RESEARCH ARTICLE



Occurrence, spatial distribution, and main source identification of ten bisphenol analogues in the dry season of the Pearl River, South China

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Abstract

Bisphenol analogues (BPs) including bisphenol a (BPA) have been broadly utilized as industrial feedstocks and unavoidably discharged into water bodies. However, there is little published data on the occurrence, distribution, and environmental risks of other BPs in surface water. In this study, ten BPs besides BPA were analyzed in surface water from the Pearl River, South China. Among these detected BPs, BPA, bisphenol F (BPF), bisphenol AF (BPAF), and bisphenol S (BPS) were the most frequently detected compounds. The median concentrations of the measured BPs were ranked in the order of BPA (34.9 ng/L) > BPS (24.8 ng/L) > BPAF (10.1 ng/L) > bisphenol F (BPF) (9.0 ng/L) > bisphenol B (BPB) (7.6 ng/L) > bisphenol C (BPC) (1.2 ng/L). Among them, BPA and BPS were predominant BPs, contributing 68% of the total ten BPs in surface water of the Pearl River. These results demonstrated that BPA and BPS were the most extensively utilized and manufactured BPs in this region. The source analysis of BPs suggested that the BPs may be originated from domestic wastewater, wastewater treatment plant (WWTP) effluent, and the leaching of microplastic in surface water of the Pearl River. The calculated BP-derived estrogenic activity exhibited low to medium risks in surface water, but their combined estrogenic effects with other endocrine disrupting compounds should not be ignored.

Keywords Bisphenol analogues · Surface water · Spatial distribution · Estrogenic effect · Pearl River

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Introduction

Bisphenol A (BPA) is a high-yield chemical, primarily utilized as an industrial feedstock to produce epoxy resins and polycarbonate plastics (Huang et al. 2012). Numerous studies have documented the various toxicities of BPA, covering reproductive toxicity, genotoxicity, neurotoxicity, embryotoxicity, and endocrine disruption (Chen et al. 2016; Rochester and Bolden 2015; Huang et al. 2018; Vandenberg et al. 2007; Gu et al. 2022). Therefore, considering the harmful health effects of BPA, countries like China, Canada, Japan, and the European Union have banned its usage in some consumer products (Huang et al. 2017; Wang et al. 2019). To further restrict the risk of BPA, Canada has proposed a BPA discharge standard of 1.75 µg/L for treated wastewater since 2009, and new regulations were proposed in 2010 requiring facilities to develop and implement plans to limit environmental release of BPA, which became the first country that tried to reduce BPA risk for human, wildlife, and ecosystem (Flint et al. 2012). To further protect human's health, BPA has been regulated in National Drinking Water Quality Standard of China, Japan, and European Union (Yuan et al. 2016; 2018; Liu et al. 2021).

To fulfill the market demand, bisphenol analogues with chemical structures similar to BPA have been widely used, and some of them are gradually being used as substitutes for BPA (Chen et al. 2016; Delfosse et al. 2012; Liao et al. 2012; Xue et al. 2015; Banderakhshan et al. 2022). Bisphenol F (BPF), bisphenol S (BPS), and bisphenol AF (BPAF) are the major alternatives of BPA in the manufacture of epoxy resins and polycarbonate plastics. BPF has a variety of usages, such as adhesives, liners, varnishes, and plumbing, as well as in food packaging and dental sealants. BPS is usually applied in thermal papers, can coatings, and dye additives. BPAF is used in electronics, optical fibers, waveguides, and high-performance monomers. Because of the broad use of basic applications extending from food packaging to thermal papers, high quantities of BPs are inevitably emitted into the water bodies through various routes such as industrial effluent and domestic sewage (Erjavec et al. 2016; Yan et al. 2017; Chiriac et al. 2021).

BPA analogues have also been proven to be detrimental to human health and associated with cardiovascular diseases, cancer, obesity, fertility, and allergies. BPS was demonstrated to promote breast cancer progression by altering the level of DNA methylation in the promoter regions of breast cancer-related genes (Huang et al. 2019). Urinary levels of BPAF and BPS were suggested to be significantly associated with type-2 diabetes mellitus (T2DM) (Duan et al. 2018). Moreover, the positive association between urinary BPF and asthma was primarily found in adults, while the correlation between asthma and BPS was only observed in men (Mendy et al. 2020). Overall, these findings have indicated that BPA analogues are not necessarily safe as the replacement compounds of BPA (Helies-Toussaint et al. 2014; Kitamura et al. 2005; Svajger et al. 2016). Thus, it is important to analyze the occurrence of BPs in surface water bodies for their environmental protection and administration (Xie et al. 2022).

The Pearl River Delta is one of the most economically prosperous and populated regions in China. The Pearl Rivers are the critical source of potable water for Guangzhou and its nearby towns. Moreover, this region has been the hub for manufacturing and other industries with a high consumption of BPs in the past decades (Chen et al. 2019). However, to the best of our knowledge, there are only three related publications on the occurrence, distribution, and environmental risks of BPs in the aquatic environment of this region (Zhao et al. 2019; Chen et al. 2020; Huang et al 2020). Among these, the main purpose of Zhao et al. (2019) was to investigate the concentration of BPs in sea and estuary water, while Chen et al. (2020) only collected 10 water samples of the Pearl River to check the river water's safety to swimmers. In the work of Huang et al. (2020), as many as 38 river water samples were collected, in which urban rainfall runoff was proven to be an important source to receiving water. However, the spatial distribution of BPs in the Pearl River remains unknown,

especially in long dry season without influence of rainfall runoff. Therefore, the main purpose of this study was to investigate the spatial distribution of ten BPs in the surface water of the Pearl River without influence of rainwater runoff, along which possible sources of BPs were analyzed.

Materials and methods

Chemicals and reagents

A total of ten BPs were chosen as the target chemicals, including BPA, BPB, BPC, BPE, BPF, BPP, BPS, BPZ, BPAF, and BPAP. Some fundamental information on these ten BPs is shown in Table S1. Deuterated bisphenol A (BPA-d16) was applied as the internal standard (IS). Information for the purity of each BP and supplies is available in our previous study (Wang et al. 2021).

Study area and sample collection

The Pearl River system is highly complicated, and the river networks are intertwined (Fig. 1). Generally, the river flows across Guangzhou city with a population of about 15 million (China Statistics Bureau 2020). The Pearl River branches into two tributaries at the turning point of S4, flowing through Guangzhou city and then converging into one river at Huangpu Port. Liuxi Reservoir is located in the northeastern of Guangzhou city that belongs to Liuxi National Forest Park. The Pearl River is a crucial potable water resource for Guangzhou city and its nearby townships.

In total, 25 sites were selected in the Pearl River, including 17 mainstream sites, 7 tributary sites, and 1 control site (Liuxi reservoir, S0) (Table S2). The sample sites were the same as our previous work (Tang et al. 2021a) and only one water sample was collected in each site. At each site, grab samples (2 L) were gathered from 0.5 m below the water surface in amber glass bottles. Water samples were immediately delivered on ice to the laboratory and kept at -20 °C before pretreatment. The collected water samples were usually treated using solid phase extraction (SPE) within 48 h. All water samples were obtained in December of 2020, which was the dry season in South China and there had been no evident precipitations for at least one month before water sample collection.

Chemical analysis

Extraction, derivatization, and GC-MS analysis

The methods for extraction, derivatization, and instrumental analysis were performed following our previous study (Wang et al. 2020). In brief, water samples were filtered through 0.45- μ m glass fiber filters and spiked with the



Fig. 1 Location map of sampling sites in the Pearl River

internal standard (50 μ L of 1 mg/L each). The filtered water samples were then loaded onto an Oasis HLB SPE cartridge (225 mg, Waters, USA) with an AQUA Loader 3 (GL Science, Japan) at a flow rate of 10 mL/min. After the sample loading, the cartridges were dried under a vacuum and then eluted with 5 mL methanol. The eluates were dried under a mild stream of N_2 in preparation for derivatization. BPs were analyzed by GC–MS, using an Agilent 7890B series gas chromatograph with a 5977B single quadrupole mass spectrometer (Agilent, USA). Detailed descriptions about the derivatization steps and instrumental analysis of BPs are provided in the Supporting Information.

Quality assurance and quality control

A procedure blank, solvent blank, and 100 ng/mL mixed standard sample were performed sequentially every 12 injections during the testing of each batch of samples to check out background contaminants, residues, and instrument properties. The calibration curve was prepared using the 7-point quadratic regression ranging from 5 to 200 µg/L. The coefficients of determination $(R^2) > 0.993$ showed the excellent linearity for the standard calibration curve. Quantification of BPs was determined by an internal standard method. For each target compound, limits of detection (LODs) and limits of quantification (LOQs) were obtained by the standard deviation (SD) of triple and tenfold the seven replicate injections of the lowest concentration of the standard calibration curve. The method recoveries were obtained by spiking standards at 20, 100, and 200 ng/L into the river water sample. Detail recoveries, LODs, and LOQs of target bisphenol analogues are described in Table 1

Risk assessment

Estrogenic activity assessment

Since the Pearl River is the primary supply of potable water for the population and BPs induce similar estrogenic effects, estrogen equivalent (EEQ) is also employed to assess the risk of BPs in water bodies (Eldridge et al. 2007; Konkel 2013). The chemically calculated EEQ of the target ten BPs is calculated with Eq. (1). Pollutants are considered to be harmful to the endocrine systems of organisms in the aquatic environment when EEQ is greater than 1.0 ng E_2/L (Yan et al. 2017; Tang et al. 2021a, b).

$$EEQ = \sum (C_i \times EEF_i)$$
(1)

where C_i indicates the levels of the target BPs in water samples and EEF_i represents the proportion of the median effective concentration (EC₅₀) of each chemical to the EC₅₀ of 17β -estradiol. As shown in Table S1, each BP has different estradiol equivalency factors and varied considerably. Hence, the choice of estradiol equivalency factor may be significantly different. In the present study, the maximum reported estradiol equivalency factor was employed for each target chemical.

Eco-toxicity assessment

The risk quotient (RQ) method was used to assess the ecotoxicity of the selected BPs in the water bodies (Xiong et al. 2016; Yan et al. 2017; Zhao et al. 2015). RQ_i value is the proportion of the maximum measured environmental concentration (MEC_i) to the predicted no-effect concentration (PNEC_i), depicted in the following equation.

$$\sum RQ = \sum RQ_i = \sum \frac{MEC_i}{PNEC_i}$$
(2)

The Σ RQ was the sum of RQ of each separately measured contaminant (RQ_i) at each sampling site (Eq. (2)). Generally, environmental risks are classified as high risk (RQ > 1.0), medium risk (0.1 < RQ < 1.0), and low risk (0.01 < RQ < 0.1) (Blair et al. 2013; Palma et al. 2014). The PNEC values are usually obtained from dividing the minimum toxicity value (i.e., lowest short-term L(E)C50 or long-term NOEC value) in the literature by an assessment factor (AF) of 1000, 100, 50, or 10. The toxicity values of the present study were derived from published studies, as shown in Table S4.

Data analysis

In the statistical analysis, the concentrations of BPs below their LODs were set one-half of their corresponding LODs (Luo et al. 2018, 2020). Statistical analyses were performed with SPSS version 17.0 software package. All of the plots were created with Origin version 8.1. The statistical significance was set at p < 0.05 or below.

Table 1 Calibration curve, R^2 , recovery (%, mean \pm standard derivation, n = 3), method limits of detection (LODs), and limits of quantitation (LOQs) of target bisphenol analogues in surface water by GC–MS (ng/L)

Calibration curve	R^2	Recovery	Recovery			
		20	100	200		
y = 1.4067x - 0.1391	0.998	76.3 ± 4.2	84.3±6.4	83.2 ± 0.93	5.2	17.5
y = 1.4587x - 0.2084	0.998	117.4 ± 2.9	89.0 ± 4.3	84.3 ± 0.49	1.5	5.9
y = 1.0184x - 0.1752	0.998	83.0 ± 2.1	91.9 ± 6.5	90.8 ± 0.20	2.4	7.9
y = 0.4953x + 0.0307	0.993	113.9 ± 6.3	104.6 ± 2.9	80.8 ± 5.3	5.4	17.9
y = 0.5841x - 0.0891	0.998	92.5 ± 3.8	91.5 ± 3.9	95.7 ± 0.48	2.4	6.1
y = 0.0582x - 0.0082	0.999	73.7 ± 5.4	79.6 ± 3.0	97.6 ± 1.3	5.6	18.7
y = 0.072x - 0.0175	0.989	98.2 ± 3.8	73.4 ± 1.1	74.3 ± 3.1	5.4	19.3
y = 0.2108x - 0.0304	0.998	67.8 ± 5.8	100.0 ± 5.7	104.1 ± 1.2	2.6	8.7
y = 0.4004x - 0.0648	0.998	126.4 ± 5.3	124.6 ± 6.9	74.6 ± 4.1	3.6	12.1
y = 0.5051x - 0.0646	0.995	92.1 ± 1.6	91.5 ± 3.9	92.3 ± 0.18	2.2	5.6
	Calibration curve y=1.4067x-0.1391 y=1.4587x-0.2084 y=1.0184x-0.1752 y=0.4953x+0.0307 y=0.5841x-0.0891 y=0.0582x-0.0082 y=0.072x-0.0175 y=0.2108x-0.0304 y=0.4004x-0.0648 y=0.5051x-0.0646	Calibration curve R^2 $y = 1.4067x - 0.1391$ 0.998 $y = 1.4587x - 0.2084$ 0.998 $y = 1.0184x - 0.1752$ 0.998 $y = 0.4953x + 0.0307$ 0.993 $y = 0.5841x - 0.0891$ 0.998 $y = 0.0582x - 0.0082$ 0.999 $y = 0.072x - 0.0175$ 0.989 $y = 0.4004x - 0.0648$ 0.998 $y = 0.5051x - 0.0646$ 0.995	Calibration curve R^2 Recovery $y = 1.4067x - 0.1391$ 0.998 76.3 ± 4.2 $y = 1.4587x - 0.2084$ 0.998 117.4 ± 2.9 $y = 1.0184x - 0.1752$ 0.998 83.0 ± 2.1 $y = 0.4953x + 0.0307$ 0.993 113.9 ± 6.3 $y = 0.5841x - 0.0891$ 0.998 92.5 ± 3.8 $y = 0.0582x - 0.0082$ 0.999 73.7 ± 5.4 $y = 0.2108x - 0.0304$ 0.998 67.8 ± 5.8 $y = 0.4004x - 0.0648$ 0.998 126.4 ± 5.3 $y = 0.5051x - 0.0646$ 0.995 92.1 ± 1.6	$\begin{array}{c c} \mbox{Calibration curve} & R^2 & \mbox{Recovery} \\ \hline 20 & 100 \\ \hline \\ \mbox{y=1.4067}x-0.1391 & 0.998 & 76.3 \pm 4.2 & 84.3 \pm 6.4 \\ \mbox{y=1.4587}x-0.2084 & 0.998 & 117.4 \pm 2.9 & 89.0 \pm 4.3 \\ \mbox{y=1.0184}x-0.1752 & 0.998 & 83.0 \pm 2.1 & 91.9 \pm 6.5 \\ \mbox{y=0.4953}x+0.0307 & 0.993 & 113.9 \pm 6.3 & 104.6 \pm 2.9 \\ \mbox{y=0.5841}x-0.0891 & 0.998 & 92.5 \pm 3.8 & 91.5 \pm 3.9 \\ \mbox{y=0.0582}x-0.0082 & 0.999 & 73.7 \pm 5.4 & 79.6 \pm 3.0 \\ \mbox{y=0.072}x-0.0175 & 0.989 & 98.2 \pm 3.8 & 73.4 \pm 1.1 \\ \mbox{y=0.2108}x-0.0304 & 0.998 & 67.8 \pm 5.8 & 100.0 \pm 5.7 \\ \mbox{y=0.4004}x-0.0648 & 0.998 & 126.4 \pm 5.3 & 124.6 \pm 6.9 \\ \mbox{y=0.5051}x-0.0646 & 0.995 & 92.1 \pm 1.6 & 91.5 \pm 3.9 \\ \hline \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Result and discussion

Concentrations of bisphenol analogues in Pearl River

Table 2 shows the range, mean, median, and detection frequency of each BP in the Pearl River water. At least one BP was detected in each water sample. The levels of the total ten BPs (Σ BPs) in the Pearl River water varied from 36.6 to 261.8 ng/L with mean (median) concentration of 114.0 (89.8) ng/L. Among the determined ten BPs, BPA, BPAF, BPF, and BPS were widely detected with detection frequencies of 100%, 92%, 84%, and 72%, respectively, while the respective detection frequencies of BPB, BPC, BPZ, and BPAP were 52%, 44%, 4%, and 4%. BPE and BPP were not detected in any water sample. Among the detected BPs, the median concentration was ranked in the order of BPA (34.9 ng/L) > BPS (24.8 ng/L) > BPAF (10.1 ng/L) > BPF (9.0 ng/L) > BPB (7.6 ng/L) > BPC (2.7 ng/L). However, BPZ and BPAP were only detected in one water sample with the concentration approaching their LOQs. Though their usage data are hardly available, the detected results of this work suggested that BPs were widely used in Guangzhou, leading to their wide distribution in the Pearl River.

Figure 2 shows the concentration contribution ratio of each BP to the Σ BPs. Based on their median concentration, BPA contributed about 39%, followed by BPS with a contribution ratio of 27%, BPAF (11%), and BPF (10%), while

Table 2 Concentrations of target compounds in surface water from the Pearl River*

Site	BPA	BPB	BPC	BPE	BPF	BPP	BPS	BPZ	BPAP	BPAF	ΣBPs
S0	29.0 ± 1.1	7.7 ± 0.07	n.d	n.d	8.4 ± 0.2	n.d	29.5 ± 0.9	n.d	n.d	14.1±1.4	89.8
S 1	18.9 ± 0.5	n.d	9.0 ± 0.0	n.d	n.d	n.d	n.d	n.d	n.d	9.9 ± 0.2	42.9
S2	13.9 ± 0.4	n.d	9.0 ± 0.0	n.d	n.d	n.d	n.d	n.d	n.d	9.7 ± 0.1	36.6
S 3	18.9 ± 0.4	n.d	9.1 ± 0.0	n.d	n.d	n.d	n.d	n.d	n.d	11.2 ± 0.5	48.6
S4	16.9 ± 0.7	7.7 ± 0.0	8.8 ± 0.0	n.d	n.d	n.d	n.d	n.d	n.d	n.d	40.1
S5	19.9 ± 0.5	7.6 ± 0.1	9.1 ± 0.1	n.d	9.1 ± 0.1	n.d	n.d	n.d	n.d	25.5 ± 1.3	71.2
S6	39.1 ± 1.1	n.d	n.d	n.d	8.9 ± 0.2	n.d	21.6 ± 0.3	n.d	n.d	9.3 ± 0.5	80.1
S 7	28.2 ± 0.3	7.7 ± 0.7	n.d	n.d	9.0 ± 0.3	n.d	24.6 ± 0.6	n.d	n.d	10.3 ± 0.7	81.0
S 8	26.1 ± 0.6	n.d	n.d	n.d	9.5 ± 0.1	n.d	12.2 ± 0.0	n.d	n.d	13.5 ± 0.5	64.0
S9	29.1 ± 0.7	n.d	9.0 ± 0.0	n.d	8.7 ± 0.3	n.d	n.d	n.d	n.d	16.3 ± 0.4	70.3
S10	17.1 ± 0.3	7.8 ± 0.2	8.8 ± 0.0	n.d	9.0 ± 0.3	n.d	n.d	n.d	n.d	11.2 ± 0.1	53.8
S11	36.0 ± 0.9	8.7 ± 0.1	9.0 ± 0.0	n.d	11.6 ± 0.3	n.d	115.9 ± 5.8	n.d	n.d	9.1 ± 0.2	194.1
S12	40.0 ± 2.2	8.8 ± 0.1	9.1 ± 0.0	n.d	13.1 ± 0.4	n.d	118.3 ± 7.3	n.d	n.d	9.4 ± 0.8	201.3
S13	64.7 ± 0.7	8.5 ± 0.2	n.d	n.d	12.4 ± 0.3	n.d	124.4 ± 6.2	n.d	n.d	n.d	214.3
S14	41.4 ± 1.7	8.3 ± 0.1	n.d	n.d	10.5 ± 0.28	n.d	57.8 ± 2.7	n.d	n.d	8.6 ± 0.1	127.8
S15	37.8 ± 0.5	8.7 ± 0.2	n.d	n.d	10.0 ± 0.4	n.d	79.8 ± 5.0	n.d	n.d	9.3 ± 0.5	146.8
S16	34.9 ± 2.7	7.6 ± 0.1	n.d	n.d	9.5 ± 0.1	n.d	39.2 ± 3.3	n.d	n.d	8.0 ± 0.1	101.9
S17	31.8 ± 3.0	7.6 ± 0.1	n.d	n.d	9.0 ± 0.1	n.d	28.2 ± 2.5	n.d	n.d	8.5 ± 0.4	87.7
S18	36.3 ± 0.3	n.d	9.4 ± 0.1	n.d	8.6 ± 0.1	n.d	18.7 ± 0.5	8.0 ± 0.3	8.9 ± 0.0	15.4 ± 0.2	107.9
S19	25.8 ± 1.4	n.d	n.d	n.d	9.2 ± 0.1	n.d	24.8 ± 3.2	n.d	n.d	11.3 ± 2.5	73.8
S20	40.5 ± 1.06	7.7 ± 0.0	9.3 ± 0.2	n.d	9.8 ± 0.2	n.d	53.7 ± 2.0	n.d	n.d	123.1 ± 2.8	246.8
S21	52.8 ± 2.2	8.2 ± 0.1	n.d	n.d	9.7 ± 0.2	n.d	48.2 ± 2.1	n.d	n.d	87.5 ± 1.4	211.5
S22	53.1 ± 1.9	n.d	n.d	n.d	9.0 ± 0.2	n.d	31.8 ± 2.5	n.d	n.d	8.8 ± 0.3	103.4
S23	126.0 ± 1.4	n.d	n.d	n.d	9.7 ± 0.5	n.d	110.8 ± 13.2	n.d	n.d	10.1 ± 0.5	261.8
S24	44.7 ± 3.3	n.d	n.d	n.d	9.0 ± 0.2	n.d	23.1 ± 2.0	n.d	n.d	17.0 ± 0.1	93.8
Range	13.9–126.0	0-8.8	0–9.4	0–2.7	0-13.1	0–2.8	0.0-124.4	0-8.0	0-8.9	0-123.1	36.6-261.8
Mean	36.9	4.6	4.3	1.5	8.3	0.2	38.7	0.5	0.65	18.3	114.0
Median	34.9	7.6	1.2	2.7	9.0	0	24.8	0	0	10.1	89.8
SD^a	22.4	4.0	4.3	1.4	3.4	0.8	40.6	1.6	1.8	27.1	68.0
RSD ^C	60.7%	87.0%	100.0%	93.3%	41.0%	400%	104.9%	320.0%	276.9%	148.1%	59.6%
DF^b	100	52	44	0	84	0	72	4	4	92	-

^aStandard deviation; ^bdetection frequency; ^crelative standard deviation; ^{*}in many samples, the BP concentrations were above LOD but below LOQ; however, their ratios of the signal to noise were all above 10; thus, their concentrations were all given; n.d: not detected

the total contribution ratio of BPA, BPS, and BPAF was over 70%. The contribution ratio of BPS was close to that of BPA, which suggested that usage of BPS has been rapidly increased in Guangzhou city in recent years, since BPs i are structurally similar to BPA, and numerous studies have confirmed the BPs as an kind of EDCs (Van Leeuwen et al. 2019). Hence, the environmental risks of BPs in surface water should be paid more attention.

Concentration comparison with previous studies

Recently, the levels of BPs in river water have been investigated in several regions, especially for BPA, and these studies were in comparison with the current work (Table 3). The concentrations of BPA in this research were less than those in previous studies in the Pearl River system (Huang et al. 2020), but comparable to those in water samples from the Hunhe River (40 ng/L), Haihe River (42 ng/L), Liaohe River (47 ng/L), West River (43 ng/L), and Yellow River (33/44 ng/L) in China (Jin and Zhu 2016; Patrolecco et al. 2006; Yamazaki et al. 2015; Zhao et al. 2020). Mean BP concentrations (39 ng/L) in this work were greater than those reported from China and Japan (Huang et al. 2020; Yamazaki et al. 2015), but lower than those in India (Yamazaki et al. 2015). The mean levels of BPAF (18 ng/L) in the present study were less than those found from the Yellow River (40/24 ng/L; dry/wet season) (Zhao et al. 2020), but higher than those of other previous studies (Huang et al. 2020; Jin and Zhu 2016). Other BPs were detected with low levels in this work, comparable to those of other studies from China (Huang et al. 2020; Jin and Zhu 2016). In comparison with the concentrations of BPA, BPS, and BPF in the Pearl River in 2015, recorded by Huang et al. (2020), the levels of



Fig. 2 Compositional profiles of detected bisphenol analogues in the surface water from the Pearl River based on their median concentrations

BPA have been decreased dramatically. Still, the concentrations of BPS and BPF were basically unchanged. This may be attributed to the ban on related applications of BPA in China (Qiu et al. 2021).

Spatial distribution and potential sources of BPs

The spatial distribution of BPs in this region (Table 2) showed that the Σ BPs in the Pearl River water varied considerably in the range of 37-262 ng/L with mean levels of 90 ng/L. For the Pearl River, the higher levels for BPA, BPS, and BPAF occurred at sites S11-S13, S20-S21, and S23, while the greatest levels of BPA (126.0 ng/L) was found at site S23, the maximum concentrations of BPS (124.4 ng/L) was observed at site \$13, with the largest concentrations of BPAF (123.1 ng/L) was measured at site S20. These sites are located in the branches of the Pearl River, adjacent to industrial zones, resulting in large quantities of industrial wastewater being released into the river with incomplete removal. Compared to other sites, the levels of BPs are well-distributed in surface water of the Pearl River, and the main contribution of BPs may be from domestic pollution. Unexpectedly, trace amounts of BPs were detected at site S0, which is an essential potable water source, raising concerns about the risk of human exposure. Exposure to these compounds may result in estrogenic effects and reproductive effects, or jeopardize the cognitive abilities of children (McDonough et al. 2021). We speculate that some of the BPs in site S0 may come from various sources, involving photo-/ microbial degradation from parent chemicals, existing as industrial additives in consumer products.

WWTP effluents are considered to be the potential source of BPs in the aquatic environment. To confirm this, the selected BPs in the upstream and downstream river waters of the seven municipal WWTPs were further compared. As shown in Fig. 3, the levels of BPA, BPS, and Σ BPs in the downstream river waters of XT WWTP were significantly higher than that of the upstream river water. However, the concentration of Σ BPs between the upstream and downstream river waters of other WWTPs has no obvious statistical relationship. In South China, industrial wastewater is initially processed in factory sewage treatment facilities and then further treated in WWTPs. The XT WWTP in the present study received both industrial and domestic sewage, while other WWTPs only received domestic sewage. Therefore, the XT WWTP effluent may have a higher concentration of BPs, leading to elevated concentrations of BPs in downtown water. The study of Huang et al. (2020) reported higher concentrations of BPs in the XT WWTP effluent than those of the other WWTPs. The results seemed to suggest that the WWTP effluent is an essential potential source of BPs. However, the concentrations of the total BPs between the upstream and downstream river waters of the other

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ND, not detected; -, not available

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Fig. 3 The total concentrations of ten BPs in the Pearl River waters collected at the upstream and downstream of seven WWTPs



Fig. 4 Score plot of principal component analysis of bisphenol analogues in surface water from the Pearl River

WWTPs have no obvious statistical relationship (p>0.05). There are several possible reasons for this, including the low concentration of BPs in WWTP effluent and the different half-life of BPs.

BPs are extensively applied in household products and urban infrastructure. As a result, BPs will be unavoidably discharged into the receiving streams through the urban rainfall runoff. A previous study suggested that the daily mass load of BPA in runoff was 2.7 times greater than that in WWTP effluents in the UK (Wilkinson et al. 2016), indicating that rainfall runoff was an important source of BPA. Consistently, other monitoring results also suggested that rainfall runoff was the main source of pharmaceuticals and personal care products (PPCPs) in the rivers. In spite of the diluting effect, PPCP levels were increased in the receiving rivers (Liu et al. 2018; Mei et al. 2018). In this study, sampling was collected during the dry season, and it has not rained for more than a month. Thus, the BPs entering rivers through rainfall runoff were unlikely to be the critical source in this study.

In addition to WWTP effluent and rainfall runoff, microplastics may be potential sources for BPs in surface water due to the release of monomers during the aging process. Numerous studies have shown that BPA will be available for leaching from microplastics in seawater and surface water (Notardonato et al. 2019; Sajiki and Yonekubo 2004; Xu et al., 2020) Meanwhile, some available studies have investigated the presence of microplastics in surface water in China, including Yongjiang River, Pearl River, Hanjiang River, and Yangtze River (Zhang et al. 2020; Lin et al. 2018; Wang et al. 2017), with the abundance ranges of 379–8920 items/m³. Thus, microplastics may contribute to BPs in surface water, although more knowledge is needed to verify the hypothesis.

As shown in Table 4, the correlations between the levels of these BPs were also performed. In the Pearl River, the correlation analysis suggested that there was a significant positive relationship between BPA and BPF (R=0.440, p < 0.05), as well as BPA and BPS (R=0.662, p < 0.01). All of these results indicated that they had shared similar contamination sources. The positive correlations between BPBand BPF, as well as BPB and BPS (R>0.4, p < 0.05) were observed. BPF has significant positive relationships with BPS (R=0.652, p < 0.01), and BPZ has significant positive relationships with BPAP (R=0.898, p < 0.01).

Based on the distribution of residential regions and industrial zones around the Pearl River, principal component analysis (PCA) was used to analyze the BPs in the Pearl River to determine their sources. In the Pearl River, the clustering could be recognized at least in the score plot of PCA: (1) S2 and S3, which had the minimum levels of BPA; S1, S4, and S9, which had the lowest levels of BPAF; S18, which contained the highest concentration of BPZ and BPAP; and (4) all of the other sampling sites.

Table 4 Pairwise correlation (R) between the concentrations of ten bisphenol analogues in surface water from the Pearl River

Compounds	BPA	BPB	BPC	BPE	BPF	BPP	BPS	BPZ	BPAP	BPAF
BPA	1									
BPB	-0.038	1								
BPC	-0.440*	0.001	1							
BPE	0.063	-0.141	0.257	1						
BPF	0.440*	0.418*	-0.399*	-0.117	1					
BPP	-0.275	-0.341	0.329	-0.036	-0.637**	1				
BPS	0.662**	0.435*	-0.210	0.068	0.652**	-0.277	1			
BPZ	0.031	-0.173	0.265	0.228	0.030	-0.098	0.009	1		
BPAP	0.158	-0.241	0.253	0.236	-0.002	-0.106	-0.015	0.898**	1	
BPAF	0.078	0.194	0.148	0.236	0.137	-0.087	0.019	0.019	-0.091	1

*: *p* < 0.05; **: *p* < 0.01





Estrogenic activities and ecological risk assessment

Estrogenic activity assessment

The BP-derived EEQ and the sum of EEQ for each sampling point were calculated (Fig. 4). For the Pearl River, Σ EEQ varied from 0.050 to 0.284 ng E₂/L. Recent research reported that the ranges of Σ EEQ were 0.004–0.18 and 0.005–0.11 ng E₂/L for surface water in the Pearl River system in wet and dry seasons, which were similar to the current results (Huang et al. 2020). These Σ EEQ were well below 1.0 ng E₂/L, suggesting that there was no detectable estrogenic risk for BPs in surface water of the Pearl River. In addition to BPs, numerous other chemicals in the surface water, such as alkylphenols, phthalates, and polychlorinated

biphenyls, as well as natural and synthetic estrogens (E1, E2, and EE2), have estrogenic effects (Tang et al. 2020; Zhao et al. 2021). Consequently, BPs may contribute only a portion of the total estrogenic activity in surface water (Fig. 5).

Eco-toxicity assessment

The risk quotient (RQ) method was applied to evaluate the eco-toxicity of BPs in the Pearl River. The total RQ of each BP was computed to investigate the potential integrated impact of these contaminants. For the Pearl River, the range of Σ RQ was 0.011–0.148. The results showed that none of the sampling sites in the Pearl River had high risks to aquatic organisms (Σ RQ < 1.0), and only 12% of the monitored water samples presented moderate risks to



Fig. 6 RQ of target bisphenol analogues in water samples

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the river ecosystem. Among the ten BPs, BPC had a comparatively greater RQ value for all the samples sites with the highest contribution of 39%. Previous studies have demonstrated that some BPs, i.e., BPF, BPS, and BPAF, etc., had similar estrogenic effects and anti-androgenic effects to that of BPA (Van Leeuwen et al. 2019). Meantime, risks may be significantly enhanced due to their elevated combined effects of complex estrogenic contaminants in the aquatic environment (Li et al. 2018). Therefore, it is vital to take more effective actions to decrease the discharge of BPs (Fig. 6).

Conclusion

Since BPA has been restricted in many countries for foodcontact-related products, several BPs, including BPF, BPS, and BPAF, have been widely used. A large number of BPs were found in surface water of the Pearl River. The predominant BPs were BPA, BPF, BPS, and BPAF. The results of the study on the spatial distribution and possible sources of BPs suggested that the distribution of BPs was comparatively uniform in surface water. This study also demonstrated no high risk of BPs in surface water samples, but their combined estrogenic effects with other EDCs should not be ignored. Further research is recommended to clearly understand the combined estrogenic effects in surface water, which would provide valuable information to understand the fate of BPs in the aquatic environment.

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Author contribution Hao Wang, data analysis and original draft preparation; Zhao Tang, data analysis; Ze-hua Liu, supervisor, funding support, writing review; Feng Zeng, co-supervisor, equipment support; Jun Zhang, sample collection; Zhi Dang, writing review.

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Data availability Not applicable.

Declarations

Ethical approval. Not applicable.

Consent to participate All authors have given consent to their contribution.

Consent for publication All authors have agreed with the content and all have given explicit consent to publish.

Competing interests The authors declare no competing interests.

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