Occurrence, Distribution and Ecological Risk of Bisphenol Analogues in the Surface Water from a Water Diversion Project in Nanjing, China

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Abstract: Owing to the widespread use of bisphenol analogues (BPs) as bisphenol A (BPA) alternatives, they have been recognized to constitute a health risk for aquatic ecosystems. The occurrence and distribution of six BPs were investigated in the truly dissolved phase (< 5 kDa), colloidal phase (5 kDa to 1 μm) and suspended particulate matter (SPM > 1 μm) in a water diversion project of Nanjing, China. With the exception of bisphenol Z, all BPs were detected in at least two phases, the total concentrations of detected BPs were 161-613 ng/L, 5.19-77.2 ng/L and 47.5-353 ng/g for the truly dissolved phase, colloidal phase and SPM, respectively. Among the detected compounds, BPA still the dominant BPs in the truly dissolved phase and colloidal phase, followed by BPS, while BPAF was the major contaminant in SPM, followed by BPA. The mean contribution proportions of colloids were 1-2 orders of magnitude greater than that of SPM, suggesting that colloids play an important role in regulating the environmental behaviors of BPs. In terms of spatial distribution, although the water diversion project could reduce the pollution levels of BPs, which might further affect the ecological security of the Yangtze River.

Keywords: bisphenol analogues; colloids; suspended particulate matter; environmental risk; water diversion project

1. Introduction

Environmental hormone bisphenol-A (2,2-bis(4-hydroxyphenyl)propane; BPA) has varying degrees of influence on animals, such as fish [1], rats [2] and human health [3]. A number of countries and regions, including China [4], San Francisco [5], Canada and the European Union [6], have issued policies banning the use of BPA in products in response to the adverse effects of BPA. However, in order to meet the market demand for products, various alternatives to BPA were widely used in industrial production. Such as, BPA analogues bisphenol-S (4,4'-sulfonyldiphenol; BPS) is widely used in the manufacture of epoxy resins [7], bisphenol-E (bis(4-hydroxyphenyl)ethane; BPE) cyanate resin [8], bisphenol-F (bis(4-hydroxypheny)methane; BPF) epoxy resin reinforced with nano polyanilines [9] and Bisphenol-AF (4,4'-(hexafluoroisopropylidene) diphenol; BPAF) was applied to polycarbonate resin production [10]. However, are the products without BPA safe worry-free? Recent studies have shown that BPS, BPF and other BPA analogues were widely detected in

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the water environment, and the pollution levels have an increasing trend [11,12]. And the current researches have indicated that BPS, BPAF and BPF can be adsorbed by aquatic organisms, and result in severe threat to the whole ecosystem as BPA [13,14]. Research is still needed to better elucidate the environmental sources, distribution and fate of bisphenol analogues (BPs).

Existing research has focused on the traditionally dissolved phase, which was subdivided from natural waters according to an operationally defined limit (e.g., 0.7 or 1.0 μm). However, natural colloids (1.0 nm–1.0 μm) are ubiquitously present in aquatic environment. Due to its large specific surface areas and multiple adsorption sites, colloids may be significant both in terms of the proportion of bound contaminant and its subsequent fate and behavior [15]. Previous studies reported that 76% fraction of total organic carbon were contributed by colloidal organic carbon, these colloids are important sinks for BPs, pharmaceuticals and oestrogenic chemicals [11,16]. And up to 50% of antibiotics and BPs were associated with natural colloids in traditionally dissolved phase of surface water [11,17]. However, few studies on the distribution and toxicological characteristics of BPs in the truly dissolved phase (<1 nm) and colloidal phase are investigated, further studies on the multi-phase partitioning and ecological risk of BPs in aquatic system are needed.

Qinhuai River, called as the Mother River of Nanjing city, is connected with Gucheng Lake, Shijiu Lake and Yangtze River, the chief receiving water body of domestic wastewater. Due to the rapid economic growth and high population density, the water quality of the Qinhuai River was gradually deteriorating. To improve water environmental quality of Qinhuai River, a project of Yangtze River Diversion was implemented. The route of water diversion is: the Yangtze River→the New Qinghuai River→the Qinhuai River→the Yangtze River. By mean of the project of Yangtze River Diversion, contaminants can be diverted and diluted, and the water flow can be promoted. However, it is worth noting that the diversion of water is finally discharged into Yangtze River, which may pose a threat to the ecological health of the river. In this study, thirteen sampling sites were settled up along the route of water diversion and the Nanjing section of Yangtze River. The distribution of six BPs in multiple environmental media, including the truly dissolved phase, colloidal phase and suspended particulate matter of surface water were investigated. Based on the knowledge, the environmental risk of BPs was evaluated to determine potential implication to

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ecosystem of water diversion project.

2. Materials and methods

2.1. Chemicals

Standard substances for BPA, BPS, BPE, BPF, BPAF and bisphenol Z (BPZ) were purchased from J&K Chemical Co., Ltd. (Shanghai, China). Methanol, formic acid and ammonia were obtained from Merk Corporation (Darmstadt, Germany).

2.2. Sample collection

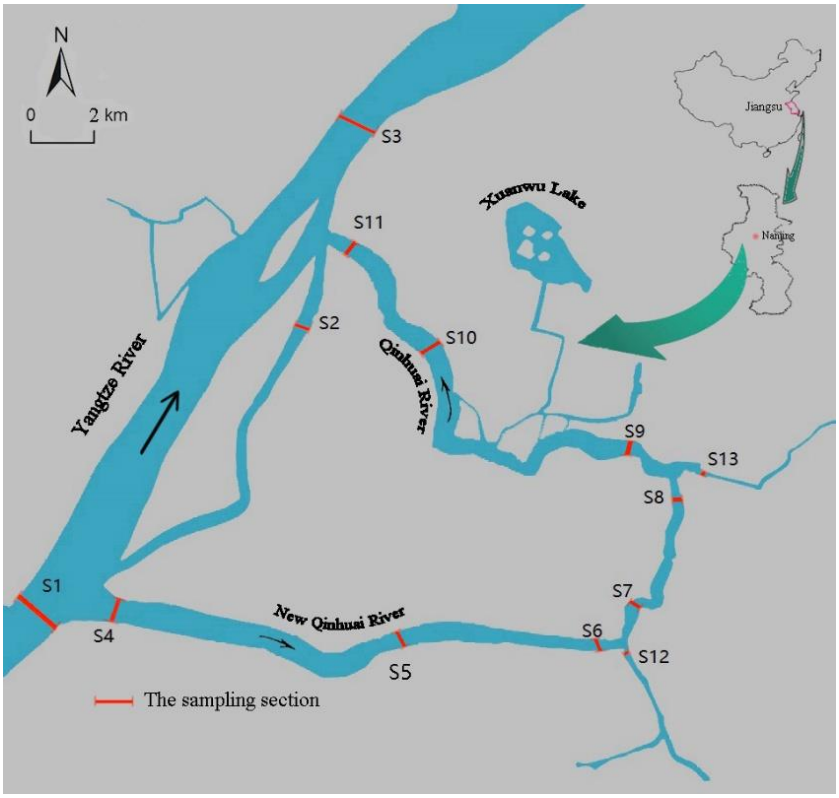

Figure 1. The locations of 13 sampling sites in the survey region.

As shown in Figure 1, a total of thirteen sampling sites were selected along the Yangtze River (S1-S3) and urban river (S4-S13). At each sampling site, 2 L of water sample was collected in triplicate in July 2018, according to the technical specifications of surface water monitoring [11]. The water samples collected were stored in containers containing dry ice, and quickly transported to the laboratory for further processing. According to the pretreatment method reported by previous study [16], the water samples were divided into three parts (i.e., the truly dissolved phase, colloidal

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phase and SPM) by vacuum filter unit and cross-flow cell, using 1 μm glass fiber filters and 5 kDa polyether sulfone membrane, respectively.

2.3. Sample extraction and instrument analysis

The method for extraction and analysis of BPs in the truly dissolved phase and colloidal phase was described in our previous study [11]. Briefly, solid-phase extraction (SPE) system was used to extract the exposure water samples through an Oasis HLB (6 mL, 200 mg) cartridge (Waters, Massachusetts, USA), which were eluted using 9 mL of methanol with 2% ammonia. The extraction method of BPs in SPM samples were developed based on the previous study [18]. Briefly, the SPM samples were extracted using 20 mL of mixture solvent of methanol/acetone (50:50 v/v) with sonication for 30 min, and then centrifuged at 4000 r/min for 10 min. The above steps were repeated two times; the supernatant was merged and concentrated to 2 mL. Next, 200 mL of ultrapure water was added to the solution for further cleanup using SPE method, which was similar to that in water samples.

The BPs were analyzed using Waters Acquity ultra-high performance liquid chromatograph coupled with a Waters Acquity Xevo TQ triple quadrupole mass spectrometer (UPLC/MS/MS) with multiple reaction monitoring. The mobile phase comprised of 0.01% Ammonium hydroxide and 100% acetonitrile. The column temperature, the injection volume and the flow rate were 40 °C, 5 μL and 0.3 mL/min, respectively. Other instrumental parameters of UPLC/MS/MS were shown in the Supplementary information (SI, Table S1 and S2).

2.4. Quality assurance and quality control

In the process of field sample pretreatment, a solvent blank, a standard and a procedure blank were run in sequence to check for background BPs. The sensitivity of the method was evaluated by limit of quantitative (LOQ). The LOQs of BPs in water samples and SPM samples are 0.53-11.1 ng/L and 0.25 -1.5 ng/g, respectively, and the linear range is 1-200 ng/L (R^2>0.991). The recovery rates of BPs in water samples and SPM samples are 70.3%~108% and 73.5%~110% (Table S3), respectively. The relative standard deviation is less than 20%. The detail information was presented in SI.

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2.5. Parameter measurement and statistical analysis

Using the risk quotient (RQ) of algae, daphnias and fish to conduct an ecological risk assessment of BPs detected in the traditional dissolved phase of surface water [19]. According to oestrogen equivalent factor (EEF), 17β-oestradiol equivalency quantity (EEQ) was calculated based on the measured concentrations of BPs [16]. The results were described using mean, median, and concentration ranges. The detail information was showed in SI.

Table 1. Concentrations of detected BPs in the truly dissolved phase, colloidal phase and SPM samples.

Compounds	Truly dissolved phase (ng/L)				Colloidal Phase (ng/L)				Suspended Particulate Matter (ng/g)			
	Mean	Median	Range	DF[a] (%)	Mean	Median	Range	DF (%)	Mean	Median	Range	DF (%)
BPA	253	222	120-554	100	27.4	22.3	4.54-66.7	100	38.8	42.8	28.2-89.8	100
BPS	39.2	38.3	2.24-73.3	100	4.21	4.20	0.14-10.2	100	12.6	14.5	2.78-19.0	100
BPAF	5.10	3.47	1.50-16.2	100	1.12	0.97	0.12-2.47	100	46.7	38.1	28.2-89.8	100
BPF	2.20	1.90	0.00-4.76	61.5	0.35	0.33	0.00-0.82	69.2	2.10	0.00	0.00-17.3	23.1
BPE	0.83	0.94	0.00-2.12	53.8	0.25	0.23	0.00-1.11	53.8	0.00	0.00	0.00-0.00	0.00

[a] DF: detection frequency

3. Results and discussion

3.1. Truly dissolved phase of surface water

The concentrations of BPs including min-max, mean and median values in surface water from study area are shown in Table 1. Five of the six BPs were detected in truly dissolved phase, with detection frequencies of 53.9%-100%, whereas BPZ were not detected. BPA is the predominant compound with a mean concentration of 253 ng/L, followed by BPS (39.2 ng/L) > BPAF (5.10 ng/L) > BPF (2.20 ng/L) > BPE (0.83 ng/L). As shown in Figure 2, the total concentrations of detected BPs (ΣBPs) are from 161 to 613 ng/L (mean concentration 300 ng/L). Spatially, the tributary Yunliang River (S13) had the highest mean concentrations of ΣBPs, followed by Qinhuai River outlet (S11), downstream of the Yangtze River (S3), and Qinhuai River. The Yunliang River as an urban receiving river, receives effluent of a sewage treatment plant (STP, Sewage treatment capacity: 20 0000 m^3/d) [16,20], overflow water of rainwater and some untreated domestic sewage, which may be the main reason for high ΣBPs in S13. The lowest ΣBPs were found in upstream of

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the Yangtze River, which ensure the availability of water quality of the Yangtze River Diversion. Compared to the pollution levels of BPs in upstream of the Yangtze River, the concentrations of ΣBPs in downstream of the Yangtze River (S3) and Qinhuai River outlet (S11) are 2.45 and 2.94 times higher, respectively. These results suggests that the water diversion project from the Yangtze River to urban river mitigated the adverse effects of BPs in the aquatic environment of urban river, however, it could also increase the ecological risk of BPs in downstream of the Yangtze River.

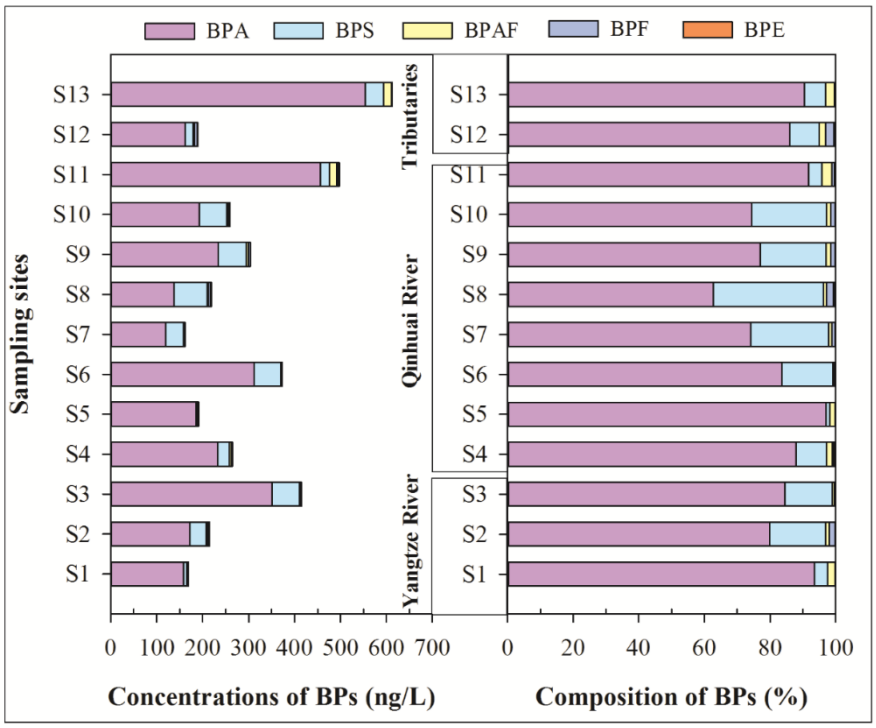

Figure 2. Concentrations and composition of BPs in the truly dissolved phase of the surface water.

In terms of monomer composition, the compositions of BPs in the truly dissolved phase at each sampling site are generally similar, the dominant BP is BPA with the mean contribution of 83.4%, followed by BPS (13.5%), BPAF (1.8%) and BPF (1.0%) (Figure 2). Similar results were also found river-lake system of Taihu Lake basin, where the mean contribution rates of BPA, BPS and BPF were 81.8%, 12.5% and 4.7%, respectively [11]. The pollution levels of BPA in sampling sites S3, S6, S11 and S13 were above 300 ng/L, while BPS in S3, S6, S8, S9, S10 and S13 were higher than 40 ng/L, which were similar with Taihu Lake basin [11]. Among the alternatives to BPA, BPS was the highest BPA alternative in Nanjing section of the Yangtze River and Taihu Lake basin [21], which were clear different from the Pearl River Delta, where BPF was the dominant BP with the

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contribution rate of 78.8%. These results suggest that BPS is being widely used in the Yangtze River basin.

3.2. Colloidal phase of surface water

Colloids, as important sink of emerging contaminants is a widely existing in aquatic environment [22], which can cause some adverse effects on the growth of aquatic organism [23,24]. As shown in Figure 3, five of six BPs in the colloidal phase were widely detected with the detection rates of 53.8%-100%, among them, the detection rates of BPA, BPS and BPAF were 100%. The mean concentrations of ΣBPs were from 5.19 ng/L (site S1) to 77.2 ng/L (site S4), which were clearly lower than those in the truly dissolved phase, suggesting the high biological availability of BPs. Similar with the monomer distribution of BPs in the truly dissolved phase, BPA was still the dominant BPs, followed by BPS and BPAF, with the mean concentrations of 27.4, 4.21 and 1.12 ng/L. These results were consistent with Taihu Lake basin, where BPA and BPS were the dominant BPs [11]. In terms of monomer composition, the compositions of BPs in colloidal phase were generally similar with that in truly dissolved phase, the mean contribution of BPA is 80.6%, followed by BPS (13.6%), BPAF (4.0%) and BPF (1.2%), which was also similar to that of monomer distribution of BPs in Taihu Lake basin [11].

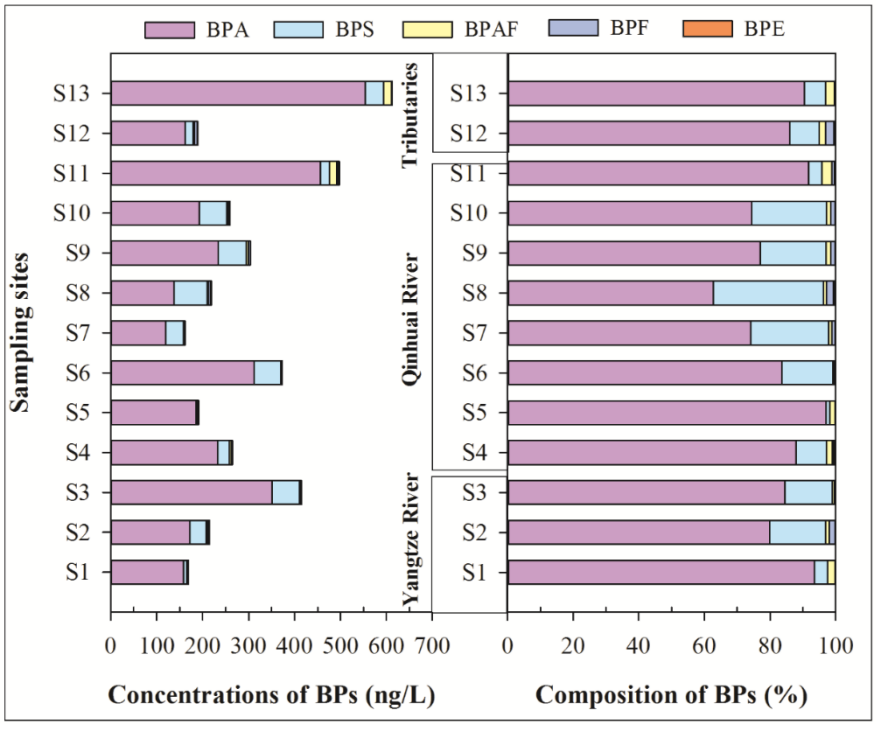

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Figure 3. Concentrations and composition of BPs in the colloidal phase of the surface water.

3.3. Suspended particulate matter of surface water

The concentrations of BPs in SPM are shown in Figure 4. Four of six target compounds were detected in the SPM samples, with the detection frequencies of 23.1%-100%. Neither BPZ nor BPE was detected in all sampling sites. The mean concentrations of ΣBPs ranged from 47.5 ng/g to 353 ng/g. Among them, BPAF was the predominant BP with the mean concentration of 46.7 ng/g, followed by BPA (38.8 ng/g), BPS (12.4 ng/g) and BPF (2.10 ng/g). The concentrations of BPA in SPM from Taihu Lake basin ranged from ND to 877 ng/g dw (mean concentration 76.8 ng/g dw) [25], which were comparable to that of our study, but much lower than that from the Yangtze River (Nanjing section), ranged from ND to 364 μg/g (mean concentration 51.8 μg/g) [18]. However, little research was focus on the residues of other BPs in SPM phase.

The compositions of BPs in SPM phase have been given in Figure 4. In contrast to the truly dissolved phase and colloidal phase, BPAF exhibited relatively higher concentrations, the mean contribution of BPAF to the ΣBPs (46.7%) was much higher than that in truly dissolved phase (1.8%) and colloidal phase (4.0%). While the mean contribution of BPA to the ΣBPs (38.8%) in SPM phase was lower than that in in truly dissolved phase (83.4%) and colloidal phase (80.6%), which was probably because of its strong capacity of bind SPM owing to the relatively high K_{ow} of BPAF. Especially, the mean contributions of BPAF in S6, S7 and S8 reached more than 72%, the three sites were located at the downstream of Jiangning STP, which may be related to the contribution variation of BPAF.

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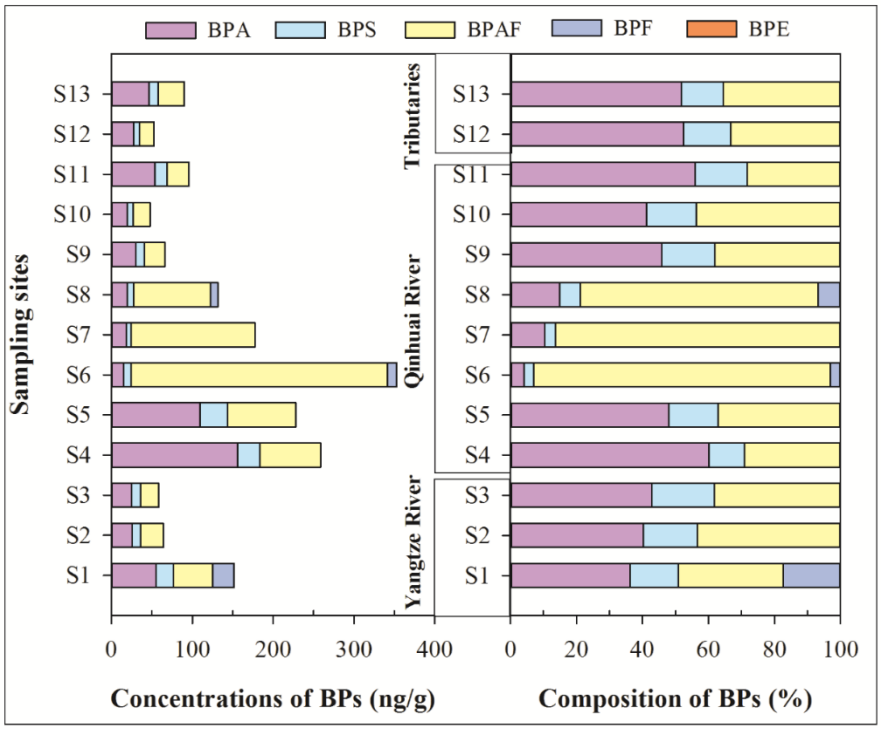

Figure 4. Concentrations and composition of BPs in the suspended particulate matter of the surface water.

3.4. Partitioning among SPM, colloidal and truly dissolved phases of surface water

To evaluate the potential importance of particulate matter to environmental behavior of BPs in the aquatic system, the adsorption contribution proportions of SPM and colloids to BPs were calculated in Figure 5. On average, 90.0% of BPA, 89.9% of BPS, 65.3% of BPAF, 84.2% of BPF and 76.5% of BPE were soluble in the truly dissolved phase. These finding were similar with those reported in the Pearl River [26], where between 24.4% and 94.1% of BPA were soluble in the truly dissolved phase. These results suggested that the majority of BPs were existing as dissolved state in surface water. In colloidal phase, 9.7% of BPA, 9.6% of BPS, 14.4% of BPAF, 13.5% of BPF and 23.5% of BPE were associated with colloids, which were covered in the ranges reported by Gong et al. [26], who found that colloid-bound BPs varied from 3.6% to 52.4% for BPA, 16.7% to 63.1% for 4-nonylphenol ($\log K_{ow}$ = 4.48). Si et al. found that 50.4% of BPAF, 25.2% of BPF, 10.9% of BPA and 9.5% of BPS were bound with colloids in surface water from Taihu Lake basin (Wujin district) without taking SPM into account [11]. In the present study, 0.2% of BPA, 0.5% of BPS, 20.3% of BPAF and 2.3% of BPF were bound with SPM, which were much lower than that of

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colloids with the except of BPAF. The findings indicate that colloids are a potential reservoir of BPs, which might influence the environmental behaviors of BPs due to its ubiquity, abundance and mobility in aquatic systems.

Information on the occurrence of BPs mainly focuses on the traditionally dissolved phase, and the pollution levels of BPs in the truly dissolved and colloidal phases are little. In the present study, the mean concentrations of BPs in the traditionally dissolved phase ranged from 174 ng/L to 642 ng/L (mean concentration: 344 ng/L). The mean contribution proportions of the traditionally dissolved phase were 99.8% of BPA, 99.5% of BPS, 79.7% of BPAF, 97.7% of BPF and 100% of BPE. The concentrations of BPs in the traditionally dissolved phase of surface water reported in all over the world are shown in Table S4. Based on frequent detection of BPs (BPA, BPS, BPF and BPAF), the total concentrations of BPs in our study area were similar to those from Taihu Lake basin investigated in 2018 [11] and the Pearl River Delta investigated in 2015 [27], with the concentration ranges of 98.8−726 ng/L and 107−987 ng/L, respectively. However, the contrast between composition of BPs by BPA and BPF between Taihu Lake basin/Yangtze River (Nanjing section) and Pearl River Basin (China)/Han River (Korea)/Tamagawa River (Japan) suggests the obvious difference in the use and discharge of BPs in these regions/countries [21,27]. BPA was still the predominant in Taihu Lake basin and Yangtze River (Nanjing section) with mean concentrations of 217 ng/L and 291 ng/L, respectively [11], while BPF was predominant in the Pearl River basin, Han River and Tamagawa River (mean concentrations > 630 ng/L) [27].

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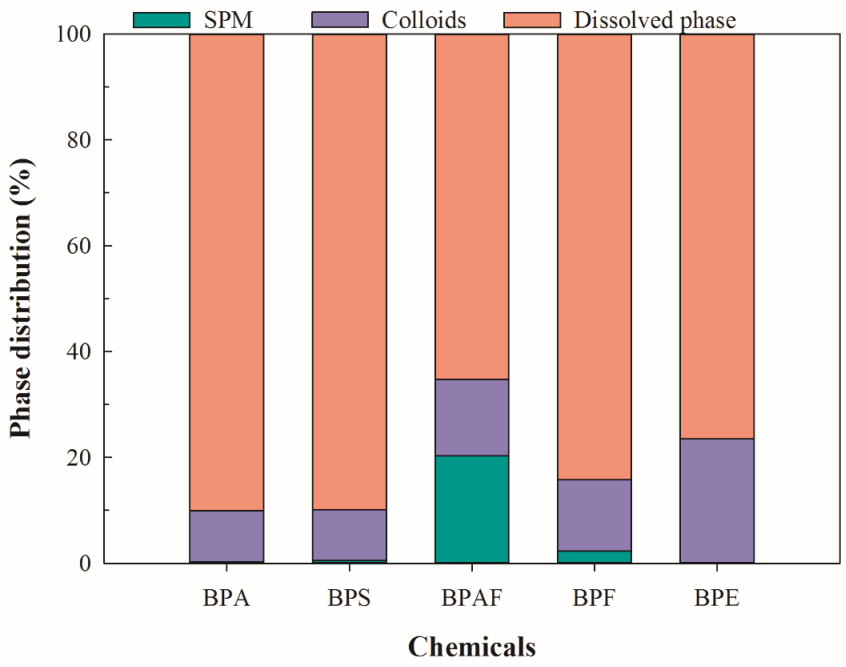

Figure 5. The phase distribution of BPs in the truly dissolved phase,colloids and SPM of the surface water.

3.5. BPs flux and environmental implication

On the basis of flow rates and mean concentrations of BPs, the flux of BPs through water diversion project into the Yangtze River were estimated. The total flow rate of water diversion project was 1.5×10^8 m^3/month during July. Based on the mean concentrations of BPs measured in the surface water of sampling site S11, the flux of BPs was calculated to be 75.6 kg/month for BPA, 3.05 kg/month for BPS, 2.75 kg/month for BPAF, 0.59 kg/month for BPF and 0.36 kg/month for BPE through the water diversion project. The Total flux of BPs through the water diversion project was 82.4 kg/month.

Because of the increased emission and widespread presence of BPs in water bodies, which may have adverse effects on the ecosystem. A screening level risk assessment for detected BPs was performed based on the environmental concentrations of BPs in the traditionally dissolved phase and the toxicity data of BPs for the most sensitive aquatic organisms (Table S5). According to the common risk level evaluation criteria in the water environment [28]: Low risk $0.01 < RQ < 0.1$; medium risk $0.1 < RQ < 1$; high risk $1 < RQ$, a large majority of RQ values for detected BPs (except

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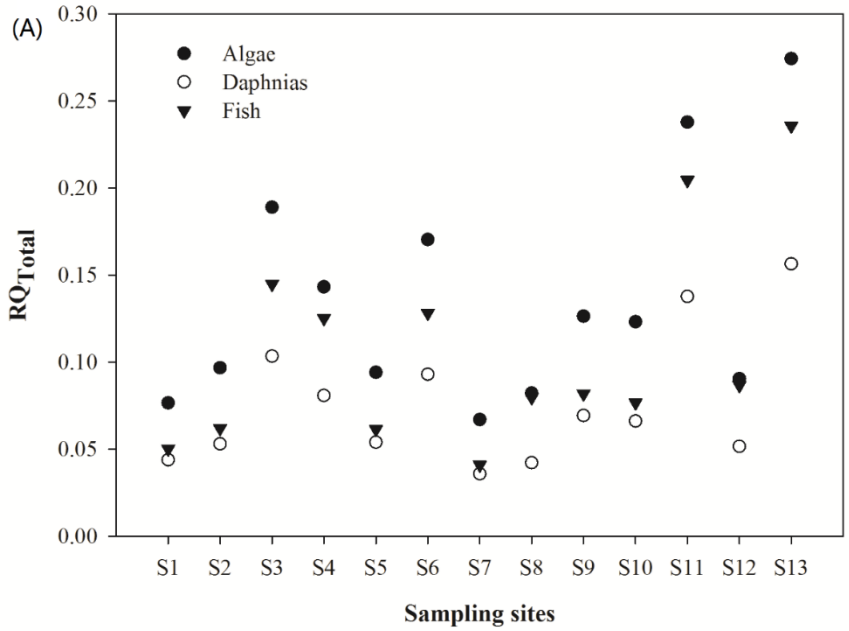
of BPA) were below 0.01, suggesting no high risk was existing for the relevant sensitive aquatic organisms by BPA alternative in the study area. The RQ values of BPA in most sampling sites exceeded 0.1 for algae, indicating medium risk for growth status of *Selenastrum capricornutum* might exist [29]. Due to co-existence of BPs and their similar action patterns, the total RQ of detected BPs (RQ_{Total}) was calculated characterize the worst-case scenario (Figure 6A). The RQ_{Total} ranged from 0.067 to 0.274 for algae, 0.036 to 0.156 for daphnias, and 0.041 to 0.236 for fish, respectively. The most sensitive species are fish, followed by daphnia and algae. In general, the mean contribution values of each BP for RQ_{Total} declined according to the following order: BPA (87.4%) > BPE (5.9%) >BPAF (3.8%) > BPS (2.0%) > BPF (0.9%).



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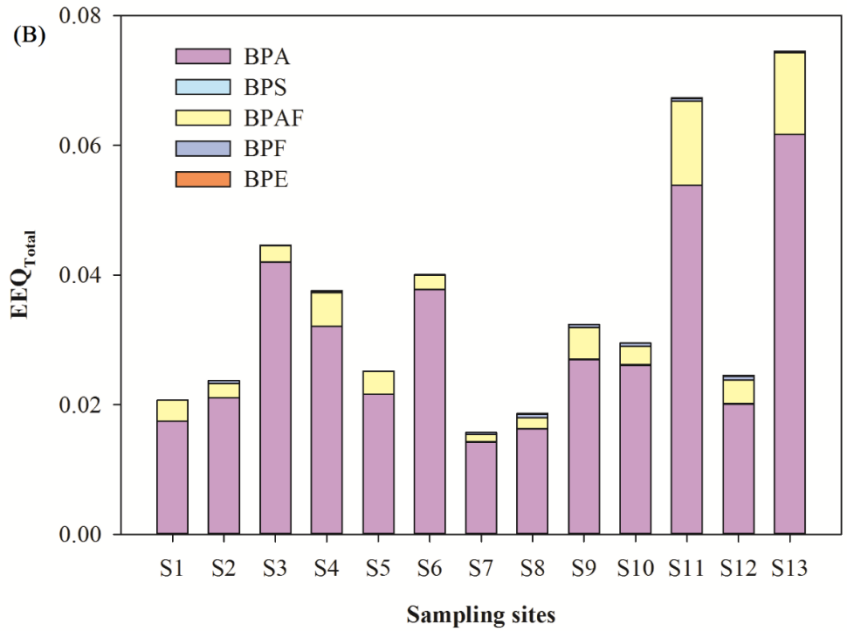

Figure 6. The RQ_{Total} (A) and EEQ_{Total} (B) of BPs for aquatic organisms of the surface water.

Studies have shown that BPs can cause oestrogenic effect on aquatic organisms by combining estrogen receptors. According to the EEF value in Table S5, 17β-oestradiol equivalency quantity (EEQ) method was used to calculate the estrogen activity of BPs. When the total of EEQ (EEQ_{Total}) >1.0 ng E_2/L, it was shown that the chemical could have a negative effect on the endocrine system of aquatic organisms. The results of our study showed that EEQ_{Total} in the waters was 0.0157-0.0745 ng E_2/L (Figure 6B), all the sampling points were less than the threshold of 1.0 ng E_2/L. The contribution rate of BPA to estrogen activity was the highest, which was 86.2%, followed by BPAF (12.9%), BPF (0.8%) and BPS (0.1%). From the perspective of spatial distribution, the higher environmental risk of BPs were found in sampling sites S11 and S13. These two sampling sites are located in the estuarine of water diversion project into Yangtze River and ravine stream into water diversion project. These suggest that the flushing and dilution effects of water diversion project were existing for the mitigation of BPs contamination in urban river, however, potential environmental risks transferring into the Yangtze River also needs to be taken into consideration.

4. Conclusions

The occurrence and distribution of six BPs in surface water were investigated in the water

diversion project. The results showed that BPA, BPAF, BPS and BPF were widespread in truly dissolved phase, colloidal phase and SPM, with the total concentration ranges of 161−613 ng/L, 5.19−77.1 ng/L and 47.5−353 ng/g, respectively. In terms of medium partitioning, the majority of BPs were existing as dissolved state in surface water, followed by colloids and SPM adsorption. The mean distribution ratios of the three medium were 89.4%, 9.9% and 0.7% for the truly dissolved phase, colloidal phase and SPM, respectively. Among the detected BPs, BPA and BPS were most abundant in the truly dissolved phase and colloidal phase, while BPA and BPAF were the major contaminants in the SPM. Particulate matter showed significant binding capacity for BPs, especially for colloids, which maybe further influence the environmental behaviors of BPs. The spatial distribution of BPs in surface water indicated that higher concentrations and environmental risks of BPs were found in the estuarine of water diversion project into Yangtze River, which may further affect the ecological security of the Yangtze River.

Supplementary Materials: Supplementary data to this article can be found online at http://www.mdpi.com/xxx/s1. Table S1: The mobile phase compositions of the separation methods. Table S2: The six BPs of the optimized MS/MS parameters. Table S3: Recovery values obtained for the three independent concentrations of spiked quality control samples. Table S4: The mean (median) and minimum-maximum concentrations of BPs in other sampling locations. Table S5: Aquatic toxicity data of the BPs to the most sensitive aquatic species.

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Conflicts of Interest: The authors declare no conflict of interest.

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