen was used for both carrier gas and makeup gas at flow rates of 1 ml/min and 50 ml/min, respectively. Oven temperature was initially set at 80 °C, held for 2 min, increased at 10 °C/min to 140 °C, increased again at 4 °C/min to 280 °C and held for 5 min. The injector temperature was 240 °C and the detector temperature was 300 °C.

2.2.4. QA/QC

Strict quality controls were implemented to ensure the correct identification and accurate quantification of the target compounds. Field blank samples were 3 g fully activated and cleaned silica gel, which were exposed to the air at the sampling site during the sample collection. Sample preparation and analysis were conducted in a clean room with double HEPA air filtration and positive ambient pressure. All glassware was thoroughly rinsed before and after use with dichloromethane. Before Soxhlet extraction, all the condensers were pre-extracted for over 6 h using 150 ml dichloromethane. A method blank sample was included in each batch of 12 samples to monitor the contamination. The results showed all targeted PBDEs in blanks were below the detection limits. Mean recoveries of ^{13}C-labeled PBDE congeners 47, 99, and 153 were 61.1 ± 10.0%, 88.0 ± 20.1%, 100.2 ± 19.1%, respectively, which are well within the limits specified in USEPA Draft

Table 1
Primary statistical result of BDE congeners and OCPs in sludge samples (ng/g, dw) of this study

Compound	Median	Mean	Min.	Max.	LOD (pg/g)
BDE-17	0.3	0.7	0.1	3.8	6
BDE-28	1.2	2.3	0.3	17.6	5
BDE-47	2.3	5.0	0.4	58.7	4
BDE-66	0.8	1.7	<LOD	21.7	18
BDE-71	1.1	3.1	<LOD	17.2	7
BDE-85	0.1	0.3	<LOD	5.0	7
BDE-99	1.9	4.5	<LOD	69.7	6
BDE-100	0.4	1.0	<LOD	18.4	6
BDE-138	0.3	0.9	0.1	4.5	3
BDE-153	0.6	1.8	<LOD	30.2	2
BDE-154	0.8	2.2	<LOD	9.6	2
BDE-183	1.5	2.1	<LOD	7.0	12
BDE-209	25.5	68.5	<LOD	1108.7	1 ng/g
Total PBDE[a]	43.8	94.0	5.1	1114.9	
α-HCH	<LOD	1.6	<LOD	42.2	0.04[b]
β-HCH	<LOD	16.8	<LOD	134.4	0.11
γ-HCH	<LOD	0.6	<LOD	7.4	0.04
δ-HCH	<LOD	0.9	<LOD	7.3	0.05
p,p′-DDE	91.2	142.8	10.5	730.3	0.05
p,p′-DDD	29.1	64.9	<LOD	339.8	0.06
o,p′-DDT	7.8	11.7	<LOD	46.7	0.12
p,p′-DDT	2.4	10.0	<LOD	100.7	0.10
HCB	133.8	145.3	7.5	318.7	0.06
Total OCPs	328.5	394.6	22.3	1151.1	

[a] Total PBDE is the sum of ∑PBDE and BDE-209.
[b] For OCPs, the unit of LOD is ng/g.

Method 1614. The reported concentrations were not corrected for recoveries. The limit of detection (LOD) (Table 1) ranged from 3.4 to 24.4 pg/g. For BDE-209, the LOD was 1 ng/g. Concentrations of HCH, HCB, and DDT in sludge was quantitatively determined by internal standard procedure. The recovery tests of T-HCH (sum of α-HCH, β-HCH, γ-HCH and δ-HCH), T-DDT (*p*,*p*′-DDT, *o*,*p*′-DDT, *p*,*p*′-DDE and *p*,*p*′-DDD) and HCB were $74.1 \pm 3.2\%$, $94.3 \pm 10.1\%$, $98.4 \pm 3.3\%$, respectively. Limit of detection, calculated as a signal-to-noise ratio of 3, were typically 0.04–0.12 ng/g sludge (dry weight). The relative standard deviation (RSD) for replicate analyses was less than 14% ($n = 3$). More detailed QA/QC procedures can be found in our previous papers (Yang et al., 2004; Liu et al., 2006).

3. Results and discussion

3.1. Concentrations in sludge

All concentrations reported are on a dry weight (dw) basis.

Concentrations of PBDEs in sewage sludge are summarized in Table 1. ∑PBDE refers to the sum of all 12 targeted tri-through hepta-BDE congeners. Fig. 2 illustrates the frequency distributions of ∑PBDE and BDE-209. The concentration of ∑PBDE ranged from 6.2 to 57.0 ng/g (mean: 19.6 ng/g; median: 16.0 ng/g). Seventy percent of the concentrations were within the range of 5–30 ng/g. Relatively high concentrations of ∑PBDE were found in Lanzhou (57.0 ng/g) and Datong (44.7 ng/g). The concentrations of BDE-209 ranged from <LOD to 1109 ng/g (mean: 70.8 ng/g; median: 25.5 ng/g) and were below 100 ng/g in more than 80% of the samples. Both the highest concentration of BDE-209 and the lowest concentration of ∑PBDE were found in the sample collected from Hangzhou.

TOC of the sludge samples ranged from 217 to 814 mg/g with an average value of 493 mg/g. On the basis of organic carbon, the corresponding values of ∑PBDEs and BDE-209 in sludge range from 11.0 ng/g to 96.5 ng/g and from below limit of detection to 5115 ng/g, respectively.

Globally, PBDE concentrations in sewage sludge vary substantially among geographic regions (Table 2). In the

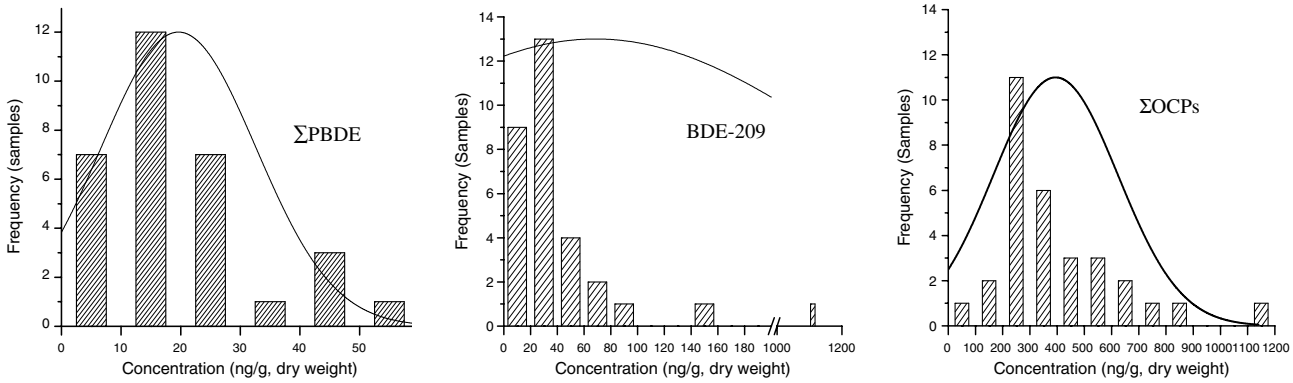

Fig. 2. Frequency distributions of concentrations of ∑PBDE, BDE-209, and ∑OCPs in sewage sludge in China.

Table 2
Comparison of PBDE concentrations in sludge among countries[a]

Location	Congener	Concentration ng g^{-1}	Reference
Lake Superior watershed communities	47, 99, 209	767, 1327, 510, respectively	Hale et al. (2003)
Michigan watershed communities (USA)	47, 99, 209	507, 706, 466, respectively	
Virginia, Maryland, New York, and California (USA)	Sum of 47, 99, 100, 153, 154	1100–2290	Hale et al. (2001)
Netherlands	Sum of 47, 85, 99, 138, 153 BDE 209	0.49–104.8 1.1–920	de Boer et al. (2003)
Germany	Total PBDEs	162 (average)	Kuch et al. (2001)
Sweden	Sum of 47, 99, 100	105–205	de Wit (2002)
Sweden (digested sludge)	Sum of tri- to penta-BDEs	20–30	Nylund et al. (1992)
Germany (sewage sludge)	Sum of tri- to hepta-BDEs	0.4–15	Hagenmaier et al. (1992)
Sweden (sewage sludge)	Total BDE47, 85, 99, 100, 138, 153, 154, 209	ND-220 (wet weight)	Öberg et al. (2002)
China	Sum of tri- to hepta-BDEs 209	6.2–57 ND-1108	This work

[a] Concentrations are based on dry weight unless otherwise indicated.

United States, a survey of biosolids from 26 publicly owned treatment works in several states revealed that the PBDE concentrations ranged from 1100 to 2290 ng/g (dw) of ∑PBDE (excluding BDE-209) (Hale et al., 2001, 2003). European samples contained up to 510 ng/g (dw) PBDEs (Hagenmaier et al., 1992; Kuch et al., 2001; de Wit, 2002; Öberg et al., 2002; de Boer et al., 2003). Results of this work indicate that the concentrations of PBDEs in sewage sludge in China are approximately 10–100 times lower than those in Europe and North America. In fact, even the highest ∑PBDE values obtained in this work were lower than the average concentrations in Germany (Knoth et al., 2007) and other European countries.

Concentrations of ∑OCP (sum of HCHs, DDTs and HCB) ranged from 22.3 ng/g to 1151 ng/g (with a mean of 395 ng/g and a median of 329 ng/g) (Fig. 2). The concentrations of ∑OCP in 74% of the samples are lower than 500 ng/g. Concentrations of DDTs were higher than other OCPs in all samples, with T-DDT ranging from 10.5 ng/g in Linyi to 1065 ng/g in Chongqing. Compared with other countries (Table 3), OCPs levels in sludge in China are relatively high. Concentration were in the order of T-DDT > HCB > T-HCH (Fig. 3). For HCHs and HCB, the concentrations are comparable to the results reported from other countries. However, the concentrations of DDTs are much higher than those found in developed countries. This may relate to the protracted use and high percentage of the total DDT production and usage in China than in those countries (Li et al., 1998). Furthermore, dicofol, containing DDT as an impurity, is still used in China (Zhang et al., 2005) and may partially account for the DDT residues in Chinese sewage sludge.

HCB was present in all sludge samples collected in this work. Concentration of HCB ranged from 7.5 ng/g to 319 ng/g, with an average of 145 ng/g. HCB found in sludge may originate from several sources. For example, HCB occurred as a waste in the manufacture of several chlorinated products and some pesticides such as the fungicide PCNB (Courtney, 1979). In addition, HCB emissions have been linked to combustion and metallurgical processes involving the use of chlorine (Öberg and Bergström, 1985; Ballschmiter and Wittlinger, 1991).

3.2. Composition analysis

BDE-209 was found in all sludge samples except the four collected from Pingdingshan, Zaozhuang, Zhengzhou and Beijing1. The fraction of BDE-209 in the total PBDEs averaged 55% (all percentages in this section are weight based), with a median of 69%. Despite the fact that BDE-209 is the dominant congener in most samples, its fraction in sludge samples is generally lower than those found in the sediments of natural waters. Mai et al. (2005) found that BDE-209 constituted >90% of the total PBDEs in 70% of the surface sediment samples collected from the Pearl River Delta in southern China. We speculate that the relatively low BDE-209 fractions found in

Table 3
Comparison of OCP concentrations in sludge among countries (μg/g, dw)

Area	HCB	α-HCH	β-HCH	γ-HCH	δ-HCH	*p,p′*-DDE	*p,p′*-DDD	*o,p′*DDT	*p,p′*-DDT	*t*-HCH	*t*-DDT	Reference
China	0.145	0.002	0.017	0.001	0.001	0.143	0.065	0.012	0.010	0.020	0.229	This work
Canada	0.042	–	–	–	–	0.013	–	–	–	–	–	Webber et al. (1996)
UK	0.033	–	–	–	–	0.013	–	–	–	–	–	Stevens et al. (2003)
Greece	0.013	0.009	0.021	0.002	–	0.024	0.008	–	ND	–	–	Katsoyiannis and Samara (2005)
Switzerland	0.035	–	–	0.039	–	–	–	–	–	–	0.070	Frost et al. (1993)

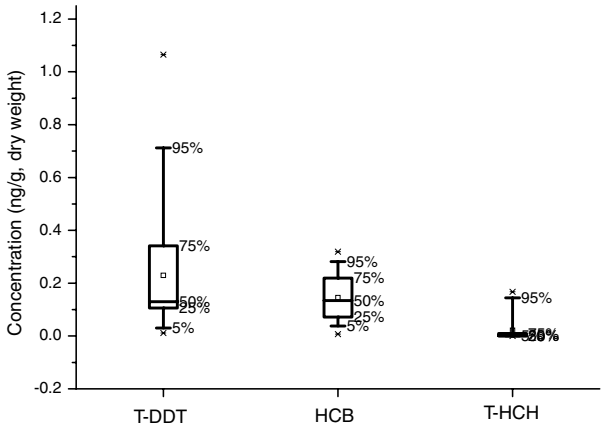

Fig. 3. Box-and-whisker plots for the concentrations of T-DDT, HCB, and T-HCH in sewage sludge in China. In the layout, the horizontal line in the box represents the median and the vertical bars display the range of the data.

sludge are the results of water treatment and sludge processing in the sewage treatment plants, especially the anaerobic sludge digestion, in which a portion of the BDE-209 can be transformed.

Among the other targeted PBDEs, it is obvious that BDEs-47, 99, and 183 were the dominant congeners (Fig. 4a), with their contributions ranging from 5.7% to 31% (average 24%), 0.5% to 33% (average 22%), 0.8% to 30% (average 13%), respectively. The relative abundance of these major congeners differs among reported sludge studies. For example, BDE-99 was found to be generally higher than BDE-47 in the 22 sludge samples in Sweden (Hagenmaier et al., 1992). The congener patterns can be affected by the sources, processing, age of the sludge as well as other factors.

Significant correlations were found between major congener pairs (Table 4). Strong correlation ($R = 0.814$, $P < 0.001$) existed between BDEs-47 and 99, the two major

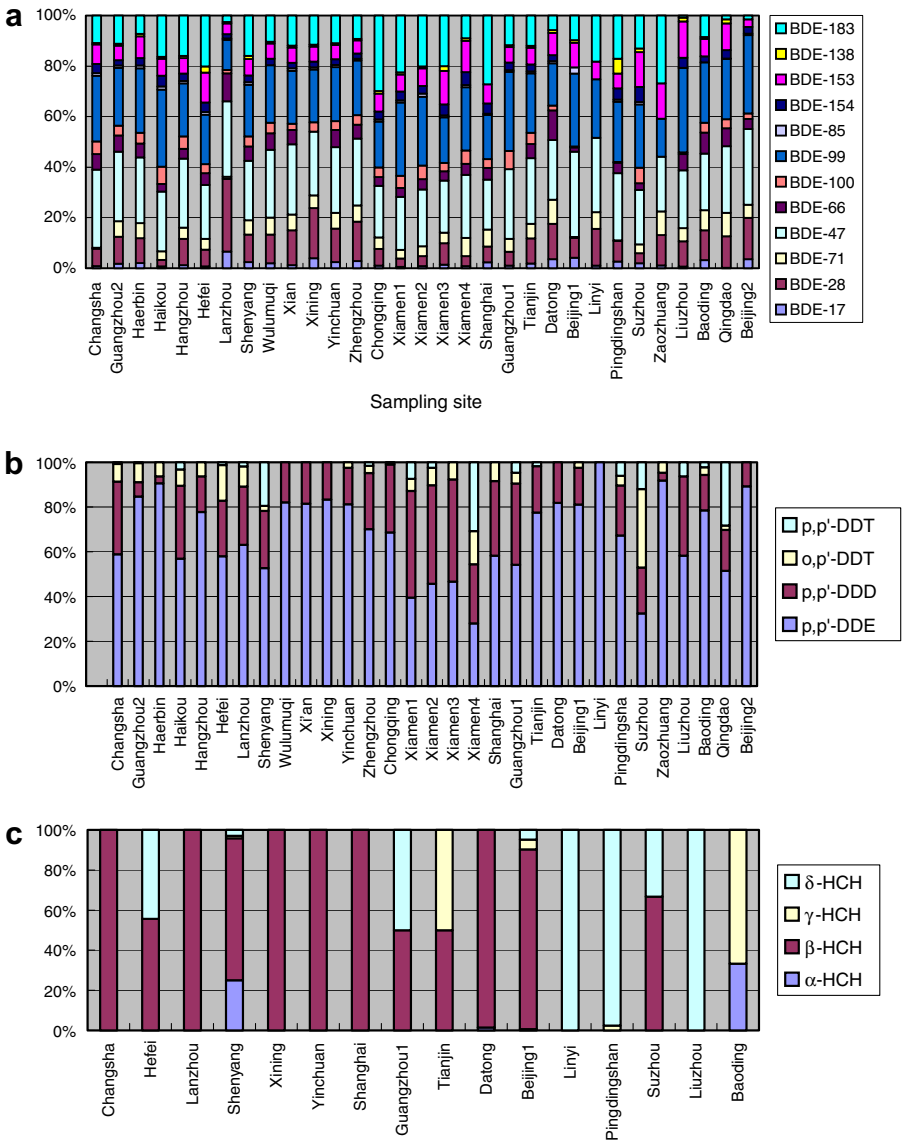

Fig. 4. The percent stacked columns of PBDE congeners, DDT, and HCH: (a) PBDE; (b) DDT; (c) HCH.

Table 4
Correlation matrix of the concentrations of PBDE congeners

	BDE-17	BDE-28	BDE-47	BDE-99	BDE-100	BDE-154	∑PBDE
BDE-28	0.950						
BDE-47	0.704	0.780					0.982
BDE-66	0.900	0.930	0.734				
BDE-99			0.814		0.841		0.851
BDE-138						0.984	
BDE-153				0.765			0.777
BDE-154							0.756

Correlation coefficient $R > 0.7$ ($P < 0.001$) indicates that the correlation between concentrations of the two congeners is statistically significant. Correlation coefficients are listed only when two congeners have significant linear relationship.

components of PeBDE technical mixture. Öberg et al. (2002) investigated PBDE concentrations (wet weight) in 104 sewage sludges, and found that tetra-, penta- and hexa-BDEs correlated well (with R between 0.92 and 0.98). The correlations with ∑PBDE were significant for BDEs-47 and 99 ($R = 0.98$ and 0.85, respectively; $P < 0.001$), but weak for BDE-183 (Table 4). The ratio of BDE-99 to BDE-100 ranged from 90:10 to 80:20 except for four samples. It is consistent with the mean of 86:14 by Knoth et al. (2007) and the value of 84:16 reported for technical PeBDE (Bromkal 70-5DE) (Sjödin et al., 1998). The results imply that the ratio of these two congeners did not change significantly through the wastewater processing. It was not surprising that a significant linear relationship was also found between BDE-209 and the total PBDEs ($R^2 = 0.99$, $P < 0.0001$).

Composition analysis showed that the major component of T-DDTs were *p,p′*-DDE and *p,p′*-DDD (Fig. 4b), with mean concentrations of 142.8 and 64.9 ng/g, respectively, compared with 10.0 ng/g for *p,p′*-DDT. It is well known that *p,p′*-DDT can be metabolized into *p,p′*-DDE and *p,p′*-DDD. High compositional percentage of *p,p′*-DDE and *p,p′*-DDD suggested that transformation of *p,p′*-DDT occurred either before or during the wastewater treatment process.

Half of the sludge samples contained detectable HCHs and the concentrations ranged from <LOD to 166.9 ng/g. The commercial HCH mixtures contain 60–70% α, 5–12% β, 6–10% γ, and 3–4% δ isomers (Kutz et al., 1991). Fig. 4c shows that β-HCH was the major HCH accounting for about 84% of total HCH in the sludge samples of this study. The β-isomer had the lowest water solubility and vapour pressure and thus a high affiliation to solids (Baschmann et al., 1988). α-HCH, although the dominant component in technical HCHs, can be easily dissipated from sludge due to its high Henry's Law constant. γ-HCH has a higher water solubility and Henry's Law constant than β-isomer. β-HCH is more stable and resistant to microbial degradation than other HCH isomers (Baschmann et al., 1988). The above factors are reflected by the high percentage α, β-HCH in sewage sludge found in this work.

3.3. Principal component analysis

Neither a longitudinal nor latitudinal geographic trend was identified in this work for the PBDE levels in sludge generated in sewage treatment plants in China. In order to examine the factors that may affect the PBDE levels in sludge, principal component analysis (PCA) was executed with SPSS 12.0 for Windows Release 12.0.0 (SPSS Inc.,

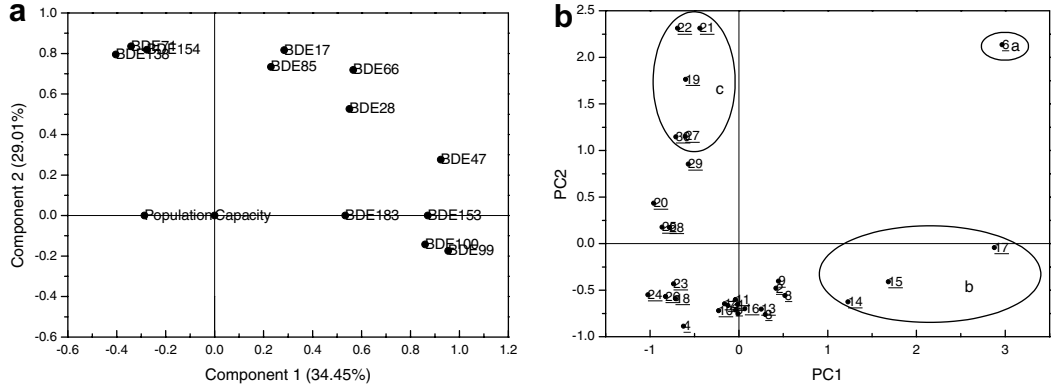

Fig. 5. Loading plot and score plot of PCA based on the PBDEs database. (a and b) Loading plot and score plot of PBDEs, respectively: (1) Changsha; (2) Guangzhou2; (3) Haerbin; (4) Haikou; (5) Hangzhou; (6) Hefei; (7) Lanzhou; (8) Shenyang; (9) Wulumuqi; (10) Xi'an; (11) Xining; (12) Yinchuan; (13) Zhengzhou; (14) Chongqing; (15) Xiamen1; (16) Xiamen2; (17) Xiamen3; (18) Xiamen4; (19) Shanghai; (20) Guangzhou1; (21) Tianjin; (22) Datong; (23) Beijing; (24) Linyi; (25) Pingdingshan; (26) Suzhou; (27) Zaozhuang; (28) Liuzhou; (29) Baoding; (30) Qingdao; (31) Beijing.

1989–2003). PCA extracted four components with eigenvalues greater than 1, which accounted for 89.3% of the variability in the original data. The first two components explained 63.5% of the variability in the data set. Fig. 5 depicts the loading and score plots for the PBDEs concentration data. In the loading plot, component 1 is highly correlated with BDEs-47 ($R^2 = 0.853$, $P < 0.05$), 99 ($R^2 = 0.909$, $P < 0.05$), 100 ($R^2 = 0.740$, $P < 0.05$), and 153 ($R^2 = 0.758$, $P < 0.05$), which are the dominant congeners of $\sum$PBDE. It accounts for 35% of the total variance. Component 2 accounts for 29% of the total variance and is positively characterized by BDEs-17 ($R^2 = 0.668$, $P < 0.05$), 85 ($R^2 = 0.540$, $P < 0.05$), 71 ($R^2 = 0.698$, $P < 0.05$), 138 ($R^2 = 0.632$, $P < 0.05$), 154 ($R^2 = 0.669$, $P < 0.05$), etc. This result implies that concentrations of different PBDE congeners in sludge do not correlate with the facility location, serving population, and processing capacity. This is consistent with the conclusions made by Hale et al. (2003) for North America, although in Europe higher levels were found in larger WWTPs (Gawlik and Bidoglio, 2004). The plot of PC1 versus PC2 (Fig. 5b) illustrates the two dimensional distribution of the samples into four clusters, which were characterized by varying proportions of particular PBDEs congeners. Cluster A has higher concentrations of all PBDE congeners, cluster B is characterized by high concentrations of BDEs-47, 99, 100, and 153, and cluster C by BDEs-17, 85, 71, 138, 154, etc. For cluster D, the PBDEs concentrations are lower than those of other three clusters. This plot highlights the lack of relationship between the concentrations of PBDE congeners in Chinese sewage sludge and sampling locations.

PCA was not used for data analysis of OCPs because some data points for the HCH isomers were below the limit of detection.

Analysis of concentrations of PBDEs along with OCPs in sewage sludge allowed these two classes of contaminants to be compared. Statistical analysis showed no correlation between PBDE and OCPs in sewage sludge, suggesting differences in their sources and behavior during wastewater treatment.

4. Conclusions

This work investigated the residue of levels of PBDEs and OCPs in sewage sludge collected from 31 WWTPs in 26 cities in China. The concentrations of $\sum$PBDEs in the sewage sludge in China are much lower than those in Europe and North America, despite the fact that the demand for deca-BDE reached to 13 500 tonnes in 2001 compared to the global demand of 70 000 tonnes in 2004. PCA analyses generated clusters characterizing different PBDE levels and congener patterns. Strong correlations between major PBDE congeners were found. OCPs levels in sludge in China were generally higher than those in other countries, which are believed to be the result of protracted use of DDTs in China.

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