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BROMINATED FLAME RETARDANTSIN A WASTEWATERTREATMENT PLANT (WWTP) FROM HARBIN, CHINA:LEVELS, INPUT SOURCE AND MASS LOADING

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1. Introduction

Polybrominateddiphenyl ethers (PBDEs) are a group of additive brominated flame retardants (BFRs) that are extensively used in various polymers. Although manufacturers in the European Union (EU) and the United States (U.S.) have begun to phase out deca-BDE voluntarily, it is still extensively consumed in China with an annual production of approximately 36,000 tones[1]. The phase out of PBDEs in the worldwide has paved the way for use of "novel" BFRs (NBFRs) as replacements for the banned formulations[2]. Currently, many NBFRs have been produced for commercial use. In many areas, PBDEs are widely distributed in the environment including air, sludge, sediment, fish, birds, marine mammals, humans and levels of PBDEs in biota show a steady increase that parallels the historic rate of their production[3]. Among NBFRs, DBDPE and BTBPE were the most frequently detected compounds in the environment. As a sink for municipal wastewater along with street runoff and dry/wet deposition, wastewater treatment plant (WWTP) was considered to be an important medium for the transport and transformation of organic pollutants, such as PBDEs andNBFRs. The occurrence and fate of PBDEs in WWTPs have been investigated in several earlier studies [4]. However, for NBFRs, data on their occurrence and fate was scarce. To our knowledge, as the carrier and sink of many pollutions including PBDEs and NBFRs released from household products, indoor dust are also considered to be a main source of those pollutants in WWTPs receiving domestic wastewater[1, 4]. Harbin as the capital of Heilongjiang province is one of the main "Old Industrial Base" in China, which is located at the middle stream of the Songhua River in Northeast China. In this study, influent and effluent wastewater, sludge from a WWTP was collected in Harbin for the comprehensive study of PBDEs and NBFRs.

2. Materials and methods

The biggest WWTP in Harbin was chose for the study with a capacity of 650,000 m3/d. Wastewater samples (n = 12) were collected for the influent, final effluent of the WWTP in November of 2012, January, March, May, July and September of 2013. The sludge samples were collected from the dewater sludge (DS) (n=6) and anaerobic-oxic sludge (AOS)(n=6) with stainless steel jars from the WWTP synchronized with wastewater sampling. Sample treatment method was modified according to the previous methods[5]. Quantification of target BFRs was performed using an Agilent 6890 GC coupled with an Agilent 5975B mass spectrometer with electron capture negative ionization mode.

3. Results and discussions

The concentration of BFRs in the wastewater and sludge in the WWTP was summarized in the Table 1.The mean concentration of Σ13PBDEs in influent was 152 ng/L. The major congeners of PBDEs detected in the influent were BDE 17, 28, 47, 49, 99, 85, 153, 183, 209. Among the major congeners, BDE-209 was the most abundant congener in the influent with the mean concentration of 150 ng/L. The concentration of Σ12PBDEs (without BDE-209) was several orders of magnitude lower than that of BDE-209. The result may because the major PBDE product was deca-BDE and only a very small market existed for Penta-BDE in China, which was banned for production in 2007. The mean concentration of PBDEs in the effluent of the WWTP in Harbin was 16.2 ng/L (range: 0.315 to 30.6 ng/L). The mean concentrations of NBFRs in influent were 57.9 ng/L (24.5-107 ng/L). NBFRs in the influent were dominated by DBDPE and BEHTBP with the average concentrations of 29.2 and 11.2 ng/L, respectively. The concentrations of NBFRs in influent were 2-3 folds lower than that of PBDEs. This concentration trend was in accordance with the production and usage of these three flame retardants. The mean concentration of NBFRs in the effluent was 13.7 ng/L (0.95 - 20.3 ng/L). DBDPE was the predominant congeners in the effluent with mean concentration of 5.61 ng/L, respectively.

The mean concentration of Σ13PBDEs in anaerobic-oxic sludge and dewatered sludge were 356 ng/g dw (214 - 597 ng/g dw) and 633 ng/g dw (278 - 823 ng/g dw), respectively. The mean concentration of Σ13PBDEs in dewatered sludge was higher than that in anaerobic-oxic sludge. Furthermore, significant

difference of ΣPBDEs in anaerobic-oxic sludge and dewatered sludge was found using One-way ANOVA ($p<0.05$).This result may be caused by that BDE-209 was more easily biodegradated during the A/O process compared BAF process.The mean concentration of ΣNBFRs in dewatered sludge (687 ng/g dw) was a little higher than that in anaerobic-oxic sludge (674 ng/g dw). However, there is no significant difference between anaerobic-oxic sludge and dewatered sludge ($p= 0.539$). Among NBFRs, the dominant compound was DBDPE with the mean concentration of 303 ng/g dw (50.8-911 ng/g dw) and 316 ng/g dw (57.6-177 ng/g dw) in anaerobic-oxic and dewatered sludge, respectively.The ratio for DBDPE/BDE-209 (0.62±0.42) was found less than 1 in sludge from the WWTP indicating that Deca-BDE is still the major BFR product in this city.BEHTBP was the second most abundant alternative BFR in aerobic and dewatered sludge. The concentrations of BEHTBP in anaerobic-oxic and dewatered sludge were 172 ng/g dw (80.9-314 ng/g dw) and 242 ng/g (85.7-637 ng/g dw), respectively.

The overall removal rate of PBDEs and NBFRs was calculated to be 89.34% and 76.2%, respectively, by compared the total concentrations in the influent and the final effluent. Lager proportions of PBDEs and NBFRs were discharged via dewatered sludge which was 57.7% and 57.0%, respectively. The loading mass of final effluent was determined to be 10.5 g/d and 8.91 g/d for PBDEs and NBFRs, suggesting that 3.84 kg and 3.25 kg of PBDEs and NBFRs were discharged to the Songhua River annually, respectively. Additionally, consider the water content of 70%, there was approximately 20.8 kg and 7.79 kg of PBDEs and NBFRs on annually basis removed with the sludge. As shown in the Fig.1, the fates of PBDEs and NBFRs in the WWTP from Harbin were investigated. In general, absorbed on sludge was the major remove pathway of PBDEs and NBFRs in the WWTP, this may be due to the higher KOW value of those congeners. In addition, it should be note that there was mass losing of PBDEs and NBFRs in the WWTP, which account for 31.6% and 19.2% for PBDEs and NBFRs, respectively. This fraction of mass loss could be explained by the volatilization, degradation, and/or transformation of PBDEs and NBFRs, during the wastewater treatment process.

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Table 1 The mean concentration and Fractions of target compounds in wastewater and sludge in the WWTP in Harbin, China

	Concentration				Fraction			
	Influent (ng/L)	Effluent (ng/L)	DS (ng/g dw)	AOS (ng/g dw)	Influent (%)	Effluent (%)	DS (%)	AOS (%)
ATE	1.76	0.13	22.7	0.315	2.91	0.90	3.28	0.05
TBCT	0.02	0.09	13.9	1.83	0.03	0.62	2.01	0.27
PBT	0.33	2.22	6.00	10.3	0.55	15.34	0.87	1.53
PBEB	0.04	0.07	0.27	1.11	0.07	0.48	0.04	0.16
DPTE	0.74	0.7	2.97	8.15	1.23	4.84	0.43	1.21
HBBZ	0.6	0.26	3.59	7.55	0.99	1.80	0.52	1.12
HCDBCO	0.65	0.64	15.8	34.8	1.08	4.42	2.28	5.17
EHTBB	5.81	1.35	15.9	6.03	9.62	9.33	2.29	0.90
HBCD	9.57	1.78	11.2	124	15.9	12.3	1.62	18.4
BTBPE	0.47	0.03	42.5	4.41	0.78	0.21	6.13	0.65
BEHTBP	11.23	1.59	242	172	18.6	11.0	34.9	25.5
DBDPE	29.17	5.61	316	303	48.3	38.8	45.6	45.0
ΣNBFRs	60.4	14.5	693	673				
BDE 17	0.09	-	3.08	2.3	0.06	0.00	0.49	0.64
BDE 28	0.11	0.07	6.98	3.33	0.07	0.43	1.10	0.93
BDE 49	0.32	0.134	6.63	2.01	0.21	0.82	1.05	0.56
BDE 47	0.55	0.013	4.25	7.32	0.36	0.08	0.67	2.05
BDE 66	0.13	-	0.29	0.12	0.09	0.00	0.05	0.03
BDE 100	0.6	0.012	1.38	0.47	0.39	0.07	0.22	0.13
BDE 99	0.08	0.04	3.54	6.99	0.05	0.25	0.56	1.96
BDE 85	0.01	0.004	0.69	0.05	0.01	0.02	0.11	0.01
BDE 154	0.06	0.118	0.08	0.32	0.04	0.73	0.01	0.09
BDE 153	0.06	0.07	1.35	1.02	0.04	0.43	0.21	0.29
BDE 138	0.06	0.077	2.6	8.58	0.04	0.47	0.41	2.40
BDE 183	0.18	0.022	0.84	1.41	0.12	0.14	0.13	0.40
BDE 209	150	15.7	602	323	98.5	96.6	95.0	90.5
ΣPBDEs	152	16.3	634	357				

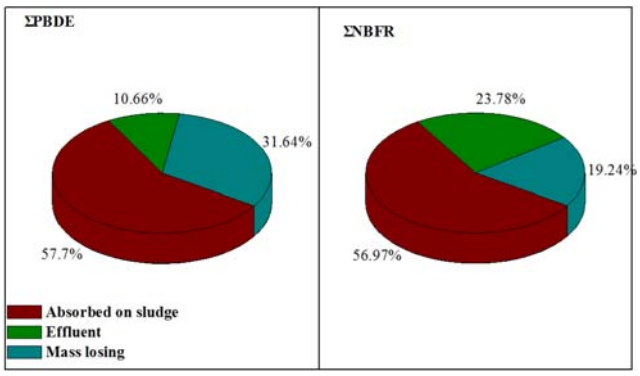

Fig.1 The fate of the PBDEs and NBFRs in the WWTP in Harbin, China