



Occurrence and partitioning of bisphenol analogues in water and sediment from Liaohe River Basin and Taihu Lake, China



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ABSTRACT

Bisphenol analogues are widely used in the manufacture of polycarbonate plastics and epoxy resins, and the demand and production capacity of these compounds are growing rapidly in China. The occurrence and distribution of bisphenol analogues other than bisphenol A (BPA) in the aquatic environment is still poorly understood. In this study, nine bisphenol analogues were measured in water and sediment samples from Taihu Lake (TL), Liaohe River basin, including Liaohe River (LR) and Hunhe River (HR), China. Water samples from LR and HR contained much higher total bisphenols (\sum BPs) concentrations. BPA and bisphenol S (BPS) were predominant with a summed contribution of 55, 75, and 75% to the \sum BPs in TL, LR, and HR waters, respectively. This suggests that BPA and BPS were the most widely used and manufactured bisphenols in these regions. In sediment, BPA was always predominant, with the next abundant compound bisphenol F (BPF) in TL and HR sediment, but BPS in LR sediment. The average field sediment–water partitioning coefficients ($\log K_{oc}$) were calculated for the first time for certain bisphenols and were determined to be 4.7, 4.6, 3.8, 3.7, and 3.5 mL/g for BPF, BPAP, BPA, BPAF, and BPS, respectively.

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1. Introduction

Bisphenol analogues are a group of anthropogenic chemicals with two hydroxyphenyl functionalities and are widely used as raw materials in manufacturing of epoxy resins and polycarbonate plastics, food cans (i.e., lacquer coatings), and dental composites (Howdeshell et al., 1999; Liao et al., 2012a,b,c,d; Sui et al., 2012). Bisphenol A [2,2-bis(4-hydroxyphenyl)propane; BPA], a ubiquitous endocrine disruptor, has been the most highly produced bisphenol analogues, and over eight million tons of BPA were manufactured and applied annually worldwide (Chen et al., 2002). During its manufacturing, usage, aging, and disposal of BPA related consumer products, BPA is inevitably released into the environment. The occurrence of BPA has been reported in various environmental matrices (Lee et al., 2015; Liao et al., 2012a,b,c,d) and

humans (Liao et al., 2012a,b,c,d) from around the world (Yang et al., 2014a). Huang et al. reviewed the concentration of BPA in surface waters from different regions of China, and reported that the BPA level was generally $<1.0 \mu\text{g/L}$ (Huang et al., 2012). Meanwhile, BPA concentrations in sediments from various rivers in China were in the range of 0.58–60 ng/g dw (Huang et al., 2012). It has been well documented that BPA is related to adverse health effects in wildlife and humans (Chen et al., 2002). As a consequence, the production and usage of BPA have been strictly regulated in European Union, North America, and China (Ministry of Health of P. R. China, 2011; Kärman et al., 2007; Migeot et al., 2013).

To meet the market demand, several bisphenol analogues that are structurally similar to BPA have been introduced as alternatives in industrial applications (Liao et al., 2012a,b,c,d; Yang et al., 2014c). These include bisphenol S (4,4'-sulfonyldiphenol; BPS), bisphenol AF [4,4'-(hexafluoroisopropylidene)diphenol; BPAF], bisphenol F (4,4'-dihydroxydiphenylmethane; BPF), bisphenol B [2,2-bis(4-hydroxyphenyl)butane; BPB], bisphenol Z [4,4'-(cyclohexane-1,1-diyl)diphenol; BPZ], and bisphenol AP [4,4'-(1-phenylethylidene)bisphenol, BPAP]. They have broad applications in manufacture of epoxy resins and polycarbonate

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plastics for food contact materials, thermal receipt papers, polyesters, and phenolic resins (LaFleur and Schug, 2011; Wang et al., 2007; Yang et al., 2014b). Among them, BPAF and BPS are generally the most extensively applied BPA substitutes. The reported annual production of BPAF was approximate 10,000–500,000 pounds in America during 1986 and 2002 (Zhang et al., 2013).

Recently, many concerns have been raised on the occurrence and adverse effects of BPA alternatives. These analogues were found to display potential ecotoxicities and similar or even stronger estrogenic activities than BPA (Kitamura et al., 2005; Okuda et al., 2011). For instance, Kitamura et al. evidenced that BPB (EC₅₀, 0.07 μM), BPAF (EC₅₀, 0.05 μM), and BPZ (EC₅₀, 0.21 μM) exhibited higher estrogenic activities than BPA in human breast cancer cell line MCF-7. BPF (EC₅₀, 1.0 μM) and BPS (EC₅₀, 1.1 μM) also showed such but relatively weaker activities (Ji et al., 2013; Kitamura et al., 2005; Yoshihara et al., 2004). *In-vitro* studies demonstrated that BPAF had a stronger binding affinity with estrogen receptor ER alpha in HeLa cells than BPA, and meanwhile acted as an antagonist on ER-beta receptor (Matsushima et al., 2010).

BPA substitutes could be discharged into the aquatic environment through similar ways as BPA and were expected to have adverse effects on aquatic ecosystems. Only few small studies reported concentrations of BPA alternatives (mainly BPAF, BPF, and BPS) in the aquatic environment (Yang et al., 2014a; b; c; Zeng et al., 2012; Chen et al., 2015). For example, in 5 river water and sediment samples from Hangzhou Bay, China, concentrations of BPAF, BPF, and BPS varied from <0.02 to 246 ng/L in waters and from <0.02 to 2010 ng/g dw in sediments, respectively. Meanwhile, in 2 water and 4 sediment samples, BPAF had higher concentrations than BPA (Yang et al., 2014b). Systematic studies on the occurrence and profiles of bisphenol analogues in waters and sediments, especially from large-scale watersheds, are still scarce. Sediment can act as an important reservoir or sink for organic compounds (Liao et al., 2012a,b,c,d). Partitioning of organic compounds between the water and sediment plays an important role in their environmental transport and fate, and which are still poorly understood for bisphenol analogues.

Taihu Lake (TL), a typical watershed in southern China, is the second largest freshwater lake in China and an important drinking water source for megalopolises in this basin (e.g., Shanghai and Suzhou) (Qiu et al., 2004; Tao et al., 2013). TL receives much agricultural and domestic sewages from surrounding cities, and might be the sink of many anthropogenic organic pollutants. Liaohe River Basin mainly consists of Liaohe River (LR) and Hunhe River (HR), and, right now, is the largest industrial region in northeastern China (Bai et al., 2014; Zeng et al., 2012; Zhang et al., 2010a,b). Recent studies reported high levels of various organic chemicals (e.g., organochlorines and perfluoroalkyl substances) in waters from the Liaohe River Basin (Bai et al., 2014; Chen et al., 2015; Nakata et al., 2005; Ren et al., 2013).

In this study, paired water and sediment samples (totally 88 samples) were collected from the TL, LR, and HR, and were analyzed for nine bisphenol analogues. Field based distribution coefficients between the water and sediment were calculated for the first time for bisphenol analogues. To our knowledge, this is the first study to report the occurrence of bisphenol analogues other than BPA in waters and sediments from natural and large-scale watersheds in China.

2. Materials and methods

2.1. Standards and reagents

BPAF (97%), BPAP (99%), bisphenol C (BPC; 98%), BPB (99%), BPF (98%), bisphenol FL [4,4'-(1-phenylethylidene)bisphenol; BPFL;

97%], BPS (98%), and BPZ (98%) were purchased from Sigma–Aldrich (St. Louis, MO, USA). BPA (97%) and ¹³C₁₂-labeled BPA (99%) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Full names and acronyms of these analytes are provided in Table S1 of the Supporting Information (SI). HPLC-grade solvents, Milli-Q water, methanol, acetone, formic acid (99%), ammonium hydroxide (28–30 wt % solution of NH₃ in water), ammonium acetate (≥97%), and sodium hydroxide (≥98%) were purchased from Fisher Scientific (Ottawa, ON, Canada).

2.2. Sample collection

Water and sediment samples were collected from Taihu Lake, Liaohe River, and Hunhe River in September of 2013. The distribution of sampling sites is shown in Fig. 1. There are 23 sites (TL1–23) in the Taihu Lake. Fifteen sites were distributed along the LR (LR1–15) and ten were along the HR (HR1–10). River water samples were collected at least 5 m off riverbank with a stainless steel bucket (~5 L volume). At each sampling site, surface sediment was concurrently collected with a hand piston sediment sampler, although sediment was not available at some sampling sites. Totally 23 sediment samples in TL, 12 in LR, and 7 in HR were collected. At each site, at least three individual sediment or water sub-samples were collected and thoroughly pooled to obtain one composite sample.

Water samples were stored in 750 mL polypropylene (PP) bottles and sediment samples were stored in PP plastic bags. All containers and sampling tools were pre-cleaned with methanol and Milli-Q water before each sampling to avoid cross-contamination. Field blanks of laboratory water were also transported with the real samples during the sampling campaign. Water and sediment samples were immediately transported with ice (~4 °C) to the laboratory and stored at –20 °C until pretreatment. No flood event was recorded within one year before our sampling campaigns and the surface water flow velocity was around 1.5 m/s for both LR and HR. Detailed description of water quality parameters can be found in Table S2.

2.3. Sample pretreatment and total organic carbon determination

Water and sediment samples were extracted following the method described elsewhere (Yang et al., 2014b), but with some modifications. Briefly, water samples (500 mL) and blanks were spiked with the internal standard (¹³C₁₂-labeled BPA), and were then filtered through 0.45 μm glass fiber filters (APFF14250, Millipore, USA). Subsequently, water samples were loaded onto Oasis HLB cartridges (500 mg, 6 cc volume, Waters, USA) that were pre-conditioned sequentially with 6 mL of methanol and 6 mL of water at a flow rate of ~5 mL/min. Cartridges were washed with 6 mL of methanol/water (30: 70, v/v) and 6 mL of Milli-Q water to remove interferences, and then pumped until dry. The analytes were eluted from the HLB cartridges using 6 mL of 1.0% ammonia in methanol. These eluates were evaporated to dryness under a gentle stream of pure nitrogen gas, and then reconstituted with 200 μL of methanol/water (50: 50, v/v) for instrumental analysis.

Once in the laboratory, sediment samples were homogenized, freeze-dried, and ground to particles smaller than 80-mesh. A total of 0.5 g of freeze-dried sediment samples were transferred into 15-mL glass centrifuge tubes. After spiking with the ¹³C₁₂-BPA (internal standard), the sediment was extracted with 5 mL of mixed solution of methanol and acetone (50: 50, v/v) by shaking for 60 min. The slurry was centrifuged at 4000g for 10 min (Eppendorf Centrifuge 5804, Hamburg, Germany), and the supernatant was transferred into a clean glass tube. The above extraction steps were repeated one more time. The combined extract was

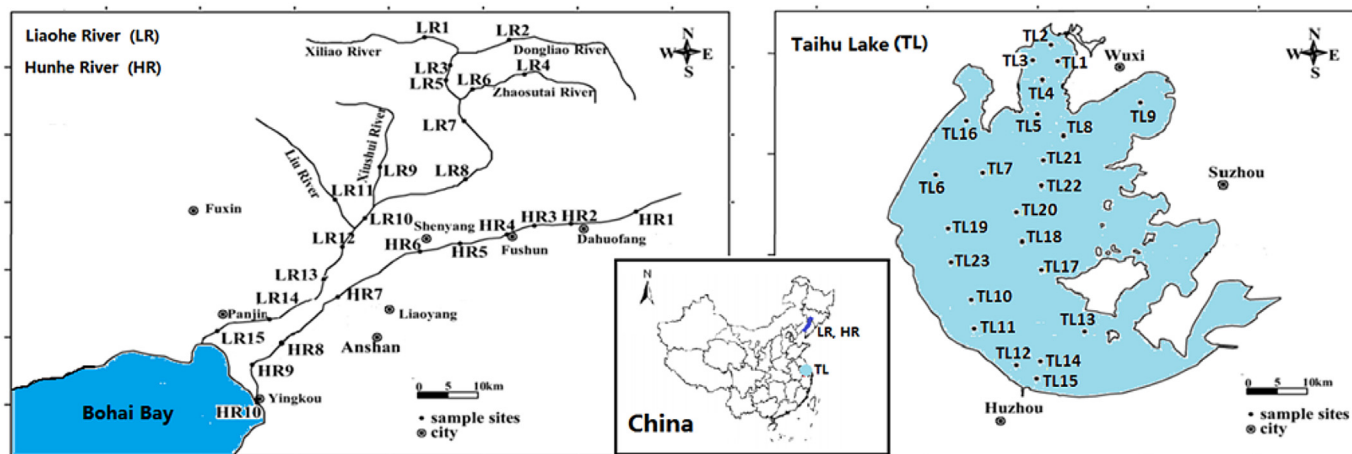


Fig. 1. Sampling sites in Taihu Lake (TL; right), Liaohe River (LR; left), and Hunhe River (HR; left), China.

concentrated to 1.5 mL under a gentle nitrogen stream, and then diluted to 10 mL with water containing 0.1% formic acid (pH = 4). Subsequently, the extract was directly applied to the HLB cartridge for further concentration and purification, following procedures described above.

The organic carbon fraction of sediment (f_{oc} , %) was determined based on the wet chemistry technique (Potassium Dichromate Oxidation–Ferrous Sulfate Titrimetry) suggested by the U.S. Environment Protection Agency using a Vario EL cube elemental analyser (Elementar, Germany) (Chen et al., 2015).

2.4. Instrumental analysis

Identification and quantitation of bisphenol analogues in sample extracts were performed using ultra–performance liquid chromatography tandem mass spectrometry (UPLC–MS/MS) with a Waters ACQUITY liquid chromatography system coupled to a Xevo T_QS triple quadrupole mass spectrometer (ESI–MS/MS; Waters Co., Milford, MA, USA). An analytical column (XBridge™ BEH Shield RP C18, 2.5 μ m, 150 \times 3.0 mm; Waters, MA, USA), connected to a guard column (Thermo Fisher–Hypersil Betasil C18, 1.0 \times 2.1 mm, San Jose, USA), was used for chromatographic separation of analytes. The mobile phase comprised of 2.5 mM ammonium acetate (phase A) and methanol (phase B) at a flow rate of 0.3 mL/min. The gradient increased to 40% B at 1.5 min, and then increased to 100% methanol at 12.5 min before reverting to the initial condition (20% B) at 15 min, and was then maintained until 20 min. A total of ten micro liter of extract was automatically injected and the temperature of column was maintained at 40 °C. Chromatograms were recorded using negative ion multiple reaction monitoring mode. Detailed UPLC conditions, MS/MS parameters, and transitions of ions monitored for quantification and qualification can be found in the SI.

2.5. Limits of detection (LODs) and recoveries

Trace levels of BPA and BPS were detected in the blank HLB cartridges, by rinsing them with 6 mL of methanol or acetonitrile. Therefore, all HLB cartridges were washed three times with HPLC grade methanol (6–10 mL each) prior to use. Internal standard calibration curves were established for the quantitation of all target analytes (highly linear with $R^2 > 0.995$). The limits of detection (LODs) were determined by measuring the means of signals from procedural blank samples ($n = 3$), and reported as the mean plus

three times the standard deviation. If the specific analyte was not detected in the blanks, LODs were defined as the concentration with a signal–to–noise ratio of three. The LODs for the target compounds in waters and sediments were in the range of 0.011–0.077 ng/L and 0.0075–0.10 ng/g dw, respectively. Procedural blanks ($n = 3$) were conducted along with each batch of samples, and trace level of BPA (around its LOD) was occasionally identified. Therefore, when possible, glass centrifuge tubes were used in extraction processes, instead of PP centrifuge tubes that commonly used. Recoveries of the target compounds in spiked Milli–Q water ($n = 4$) ranged from $80 \pm 17\%$ (mean \pm SD) for BPF to $121 \pm 14\%$ for BPZ, and were in the range of $69 \pm 8\%$ (BPAP)– $114 \pm 9\%$ (BPFL) in spiked sediment samples ($n = 4$). Further details regarding LODs and recoveries are provided in Table S1.

2.6. Data analysis

The partition coefficients of bisphenol analogues between sediment and surface water were estimated using the concentrations in sediment and in overlaying water at the same sampling sites. The partition coefficient K_d was calculated using the following equation:

$$K_d = C_s / C_w \quad (1)$$

where C_s and C_w are the concentrations of bisphenol analogues in sediment (ng/g dw) and in corresponding overlaying water (ng/L).

Field–based K_{oc} was calculated using the following equation to describe the partitioning of bisphenols between water and sediment in field.

$$K_{oc} = K_d \times 100 / f_{oc} \quad (2)$$

where K_{oc} is the organic carbon–normalized partition coefficient and f_{oc} is the percentage of total organic carbon in sediment.

3. Results and discussions

3.1. Concentrations of bisphenol analogues in water samples

The mean and median concentrations of bisphenol analogues in the water samples collected from TL, LR, and HR, China are listed in Table 1 and Table S3. All water samples contained measurable bisphenol analogues. The concentration of total bisphenol analogues (Σ BPs) in LR water (mean: 63 ng/L, range: 8.7–173 ng/L)

Table 1
Concentrations of nine bisphenol analogues in the water (ng/L) and sediment (ng/g dw) samples from TL, LR, and HR, China.

	Taihu Lake (n = 23)				Liaohe river (n = 13)				Hunhe river (n = 10)			
	Mean	Median	Range	DF ^a	Mean	Median	Range	DF	Mean	Median	Range	DF
Water												
BPA	8.5	7.9	4.2–14	100	47	29	5.9–141	100	40	42	4.4–107	100
BPAF	0.28	0.21	0.13–1.1	100	1.9	1.0	0.50–9.6	100	2.4	0.94	0.61–11	100
BPAP	0.033	0.018	n.d.–0.39	52	0.0035	n.d.	n.d.–0.045	7.7	n.d.	n.d.	n.d.	0
BPB	n.d. ^b	n.d.	n.d.	0	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0
BPC	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0
BPF	0.83	0.50	n.d.–5.6	87	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0
BPFL	n.d.	n.d.	n.d.	0	0.0095	n.d.	n.d.–0.067	15	0.0069	n.d.–0.069	n.d.	10
BPS	6.0	2.0	0.28–67	100	14	8.9	0.22–52	100	11	8.4	0.61–46	100
BPZ	n.d.	n.d.	n.d.	0	0.054	n.d.	n.d.–0.70	7.7	n.d.	n.d.	n.d.	0
∑BPs	16	12	5.4–87	100	63	42	8.7–173	100	53	49	7.6–160	100
Sediment												
BPA	1.3	0.72	0.19–7.4	100	0.14	0.11	n.d.–0.45	67	1.0	0.93	0.15–2.1	100
BPAF	0.032	0.014	0.010–0.36	100	0.0016	n.d.	n.d.–0.010	17	0.0017	n.d.	n.d.–0.012	14
BPAP	0.031	0.026	n.d.–0.40	61	0.022	0.018	0.010–0.059	100	0.026	0.024	0.014–0.053	100
BPB	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0
BPC	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0
BPF	0.47	0.47	n.d.–1.2	91	0.034	n.d.	n.d.–0.41	8.3	0.92	n.d.	n.d.–3.8	43
BPFL	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0
BPS	0.15	0.071	n.d.–0.76	57	0.092	n.d.	n.d.–1.1	8.3	0.0073	n.d.	n.d.–0.051	14
BPZ	0.12	n.d.	n.d.–2.5	26	0.050	n.d.	n.d.–0.36	17	0.060	n.d.	n.d.–0.42	14
∑BPs	2.1	1.4	0.37–8.3	100	0.34	0.27	0.013–1.3	100	2.0	1.4	0.23–6.0	100

^a DF = detection frequency (%).

^b n.d. = not detected.

and in HR water (53 ng/L, 7.6–160 ng/L) was comparable to each other, while the ∑BPs in TL water (16 ng/L, 5.4–8.7 ng/L) was much lower. BPA, BPAF, and BPS were measurable in all of the 46 water samples with detection frequencies of 100%. LR and HR waters consistently had higher levels of BPA and BPAF than TL water. The mean water concentrations of BPA and BPAF were 47 ng/L and 1.9 ng/L in LR, 40 ng/L and 2.4 ng/L in HR, and 8.5 ng/L and 0.28 ng/L in TL, respectively. The highest concentration of BPS was found in LR (mean 14 ng/L, range 0.61–46 ng/L) water samples, followed by HR (mean 11 ng/L, range 0.61–46 ng/L) and then TL (mean 6.0 ng/L, range 0.28–67 ng/L). Low level of BPAP (mean 0.033 ng/L, n.d.–0.39 ng/L) was detected in 59% of TL water samples, but was only measurable in one sample (0.045 ng/L at LR8) from Liaohe River Basin. Similarly, BPF was frequently detected (87% detection frequency) in TL water with the concentration in the range of n.d.–5.6 ng/L (mean 0.83 ng/L), but was not detectable in Liaohe River Basin. BPFL and BPZ were only found in one or two water samples in Liaohe River Basin at concentrations generally close to their LODs. For instance, BPFL was measurable in two samples (at 0.056 ng/L and 0.067 ng/L) from LR and one sample (at 0.069 ng/L) from HR. Other bisphenol analogues, such as BPB and BPC, were not identified in any of water samples.

The concentration percentage of each analogue in the ∑BPs is shown in Fig. 2. The compositional profile of bisphenol analogues in water samples from HR and LR was generally similar to each other; whereby BPA (mean contribution of ~75% in HR and LR waters) was predominant, followed by BPS (mean 21% and 19% in LR and HR, respectively) and BPAF (both <5%). BPA and BPS collectively contributed >95% of the ∑BPs in HR and LR waters. Although BPA was also predominant (~55%) in TL waters, BPS made a higher contribution (38%) to the ∑BPs than that in HR and LR. In addition, BPF made a significant contribution (mean 5.3%) to the ∑BPs in TL waters while it was absent in HR and LR water samples. The predominance of BPA in all of the water samples suggests that BPA is

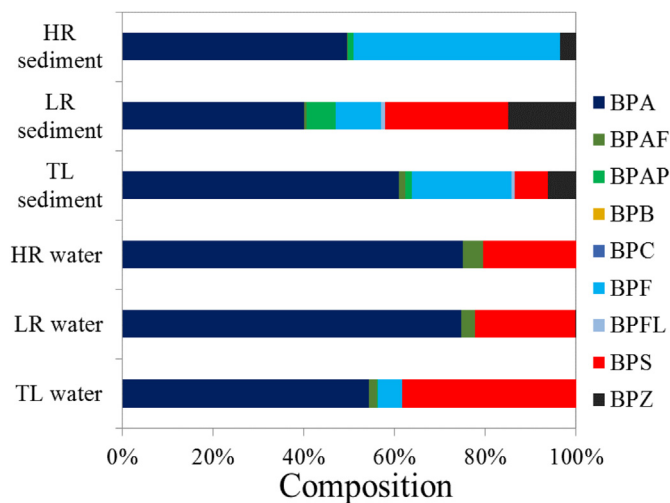


Fig. 2. Compositional profiles of detected bisphenol analogues in the water and sediment samples from TL, LR, and HR, China.

still the most widely manufactured and used bisphenol analogue in China, and followed by its main alternative, BPS. BPA was a chemical of high-production-volume in China, and its production was ~167,000 t/year (Huang et al., 2012). Since the production and usage of BPA were regulated in China around 2008, it has been gradually replaced with BPS and BPF (Liao et al., 2012a,b,c,d), and this is consistent with our monitoring results. BPS was introduced as a BPA substitute partially because it is more resistant to biological degradation in aquatic environment (Liao et al., 2012a,b,c,d). The different compositions between TL and Liaohe River Basin suggest that various BPA alternatives are demanded and/or manufactured in these regions.

3.2. Comparison of water concentrations of bisphenol analogues with those reported previously

Several studies have reported the concentrations of BPA in river and lake waters from around the world (Table 2), and we hereby compared BPA concentrations in the present study with those from literature. The BPA concentration in Liaohe River Basin (4.4–141 ng/L) was comparable to those reported in water samples from the Mississippi River (6.0–113 ng/L) and Canals River (1.9–158 ng/L) in USA and that from the Tiber River in Italy (<30–140 ng/L), but much lower than that from the Pearl River (43–639 ng/L) and Songhuajiang River (23–714 ng/L) in China. The BPA level in Taihu Lake (4.2–14 ng/L, this study) was similar to that in rivers and creeks in Germany (0.5–14 ng/L), but was much lower than that in other water bodies listed in Table 2. For instance, the concentration of BPA in water samples from the Lake Pontchartrain, USA was in the range of 1.5–57 ng/L (mean 21 ng/L).

Information on the environmental occurrence of other bisphenol analogues is scarce, and only a few studies have reported their concentrations in natural waters (Table 3). Mean BPS concentrations in waters from TL (6.0 ng/L), HR (11 ng/L), and LR (14 ng/L) were higher than those from three rivers (3.4, 4.6, and 4.7 ng/L) in Japan (Yamazaki et al., 2015), but much lower than those from the Pearl River, China (135 ng/L), Cooum River, India (768 ng/L) (Yamazaki et al., 2015), and 2 orders of magnitude lower than those found in the Buckingham Canal, India (1080 ng/L) (Yamazaki et al., 2015). For BPF, it was not detected in the LR and HR waters. Its concentrations in waters from TL (mean: 0.83 ng/L, range: n. d.–5.6 ng/L) were considerably lower than those from the Jiuxiang River, China (15–25 ng/L) (Zheng et al., 2015), West River, China (64 ng/L, n. d.–105 ng/L), Arakawa River, Japan (79 ng/L, 76–82 ng/L), and Han River, Korea (633 ng/L, 121–1300 ng/L) (Yamazaki et al., 2015). This may be because BPF was manufactured and applied on a small scale in the studied regions.

3.3. Spatial distribution of bisphenol analogues in water samples

The spatial distribution of bisphenol analogues in the selected watersheds (Fig. 3 and Fig. S1) showed that the Σ BPs in TL waters varied in a narrow range (5.4–30 ng/L, mean 13 ng/L) except a spike at sampling site TL16 (87 ng/L), which contained a comparatively higher level of BPS (67 ng/L). TL16 is close to Wuxi city, where many manufacturers of textile, plastic, and electronics are located (Zhang et al., 2010a,b). Emissions from these factories may contribute to the high level of BPS observed.

In LR, waters from LR2 (140 ng/L), LR4 (173 ng/L), and LR12 (155 ng/L) had relatively higher levels of Σ BPs (8.7–59 ng/L in the other LR water samples). Consistently, other monitoring results demonstrated that the water from site LR12 also contained relatively higher concentrations of various organic pollutants (e.g., polycyclic aromatic hydrocarbons and organochlorine pesticides) than surrounding sampling sites (Yang et al., 2011). It was unexpected that waters from the headstream of LR (i.e., LR2 and LR4) displayed such high levels of Σ BPs (mainly BPA and BPS), suggesting anthropogenic emissions of these chemicals nearby. Relationships among concentrations of measurable bisphenol analogues in LR water samples were tested with Pearson correlation analysis, and significant ($p < 0.05$) relationship was only found between BPA and BPS (sample LR12 was excluded) (Fig. S3). This result suggests that BPA and BPS may have a common source.

In the upstream Hunhe River (HR1–3), the Σ BPs was relatively low (7.6–21 ng/L) (Table S3). It gradually increased at the sites of HR4 (38 ng/L) and HR5 (49 ng/L) as the river flows through industrial areas (such as Fushun) (Figs. 1 and 3), and reached the highest at HR6 (164 ng/L), which located at the vicinity of Shenyang. Shenyang is an industrial city famous for its heavy industries in northern China. It was reported that a considerable amount of waste plastics (e.g., polystyrene foam, polyethylene, polypropylene, etc.) are recycled in Shenyang and the total amount of waste plastics in Shenyang was 631,000 t in 2008 (Chen et al., 2011). In the collection, pretreatment and recycle processes, bisphenol analogues could escape from waste plastics and finally enter the HR. Industrial and municipal activities may also contribute to the high level of Σ BPs at HR6. As the water flows further to the downstream region, the Σ BPs gradually decreased, but the level was generally still higher than those at the upstream sites. A significant relationship (positive, $p < 0.05$) was observed between the BPA and BPS concentrations in water samples from HR, further supporting that they may share similar environmental sources.

3.4. Concentrations of bisphenol analogues in sediment samples

Concentrations of individual bisphenol analogues and Σ BPs in sediment samples are shown in Table 1 and Table S4. The majority (88%) of the analyzed sediment samples contained at least three bisphenol analogues at measurable levels, and no obvious spatial trend was observed (Fig. S3). The Σ BPs ranged from 0.37 to 8.3 ng/g dw in TL, and was followed by that in HR (0.23–6.0 ng/g dw, mean 2.0 ng/g dw) and LR (0.013–1.3 ng/g dw, mean 0.34 ng/g dw). Similar to the water samples, BPA, BPAP, BPF, and BPS were among

Table 2
Comparison of BPA concentrations (ng/L) in TL, LR, and HR waters with those reported from various areas globally.

Location	Year	Mean	Median	Range	DF ^b	Reference
Four rivers and three creeks, Germany ^a	2000	4.7	3.8	0.5–14	100	Kuch and Ballschmiter (2001)
Taihu Lake, China	2013	8.5	7.9	4.2–14	100	This study
Lake Pontchartrain, USA	2003	21	19	1.5–57	100	Boyd et al. (2004)
Haihe River, China	2003	41	35	<0.17–106	93	Jin et al. (2004)
Hunhe River, China	2013	40	42	4.4–107	100	This study
Mississippi River, USA	2003	38	33	6.0–113	100	Boyd et al. (2004)
Tiber River, Italy	2002–2003	78	80	<30–140	90	Patrolecco et al. (2006)
Liaohe River, China	2013	47	29	5.9–141	100	This study
Canals River, USA	2004	^c		1.9–158		Gonzalez-Casado et al. (1998)
Granada, Spain	1998			52.0–219		Gonzalez-Casado et al. (1998)
Pearl River, China	2006–2007	232	136	43–639	100	Gong et al. (2009)
Songhuajiang River, China	2007			23–714	100	Shao et al. (2008)
Two rivers, Japan ^d	2006			<500–900	25	Kang and Kondo (2006)

^a Four rivers: Danube, Nau, Blau, and Iller; three creeks: Schussen, Laiblach, and Argen.

^b DF = detection frequency (%).

^c Not available.

^d Kogawauchi River and Kiyotake River.

Table 3
Comparison of BPS and BPF concentrations (ng/L) in TL, LR, and HR waters with those reported from various areas globally.

Location	Sample size	BPS			BPF			Reference
		Mean	Median	Range	Mean	Median	Range	
Edogawa River, Japan	3	3.4	2.8	2.7–4.7	340	316	259–445	Yamazaki et al. (2015)
Arakawa River, Japan	2	4.6	^a	1.6–7.6	79		76–82	Yamazaki et al. (2015)
Tamagawa River, Japan	3	4.7	3.9	1.5–8.7	1740	2290	90–2850	Yamazaki et al. (2015)
Taihu Lake, China	23	6.0	2.0	0.28–67	0.83	0.50	n.d.–5.6	This study
Korttalaiyar River, India	2	8.7	8.7	n.d.–8.7				Yamazaki et al. (2015)
Hunhe River, China	10	11	8.4	0.61–46				This study
Liaohe River, China	13	14	8.9	0.22–52				This study
Han River, Korea	4	41	41	n.d.–42	633	555	121–1300	Yamazaki et al. (2015)
Pearl River, China	3	135	135	n.d.–135	773	757	448–1110	Yamazaki et al. (2015)
Buckingham Canal, India	2	1080		58–2100	164		38–289	Yamazaki et al. (2015)
Adyar River, India	3	6840	6840	n.d.–7200	20	20	n.d.–27	Yamazaki et al. (2015)
West River, China	3				64	64	n.d.–105	Yamazaki et al. (2015)
Jiuxiang River, China	14						15–25	Zheng et al. (2015)
Several rivers, lakes, and channels, Germany	30						0.1–180	Fromme et al. (2002)

^a Not available.

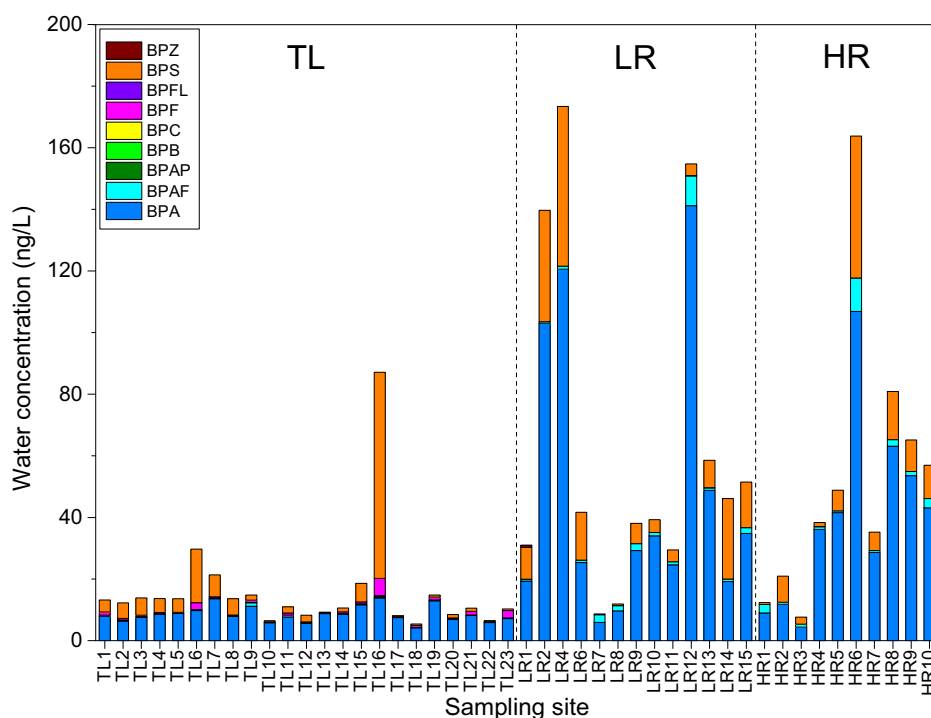


Fig. 3. Concentrations of bisphenol analogues in the water samples from TL, LR, and HR.

the most frequently identified bisphenol analogues in all sediment samples, and the detection frequencies of all analogues were relatively higher in TL sediments. The concentration of BPA was comparable between TL sediments (mean: 1.3, median: 0.72 ng/g dw, detection frequency: 100%) and HR sediments (1.0, 0.93 ng/g dw, 100%), which was ~10 times higher than that in LR sediments (0.14, 0.11 ng/g dw, 67%). Concentrations of BPAF (0.010–0.36 ng/g dw, mean 0.032 ng/g dw, 100%), BPF (n.d.–1.2 ng/g dw, mean 0.47 ng/g dw, 91%), and BPS (n.d.–0.76 ng/g dw, mean 0.15 ng/g dw, 57%) in TL sediments were higher than those from Liaohe River Basin, and were generally >3 times lower than that of BPA. BPS was only detected in one sediment sample from LR and HR, with the concentration of 1.1 and 0.051 ng/g dw, respectively. BPF, BPB, and BPC were not identified in any of the sediment samples.

The concentrations of \sum BPs measured in the sediments in this study were generally lower than those reported in previous studies.

For example, BPA concentrations in the sediments of TL (mean: 1.3, range: 0.19–7.4 ng/g dw) and HR (1.0, 0.15–2.1 ng/g dw) were lower than those of Saginaw River watershed and Michigan inland lakes, USA (3.1, <0.25–13 ng/g dw) (Liao et al., 2012a,b,c,d), Pearl River Estuary, China (3.1, 2.0–4.3 ng/g dw, $n = 2$) (Peng et al., 2007), Tokyo Bay, Japan (8.2, 1.9–23 ng/g dw) (Liao et al., 2012a,b,c,d), Medway River, UK (7.7–56 ng/g dw) (Hibberd et al., 2009), and Elbe River, Germany (163, 66–343 ng/g dw) (Heemken et al., 2001). Liao et al. firstly reported the concentrations of several bisphenol analogues in the sediments of several industrialized areas in the USA, Japan, and Korea (Liao et al., 2012a,b,c,d). The BPS concentrations in TL sediments (mean: 0.15, range: n.d.–0.76 ng/g dw) were slightly lower than that in USA (0.21, n.d.–4.6 ng/g dw), but much lower than that from Korea (61, n.d.–1970 ng/g dw) (Liao et al., 2012a,b,c,d). The level of BPF in TL and HR sediments was also lower than those from USA (3.2, n.d.–28 ng/g dw) and Japan (4.0, n.

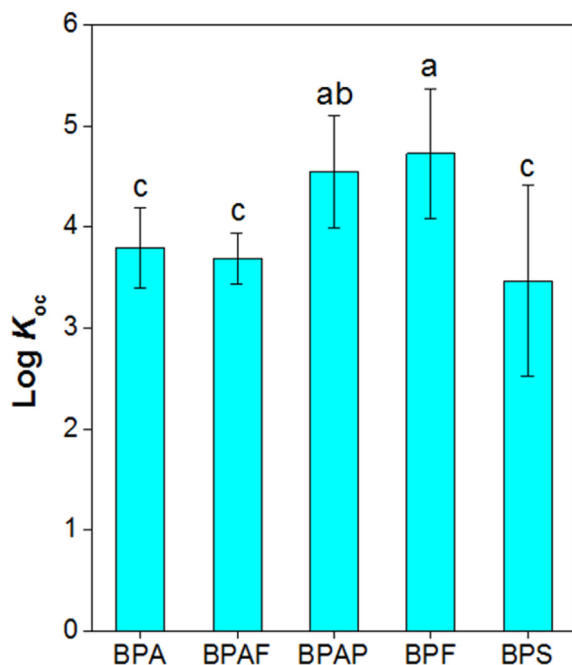


Fig. 4. Log K_{oc} values of bisphenol analogues determined in samples from TL. Different letters indicate statistically significant differences ($p < 0.05$).

d.—9.1 ng/g dw) (Liao et al., 2012a,b,c,d).

The compositional profiles of individual bisphenol analogues in the sediments were distinctly different from that in the corresponding waters (Fig. 2). Although BPA was always predominant in the sediments, its average contribution to \sum BPs (61, 40, and 50% in TL, LR, and HR sediments, respectively) was lower than its contribution in the corresponding waters, especially in LR and HR. The next predominant analogue was BPF in TL and HR sediments (22 and 46%, respectively), but was BPS in LR sediments (27%). BPZ, occasionally detected in water samples, contributed 6.1, 15, and 3.5%, on average, of the \sum BPs in TL, LR, and HR sediments, respectively. Total contribution of other BP analogues was generally less than 5% in sediments. The distinctly different profiles of bisphenol analogues in the sediment and water could be explained by the different partitioning behaviors of individual analogues and their different microbial degradation in the sediment.

3.5. Partitioning of bisphenol analogues between water and sediment

In TL, the partition coefficients could only be calculated for BPA, BPAF, BPAP, BPF, and BPS, since other bisphenol analogues were below detection limit either in waters or in sediments; similarly, that of BPA was calculated in LR and HR. The log K_{oc} s of bisphenol analogues determined in TL followed the order of BPF (mean \pm SD,

4.7 \pm 0.64 mL/g) > BPAP (4.6 \pm 0.56 mL/g) > BPA (3.8 \pm 0.40 mL/g) > BPAF (3.7 \pm 0.25 mL/g) > BPS (3.5 \pm 0.95 mL/g) (Fig. 4). For LR and HR, only the log K_{oc} of BPA could be calculated as other analytes were not detected in either water or/and sediment. The log K_{oc} of BPA in LR and HR (3.0 \pm 0.69 and 3.1 \pm 0.45 mL/g, respectively) was comparatively lower than in TL (Table 4 and Table S5). The field based log K_{oc} could be affected by many field factors, including compositional properties of sediment, hydrology conditions and etc. The different physicochemical properties of sediment compositions may contribute to the different log K_{oc} of BPA in TL and in LR and HR (Ahrens et al., 2009; Higgins and Luthy, 2006). In addition, water flows much faster in river than in lake. Thus, the partitioning from water to sediment in LR and HR may not reach dynamic equilibrium. The relatively lower log K_{oc} of BPA, especially in LR and HR, could also explain its lower contribution in sediments than in waters, as discussed above.

Until now, sparse information is available for the log K_{oc} values of BP analogues. To our knowledge, this is the first study to report the log K_{oc} of BPAP based on real environmental samples. Patrolecco et al. reported a log K_{oc} value of 4.05–4.23 mL/g for BPA which was determined in water and bed sediment collected from Tiber river, Italy (Patrolecco et al., 2006). This value was slightly higher than that derived from TL in the present study. The log K_{oc} of BPAF was reported to be 3.28 \pm 0.4 mL/g, based on the results of a field sampling around a major BPAF manufacturing park in China (Song et al., 2012), and this value was slightly lower than that from TL in this study.

We estimated log K_{oc} values for bisphenols using the EPISuite™ software (based on the molecular connection index; KOCWIN v2.00, EPA, America) (US EPA, 2012) and the calculated log K_{oc} values for BPA (4.6 mL/g) and BPAF (5.9 mL/g) were 0.8 and 2.1 log units higher than those obtained from TL field data, respectively, but the model simulated values for BPF (4.2 mL/g), BPAP (4.5 mL/g), and BPS (3.3 mL/g) were generally comparable to those from TL. If based on their water–octanol partition coefficients (log K_{ow} s; obtained with KOWWIN v2.00) and still using the EPISuite™ software (KOCWIN v2.00) (US EPA, 2012), the derived log K_{oc} s were 2.9, 3.9, 3.1, 3.7, and 2.2 mL/g for BPF, BPAP, BPA, BPAF, and BPS. These log K_{oc} values (except BPAF) were much lower than our field measured values in TL (except BPAF), suggesting that the affinities of the bisphenol analogues with sediment are stronger than that anticipated from their hydrophobicity (i.e., log K_{ow}), and specific chemical interactions, such as hydrogen bonding, could occur between bisphenol analogues and sediment besides nonspecific hydrophobic interaction (Patrolecco et al., 2006). For BPAF, the estimated value (3.7 mL/g) was nearly equal to the field measured log K_{oc} in TL (3.7 \pm 0.25 mL/g). This suggests that nonspecific hydrophobic interaction was predominant between BPAF and sediment. This is also in agreement with the results of Song et al. who observed a good linear relationship between BPAF concentrations in river waters and that in sediments (total organic carbon normalized) (Song et al., 2012). These results suggest that the organic carbon is an important factor in affecting the distribution of BPAF between

Table 4

Organic carbon–normalized partition coefficients (log K_{oc}) of bisphenol analogues determined in this study.

Compound	Taihu Lake					Liaohu river					Hunhe river				
	n	Mean	Median	SD	Range	n	Mean	Median	SD	Range	n	Mean	Median	SD	Range
BPA	23	3.8	3.7	0.40	2.9–4.7	6	3.0	2.8	0.69	2.0–4.0	7	3.1	3.0	0.45	2.4–3.8
BPAF	23	3.7	3.6	0.25	3.1–4.3	a									
BPAP	9	4.6	4.5	0.56	3.9–5.7										
BPF	18	4.7	4.7	0.64	4.1–6.4										
BPS	17	3.5	3.7	0.95	1.6–5.2										

^a Not available.

water and sediment. Yang et al. reported log K_{oc} s of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) (2.88 ± 0.62 and 2.28 ± 0.55 mL/g, respectively) obtained through a field study in TL (Yang et al., 2011). These values were much lower than those of bisphenol analogues calculated from the field samples collected from the same places. This implies that sediment is probably an important sink for the BPA alternatives (Ju et al., 2008). Further research is warranted to understand the partitioning and fate of bisphenol analogues in environmental matrices.

4. Conclusions

Since many European and North America countries regulated and phased out BPA around 2008, several bisphenol substitutes such as BPS, BPAF, BPAP and BPF have been massively applied. Results in the current study showed widespread presence of these chemicals in TL and Liaohe River Basin. Water samples from LR and HR contained comparatively higher total bisphenols (Σ BPs) concentrations. BPA and BPS were predominant with a summed contribution of 55, 75, and 75% to the Σ BPs in TL, LR, and HR waters, respectively. In sediment, BPA was always predominant, with the next abundant compound BPF in TL and HR sediment, but BPS in LR sediment. For the first time, we estimated average field-derived sediment–water partitioning coefficients for certain bisphenols, which was 4.7, 4.6, 3.8, 3.7, and 3.5 mL/g for BPF, BPAP, BPA, BPAF, and BPS, respectively. These results would provide useful information to understand the fate of bisphenols in aquatic environment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.07.059>.

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