Current Levels and Composition Profiles of Emerging Halogenated Flame Retardants and Dehalogenated Products in Sewage Sludge from Municipal Wastewater Treatment Plants in China

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Supporting Information

ABSTRACT: Occurrence of new toxic chemicals in sludge from wastewater treatment plants (WWTPs) is of concern for the environment and human health. Alternative halogenated flame retardants (HFRs) are a group of potentially harmful organic contaminants in the environment. In this study, a nationwide survey was carried out to identify the occurrence of HFRs and their potential dehalogenated products in sewage sludge from 62 WWTPs in China. Of all 20 target chemicals analyzed, decabromodiphenyl ethane (DBDPE), hexabromocyclododecane (HBCD) and 1, 2-bis (2,4,6-tribromophenoxy)-ethane (BTBPE) were detected in all sludge samples, and the concentrations were in the range of 0.82–215, 0.09–65.8, and 0.10–2.26 ng g⁻¹ d.w., respectively. Dechlorane Plus (DP) was found in 60 of 62 samples, and the concentration ranged from nd–298 ng g⁻¹ with a mean of 18.9 ng g⁻¹ d.w. The anti-DP fractional abundance f_{anti} (0.79) in the samples was much higher than the commercial DP composition ($f_{\text{anti}} = 0.59$), indicating a stereoselective degradation. Comparison with global sludge concentrations of HFRs indicate that China is at the medium pollution level in the world. Principal components analysis revealed that strong correlations existed between ln-transformed concentrations (natural logarithm) of the dominant BFRs and total organic carbon (TOC) as well as industrial wastewater proportion, influent volume and serving population. Significant linear relationships ($R = 0.360\text{--}0.893$, $p < 0.01$) were found among emerging brominated flame retardants (BFRs), suggesting their common commercial applications and release sources to the environment. Two kinds of dehalogenated products, pentabromocyclododecane (PBCD) and undecachloropentacyclooctadecadiene (Cl₁₁-DP), derived from HBCD and DP, were also identified in sewage sludge for the first time.

INTRODUCTION

Halogenated flame retardants (HFRs) mainly include two classes of commercial organobromine and organochlorine compounds for fire-retardant application in common household objects such as furniture, mattresses, textiles, plastics, resins, baby products, and electronic equipment.¹ Many HFRs have been synthesized and used extensively in high volumes for a decade or more and therefore prevalent in the environment.^{2,3} Of the commercialized HFRs, brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) were most widely used.⁴ However, due to the environmental and public health concerns, penta-BDE and octa-BDE have been banned under the Stockholm Convention on Persistent Organic Pollutants (POPs) and Deca-BDE are also being phased out in many countries.²

Restrictions of PBDEs have led to the increasing production and use of other alternative HFRs.⁵ As a result, a number of

emerging HFRs have been widely identified in diverse environmental matrices worldwide and pose a potential risk to the environment and human health.⁶ Representative emerging HFRs include 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE), pentabromoethylbenzene (PBEB), decabromodiphenyl ethane (DBDPE), tetrabromo-*o*-chlorotoluene (TBOCT), hexabromocyclododecane (HBCD), 1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane (TBECH), polybrominated biphenyls (BB153 and BB209), hexabromobenzene (HBB), pentabromotoluene (PBT), hexachlorocyclopentadienyl dibromocyclooctane (HCDBCO), tetrabromo-*p*-xylene (pTBX), tribromobenzene (TBB) and Dechlorane Plus (DP).^{2,7,8}

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Among these emerging HFRs, DBDPE, BTBPE, HBCD, and DP were the most frequently detected contaminants in the Chinese environment.^{9–12}

DBDPE is structurally similar to BDE209 and has been introduced into the market as a principal alternative for Deca-BDE since the early 1990s.⁷ Both DBDPE and BDE209 are mainly used in textile and plastic applications. Recently, DBDPE have been frequently detected in diverse environmental matrices.^{11,12} Zhu et al. reported an increasing trend substitution of deca-BDE for DBDPE in China.¹³ HBCD is widely used as an additive BFR in the polystyrene foams, thermal insulation, and electrical products, which have been identified to be ubiquitous contaminants and now considered as POPs candidates.^{1,9,14} Polybromobenzenes including HBB, PBT, PBEB were manufactured from 1980s and have been used in polyester, latex, textiles, electronics, and plastic goods.¹⁵ Some polybromobenzene pollutants have been demonstrated to be bioaccumulative and toxic.^{16,17} DP is a highly chlorinated flame retardant with a similar structure to the pesticide mirex and consists of two isomers (*syn*- and *anti*-DP). It was suggested as a substitute to Deca-BDE in polymeric applications since the 1960s.¹⁸ DP analogues including Dechloranes 602 (Dec602), 603 (Dec603), and 604 (Dec604) were commercialized as fire retardants in the 1970s. DP is now categorized by the U.S. EPA as a high production volume chemical with the annual U.S. production up to 450 tons.³ Dec602, 603, and 604 are on the Canada's Nondomestic Substances List. Since the first reports on environmental occurrence of DP in 2006¹⁹ and other Dechloranes in 2009,²⁰ subsequent studies have indicated that DP and some analogues are potentially worldwide contaminants.^{3,21}

Wastewater treatment plants (WWTPs) are commonly considered as a major sink for many organic contaminants through receiving domestic and/or industrial sewage.^{22,23} Due to high octanol–water partition coefficient (K_{OW}) and organic carbon–water partition coefficient (K_{OC}), HFRs are preferentially disposed into sludge partition during wastewater treatment.^{24,25} Therefore, sewage sludge can be an excellent medium for determining the environmental occurrence and discharge of emerging HFRs, which could also re-enter the ambient environment via biosolids application.^{25,26} Detailed investigations on several emerging HFRs in sludge have been carried out in Spain,^{25,27} Korea,^{22,28} and the U.S.,²⁹ whereas only limited number of samples or types of HFRs have been analyzed in other countries.^{30–34} However, very few studies have been reported on alternative HFRs and their potential degradation products in sewage sludge from China.¹¹

China is now one of the world's major flame retardants manufacturers with an total annual production up to 200 000 tons.^{35,36} Among them, the annual production volumes for Deca-BDE, DBDPE, HBCD and DP have been reached 20 000, 12 000, 7500, and 300–1000 tons in recent years, respectively.^{11,14,37} BTBPE, HBB, and PBT are also produced and used in China, but their production volumes are not available.¹⁰ No manufacturing information is available in China for other HFRs to date. China is also one of the world's largest consumers of flame retardants with an annual growth rate at 7% in consumption demand.^{38,39} With the increasing production and usage for HFRs in China, discharges from industrial process and emission from household products could result in elevated levels of emerging HFRs in the Chinese environment.^{9,11,40,41} Since WWTP usually receives input from large

communities or commercial zones, the resulting sewage sludge can be used as an indicator for investigating the integrated emission of organic pollutants at a population based level. In this work, we carried out the first nationwide survey to determine emerging HFRs and several degradation products in sludge from WWTPs in China. The objectives of this study are to reveal current pollution levels of emerging HFRs, identify the occurrence of potential dehalogenated products in sewage sludge, examine potential factors affecting the accumulated concentrations, and evaluate environmental emission of HFRs via land-application sludge in China.

MATERIALS AND METHODS

Sample Collection. A total of 62 sewage sludge samples from municipal WWTPs representing various regions in China were collected during August 2010 to August 2013, covering 36 cities in 21 provinces and municipalities across China. The sampling map is shown in Supporting Information (SI) Figure S1. About 0.5–1.0 kg wet weight of the freshly digested sludge as grab samples was obtained from WWTP dehydration process, packed in aluminum foil, sealed in Ziplock bags and then immediately transported to the laboratory. All samples were freeze-dried, homogenized, and stored in a freezer at -20°C until extraction. Basic characteristics of the selected WWTPs are provided in the SI Table S1, including wastewater treatment capacity, daily processing volume, serving population, sewage sources (domestic, industrial, or mixed) and biotreatment techniques during secondary treatment process as well as total organic carbon (TOC) for individual sludge samples.

Instrumental Analysis and Quantification. In this study, 13 current-use non-PBDE BFRs (TBECH, pTBX, TBOCT, PBT, PBEB, HBB, TBB, HCDBCO, BB153, BB209, BTBPE, HBCD, and DBDPE), four CFRs (*syn*- and *anti*-DP, Dec602, Dec603, and Dec604) and three dehalogenated products (pentabromocyclododecane, PBCD for HBCD, *anti*-Cl₁₁-DP, and *anti*-Cl₁₀-DP for DP) were measured in sludge samples (full name and structure information on the compounds are shown in Table S2, SI). The procedures of sample extraction, cleanup, and instrumental analysis were based on our previously developed methods with minor modifications.^{7,42,43} Briefly, 0.5–1.0 g of sample were spiked and then extracted with accelerated solvent extractor (ASE). Five g of acidic silica (40%, w/w) was added into the extract to remove most of lipids. After primary purification, a multilayer silica column was used for further cleanup with 70 mL of hexane/dichloromethane (5:1, v/v). Detailed sample preparation procedure can be found in the SI.

Target chemicals were analyzed using a high-resolution gas chromatograph/low-resolution mass spectrometer (HRGC/LRMS, SHIMADZU2010 Ultra, Japan) with electron capture negative ionization (ECNI) in selected ion monitoring (SIM) mode. The MS ion source and interface temperatures temperature were 150 and 280 $^{\circ}\text{C}$, respectively. Helium and methane were used as carrier and reagent gas, respectively. The analytes were separated on a 15 m DB-5MS capillary column (0.25 mm i.d. $\times$ 0.1 μm film thickness, J&W Scientific, U.S.) with a constant flow rate of 1 mL/min. The GC temperature program was as follows: hold at 100 $^{\circ}\text{C}$ for 4 min; then increase to 150 $^{\circ}\text{C}$ at 8 $^{\circ}\text{C}/\text{min}$ and hold for 4 min; finally ramp to 300 $^{\circ}\text{C}$ at 12 $^{\circ}\text{C}/\text{min}$ and hold for 13 min. The injection was performed with 1 μL in splitless mode. The following primary/secondary ions (m/z) were used for quantification and confirmation: 79/81 for all non-PBDEs BFRs, 340.8/613.6

Table 1. Descriptive Statistics of Concentrations of the Identified Halogenated Flame Retardants and Their Selected Dehalogenated Products in Sludge from WWTPs in China (ng/g d.w.)

type	analyte	DF ^a (%)	mean	median	P95 ^b	range	AP ^c (%)
BFRs	PBT	82.3	0.07	0.06	0.20	nd ^d –0.29	0.1
	PBEB	75.8	0.04	0.04	0.09	nd–0.12	0.1
	HBB	88.7	0.68	0.55	1.54	nd–3.22	0.9
	BTBPE	100	0.95	0.86	2.08	0.10–2.26	1.3
	DBDPE	100	52.2	41.1	154	0.82–215	73.1
	∑HBCD	100	17.3	16.0	39.3	0.09–65.8	24.2
	∑PBCD	67.8	0.21	0.20	0.46	nd–0.72	0.3
CFRs	Dec602	14.5	0.02	n.d.	0.08	nd–0.21	0.1
	Cl ₁₁ -DP	41.9	0.18	n.d.	0.61	nd–4.15	0.9
	<i>syn</i> -DP	74.2	3.77	1.13	13.9	nd–59.6	20.0
	<i>anti</i> -DP	96.8	15.2	3.28	74.5	nd–238	79.0
	∑DP	96.8	18.9	4.25	91.1	nd–298	99.0

^aDetection frequency. ^b95th percentile. ^cAveraged proportion in each group. ^dNot detected or below detection of limitation.

for Dec602, 635.6/637.6 for Dec603, 79/81 for Dec604, 651.8/653.8 for *syn*- and *anti*-DP, 617.7/619.7 for Cl₁₁-DP, 583.8/585.8 for Cl₁₀-DP, 369.7/371.7 for ¹³C₁₂-PCB138, and 507.9/509.9 for ¹³C₁₂-PCB209. Considering possible thermal decomposition of HBCD in GC analysis,^{7,44} we assessed the possible factors resulting in the thermal degradation and found the injection port temperature was a critical factor when optimizing the temperature program on a 15 m column (SI Figure S2). The low injection port temperature was suitable for determination of HBCD but not for sensitive determination of other high molecular weight analytes. Therefore, two injections for each sample at different injection temperature were performed in GC analysis (220 °C for HBCD and PBCD and 280 °C for other targeted HFRs, SI Figure S3). The α , β and γ -HBCD isomers could not be separated by GC, so only the sum of three isomers ($\sum$ HBCD) was reported.⁷ All the target compounds can be well resolved with different response factors (Figure S4, SI). Due to possible interference from 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE154) in analysis of BB153 on 15 m column,⁷ the qualitative results were checked on DB-XLB (30m $\times$ 0.25 mm i.d., 0.25 μ m film thickness) column. Quantification was performed by internal standard calibration, using the primary ion of each analyte. Seven point calibration curves with concentration from 0.2 to 200 ng/mL were used for the quantification of HFRs and potential dehalogenated products with the regression coefficients of $R^2 \geq 0.99$.

Quality Assurance and Quality Control (QA/QC). Strict quality assurance and control measures were implemented to ensure accurate identification and quantification of the analytes. All glassware was soaked in a detergent and solvent rinsed, then heated at 450 °C overnight prior to use. A procedural blank was analyzed with every batch of eight samples. The concentrations of HFRs and selected dehalogenated products in procedural blanks were all below the method detection limit (MDL). All data reported herein were not blank corrected and on a dry weight basis. Estimating the recoveries in this study was similar to that described lately.²³ One sample was randomly selected for matrix spike and sample duplicate analyses, with every batch of samples analyzed. HFRs and their corresponding surrogate standards were spiked at 10 ng and passed through the entire analytical procedure. The average recoveries of target analytes and three surrogates in spiked samples were $92.6 \pm 15.2\%$ and $88.5 \pm 16.7\%$, respectively. The average coefficient of variation

of triplicate analyses was $\leq 18\%$. The surrogate standard recoveries in all sludge samples ($n = 62$) ranged from 80.5% to 114.8%. The concentrations reported in this study were corrected based on the surrogate recoveries. The MDL was calculated based on 5 times the signal-to-noise (s/n) ratio, which ranged from 0.01 (PBT) to 0.2 (DBDPE) ng g⁻¹ for non-PBDEs BFRs, and from 0.01 (Dec602) to 0.05 (DP) ng g⁻¹ for Dechloranes.

Statistical Analysis. The concentrations below MDL were replaced by half of the MDL. Pearson's correlation analysis was conducted to investigate the correlations among the concentrations of different HFRs and their potential dehalogenated products in sewage sludge samples. Principal component analysis (PCA) was performed to examine the relationships between HFRs in the sludge and the WWTP characteristics using the varimax rotation method with Kaiser normalization. All statistical analysis were performed using IBM SPSS Statistics 20.0 (IBM Corp, 1989–2011) and statistical significance was set at $p < 0.05$ unless otherwise specified.

RESULTS AND DISCUSSION

Of all target chemicals analyzed, DBDPE, BTBPE, HBCD, PBT, PBEB, HBB, DP, Dec602 and two dehalogenated products (PBCD and Cl₁₁-DP) could be detected in sludge from Chinese WWTPs. Other non-PBDEs BFRs, Dec603, Dec604 and the dehalogenated product Cl₁₀-DP were all under MDL in all sludge samples. Therefore, the following discussion was focused on the detectable HFRs and emerging dehalogenated products in WWTPs. All measured concentrations were presented on a dry weight (d.w.) basis. The detailed dry-weight and TOC-normalized concentrations for individual analyte in sewage sludge are shown in the SI Table S3 and S4, respectively.

Emerging Brominated Flame Retarders and Potential Dehalogenated Products in Sludge. Statistical results of concentrations for the identified HFRs and their potential dehalogenated products in sewage sludge are summarized in Table 1 and illustrated by Box-Whisker plots in the SI Figure S5. DBDPE, HBCD, and BTBPE were more frequently detected than PBT, PBEB, and HBB. Thereinto, DBDPE was the most abundant and predominant BFR, which accounted for 73.1% of total emerging BFRs, with the range of 0.82–215 ng g⁻¹ (mean 52.2 ng g⁻¹), followed by HBCD and BTBPE, with the range of 0.09–65.8 ng g⁻¹ (mean 17.3 ng g⁻¹) and 0.10–

Table 2. Pearson's Correlation Matrix for Concentrations of Emerging HFRs and Their Selected Dehalogenated Products in Municipal Sludge Samples^a

	PBT	PBEB	HBB	BTBPE	DBDPE	ΣHBCD	ΣPBCD	ΣDP	Cl ₁₁ -DP
PBEB	0.551**								
HBB	0.552**	0.377**							
BTBPE	0.477**	0.377**	0.568**						
DBDPE	0.556**	0.360**	0.631**	0.558**					
ΣHBCD	0.517**	0.475**	0.612**	0.494**	0.893**				
ΣPBCD	0.516**	0.556**	0.517**	0.599**	0.750**	0.888**			
ΣDP	0.161	0.189	0.128	0.203	0.143	0.082	−0.019		
Cl ₁₁ -DP	0.078	0.173	0.064	0.251*	0.112	0.053	−0.013	0.921**	
Dec602	0.142	0.216	0.099	0.148	0.086	0.047	−0.054	0.982**	0.889**

^aThe symbols ** and * represent significant correlation at $p < 0.01$ and < 0.05 levels, respectively.

2.26 ng g^{−1} (mean 0.95 ng g^{−1}), respectively. The concentrations of DBDPE and HBCD were slightly lower than our previously reported levels of BDE-209 (not detected (nd)–1109 ng g^{−1} with an average level of 68.5 ng g^{−1}) in sewage sludge.⁴⁵ It is noteworthy that, the nationwide average level of DBDPE in sewage sludge were far less than those (266–1995 ng g^{−1} with average level of 1183 ng g^{−1}) from the Pearl River Delta, which is one of the most industrialized and urbanized electronic/electrical equipment manufacturing bases in southern China.¹¹

The emerging compounds PBT, HBB, and PBEB were also identified in most sludge samples but with much lower levels compared with DBDPE and HBCD. PBT and HBB were detected in 51 and 55 of the 62 samples, respectively, and their concentrations ranged between nd–0.29 and nd–3.22 ng g^{−1}, respectively. PBEB was detected in quantifiable level in 47 of the 62 samples with the range of nd–0.12 ng g^{−1}. To date, there are no comparable sludge data on the occurrence of emerging BFRs other than DBDPE and BTBPE in China.¹¹ Considering the results in other environmental matrices, the total concentrations of PBT, HBB and PBEB in sewage sludge were comparable to those in surface sediments (nd–2.96 ng g^{−1}) from Pearl River Delta.¹⁰

Significantly linear relationships ($R = 0.360–0.893$, $p < 0.01$) were found among these emerging BFRs in sludge from these WWTPs (Table 2), suggesting their similar commercial applications and release sources in the environment. A distinguishable geographical trend of higher concentrations of emerging BFRs, especially for DBDPE and HBCD, was found in the eastern regions than the central and western regions of China (Figure 1), which was similar to the geographical distributions of OH-PBDEs and emerging quaternary ammonium compounds in sewage sludge of China in our previous works.^{46,47} The spatial distribution pattern might stem from high-volume usage of BFRs-containing consumer products and the corresponding industrial production and application in the eastern regions of China (Figure S6, SI). The production of DBDPE is growing rapidly in recent years as substitutes to BDE-209.⁴⁸ The higher concentrations of DBDPE in sewage sludge may imply that it is likely becoming one of the major emerging BFRs in the Chinese environment.¹⁰

Identification of potential degradation and/or biotransformation products of parent compound BFRs during sewage treatment in WWTPs has raised concerns on their environmental fate and potential adverse effect to the ecosystem. In the present study, a degradation product of HBCD, pentabromocyclododecane (PBCD) could be found in 42 of the 62 sludge samples with the concentration range of nd–0.72 ng g^{−1} and an

Figure 1. Spatial distributions of average levels for emerging BFRs (A), and ΣHBCD, ΣDP and their selected dehalogenated products (B) in sewage sludge samples in different provinces/municipalities across China.

average value of 0.21 ng g^{−1}. The degradation product PBCD had also been previously identified in other environmental matrices. The concentrations of ΣPBCD in sludge was lower than those reported in sediments (nd–20 ng g^{−1}) from Japanese riverine environment⁴⁹ and indoor dust (nd–6438 ng g^{−1}) in UK.⁵⁰ Moreover, the breakable carbon–bromine bond of HBCD can be expected to generate significant degradation or biotransformation in biological systems.⁵¹ In the present study, a significantly high correlation between concentrations of

$\sum$ PBCD and $\sum$ HBCD in the sludge samples ($R = 0.888$, $p < 0.01$, Table 2) could suggest a concentration-dependent degradation of HBCD via reductive debromination in the sludge. Although there are a few reports on biotransformation of HBCD in biota,^{52–54} to our knowledge, this is the first report about the extensive occurrence of PBCD in municipal sewage sludge.

Emerging Chlorinated Flame Retarders and Dechlorinated Products in Sludge. As shown in Table 1, DP could be detected in 96.8% of the sludge samples, and the concentrations ranged from nd to 298 ng g^{-1} with a mean value of 18.9 ng g^{-1} , which indicated widespread distribution of this group of compounds in the Chinese sludge. Similar to the spatial distribution of emerging BFRs (Figure 1), relatively higher concentrations of DP was found in the eastern regions, especially in coastal areas, where the higher urbanization and industrialization may contribute to the higher DP level.¹² Comparing to the other targeted compounds, DP exhibited higher concentrations than HBCD, but lower than DBDPE. Dec602 were only found in small proportions of the samples (10 WWTPs) with the maximum of 0.21 ng g^{-1} whereas Dec 603 and Dec 604 were not detected in sludge, showing less contamination by these three chemicals due to their low usage in China. No significant correlations were found between the measured concentrations of emerging BFRs and Dechloranes in sludge samples except for BTBPE versus Cl_{11} -DP ($R = 0.251$, $p < 0.05$) (Table 2).

For two DP isomers analyzed, the detection frequencies of *anti*-DP and *syn*-DP were 96.8% and 74.2%, respectively, and *anti*-DP was the dominant residue observed in sludge. The *anti*-DP fractional abundance (f_{anti}) is generally used to elucidate the behavior and fate of DP in the environment, which is expressed as $f_{\text{anti}} = [\text{anti-DP}] / ([\text{anti-DP}] + [\text{syn-DP}])$.⁴³ In this study, the average f_{anti} value of sewage sludge ($f_{\text{anti}} = 0.79$) was significantly higher than the commercial DP composition in the Chinese market ($f_{\text{anti}} = 0.59$), indicating a preferential depletion of *syn*-DP relative to *anti*-DP isomer during the sewage treatment processes. The high f_{anti} profiles in sewage sludge were consistent with previously reported data in soil and sediment,^{14,41,55–57} further demonstrating that stereoselectively microbial mediated degradation of DP could lead to the relative enrichment of *anti*-DP in sludge, soil and sediment.

For two potential degradation products from DP analyzed, Cl_{11} -DP [DP-1Cl] was detected in 26 of the 62 sludge samples while Cl_{10} -DP [DP-2Cl] was not detected in any of the WWTPs investigated. This is consistent with the recent reports in wildlife^{58,59} and human beings.⁶⁰ The concentrations of Cl_{11} -DP were in the range of nd– 4.15 ng g^{-1} with an average of 0.18 ng g^{-1} , which were apparently higher than those in coastal sediments (nd– 0.04 ng g^{-1}) in north China.⁶¹ A significant correlation was also found between the concentrations of Cl_{11} -DP and DP in sewage sludge ($R = 0.921$, $p < 0.01$). Both high correlations between Cl_{11} -DP vs DP and $\sum$ PBCD vs $\sum$ HBCD in sewage sludge could imply that dehalogenation is a degradation pathway for HFRs during wastewater treatment.

Global Comparisons of HFR Concentrations in Sludge among Different Countries. There is still lack of environmental data about emerging HFRs, especially for BTBPE, HBB, PBEB, PBT, and their dehalogenated products, in sludge among different countries in the world. So only comparisons for the surveyed concentrations of emerging BFRs, HBCD and Dechloranes in sludge from Chinese WWTPs with those available from other countries are presented in SI Table S5–S7,

respectively. As shown in SI Table S5, the mean DBDPE concentration (52.2 ng g^{-1}) in sludge in China was comparable to those reported in Spain,^{25,27,31} Singapore, Sweden, England, Germany, the Czech Republic and South Africa,³⁰ and comparatively higher than those in Australia, the U.S., Canada, New Zealand,³⁰ and Norway,³³ but evidently lower than the values found in Korea (237 ng g^{-1})²² and Switzerland (128 ng g^{-1}).³⁰ The mean sludge BTBPE concentration (0.95 ng g^{-1}) in this study was similar to those reported for Korea (1.57 ng g^{-1})²² and Norway (1.27 ng g^{-1}),³³ but much lower than the level found in the U.S. (10.1 ng g^{-1}).²⁹ The mean sludge HBB concentration (0.68 ng g^{-1}) was equivalent to that in Spain (0.44 ng g^{-1}),²⁵ but 3 orders of magnitude lower than the value in Germany (329.4 ng g^{-1}).⁶² For PBEB, a lower mean level (0.04 ng g^{-1}) was observed in China compared to Spain (0.25 ng g^{-1}).²⁵ No PBT concentration data in sludge are available for comparison.

As shown in SI Table S6, the mean levels of $\sum$ HBCD (17.3 ng g^{-1}) in this work were lower than those reported in Korea²⁸ and European countries including Spain,^{25,63} Sweden,⁶⁴ Switzerland,⁶⁵ England, Ireland and Netherland.⁶⁶ The relatively higher $\sum$ HBCD levels in European sludge might be attributed to the larger consumption in Europe in the past years.⁶⁷ As shown in SI Table S7, the mean level of $\sum$ DP in sludge samples from China (18.9 ng g^{-1}) was comparable to the concentrations reported from Spain (32.5 ng g^{-1})³² and the U.S. (25 ng g^{-1}),²⁹ whereas the fractional abundance f_{anti} (0.79) was higher than the values in Spanish (0.69, 0.71) and U.S. (0.60) sewage sludge. Dec602 was sporadically detected in Chinese and Spanish sludge with similarly low concentrations, while Dec603 could be widely detected in Spain, but not found in China in the present study.²⁷

PCA for Evaluating Potential Factors Affecting HFRs Levels in Sewage Sludge. A wide range of potential factors could influence pollutant concentrations in sludge from different WWTPs. These factors would involve treatment capacity, influent volumes, serving population, treatment techniques as well as different residential and industrial sources.^{23,29} Additionally, TOC could also affect the final concentrations of pollutants in sludge. In this study, principal component analysis (PCA) was used to examine how these factors might affect the HFR concentrations in the sludge samples.

DBDPE, BTBPE, HBCD, and DP with detection frequency over 95% were included in the analysis. PCA extracted two components with eigenvalues greater than 1, which contributed to a total of 72.4% of the cumulative variances. Figures 2 illustrated the loading and score plots of the two principal components. In the loading plot, component 1 accounted for 59.4% of the total variance and had high correlation with DBDPE, HBCD, TOC, IWF (industrial wastewater fraction) and BTBPE, but also had moderate correlation with APV (actual processing volume) and SP (serving population). Component 2 accounted for 13.0% of the total variance and had strong positive loadings on DP, APV, SP. The score plot of PCA in Figure 2 was grouped by sewage source of WWTPs (DW: domestic wastewater; MW: mixed domestic and industrial wastewater), which indicated the pattern profiles of HFRs in DW and MW in China are rather different. Combining the visualization of loading and score plot, PCA results implied DBDPE, HBCD, and BTBPE were the predominant compounds among the targeted HFRs in most of the MW source sludge. The cluster of these compounds with TOC

Figure 2. Loading plot (A) and score plot (B) (grouped by sewage source, DW: domestic wastewater; MW: mixed domestic and industrial wastewater) of HFRs concentrations in all sludge samples from the principal component analysis.

suggested that TOC might be a major factor for BFRs governing the transport and solids-liquid distribution. Industrial wastewater could be a more important source for the BFRs relative to domestic wastewater. Moreover, DP was separated from the three HFRs and negatively correlated with the three HFRs and TOC in some WWTPs, likely reflecting different use patterns of these chemicals in the regions. Leakage of DP from consumer goods via domestic wastewater could favor the association of DP with the DW source sludge.

Pearson's correlation analysis show significant relationships exist between ln-transformed HFRs concentrations (ln HFRs) and industrial wastewater fraction (ln IWF) ($R = 0.544\text{--}0.662$, $p < 0.05$), further suggesting that release of these compounds is associated with industrial activity, which is in agreement with De la Torre's previous report.³² Besides, ln-transformed concentrations of DBDPE, HBCD, BTBPE and DP were also correlated with sludge TOC (ln TOC) ($R = 0.562\text{--}0.848$, $p < 0.05$), actual processing volume (ln APV) ($R = 0.555\text{--}0.659$, $p < 0.05$) and serving population (ln SP) ($R = 0.632\text{--}0.731$, $p < 0.05$). A similar relationship between population density and HFRs concentrations can also be observed for the council districts of Hong Kong.¹² This provides a general indication that levels of emerging HFRs in sewage sludge tend to be higher in those WWTPs with larger daily loading per capita. So, highly elevated levels of DBDPE, HBCD, and DP in sludge samples (NO.5, 6, 43, 44 in SI Table S3) could be influenced by the dense population and intensive industrial activities.

MLR Modeling to Help Predict HFR Levels in Sewage Sludge with TOC and the Major WWTP Characteristics. Multivariate linear regression (MLR) was tentatively performed

to predict HFR levels in Chinese sewage sludge with TOC and the major concentration-related WWTP characteristics, including IWF, APV, and SP. The concentrations of the dominant HFRs such as BTBPE, DBDPE, $\sum$ HBCD, and $\sum$ DP in sewage sludge could be predicted from TOC and three major WWTP characteristics using the four-variable models with statistical significance. The linear regression equations as $\text{Ln Analyte} = a + b \times \text{Ln TOC}\% + c \times \text{Ln APV} + d \times \text{Ln IWF} + e \times \text{Ln SP}$ ($p < 0.05$) are shown in Table 3.

Table 3. Multivariate Linear Regression Equation as Ln Analyte = $a + b \times \text{Ln TOC}\% + c \times \text{Ln APV} + d \times \text{Ln IWF} + e \times \text{Ln SP}$ ($p < 0.05$) for Four Dominant Flame Retardants in Chinese Sewage Sludge

analyte	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	R^2
BTBPE	−2.08	0.17	0.22	0.21	0.22	0.490
DBDPE	0.13	0.32	0.40	0.38	0.41	0.591
$\sum$ HBCD	−0.06	0.25	0.31	0.30	0.32	0.666
$\sum$ DP	−2.10	0.36	0.46	0.44	0.47	0.506

The MLR analysis can explain about 49–67% of the variability in predicting the concentrations of BTBPE, DBDPE, $\sum$ HBCD, and $\sum$ DP in sludge. Comparisons of the predicted with measured concentrations are shown in Figure 3.

Figure 3. Predicted versus measured concentration (ng/g, d.w.) for BTBPE ($n = 62$, $R^2 = 0.490$, $p < 0.05$), DBDPE ($n = 62$, $R^2 = 0.591$, $p < 0.05$), $\sum$ HBCD ($n = 61$, $R^2 = 0.666$, $p < 0.05$), and $\sum$ DP ($n = 60$, $R^2 = 0.506$, $p < 0.05$) in the sludge samples by the principal component regression.

The deviation of the slope from the 1:1 ideal line indicates that the models overestimate the measured values at their lower levels while somewhat underestimate them at their higher levels, which might be due to failure to consider hydraulic retention time (HRT) during wastewater treatment and other unknown factors. The models can help to evaluate the pollution levels of these PBDE substitutes in WWTPs sludge, but their subsequent environmental emission through sludge disposal remain unclear.

Estimation of HFR Accumulation in Sewage Sludge and Their Release into Biosolids-Applied Soils. In China, there were 4136 municipal WWTPs treating about 126 000 tons wastewater on a daily basis in 2013.⁶⁸ Approximately 30 million tons of sludge were produced on annual basis from the nationwide WWTPs.⁶⁹ Sludge disposal in China is generally composed of landfill burial (63%), land application (15%), incineration (2%), building materials (3%), and other (17%).⁶⁹ To evaluate impact of these contaminants in the environment, the nationwide annual emission fluxes of DBDPE, HBCD, DP, and BTBPE were calculated using total sludge production volume. Based on the measured concentrations, the estimate emission fluxes were 1566, 519, 567, and 28.5 kg/year for DBDPE, HBCD, DP, and BTBPE, respectively. Comparing the total annual accumulation in sewage sludge to the annual production volume in China suggests that the leakage of DBDPE, HBCD, and DP from the technosphere via municipal wastewater was of the order of 0.01%, 0.01%, and 0.06–0.2%, respectively. These small fractions may be attributed to low treatment rate of wastewater and large exportation of the produced HFRs in China. The proportion of biosolids for land application in China is relatively low. Most of them were directly used as fertilizers in agriculture fields near the WWTPs. The amounts of DBDPE, HBCD, DP, and BTBPE released into the biosolids-applied soils were estimated to 235, 78, 85, and 4.3 kg/year. Up to now, little is known about the ultimate fate and environmental impact of emerging HFRs in the biosolids-applied soils. More monitoring studies are urgently needed to provide more information for future environmental risk assessment and management.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional information on sample preparation and cleanup, WWTP characteristics for each sludge samples (Table S1), structure information for all analytes (Table S2), dry-weight basis and TOC-normalized concentration data (Table S3 and S4), tables of data for global comparison on the basis of available concentrations (Table S5–7), the sampling map (Figure S1), representative chromatograms (Figure S2–4), Box-Whisker plots (Figure S5) and spatial distribution in two typical regions (Figure S6). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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