

**DETERMINATION OF ORGANOCHLORINE PESTICIDES, POLYBROMINATED
DIPHENYL ETHERS IN SEWAGE SLUDGE IN CHINA**

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Introduction

A huge amount of the components consumer goods, such as polyurethane foam in upholstered furniture, enter sewers after being discarded and fragmented¹. So, various pollutants can enter the wastewater treatment plants via to sewers. As organohalogen compound, such as organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs) are hydrophobic, resistant to degradation and used in a completely uncontrolled and open manner, sewage sludge is assumed to be an environmental compartment in which these chemicals are re-enriched, and therefore the concentration of OCPs, PBDEs in sewage sludge from wastewater treatment plants can be used as an indicator of the general exposure and use of these compounds in a region². So, it is of interest to analyze the organic contaminants in sludge. However, available information concerning the concentrations of organic contaminants in Chinese sludge is rather limited.

In China, the usage of OCPs has been banned in 1983, but the recent study showed that their residues were still high³. Polybrominated diphenyl ethers (PBDEs) have widely distributed as environmental contaminates due to their use in abundance as additive flame-retardants³. They are emerging as a significant class of environmental contaminants, having been detected in a wide range of environmental samples and other samples such as human milk, blood plasma, and adipose tissue^{4,5}. Temporal trends in China indicate an increase in PBDE concentrations in experimental matrices, which parallels the rapidly increasing market demand for these compound⁷.

In this present study, a survey on OCPs and PBDEs in the sewage sludge from 31 wastewater treatment plants in China was carried out to reveal the contamination status, which may provide useful scientific contemporary data on the strategies for the corresponding pollution control.

Material and methods

A total 31 sewage sludge samples were collected from 26 cities in China between February 2005 and June 2005. These cities were selected to cover most regions of China.

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). EO5103 (including BDE-17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183) was purchased from Cambridge Isotope Laboratories (Andover, MA). ¹³C-labeled injection standard solutions of PCBs (1668a-IS) and ¹³C-labeled surrogate standard solutions of PBDEs (BDE-47, 99, 153) 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

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Corp (West Lafayette, IN) and used as calibration standard for BDE-209.

PBDEs analysis Sewage sludge were freeze-dried and homogenized by sieving through a stainless steel 75-mesh (0.5mm) sieve. Samples were spiked with ^{13}C -labeled surrogate standards and extracted with a mixture of 1:1 (v : v) dichloromethane (DCM): hexane for 24 h on a Soxhlet extractor. After extraction, about 15 g acidic silica (30%, w/w) was added to the flask to remove lipid. Activated copper powder was added to the extract to remove element sulfur.

The cleanup silica column (glass column with 15 mm inner diameter and 30 cm long) was packed from bottom to top with 1 g activated silica, 4 g basic silica (1.2%, w/w), 1 g activated silica, 8 g acid silica (30%, w/w), 1 g activated silica, 2 g AgNO_3 silica (10%, w/w) and 4 g anhydrous sodium sulfate. The extract was subjected to two multi-layered silica gel columns for cleanup. The concentrated extract (about 2 mL) was transferred to the column with multiple rinses and PBDE were eluted with 70 mL 1:1 (v:v) dichloromethane (DCM): hexane. The volumes of extract were further reduced with gentle nitrogen flow and the solvent was changed to 20 μL nonane in a minivial. Then, ^{13}C -labeled internal standards, 1668A-IS was added and the vial was vortexed to mix completely prior to GC injection. The quantification of PBDEs (expect for BDE-209) was performed on an Agilent 6890 gas chromatography coupled with an Autosepc Ultima high-resolution mass spectrometer (HRMS) (Waters Micromass, Manchester, UK) with an electron impact (EI) ion source. The column is a HP-5 (30 m \times 250 μm i.d. \times 0.1 μm film thickness) capillary column. Helium was as carrier gas at a constant flow rate of 1.2 mL min^{-1} . The oven temperature program was as following: the initial oven temperature was 90 $^\circ\text{C}$, which was held for 2 min. It was then increased to 210 $^\circ\text{C}$ at 25 $^\circ\text{C}$ min^{-1} , held for 1 min, 210 increased to 275 $^\circ\text{C}$ at 10 $^\circ\text{C}$ min^{-1} held for 10 min, finally to 330 $^\circ\text{C}$ at 25 $^\circ\text{C}$ min^{-1} and held for 10 min. Quantitative analyses of BDE209 was performed on an Agilent Model 6890 GC coupled with a Model 5975 MS with an electron impact (EI) ion source. Exact 2 μL of concentrated extract was injected into a DM-5MS (15 m \times 250 μm i.d. \times 0.1 μm film thickness) capillary column. Using helium as carrier gas at a constant flow rate of 1.2 mL min^{-1} , the oven temperature program was: the initial oven temperature was 90 $^\circ\text{C}$, which was held for 1 min. It was then increased to 340 $^\circ\text{C}$ at 20 $^\circ\text{C}$ min^{-1} 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 BDE209. The LOD for BDE-209 was 1 ng g^{-1} .

OCPs analysis The mixed OCPs standard solution including α -, β -, γ -, δ - HCH, *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, HCB was purchased from National Research Center for Certified Reference Materials of China and diluted to the desired concentration. The corresponding individual standards were also prepared for qualitative purpose. Florisil (100-200 mesh) was activated at 160 $^\circ\text{C}$ for 8h.

Prior to extraction, 100 μL of n-hexane containing 0.2 μg mL^{-1} PCB209 was added to 1 g freeze-dried samples. Sludge samples were ultrasonically extracted using 60 mL of 1:1 n-hexane:DCM. Lipids and other high molecular weigh interfering components were removed by adding acid silica gel to each flask after extraction. Then the extracts were cleaned up through a Florisil column (containing 6 g activated Florisil), and the column was eluted with 60 mL 4:1 n-hexane:DCM. Elution was concentrated, exchanged into hexane, and then adjusted to a volume of 0.5 mL with gentle nitrogen flow.

Samples were quantified on a Hewlett-Packard 6890 GC with electron capture detection (ECD), using DB-5 column (30 m \times 0.25 mm I.D., phase thickness 0.25 μm). GC conditions were as follows: carrier gas, N_2 at a rate of 1 mL/min; makeup gas, N_2 at 50 mL/min; temperature program, initial temperature 80 $^\circ\text{C}$, hold for 2min, increase at 10 $^\circ\text{C}$ /min to 140 $^\circ\text{C}$, increase at 4 $^\circ\text{C}$ /min to 280 $^\circ\text{C}$, hold for 5 min; injector temperature, 240 $^\circ\text{C}$; detector temperature, 300 $^\circ\text{C}$. Recovery test was conducted by spiking a standard solution of organochlorines

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(0.01-0.15 $\mu\text{g mL}^{-1}$). While t-HCH was expressed as a sum of α -HCH, β -HCH, γ -HCH and δ -HCH, t-DDT was defined as a sum of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD. The recovery tests of t-HCH, t-DDT and HCB yielded $74 \pm 3\%$, $94 \pm 10\%$, $98 \pm 3\%$, respectively. Detection limits, calculated as a signal-to-noise ratio of 3, were typically 0.04-0.12 ng g^{-1} sludge (dry weight). The relative standard deviation (RSD) for replicate analysis was less than 14% ($n = 3$).

Results and discussion

PBDE levels in sludge \sum PBDE refers to the sum of all 12 targeted PBDEs except for BDE209. Figure 1 is a stacked plot of concentration of PBDEs in sewage sludge. The concentration of \sum PBDE ranged from 6.2 ng g^{-1} to 57.0 ng g^{-1} (d.w.), with an average concentration of 20.0 ng g^{-1} . Relatively high concentrations of \sum PBDE was found in Lanzhou and Datong, reached to 57.0 ng g^{-1} and 44.7 ng g^{-1} , respectively. Figure 2 is a column plot BDE209 concentrations in sewage sludge. The concentrations of BDE209 ranged from ND (not detected) to 1108.7 ng g^{-1} (d.w.) with an average of 70.8 ng g^{-1} (d.w.). BDE-209 was found in all but four sludge samples, and is the dominant congener in most samples. Its fractions in the total PBDEs averaged at 55% (all percentages in this section are weight based), with a median of 69%. Among the other targeted PBDEs, it is obvious that BDEs 47, 99, and 183 are the dominant congeners (Figure 4), with their contributions ranging from 5.7% to 31% (average 24%), 0.5% to 33% (average 22%), 0.8% to 30% (average 13%), respectively.

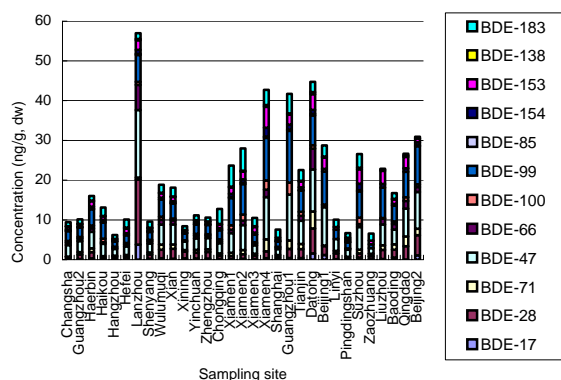


Figure 1. Stacked column of concentration of PBDEs in sludge.

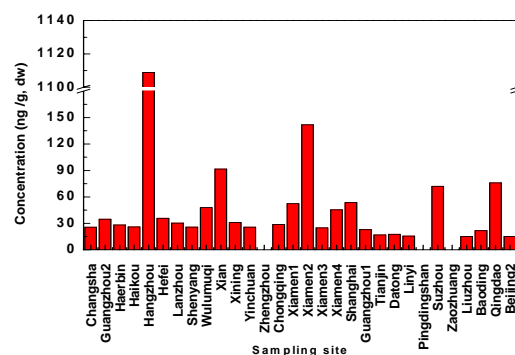


Figure 2. Column of concentration of BDE-209 in sludge.

OCP levels in sludge \sum OCP refers to the sum of HCHs, DDTs and HCB. The concentration of \sum OCP ranged from 0.02 $\mu\text{g g}^{-1}$ to 1.15 $\mu\text{g g}^{-1}$ (dw), with an average concentration of 0.39 $\mu\text{g g}^{-1}$. Contamination levels of each OCP were found to be in the order of t-DDT > HCB > t-HCH. For HCHs and HCB, the contamination is comparable to other results except for DDTs, which has much higher concentrations than those in developed countries. Composition analysis of DDTs showed that the major DDT component in sludge is *p,p'*-DDE and *p,p'*-DDD (Figure 3). The mean concentrations of *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT in the sludge being 0.14 $\mu\text{g g}^{-1}$, 0.06 $\mu\text{g g}^{-1}$ and 0.01 $\mu\text{g g}^{-1}$, respectively. It is well known that *p,p'*-DDT can metabolize into *p,p'*-DDE and *p,p'*-DDD. So high compositional percentage of *p,p'*-DDE and *p,p'*-DDD suggested that *p,p'*-DDT is metabolized during wastewater treatment process. Half of the sludge samples contained detectable HCHs with the concentration ranging from 0.0001 $\mu\text{g g}^{-1}$ to 0.17 $\mu\text{g g}^{-1}$. Composition analysis in Figure 4 showed that β -HCH is the major hexachlorocyclohexane isomer present in these samples. HCB is also present in all sludge samples. Concentration of HCB ranged from 0.01 $\mu\text{g g}^{-1}$ to 0.32 $\mu\text{g g}^{-1}$, with the average value of 0.15 $\mu\text{g g}^{-1}$.

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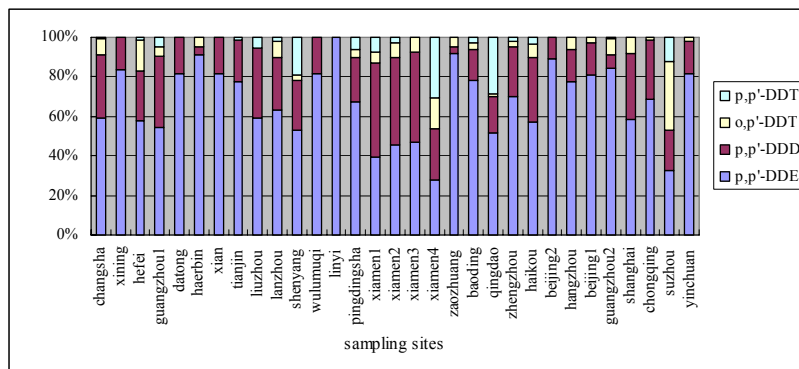


Figure 3 Composition analysis of DDTs in sludge

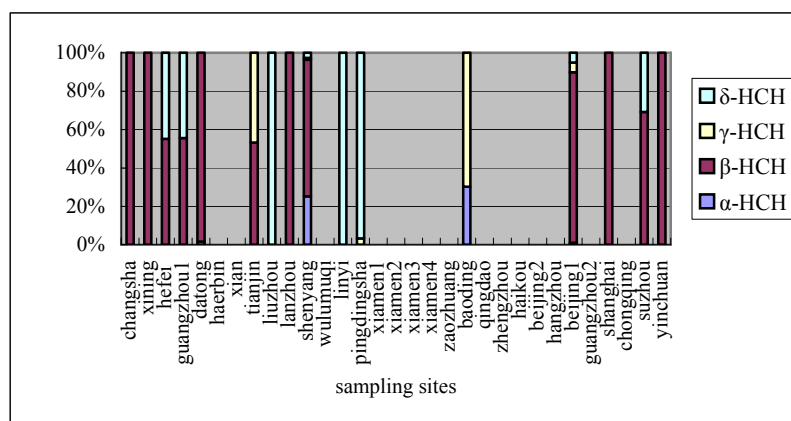


Figure 5 Composition analysis of HCHs in sludges

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