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Characterization, treatment and releases of PBDEs and PAHs in a typical municipal sewage treatment plant situated beside an urban river, East China

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Abstract

Characterization, treatment and releases of eight polybrominated diphenyl ethers (PBDEs) congeners and sixteen polycyclic aromatic hydrocarbons (PAHs) in wastewater were evaluated along the treatment processes of a typical secondary treatment municipal sewage treatment plant (STP) (in Hefei City) situated the beside Nanfei River, East China. The findings showed that the average concentrations of the total PBDEs in raw wastewater and treated effluent were 188.578 and 36.884 ng/L respectively. Brominated diphenyl ether (BDE) 209 congener, the predominant PBDE in the STP and Nanfei River, could be related to the discharge of car-industry-derived wastes. For PAHs, the average concentrations in raw wastewater and treated effluent were 5758.8 and 2240.4 ng/L respectively, with naphthalene, benzo[a]pyrene and indeno[1,2,3-c,d]pyrene being detected at the highest concentrations. PAHs mainly originate from the combustion of biomass/coal and petroleum. The STP reduced about 80% of the PBDEs and 61% of the PAHs, which were eliminated mainly by sedimentation processes. The removal rates of PBDEs/PAHs increased with the increase of their solid-water partitioning coefficients. Accordingly, the STP's effluent, containing some PBDE congeners (e.g., BDE 47, 99 and 209, etc.) and low-molecular-weight PAHs, could be an important contributor of these contaminants' input to Nanfei River. It resulted in a significant increase of PBDE/PAH concentrations and PAH toxicological risk in the river water downstream. About 4.040 kg/yr of PBDEs and 245.324 kg/yr of PAHs could be released into the Nanfei River. The current conventional wastewater treatment processes should be improved to remove the relatively low-molecular-weight PBDEs/PAHs more effectively.

Key words: polybrominated diphenyl ethers; polycyclic aromatic hydrocarbons; municipal sewage treatment plant; urban river

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Introduction

Polybrominated diphenyl ethers (PBDEs) and polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants (Ma et al., 2012; Zhang et al., 2012). The anthropogenic PAHs are mainly introduced into the environment by incomplete combustion of fossil fuels and discharge of petroleum-related materials during their use in homes and factories (Zhang et al., 2012). Increasing levels of PBDEs have been detected in e-waste, personal automobiles, cars wastes and associated dust (Ma et al., 2012; Sjödin et al., 2008; Harrad and Abdallah, 2011; Lagalante et al., 2011), of which BDE 209 normally contributes the highest proportion in Asia (Peng et al., 2009; Song et al., 2006).

The effluent discharge from a conventional municipal sewage treatment plant (STP) is frequently associated with the release of persistent organic pollutants to the receiving water bodies of local aquatic environments surrounding the location of these discharges (Rayne and Ikonomou, 2005; Alonso et al., 2005; Song et al., 2006; Li et al., 2011). PAHs, related to those commonly found in wastewaters, exist at levels up to few to tens μg/L (Pham and Proulx, 1997; Fatone et al., 2011). As far as brominated flame retardants are concerned, PBDEs are the most studied class, and the concentrations for PBDEs in wastewaters can vary from a few ng/L up to several μg/L. Although STPs can remove a large portion of hydrophobic contaminants through sedimentation of suspended solids and biodegradation by microorganisms in anaerobic processing, yet the remaining more-soluble compounds are still discharged to receiving waters (Pham and Proulx, 1997; Peng et al.,

2009). Such large contaminant fluxes into receiving waters can potentially threaten the drinking water supplies and fisheries resources (Rayne and Ikonomou, 2005).

The city of Hefei, the capital of Anhui Province in East China, is an economically fast developing region housing one of the largest groups of important automobile manufacturers and assembling plants in China (Market Analysis Report, 2010). High concentrations of PAHs were also found in the downstream sediment of Nanfei River (Wang et al., 2011a). Previous researches have revealed that the effluents of municipal STPs could be a significant source of contamination for PBDEs/PAHs (Peng et al., 2009; Song et al., 2006). Currently, very few data have been reported on the transport and release of PBDEs and PAHs from municipal STPs to the aquatic environment in the area of East China. Therefore, it is urgent to investigate the transport and release of contaminants in the wastewaters of Hefei urban STPs.

The objectives of this study were to investigate the distribution characterization (abundance and patterns) of PBDEs/PAHs during the treatment processes of a typical STP in Hefei City, East China, to assess the potential pollution sources and removal efficiencies of PBDEs/PAHs after the conventional urban STP processes and to estimate the concentration and mass releases of PBDEs/PAHs from the STP into the urban Nanfei River.

1 Materials and methods

1.1 Sewage treatment plant studied and water sampling

The test municipal STP is located in the city of Hefei (population 4.3 million) of Anhui Province, East China

(**Fig. 1a**). The treatment plant is the city's oldest and largest wastewater facility of the surrounding Chaohu Lake basin. It has three parallel and similar activated sludge-type secondary wastewater treatment systems (viz. three anaerobic tanks followed by three oxidation ditches) (**Fig. 1b**), with a total installed capacity of 300,000 m^3/day. The influent of the test municipal STP was a mixture of domestic sewage (about 60%), industrial sewage and landfill leachate. The industrial sewage is possibly produced by automobile manufacturers, chemical, and food industries. The final effluents of the STP are discharged into the Nanfei River, which is a seriously polluted urban river flowing through Hefei City (Wang et al., 2011b).

On each sampling occasion, water samples were collected according to different protocols during the treatment process, as shown in **Fig. 1**. Three parallel samples were collected every time. A five-liter water sample at each location was collected every time over a period of approximately an hour between 15:00 and 17:00, in August 2011 (wet season) and December 2011 (dry season) respectively ($n = 6$). To assess the possible contribution of the STP to the Nanfei River, surface water samples were also collected about 2 to 3 km upstream and downstream of the discharge point of the STP. All the samples were kept in coolers with ice packs and transferred to the laboratory. The samples were filtered through glass fiber filters (pore size, 0.7 μm; Whatman, Florham Park, USA), and then stored at 4°C prior to pretreatment. The water sampling flow is shown in **Fig. 1**.

1.2 Chemicals, reagents and cleanup multilayer column

The PBDE congener calibration solutions of tri- to hepta-brominated diphenyl ethers (BDE) (2 μg/mL in
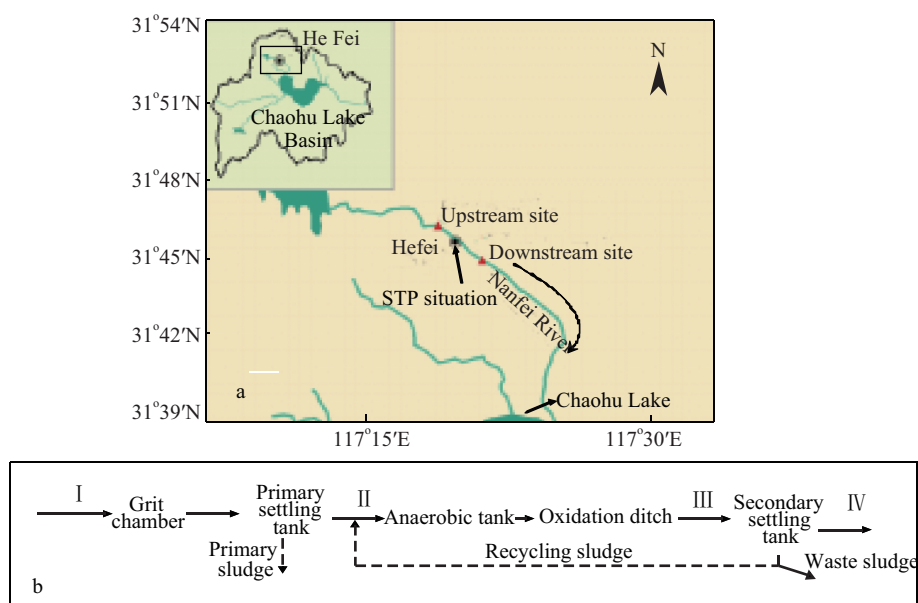

Fig. 1 Sampling sites in the largest sewage treatment plant in the Hefei City, East China (a), and schematic of the treatment process flow (b). Sampling sites: (I) influent to the grit chamber and the primary settling tanks, (II) primary settling tank effluent, (III) anaerobic tank + oxidation ditch effluent, and (IV) final effluent.

isooctane/toluene with 8:2, *V/V*) included BDE 28, 47, 100, 99, 154, 153, and 183, and deca-BDE (50 μg/mL in isooctane/toluene at 8:2, *V/V*) contained BDE 209. A stable isotopically labeled analog of ^{13}C-labeled PCB 209 (40 μg/mL in nonane) was used as the recovery surrogate. The internal standard of ^{13}C-labeled BDE 183 (5 μg/mL in isooctane) was used for the detection of BDE 28 to BDE 183, while ^{13}C-labeled BDE 209 (10 μg/mL in *n*-hexane) was used for BDE 209. All of these standard solutions were purchased from AccuStandard (New Haven, USA). All solvents used were residue analysis grade (Merck, J.T. Baker).

A mixed PAH standard solution of 2000 μg/mL containing 16 priority PAH compounds (Supelco, USA) was used. The 16 PAH compounds included: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene(BaP), indeno[1,2,3-c,d]pyrene (Ipy), dibenzo[a,h]anthracene (DahA), and benzo[g,h,i]perylene (BghiP). A deuterated PAH internal standard (phenanthrene-d_{10}, pyrene-d_{10}, and chrysene-d_{12}), and a PAH recovery standard (fluoranthene-d_{10}) were purchased from Supelco, USA.

Silica gel (70–230 mesh, Macherey-Nagel GmbH & Co. KG, Germany) was extracted for 24 hr in a Soxhlet apparatus with methanol and activated by heating at 160°C for 6 hr. Basic silica gel was obtained after 50 g neutral silica gel was eluted with addition of sodium hydroxide solution (1 mol/L) drop by drop and the mixture was shaken for 8 hr, while acidic silica gel was prepared by the method of elution of 100 g neutral silica gel with addition of 43 mL concentrated sulfuric acid (95% to 97%) drop by drop and shaking for 8 hr. The basic or acidic silica mixture was stored in amber glass bottles for approximately 1 month. Sodium sulfate was dried for 12 hr at 500°C and used to remove trace levels of water in the extracts.

The multilayer cleanup column (a glass chromatography column, i.d. × L, 25 mm × 190 mm) was prepared according to International Standard (International Standard, ISO 22032, 2006(E)). The multilayer cleanup column was deactivated with 40 mL *n*-hexane/dichloromethane (DCM) (4:1, *V/V*) and rinsed with 40 mL *n*-hexane.

1.3 Extraction and clean-up

Briefly, PBDE extraction and cleanup followed the International Standard, ISO 22032 (2006) with some modifications: a 4-L filtered water sample from each of the sites was spiked with a surrogate of 10.0 μL ^{13}C-labeled PCB 209 just before extraction. Then the sample was transferred to five paratactic 2000-mL separatory funnels, 30 g of sodium chloride was added to each, followed by extraction using continuous liquid/liquid extraction with 50 mL DCM. The aqueous fractions were back-extracted another two times

by the same method. The extracts were combined and dehydrated for 20 min by addition of anhydrous sodium sulfate (1/2 volume of the DCM phase), followed by analyte concentration by rotary evaporation of the solvent volume to 2 mL. Solvent exchange from DCM to *n*-hexane was carried out three times using 10 mL *n*-hexane addition to the 2 mL extract, followed by the extract recondensation by multiple evaporation of the solvent volume to 1 mL, in preparation for a final fraction cleanup using multilayer column chromatography. The concentrated extracts were then cleaned by column chromatography, with 125 mL *n*-hexane/DCM (4:1, *V/V*). The eluents were concentrated with rotary evaporation to 0.5 mL. The final volume was reduced to 100 μL under a gentle N$_2$ stream. The internal standard of 20.0 μL ^{13}C-labeled BDE 183 was added to all extracts before instrumental analysis for BDE 28 to BDE 183, while the internal standard of 5.0 μL ^{13}C-labeled BDE 209 was added into all extracts before instrumental analysis for BDE 209.

Samples with BDE 209 concentrations which exceeded the linear range of the analytical instrumentation were diluted. Briefly, 45.0 μL of the standard solution of ^{13}C-labeled BDE 209 was added to the final 100 μL concentrated extracts, followed by addition of 855 μL *n*-hexane, which were then gently shaken before GC-MS analysis. In addition, extraction of BDE 209 requires specific attention and, sometimes, longer extraction times than other PBDE congeners. In this study, toluene was used as an extraction solvent instead of DCM when the surrogate recoveries of BDE 209 were less than 60%.

The extraction, clean-up, recovery tests and chromatographic determination of PAHs (16) followed procedures given elsewhere (Zhang et al., 2012; Wang et al., 2011a) with small modifications. Briefly, about 1.0 L of each filtered water sample was spiked with the PAH recovery standard (fluoranthene-d_{10}, 200 ng). Then the water was extracted by liquid-liquid extraction in a separatory funnel using 350 mL of methylene chloride. The combined solvent extracts were cleaned and dried with the cleanup multilayer column and concentrated in a rotary evaporator. The residue was dissolved in *n*-hexane to give a final volume of 1.0 mL. As an injection internal standard, 20 μL of the mixed standard solution of deuterated phenanthrene, deuterated pyrene, and deuterated chrysene (10 mg/L) was added into the solution for PAH determination.

1.4 PBDE/PAH analyses

PBDEs and PAHs were analyzed with a Shimadzu Model 2010 gas chromatograph coupled with a model QP2010 mass spectrometer (Shimadzu, Japan) equipped with a fused silica capillary DB-5ms column (30 m × 0.25 mm i.d., film thickness 0.25 μm, Agilent, USA) using electron ionization and negative chemical ionization (for BDE 209) in selective ion monitoring mode. A DB-5 (30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column was

used for the determination of tri- to hepta-BDEs (BDE 28, 47, 99, 100, 153, 154, and 183) and PAHs (16). For BDE 209, a DB-1 (15 m × 0.25 mm i.d., 0.1 μm film thickness) capillary column was used.

Helium (99.999%) was used as the carrier gas at a constant flow rate of 1.0 mL/min for the determination of tri- to hepta-BDEs, and 1.3 mL/min for BDE 209. The initial gas chromatographic temperature was 60°C held for 2 min, followed by a temperature ramp of 30°C/min up to 240°C (run time, 28 min), and a ramp of 10°C/min up to 260°C (run time, 40 min), and then a ramp of 5°C/min to 320°C. The final temperature of 320°C was held for 18 min (run time, 60 min). The quadrupole and ion source temperatures were held at 106°C and 230°C, respectively. Quantification was conducted using an internal calibration method, with the ranges of the calibration standards being 1.0 to 200 μg/L for tri- to hepta-BDEs, and 100 to 2000 μg/L for BDE 209. These curves were used to derive response factors of analytes relative to the appropriate isotope-labeled internal standards. Ion fragments m/z 79 and 81 were monitored for tri- to hepta-BDEs, and m/z 486.7 and 484.7 for BDE 209. The ion of m/z 488.7 was not selected to avoid the overlap with a fragment ion from ^{13}C-labeled BDE-209. For the surrogate standard, m/z 509.9 and 511.7 were monitored for ^{13}C-labeled PCB 209. In addition, for internal standards, m/z 733.5 was used for ^{13}C-labeled BDE 183, and m/z 494.7 and 496.7 for ^{13}C-labeled BDE 209.

Helium (99.999%) was used as the carrier gas at a constant flow rate of 1.0 mL/min for the determination of PAHs. The injector, transfer line, and ion source temperatures were 250, 300, and 230°C, respectively. The oven temperature program for PAHs was as follows: initial temperature 60°C, held for 1 min; increased to 160°C at 10°C/min; increased to 260°C at 8°C/min; and increased to 300°C at 6°C/min, held for 10 min.

The concentration is expressed as nanograms per liter (ng/L) unless otherwise specified.

1.5 Quality assurance and quality control

A procedural blank analysis was performed with every 5 or 6 samples to monitor interferences and cross-contamination, and all results were blank-corrected. The quality assurance and control experiment was performed in duplicate. The relative standard deviations (RSD) ranged from 8.2% to 37.9% for PBDEs, and from 3.9% to 13.5% for PAHs (16). The spiked recovery for tri- to hepta-BDE congeners ranged from 82.7% to 105.4%, for BDE 209 ranged from 86.5% to 103.6%, and for PAHs (16) ranged from 80.6% to 96.5%. Reported concentrations were not surrogate recovery corrected. The method detection limits were around 0.003–0.005 ng/L for tri-BDE to hepta-BDE, 0.010 ng/L for BDE 209, and 0.8–1.2 ng/L for all the 16 PAHs.

1.6 Data analysis

Data analysis was performed on the statistical software of OriginPro 8.0 (OriginLab, Los Angeles, USA) and Microsoft Excel 2003. Samples with concentrations below the method detection limit were assigned a value of zero for concentration calculations.

2 Results and discussion

2.1 Abundance and patterns of PBDEs/PAHs in STP and river

The overall PBDE/PAH concentrations and their abundance and patterns in the wastewater from the STP are shown in **Table 1** and **Fig. 2**. The eight BDE congeners were all detected in raw wastewater. The mean concentration of Σ_8PBDEs was (188.578 ± 81.255) ng/L (n = 6), with BDE 209 accounting for more than 90% of the total PBDEs (**Fig. 2**). In treated wastewater, the average concentration of Σ_8PBDEs was (36.884 ± 19.530) ng/L. The lower brominated congeners (i.e., BDEs 28, 47, and 99) were also significantly found. The results in the influent were similar to that of Canadian wastewater (Song et al., 2006), but lower than that of Guangzhou (China) wastewater (Peng et al., 2009) and higher than that of Australian and Norway wastewaters (**Table 2**). However, the proportion of lower brominated congener concentrations was generally more than 10% of those reported for North America and Europe (Clarke et al., 2010; Song et al., 2006; North, 2004) (**Table 2**). This significant difference may be attributed to the much greater usage of penta-formulation PBDEs in North America and Europe (Peng et al., 2009; Vonderheide et al., 2008). In the effluent, the average PBDE concentrations were similar to those measured in Canadian wastewater, but seemed to be higher than the other studied wastewaters (**Table 2**). This might be due to the different treatment processes of the STPs.

For PAHs in raw wastewater, an average total concentration of (5758.8 ± 2238.7) ng/L was detected, with Nap, Bap and Ipy having the highest concentration levels (more than 1000 ng/L) (**Table 1**). The total PAH levels in raw wastewater were lower than those in Greek wastewater (Manoli and Samara, 2008), but higher than that of in Norway (Vogelsang et al., 2006), Italy (Fatone et al., 2011) and Canada (Pham and Proulx, 1997) wastewaters. In addition, the concentrations of Bap and Ipy found in effluent of the Hefei urban STP were much higher than those in other countries (**Table 2**). In the treated wastewater, the mean concentration of total PAHs was (2240.4 ± 187.3) ng/L. The same three PAHs ranged from 159.4 to 924.4 ng/L. These levels were in the high range of the global PAH concentrations in treated wastewaters.

Basically, the concentrations of PBDEs/PAHs in wastewater decreased gradually along the treatment pro-

Table 1   Concentrations of PBDEs and PAHs in grab samples from each stage of the Hefei urban wastewater treatment plant and the Nanfei River
(unit: ng/L)

PBDEs/PAHs	Wastewater flows				Nanfei River		MDL
	IN	PE	OD	FE	Upstream	Downstream	
BDE 28	0.023 ± 0.015	0.031 ± 0.026	0.024 ± 0.008	0.016 ± 0.007	0.035 ± 0.024	0.016 ± 0.006	0.008
BDE 47	0.172 ± 0.049	0.094 ± 0.027	0.083 ± 0.054	0.040 ± 0.024	0.256 ± 0.091	0.364 ± 0.184	0.008
BDE 99	1.639 ± 0.867	1.480 ± 0.942	0.026 ± 0.015	0.018 ± 0.009	0.253 ± 0.089	0.745 ± 0.238	0.008
BDE 100	0.242 ± 0.146	0.185 ± 0.079	<0.003	<0.003	0.036 ± 0.019	0.075 ± 0.032	0.008
BDE 153	0.259 ± 0.196	0.143 ± 0.108	0.024 ± 0.008	0.010 ± 0.005	0.191 ± 0.046	0.431 ± 0.188	0.010
BDE 154	0.148 ± 0.572	<0.003	<0.003	<0.003	<0.003	<0.003	0.008
BDE 183	0.085 ± 0.064	<0.005	<0.005	<0.005	<0.005	0.021 ± 0.008	0.012
BDE 209	186.010 ± 79.346	54.211 ± 35.461	45.214 ± 29.482	36.800 ± 19.485	7.703 ± 2.481	31.224 ± 3.046	0.125
Σ_8PBDEs	188.578 ± 81.255	56.144 ± 36.643	45.371 ± 29.567	36.884 ± 19.530	8.474 ± 2.750	32.876 ± 3.464	
Nap	1437.3 ± 645.4	1224.4 ± 256.7	1173.9 ± 184.2	924.4 ± 64.6	2.1 ± 1.6	26.4 ± 17.3	1.2
Acy	121.8 ± 26.8	106.5 ± 10.9	86.6 ± 8.4	65.0 ± 5.8	2.9 ± 1.8	6.3 ± 4.1	1.0
Ace	47.9 ± 13.7	41.8 ± 4.6	34.1 ± 3.9	32.5 ± 1.4	<1.0	5.8 ± 2.9	1.0
Flu	106 ± 48.9	95.2 ± 17.1	72.4 ± 10.5	60.1 ± 5.3	5.7 ± 3.4	8.1 ± 5.4	1.2
Phe	322.9 ± 137.5	283.6 ± 50.4	249.3 ± 32.7	226.6 ± 12.1	7.2 ± 3.1	18.7 ± 12.0	1.0
Ant	37.1 ± 10.4	30.8 ± 3.8	26.2 ± 2.5	19.0 ± 1.9	4.5 ± 0.4	9.5 ± 6.3	0.9
Flt	192.5 ± 55.8	164.1 ± 19.2	134.7 ± 8.6	104.7 ± 4.4	11.8 ± 5.1	15.9 ± 10.2	1.0
Pyr	121.0 ± 89.1	94.5 ± 29.6	74.8 ± 14.8	52.0 ± 6.7	9.1 ± 6.9	10.6 ± 3.4	1.0
BaA	64.2 ± 15.5	50.3 ± 6.7	48.1 ± 5.1	27.0 ± 1.9	13.5 ± 7.0	14.1 ± 7.1	0.8
Chr	131.6 ± 65.7	101.7 ± 28.9	94.2 ± 15.9	61.2 ± 6.6	<1.0	1.6 ± 1.0	1.0
BbF	218.4 ± 78.4	105.9 ± 24.2	90.5 ± 10.3	36.0 ± 5.1	6.4 ± 2.8	16.7 ± 6.1	1.0
BkF	212.3 ± 120.8	111.4 ± 46.7	53.6 ± 26.9	46.3 ± 8.4	8.3 ± 3.2	10.4 ± 8.6	0.8
BaP	1383.5 ± 466.1	626.7 ± 189.0	515.2 ± 96.8	380.4 ± 30.5	16.7 ± 8.5	12.8 ± 7.2	0.9
Ipy	1038.7 ± 284.3	509.4 ± 89.3	371.8 ± 50.5	159.4 ± 20.7	<1.0	3.9 ± 1.8	1.0
DahA	88.7 ± 56.4	42.5 ± 18.1	26.2 ± 8.0	12.5 ± 4.9	<0.8	2.7 ± 1.2	0.8
BghiP	234.9 ± 123.9	123.3 ± 34.0	97.6 ± 21.7	33.3 ± 7.0	3.6 ± 0.7	3.8 ± 1.0	1.0
Σ_{16}PAHs	5758.8 ± 2238.7	3712.1 ± 829.2	3149.2 ± 502.6	2240.4 ± 187.3	91.8 ± 44.5	167.3 ± 94.9	

Data are expressed as mean ± SD ($n = 6$), as the mean value of measurements for wet and dry seasons.
IN: influent, PE: primary settling tank effluent, OD: oxidation ditch effluent, FE: final effluent, MDL: method detection limit.

Table 2   Comparisons of PBDE and PAH concentrations in the wastewaters from worldwide sewage treatment plants (unit: ng/L)

Location	Site	BDE 47	BDE 99	BDE 209	ΣPBDEs	References
Hefei, China	Influent[a]	0.172 ± 0.049	1.639 ±0.867	186.010 ± 79.346	188.578 ± 81.255[e]	This study
	Effluent[a]	0.040 ± 0.024	0.018 ± 0.009	36.800 ± 19.485	36.884 ± 19.530[e]	
Guangzhou, China	Influent[b]	0.499–11.063 (3.480)	0.349–10.488 (3.404)	11.6–2412.6 (550.2)	13.3–2496.4[f]	Peng et al., 2009
	Effluent[b]	0.083–0.228 (0.123)	0.059–0.205 (0.098)	0.6–3.4 (2.6)	0.9–4.4 (3.2)[f]	
Canada	Influent[c]	102 ± 83	121 ± 93	/	265 ± 210[e]	Song et al., 2006
	Effluent[c]	14 ± 4	16 ± 4	/	36 ± 10[e]	
USA	Effluent[b]	(10.47)	(11.2)	(1.73)	(29.023)[g]	North et al., 2004
Australia	Influent[b]	13–20	13–19	31–47	(70)[h]	Clarke et al., 2010
	Effluent[b]	< 2	< 2	< 2	(0.34)[h]	
Norway	Influent[b]	/	/	/	6.3–9.3 (8.28)[e]	Vogelsang et al., 2006
	Effluent[b]	0.1–0.6	< 2	/	0.1–0.6[e]	
		Nap	Bap	Ipy	Σ16 PAHs	
Hefei, China	Influent[a]	1437.3 ± 645.4	1383.5 ± 466.1	1038.7 ± 284.3	5758.8 ± 2238.7	This study
	Effluent[a]	924.4 ± 64.6	380.4 ± 30.5	159.4 ± 20.7	2240.4 ± 187.3	
Norway	Influent[b]	100–560	5-28 (10)	/	200–1300 (620)	Vogelsang et al., 2006
	Effluent[b]	39–570	< 4–28	/	39–1030	
Italy	Influent[b]	96–634	< 5–20	< 5–20	140–1540	Fatone et al., 2011
	Effluent[b]	37–74	< 5	< 5	< 50– < 195	
Greece	Influent[b]	(7300)	(22)	(15)	(11074)	Manoli and Samara, 2008
	Effluent[b]	(5000)	(4)	(6)	(5636)	
Canada	Influent[d]	(183)	(20)	(4)	(1059)[i]	Pham and Proulx, 1997
	Effluent[d]	(88)	(1)	0	(408)[i]	

Values in brackets are mean concentrations; / means that the concentration is not available.
[a] Filtered by 0.7 μm GF, [b] dissolved + particulate, [c] filtered by 1.0 μm filterglass fiber filter, [d] pressured-filtered through 293-mm precombusted glass-fiber pads, [e] sum of 8 congeners: BDE 28, 47, 99, 100, 153, 154, 183, and 209, [f] sum of 17 congeners: BDE 28, 47, 66, 85, 99, 100, 153, 154, 183, 196, 197, 203, 205, 206, 207, 208, and 209, [g] sum of 41 congeners: BDE 1, 2, 3, 7, 8, 10, 12, 13, 15, 17, 25, 28, 30, 32, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 105, 116, 119, 126, 138, 140, 153, 181, 183, 190, 206, 207, 208, and 209; [h] BDE 17, 28 + 33, 47, 49, 66, 77, 85, 99, 100, 119, 138+166,153, 154, 183, 184, 196, 197, 206, 207 and 209, [i] sum of 21 PAHs: l-methylnaphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, 1-methylphenanthrene, and the 16 priority PAHs.
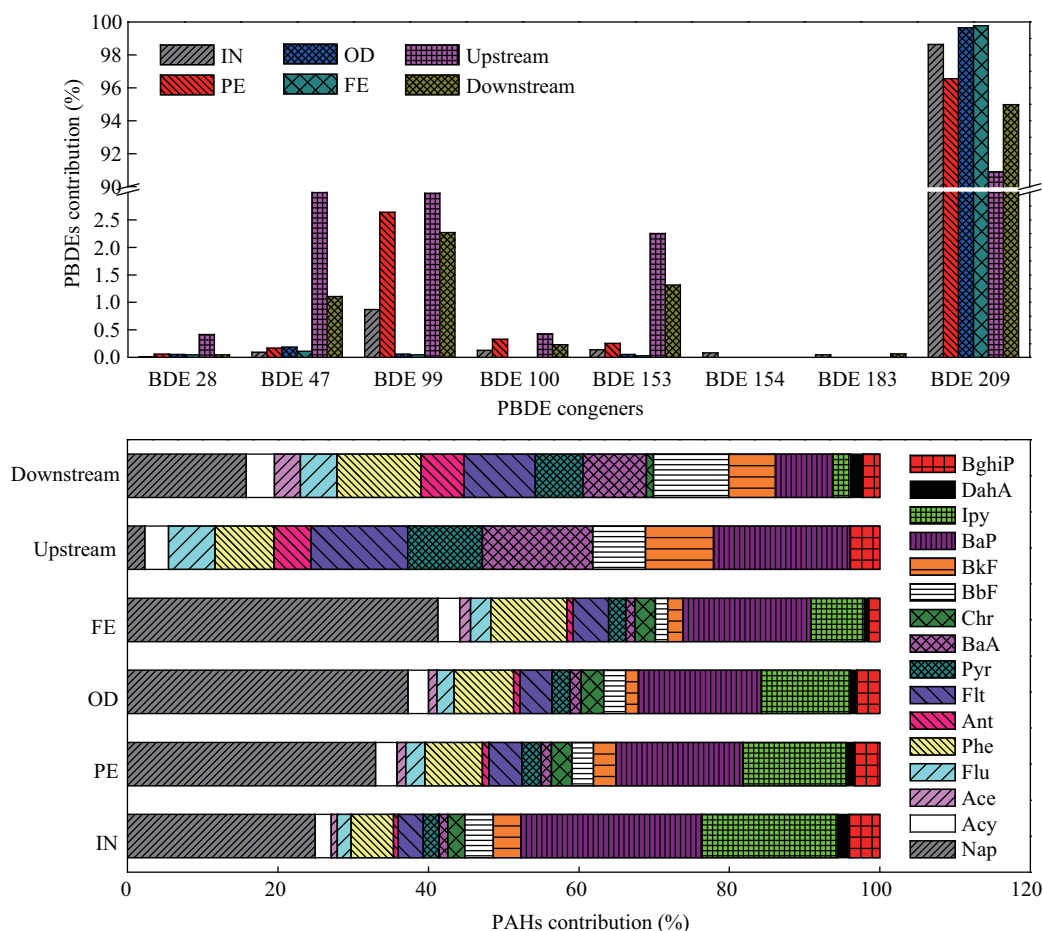
Fig. 2 PBDE and PAH contributions relative to the total concentrations in the wastewater and the Nanfei River (upstream, downstream) samples. IN: influent; PE: primary settling tank effluent; OD: oxidation ditch effluent; FE: final effluent.

cesses in the STP. During the conventional primary and secondary settling processes used in most municipal wastewater treatment plants, the concentrations of PB-DEs/PAHs were eliminated most due to PBDEs/PAHs strong tendency to be absorbed onto particles (**Fig. 2**); whereas the lower brominated BDEs and lower molecular weight (MW < 202) PAHs (e.g., Nap, Acy, Ace, Flu, Phe, Flt and Pyr, etc.) were removed at relatively lower rates. The percentages of some brominated BDEs and low-molecular-weight (MW < 202) PAHs along the treatment processes gradually increased (**Fig. 2**). This was mainly due to the adsorption properties of PBDEs/PAHs, which are hydrophobic compounds. Therefore they were expect-ed to be removed mainly by sorption on particles and subsequent sedimentation (Peng et al., 2009; Song et al., 2006). This is further discussed in the following section.

Compared to the PBDEs/PAHs in the upstream site of the Nanfei River, the concentrations of PBDE congeners and PAH compositions as well as their total concentrations were significantly increased (**Table 1**). BDE 28, 47, 99, and 153 presented higher percentage contributions in the Nanfei River than in the STP (**Fig. 2**). This was mainly due to the discharge of the urban STP. The STP discharge has contributed some PBDE congeners (e.g., BDE 47, 99 and

209, etc.) and low-molecular-weight PAHs to the Nanfei River inflowing into Chaohu Lake.

2.2 PBDE/PAH contamination sources and toxicologi-cal risk assessment

The city of Hefei houses a vast number of car manufactur-ing plants (e.g., Jianghuai Automobile) that are associated with a large amount of car accessories, which would be coated with brominated flame retardants (Market Analysis Report, 2010). High levels of PBDEs have been detected in car dust worldwide. The dominant congener in automobile dust in the United States was BDE 209, comprising 95% of the total PBDE levels with a median level of 48.1 μg/g (Lagalante et al., 2009), and BDE 209 in car dust in the UK was 100 μg/g (Harrad and Abdallah, 2011). The BDE 209 congener was also found to be the predominant PBDE in the STP and Nanfei River. Therefore, car dust may be one of the important pollutant sources in the STP and Nanfei River. This was consistent with the fact that commercial deca-BDE mixtures account for most of the total PBDE production and usage in China (Guan et al., 2007; Ma et al., 2012). The BDE 99 congener was found to be another predominant compound with the relative abundance of 0.87%–8.79%. The BDE 99 congener is

one of the dominant congeners of commercially-produced penta-BDE mixtures. Besides, the congener BDE 153 was also relatively frequently monitored. This may be because BDE 153 is the predominant hexa-BDE congener in the environment (US EPA, 2008). The typical STP likely makes it an important source of the lower brominated BDEs and BDE 209 for the Nanfei River. The widespread reports of PBDEs in effluents from municipal STPs suggest that residences and offices may be significant sources of PBDEs (Hale et al., 2006; Song et al., 2006).

As a characteristic marker of creosote or coal tar volatilization, NaP was detected with high concentration (**Table 1** and **Fig. 2**). The homologue distributions are associated with the formation mechanisms of carbonaceous materials for organic species with similar characteristics (Zhang et al., 2012). Therefore, characteristic ratios of (Flt/(Flt + Pyr), Ant/(Ant + Phe), BaA/(BaA + Chr), and IPy/(IPy + BghiP)) were calculated to identify PAH sources in the present study (**Fig. 3**) (Zhang et al., 2012). Results showed that ratios of Flt/(Flt + Pyr) were all more than 0.50, which revealed that biomass/coal combustion emission was a possible main source in the Hefei urban STP and water sample from the upstream site of the Nanfei River (Zhang et al., 2012). The results from other ratios showed that some PAHs in the STP also originated from petroleum combustion (e.g., wastewater from oil refining and car exhaust). After the STP effluents were discharged to the Nanfei River, the PAH sources represented the combustion mix of the biomass/coal and petroleum in the downstream of the river. The most potent of the carcinogenic PAHs, BaP, was detected at high concentration in the influent and effluent of the STP. This would be mainly due to the STP influents mixing with industrial wastewater. As in the case of other major cities, the source of PAHs to STPs was most likely street runoff, which combines atmospheric dust, oils and greases and road-wear particles (Pham and Proulx, 1997).

To assess the potential toxicological risk of PAHs in the surface water of the Nanfei River, toxic equivalence factors (TEFs) were applied to quantify the carcinogenicity of other PAHs (BaA, Chr, BbF, BkF, BaP and Ipy) relative to BaP and estimate BaP equivalent doses, according to

Zhang et al. (2012), Fisher et al. (2011), and Nadal et al. (2004). The calculated values of the total TEQ (toxic Bap equivalent) of PAHs in the surface water of the upstream and downstream of Nanfei River were 15.8 and 19.1 ng/L respectively, according to Eq. (1):

$$TEQ = \sum_i C_i \times TEF_i \qquad (1)$$

where, C_i (ng/L) and TEF_i are the concentration and TEF of the carcinogenic PAH i, respectively.

This indicated that the effluent discharge from the STP into the Nanfei River could increase the toxicological risk of PAHs in the river water downstream.

2.3 PBDEs/PAHs elimination efficiencies and solid-liquid partitioning

The mean elimination efficiencies of Σ_8PBDEs and Σ_{16}PAHs after the STP were 80% and 61% respectively. The average removal rates of PBDE congeners and individual PAHs varied from 30% to 100% and from 29% to 86% (**Fig. 4a** and **b**). The rates of the less brominated PBDE congener BDE 28 and low-molecular-weight PAHs (Nap, Ace, Flu and Phe) were less than 45% (**Table 1** and **Fig. 4**). The removal rates observed at the STP were comparable to the ranges (50%–99% for PBDEs and 32%–95% for PAHs) reported for different types of primary and secondary wastewater treatment systems (**Table 2**) (Pham and Proulx, 1997; Manoli and Samara, 2008). The primary settling tank contributed the highest removal efficiencies for PBDEs and PAHs (71% and 35% respectively), followed by the secondary settling tank. This was due to the fact that the PBDEs/PAHs were mainly associated with suspended particulate organic matter in the settling tanks, finally settling down in the sludge (Peng et al., 2009; Pham and Proulx, 1997). The elimination efficiencies of hydrophobic organic contaminants in the STP were highly related to their sorptive behavior, which could be indicated by the solid-liquid partitioning of hydrophobic contaminants in the STP (Pham and Proulx, 1997; Fatone et al., 2011). Therefore, the solid-water partitioning coefficient K_P is used to characterize the sorptive behavior of PBDEs/PAHs. The partitioning coefficient K_P can be calculated by Eq.
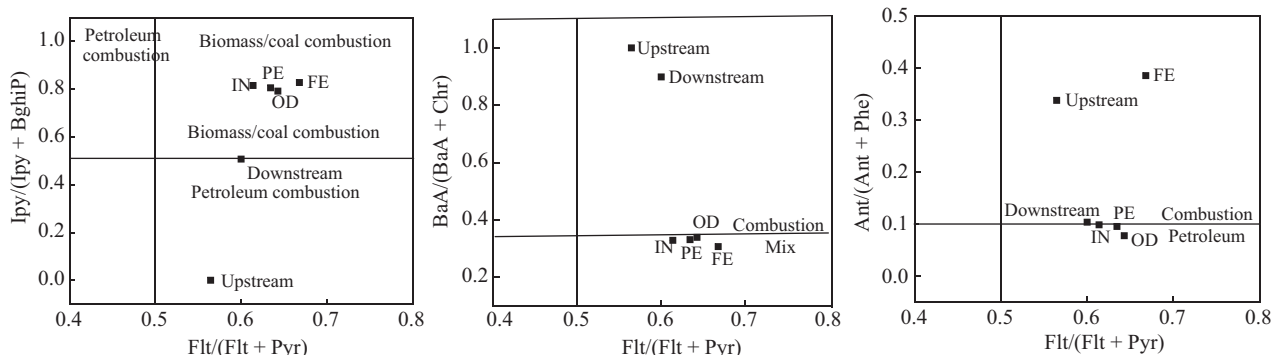

Fig. 3 Identification of the emission sources of PAHs in the sewage treatment plant and the Nanfei River.
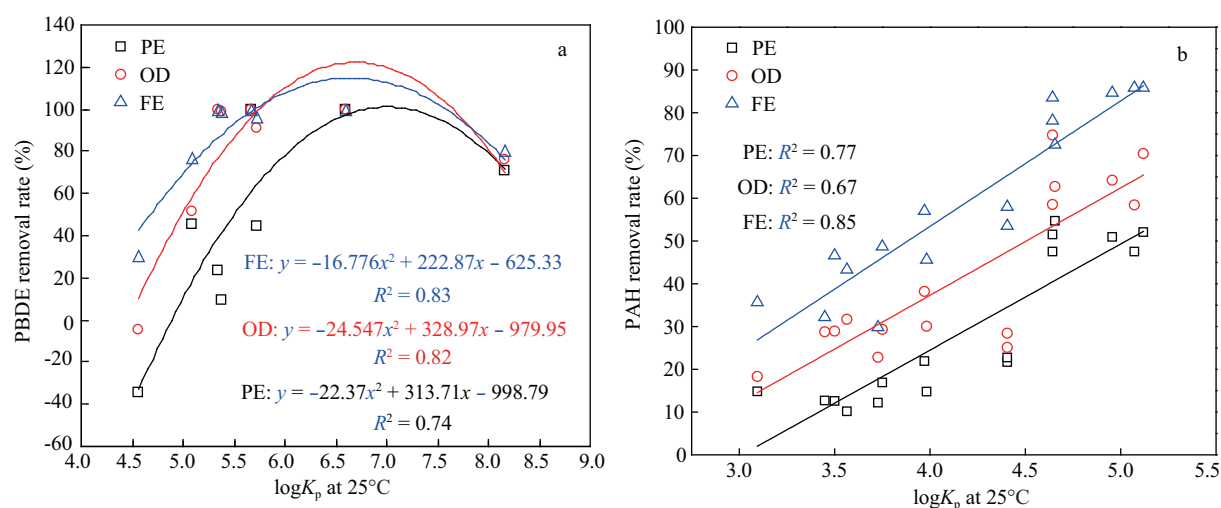
Fig. 4 Plot of average removal rate of PBDE congeners (a) and individual PAHs (b) versus $\log K_P$ over the treatment stages in the sewage treatment plant.

(2), which was reported by Dobbs et al. (1989) and Fatone et al. (2011).

$$\log K_P = 0.58 \log K_{OW} + 1.14 \qquad (2)$$

where, K_{OW} means the distribution coefficient of organic substance between n-octanol and aqueous phase.

Figure 4 shows that the removal rates were gradually increased with the increase of K_P values as a whole. The removal rates of PBDE congeners presented an evident positive quadratic relationship with their K_P values: $r = -a(\log K_P)^2 + b(\log K_P)$, while that of individual PAH showed a significantly positive linear relationship: $r = a'(\log K_P) + b'(\log K_P)$. However, an abnormal result found was that the removal rates of BDE 209 increased insignificantly during the STP treatment processes. This might be due to the special characteristics of the wastewater or the process operation conditions. Yet a reasonable interpretation of this phenomenon could not be acquired. Further research should be conducted to find out the possible reasons.

PBDEs/PAHs are hydrophobic chemicals, and the larger compounds are poorly water-soluble and have lower volatility than smaller compounds (Fatone et al., 2011). The relationships showed that the removal rate of PBDEs/PAHs increased with their decreasing solid-water partitioning coefficients or solubility of the compounds (**Fig. 4**), which indicated that the Hefei urban STP system was more effective in removing hydrophobic compounds than soluble compounds. This was similar to the results reported by Pham and Proulx (1997) for PCBs/PAHs.

The STP discharge contributed a considerable percentage of PBDE congeners (e.g., BDE 47, 99 and 209, etc.) and low-molecular-weight PAHs to the Nanfei River. Therefore, the current wastewater treatment process should be improved to further remove the relatively low-molecular-weight PBDEs/PAHs.

2.4 PBDE/PAH releases from STP to river

The PBDE/PAH mass loadings (ML) per year (kg/yr) can be calculated by Eq. (3), which was reported by Peng et al. (2009).

$$ML = (Q \times C \times 365) \times 10^9 \qquad (3)$$

where, Q (m^3/day) denotes the average flow rate of wastewater and C (ng/L) refers to the PBDE/PAH mean concentration in wastewater.

The estimated average PBDE/PAH releases per year are shown in **Fig. 5**. The input amounts of the total Σ_8PBDEs and Σ_{16}PAHs to the STP were 20.648 and 630.589 kg/yr, respectively. After the primary settling tank, the remaining 29.77% and 64.46% of the average 6.147 kg/yr Σ_8PBDEs and 406.475 kg/yr Σ_{16}PAHs concentrations were discharged to the anaerobic tank + oxidation ditch effluent. The calculated 19.55% of the total Σ_8PBDEs and 38.90% of the total Σ_{16}PAHs masses were discharged with the final effluents (**Fig. 5**) into the Nanfei River (leading to Chaohu Lake). Releases of PBDEs/PAHs from the treated wastewater were 11.068 and 672.120 g/day, which are significantly larger than the mass discharges calculated for the Palo Alto STP in California (North, 2004) and reported by Song et al. (2006) and Peng et al. (2009). Therefore, a total of 4.040 kg of PBDEs of 245.324 kg of PAHs per year could be released into the Nanfei River. This result revealed that wastewater from Hefei City was a significant contributor of PBDEs to the Nanfei River and thus the Chaohu Lake Basin, East China.

3 Conclusions

The congener BDE 209 contributed more than 90% of Σ_8PBDEs, while Nap, Bap and Ipy were detected at the highest concentration levels of Σ_{16}PAHs in the municipal
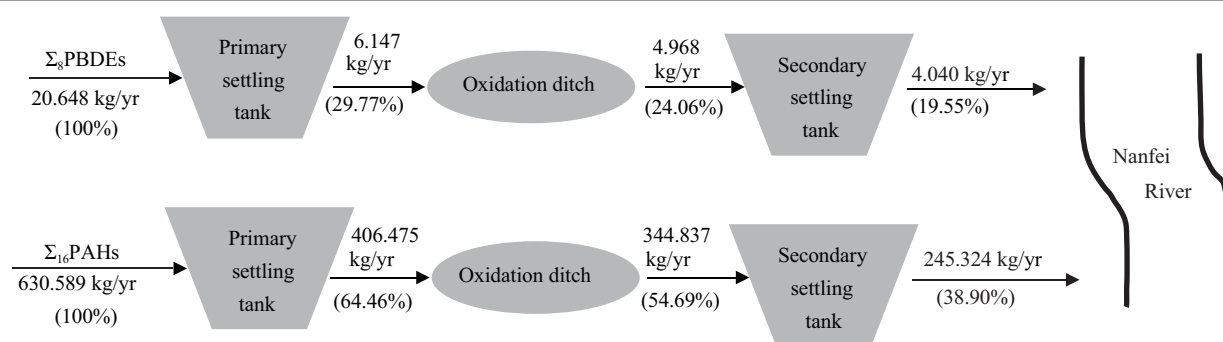
Fig. 5 PBDEs and PAHs mass releases during the sewage treatment and approximate annual inputs to Nanfei River.

STP, East China. PBDEs in the STP could be related to the discharge of the car-industry-derived wastes, and PAHs in the STP mainly originate from the combustion mix of biomass/coal and petroleum. The STP reduced on average ca. 80% of the PBDEs and ca. 61% of the PAHs. The sedimentation process was more effective than the biological process. As shown by the relationship between the removal rate of PBDE congeners and of PAHs versus their sorption partitioning coefficients, the removal of hydrophobic contaminants was more effective in contrast to smaller contaminants. The STP discharge has contributed a considerable percentage of PBDE congeners and low-molecular-weight PAHs to the Nanfei River. A total of 4.040 kg of PBDEs and 245.324 kg of PAHs per year could be released into the Nanfei River with the treated wastewater inflowing into Chaohu Lake. This could increase the toxicological risk of PAHs in the river water downstream. Therefore, the current conventional wastewater treatment processes should be improved to remove the relatively low-molecular-weight PBDEs/PAHs more effectively. In addition, the STP sludge is an important phase to absorb the PBDEs/PAHs. Thus further research is necessary on the effects of primary sludge and waste-activated sludge in the STP on the fate and transport and resulting environmental loadings of PBDEs/PAHs.

Acknowledgments

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