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Endocrine Disrupting Compounds from the Source Water of the Huai River (Huainan City), China

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Abstract The occurrence and environmental risk of eight endocrine disrupting compounds (EDCs), namely dimethyl phthalate (DMP), diethyl phthalate (DEP), benzyl butyl phthalate (BBP), dibutyl phthalate (DBP), nonyl phenol (NP), bisphenol A (BPA), 17α-ethinylestradiol (EE2) and estrone (E1), from four water sources (Pingshantou, Wanfenggang, Shisi, and Shiyi) of Huai River (Huainan section) were investigated in this study. Except for DMP only found in Pingshantou, all of the selected EDCs existed widely in the source water. DMP, DEP, BBP, DBP, NP, BPA, EE2, and E1 had the ranges of nd (cannot be detected)-130 ng/L, 25–310, 76–1351, 431–1299, 215–627, 23–107, nd-0.174, and 0.143–0.334 ng/L, respectively. Therefore, the studied water sources were associated with notable levels of EDCs, wherein the concentrations of BBP, DBP, and NP were much higher than the other five chemicals. The selected EDCs appeared to be higher in upstream than in downstream ($p < 0.05$) for each water source, suggesting that EDCs were subjected to a decreasing with water flow. Correlation analysis suggests that DEP-BP-DBP, NP-BPA, and EE2-E1 might have the same sources, respectively; and the source of NP, EE2, and E1 was different from that of BBP, BEP and BBP, and DEP, respectively. It was observed that both the TAS (total ambient severity) and RQ (risk quotient) were less than 1, indicating that EDCs in Huai River (Huainan section) posed little or no thread to the health of local inhabitants and ecological environmental.

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Endocrine disrupting compounds (EDCs), including natural androgens, natural estrogens, artificial synthetic androgens and estrogens, phytoestrogens, as well as other industrial compounds, are a heterogeneous group of chemicals, generally present in water environments in very low concentrations and causing adverse effects in living organisms (Zhang et al. 2011; Gmurek et al. 2017). The changes in sex and reproductive ability of animals are an important characteristic of EDCs (Santoro and Melvin 2017). Because the adverse biological effect of EDCs on animals was detected, there has been a raised concern due to their adverse effect to both wildlife and humans (Mirzaei et al. 2016).

EDCs from wastewater, pharmaceuticals, agricultural fertilizers, and wastes of human and animals are constantly released into environment through direct discharge, sewage treatment plant effluent, and through runoff (Carvalho et al. 2016; Tijani et al. 2013; Sackett et al. 2015). As a result, EDCs has been widely detected in different water bodies, such as wastewater effluents (Plahuta et al. 2017; Barber et al.2015), surface water (e.g., Lange et al. 2015; Feng et al. 2016; Sun et al. 2016), sediment (Wang et al. 2016; Bayen et al. 2016), and aquatic organisms (Salgueiro-Gonzalez et al. 2015; Liu et al. 2017), with concentrations ranging from ng/L to μg/L in water.

However, EDCs cannot be completely removed by the conventional water treatment processes (Guo et al. 2017). If these compounds appear in water sources, finally they also will be detected in the effluent of drinking water treatment plants (Padhye et al. 2014; Murray et al. 2017). Even the EDCs in aquatic environments exist with a low

level, but still they could lead to unfavorable reactions of the normal hormone function and physiological status in humans (Zhang et al. 2011; Omar et al. 2016). It is, therefore, necessary to detect their levels in water source to evaluate the risks to humans, protect the ecosystem, and provide useful information for drinking water treatment (Feng et al. 2016).

The Huai River with averaged water flow of 4.53×10^{10} m^3/year is one of the seven major rivers in China. It originates in Tongbai Mountain in Henan province, flows through southern Henan, northern Anhui, and northern Jiangsu and enters the Yangtze River at Jiangdu, Yangzhou City. Huai River is a very important water source, providing more than 4.0×10^{10} m^3/year water for the use of life, industry, agriculture, and municipal engineering of 15 cities from Henan, Anhui and Jiangsu Province, with population of more than 7.5×10^{10}. The estimated volume of discharges of wastewater on the river was more than 4.0×10^9 m^3/year. In Huainan City from Anhui province, the life of residents (3.8×10^6 persons) and the development of industry and economy are greatly related to Huai River, because this river is almost the only water source with water supply of more than 2.0×10^9 m^3/year. Hundreds of studies have reported the occurrence, transport, and fate in source water in China (Li et al. 2010; Dong et al. 2010; Zhang 2011; Feng et al. 2016; Yang et al. 2017). However, the studies were mainly conducted in the water source of Songhua River, Huangpu River, Yellow River, and Yangtze River. Few studies focused on the Huai River have been included in the present investigation. As a result, it is very important to pursue the EDCs appearing in the water sources from Huai River. The objectives of this study were to investigate the concentration and distribution of eight EDCs from the source water of Huai River in the section of Huainan City and to assess the environmental risk.

Materials and Methods

Study Area and Sampling Collection

The sample points were selected based on the consideration that the sample points should not only cover the area from upstream to downstream of the river but also be affected by different human (urban, industrial, and agricultural) activities upstream or in the vicinity. Therefore, based on the geographical location, Shiyi, Shisi, Wangfenggang, and Pingshantou were selected as the representative study sites. Sampling was taken from the upstream, midstream, and downstream of selected water sources during January 2010 (Fig. 1). Water samples were collected using precleaned brown glass bottle and transported to the laboratory immediately after sampling. Temperature, pH, dissolved oxygen (DO), and electrical conductivity (EC) were measured in situ. The water samples were stored under refrigeration at 4 °C until analysis. The analysis was performed within 4 days. In addition to the basic water parameters (Table 1), eight EDCs (dimethyl phthalate (DMP), diethyl phthalate (DEP), benzyl butyl phthalate (BBP), dibutyl phthalate (DBP), nonyl phenol (NP), bisphenol A (BPA), 17α-ethinylestradiol (EE2) and estrone (E1)) were determined. The goals of measuring the basic water parameters were to provide more information of source water and pursue the correlation between these basic water parameters and the selected EDCs.

Chemicals and Materials

Standard compounds, including DMP, DEP, BBP, DBP, NP, BPA, EE2, and E1, are all HPLC grade. All reagents of HPLC grade used (methanol, ether, dichloromethane, and acetonitrile) were obtained from TEDIA (USA). The other chemicals were used as 98% purity. Oasis hydrophilic lipophilic balance (HLB) cartridges (6 cc, 200 mg) (Waters Corporation, USA) and C18 cartridges (3 mL, 200 mg; 3 mL, 500 mg) (BESEP, Germany) were used for solid-phase extraction (SPE).

Sample Preparation

Water samples were filtered through prebaked glass fiber filters (0.45 μm) to remove insoluble materials, adjusted its pH to 7.0 using HCl and extracted using SPE method (Fig. 2). Three liters of source water was extracted using HLB solid-phase extraction cartridges, which had been preconditioned with a 6-mL mixture of methanol and ether (methanol: ether = 5: 95), 6 mL of methanol and 6 mL of water. During extraction, the cartridges were forced under vacuum at a flow rate of ~5 mL/min and then kept under vacuum aspiration for several min to dry the residual water. The cartridges were eluted successively with a 5-mL mixture of methanol and water (methanol: water = 5: 95) and 9-mL mixture of methanol and ether (methanol: ether = 5: 95) with a flow rate of 1 mL/min, and the elution was moved into a brown bottle, which had been added 1 g of anhydrous sodium sulfate to keep for one night. Then, the extract was blown down to 0.5 mL under a nitrogen stream and brought to the volume of 1 mL with methanol for the analysis of DMP, DEP, BBP, and DBP.

One liter of source water was extracted using C_{18} solid-phase extraction cartridges (3 mL, 500 mg, BESEP), which had been preconditioned with 10 mL of methanol and 10 mL of water. During extraction, the cartridges were forced under vacuum at a flow rate of approximately 4 mL/min. Then, the cartridges were eluted with a 10-ml mixture

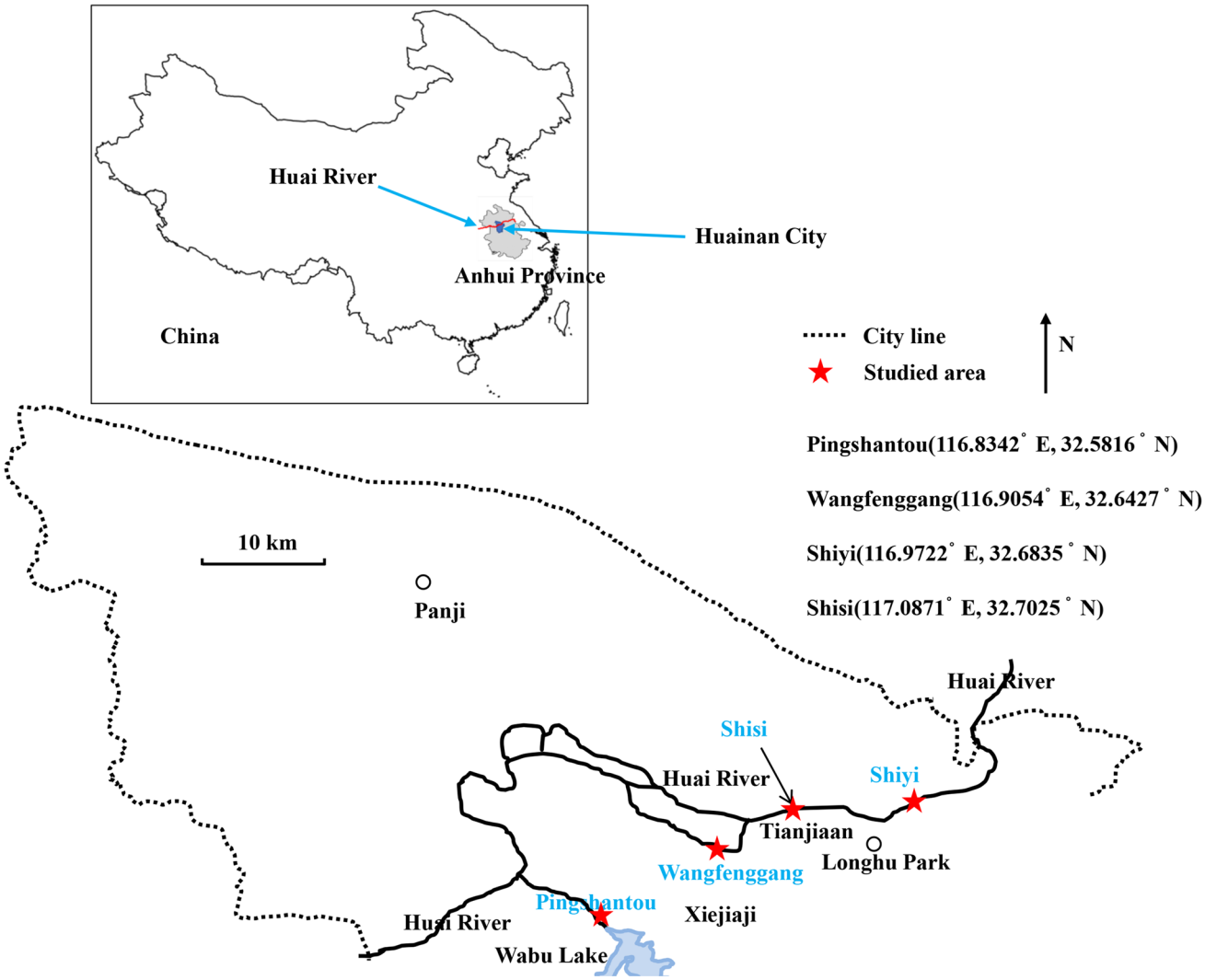

Fig. 1 Sampling methods of the studied water sources

Table 1 Basic water parameters (average of the data from upstream, midstream, and downstream)

Water source	Temperature (°C)	pH (–)	DO (mg/L)	EC (uS/cm)	Alkalinity (mg/L)*	TOC (mg/L)**
Pingshantou	3	7.62	8.87	271	64.7	5.47
Wanfenggang	4	7.59	8.33	405	146.1	5.15
Shisi	4	7.61	8.26	424	141.6	5.09
Shiyi	4	7.61	8.10	427	148.0	4.93

* Alkalinity is presented as $CaCO_3$

** Total organic carbon

of methanol and dichloromethane (methanol: dichloromethane = 20: 80) with a flow rate of 4 mL/min. Finally, the extract was blown down to 0.5 mL under a nitrogen stream and then brought to the volume of 1 mL with methanol for the analysis of NP and BPA.

Five liters of source water was extracted using C_{18} solid-phase extraction cartridges (3 mL, 200 mg, BESEP) preconditioned with 4 mL of methanol and 4 mL of water. For extraction, the cartridges were forced under vacuum at a flow rate of approximately 4 mL/min. After water dropping

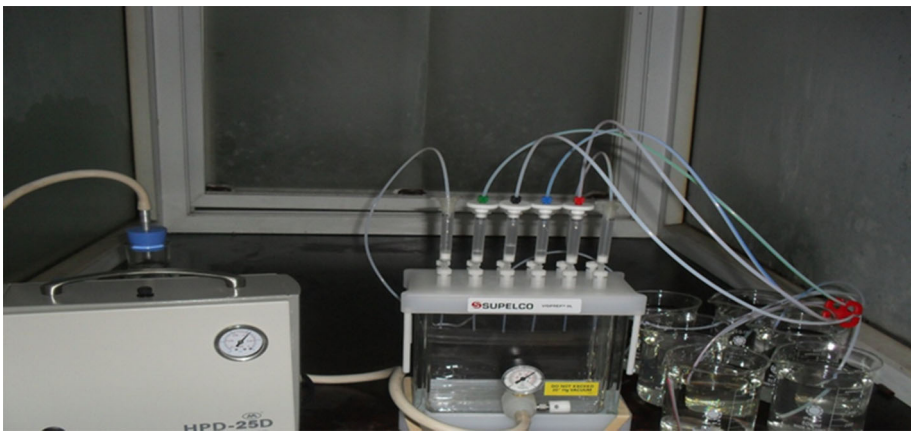

Fig. 2 Supelco Visiprep™ DL 12-tubed solid-phase extraction devices

out, the cartridges were eluted in sequence with 4 mL of water and 5 mL of methanol with a flow rate of 4 mL/min. Finally, the extract was blown down to 0.5 mL under a nitrogen stream and then brought to the volume of 1 mL with acetonitrile for the analysis of EE2 and E1.

High-Performance Liquid Chromatography Analyses

The samples were analyzed by Hitachi L-2000 high-performance liquid chromatography (HPLC) (reversed-phase), wherein a capillary column Kromasil 100-5C18 (reversed phase, 150 mm × 4.6 mm × 5 um) and L-2485 DAD detector were used for the separation of the analyses for DMP, DEP, BBP, and DBP, Apollo C18 (reversed phase column, 250 mm × 4.6 mm × 5 um) and L-2455 fluorescence detector for NP and BPA while Apollo C18 (reversed phase column, 250 mm × 4.6 mm × 5 um) and L-2485 DAD detector for EE2 and E1, respectively. The analysis conditions are summarized in Table 2 and Fig. 3.

Quality Assurance and Quality Control (QA/QC)

Recoveries were first obtained to evaluate the method performance by the analyses of spiked water samples for each chemical. The extraction and cleanup methods resembled the procedure described in the section of "sample preparation." A solvent and matrix blank were processed through the entire procedure prior to and after every six samples. The limit of detection (LOD) was determined as signal-to-noise ratio of 3:1. The LODs for source water were 0.04 ng/L for DMP, 0.03 ng/L DEP, 0.04 ng/L for BBP, 0.05 ng/L for DBP, 0.01 ng/L for NP, 0.02 ng/L for BPA, 0.12 pg/L for EE2, and 0.22 pg/L for

Table 2 Analysis conditions of reversed-phase liquid chromatography analysis

Chemicals	DMP, DEP, BBP, and DBP	NP and BPA	EE2 and E1
Scan wave	190–400 nm	–	190–400 nm
Detector wave	228 nm	–	200 nm
Excitation wave	–	208 nm	–
Emission wave	–	305 nm	–
Temperature	35 °C	30 °C	25 °C
Injection volume	10 µl	10 µl	10 µl
Carried liquid	Methanol: water = 75: 25	Acetonitrile: water = 95: 5	Acetonitrile: water = 70: 30
Flow rate	1.0 mL/min	1.0 mL/min	1.0 mL/min
Retention time	2.11 min for DMP; 2.91 min for DEP; 9.03 min for BBP; 9.61 min for DBP	2.78 min for NP; 4.75 min for BPA	4.54 min for EE2; 5.16 min for E1

The condition for DMP, DEP, BBP, and DBP was selected from Lin (2003), Yi (2002), Fang (2004), Zhang (2001), Wang (1995)

The condition for NP and BPA was selected from Hou et al. (2005), Shao et al. (2001)

The condition for EE2 and E1 was selected from Chen et al. (2009), Yang (2008), Yan et al. (2009), Wang et al. (2009), Yu et al. (2008)

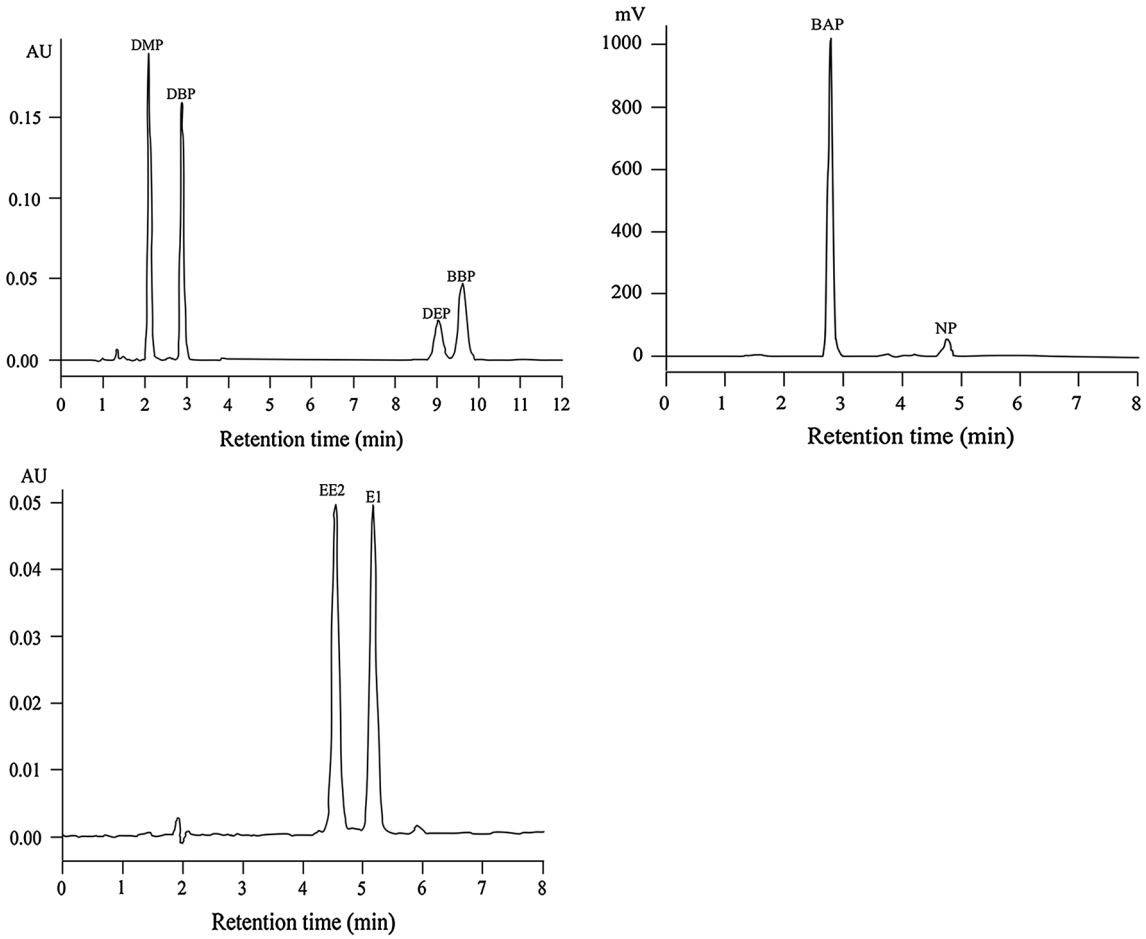

Fig. 3 HPLC chromatograms of selected EDCs

E1 for source water. The recoveries of eight EDCs ranged from 95.3 to 102.2%.

To avoid contamination during the sampling and sample preparation processes, sampling bottles and all glassware involved in the study were cleaned by soaking chromic acid solution overnight, washing three times with tap water, distilled water, acetone and methanol, and burning in an oven at 105 °C for 8 h.

Ambient Severity

Multimedia Environmental Goals (MEG), suggested by the United States Environmental Protection Agency (USEPA), are levels of significant contaminants or degradents (in ambient air, water, or land or in emissions of effluents conveyed to the ambient media) that are judged to be (1) appropriate for preventing certain negative effects in the surrounding populations or ecosystems, or (2) representative of the control limits achievable through technology (USEPA USEP 2004). The ratio of the actual concentration to the MEG is called the Ambient Severity (AS) (Gao et al. 2011). In this paper, the negative effects of certain substance on the surrounding populations and ecosystems are described as health severity (AS_H) and ecological severity (AS_E), respectively, which are calculated by the following equation:

$$AS_i = C_i/C_{MEGi}$$

in which, AS_i is AS_H or AS_E, C_i is the environmental exposure concentration and C_{MEGi} is the environmental (health or ecological) target for the chemical i in water, respectively. The grade of AS of specific chemical can be classified as: $AS < 1$, no any obvious risk; $AS > 1$, significant potential risk (Liu et al. 2014).

In fact, the synergy and antagonism between the pollutants should be taken into account; therefore, the formula above was amended as follows (Liu et al. 2014):

$$AS_i = C_i/C_{MEGi} + aC_{im}/C_{MEGim}$$

C_{im} is the lower concentration of molecule i or m and C_{MEGim} is the C_{MEGi} value considering the synergistic or antagonistic effects. When $a = 0$, there is no synergistic and antagonism; $a = 1$, there is synergy; $a = -1$, there is antagonism. However, due to the complex mechanism,

C_{MEGi} has not been worked out considering the synergistic or antagonistic effect (Liu et al. 2014). Based on the assumption that not only all organic pollutants have the same AS value and exert the same potential hazards to people and the environment, but also there is a linear relationship between AS and the potential hazards, the effect of various pollutants (Total Ambient Severity, TAS) can be calculated as follows (Liu et al. 2014):

$$\mathrm{TAS} = \sum \mathrm{AS}_i$$

Risk Quotients

Environmental risk assessment on toxic chemicals often employs risk quotient (RQ) to show the risk quantitatively. RQ is a ratio of exposure to effect, typically obtained by dividing an environmental exposure value by a toxicity end-point value (Liu et al. 2014, Peterson 2006). Therefore, RQ can be employed by risk analysts and other decision makers to evaluate whether the value exceeds any predetermined threshold levels of concern (Peterson 2006). It was calculated using the following equation:

$$\mathrm{RQ} = \frac{\text{Observed concentration of chemical } i}{\text{Allowable concentration of chemical } i}$$

To provide a better estimation of the risk, the calculation of RQ can be further elaborated by two approaches:

$$\mathrm{RQ}_{\mathrm{bcs}} = \frac{\text{Observed maximum concentration of chemical } i}{\text{Allowable concentration of chemical } i}$$

$$\mathrm{RQ}_{\mathrm{wcs}} = \frac{\text{Observed minimum concentration of chemical } i}{\text{Allowable concentration of chemical } i}$$

The best-case RQ (denoted as $\mathrm{RQ}_{\mathrm{bcs}}$) and the worst-case RQ (denoted as $\mathrm{RQ}_{\mathrm{wcs}}$) can be used to screen contaminants that may need a more refined analysis. As the $\mathrm{RQ}_{\mathrm{bcs}}$ for a certain pollutant is higher than 1, the risk posed is probably of concern; as the $\mathrm{RQ}_{\mathrm{wcs}}$ is smaller than 1, adverse effects from exposure to the pollutant may be minimal (Liu et al. 2014). When the $\mathrm{RQ}_{\mathrm{bcs}}$ is higher than 1 or $\mathrm{RQ}_{\mathrm{wcs}}$ smaller than 1, there is usually sufficient information to make a judgment on the level of risk without the aid of a more refined risk assessment (Wei et al. 2006).

Results and Discussion

Abundance of EDCs in Studied Source Water

The EDCs along the river are possibly sourced from stormwater runoff from urban and agricultural areas, effluents from wastewater treatment plants, and unorganized discharge of domestic sewage. Table 3 presents the levels of selected EDCs from all the samples. Water samples from all the 12 sampling sites contained detectable concentrations of EDCs, which means that these contaminants are widespread in the studied area. Meanwhile, the presence of the selected compounds in source water varied spatially. DEP, BBP, DBP, NP, BPA, and E1 were quantified in all water samples, with concentration ranges of 25–31, 76–1351, 431–1299, 215–627, 23–107, and 0.143–0.334 ng/L, respectively. EE2 was detected in 11 samples with 1 below LOD, ranging from nd (cannot be detected) to 0.174 ng/L. However, DMP was only quantified in two samples from upstream and midstream of Pinshantou water source, with concentrations of 20–130 ng/L. Overall, the studied water sources were associated with much higher BBP, DBP, and NP than the other five chemicals. Furthermore, correlation between basic water parameter and the level of EDCs was performer, and it is found the level of $\mathrm{EDC_S}$ was not correlated with the basic water parameter except for NP, which is negatively related to both DO and TOC. This is possibly because NP exerted toxic effect on the Algae (Yang 2013), resulting in decreased biomass (TOC) and weakened photosynthesis.

In addition, the selected EDCs appeared to have a higher level in upstream than in downstream ($p < 0.05$) for each water source while the concentration of some compound were increased from midstream to downstream (DEP and BPA in Pingshantou, BPA and EE2 in Shisi, DEP and E2 in Shiyi) (Fig. 3), which means that even though all the EDCs were subjected to a decreasing, some chemicals were still input to the water source. Based on the investigation on the activities nearby the water sources, there was no significant industrial discharge of wastewater. Therefore, from midstream to downstream of selected water source the increase of DEP and BPA in Pingshantou was due to the entrance of runoff, BPA and EE2 in Shisi related to the input of runoff and small-scale unorganized discharge of domestic sewage respectively, whereas DEP and E2 in Shiyi also was attributed to the small scale unorganized discharge of domestic sewage. However, it also was observed that the EDCs level was not always reduced or even was increased for some compounds as Huai River went through Huainan City (Fig. 3), which indicates that the Huai River was continuously contaminated by EDCs. Hence, the attention should not only be paid to the water sources area but also the places where input of EDCs possibly occurs.

Comparison with Other Sources Water in China

Table 4 summarizes the levels of selected EDCs appearing in the other water sources of China. In China the concentrations of DMP are mainly <2000 ng/L. However, the DMP from Songhua River and Yangshupu water source

Table 3 Endocrine disrupting chemicals in investigated source water (ng/L) (3 samples for each sampling area)

	DMP	DEP	BBP	DBP	NP	BPA	EE2	E1
Pingshantou								
Upstream	130	52	396	1013	429	75	0.151	0.334
Midstream	20	25	219	775	322	23	0.112	0.152
Downstream	nd	49	76	661	386	39	nd	0.143
Wanfenggang								
Upstream	nd	195	404	1100	588	73	0.127	0.307
Midstream	nd	92	291	867	445	57	0.048	0.176
Downstream	nd	101	177	462	215	40	0.093	0.161
Shisi								
Upstream	nd	84	697	1123	627	99	0.152	0.325
Midstream	nd	64	824	1008	393	31	0.051	0.195
Downstream	nd	50	292	431	247	58	0.080	0.165
Shiyi								
Upstream	nd	310	1351	1299	539	107	0.174	0.311
Midstream	nd	135	492	968	419	82	0.100	0.175
Downstream	nd	62	668	521	325	56	0.089	0.197
Range	<130	25–310	76–1351	462–1299	215–627	23–107	<0.174	0.143-0.334
Mean	13	102	491	852	411	62	0.098	0.220
SD	36	77	337	271	122	25	0.039	0.072

nd Not detected (below the detection limit)

was obviously higher, especially in Yangshupu water source where the average of DMP concentration was 124,000 ng/L. For DEP, in the source water from Suzhou City, Changzhou City, Wuxi City, Xuzhou City, and Yancheng City, the related averages were lower than 100 ng/L. Similarly, the relative high concentration of DEP also appeared in Songhua River and Yangshupu water source due to the significant contributors of DMP and DEP in these two places. Among the five cities from Jiangsu province, the content of BBP varied between <1 and 348 ng/L, and the distribution of BBP was greatly related to the economy and industry. The document available shows that the BBP concentration was 10–163,800 ng/L, wherein the highest took place in Songhua River (123,300–163,800 ng/L). It can be concluded that the source water from Huai River has been susceptible to phthalate esters (PAEs) contamination to some extent (Fig. 4).

The concentrations of $\sum$PAEs (DMP, DEP, BBP, and DBP) ranged from 1251–2960, 773–1985, 739–1699, and 785–1591 ng/L in the source water of Shiyi, Shisi, Wangfengang, and Pingshantou, respectively. Also, BBP and DBP account for the most part of $\sum$PAEs. So, BBP and DBP were main pollutants of PAEs in the studied water source. Overall, the $\sum$PAEs concentrations declined as the river flowed down due the effects, such as sorption, dilution, and degradation. However, the increase of specific species of PAEs in the water source should be paid more attention. On the other hand, the concentration of NP and BPA reported in the literatures available varied between <30 (Xiliu River) and 46,700 ng/L (Suzhou City) and between <1380 (Minhang, Shanghai city) and 26,000 ng/L (Yangshupu, Shanghai city), respectively. However, the concentrations of EE2 and E1 are widely reported in the literature. Songhua River might have higher concentrations of EE2 and E1. One-way analysis suggests that the studied water sources have been contaminated by EDCs, especially by BPA ($p < 0.05$), to a level that should be taken seriously.

Interregional comparisons based on the data available were conducted. The conclusion is that the major rivers in China, including Yangtze River, Yellow River, Songhua River, and Huai River, have been subjected to EDCs pollution to some degree. The levels of EDCs in the water possibly are governed greatly by the chemical industry from upstream reach of water source. Concentrations of EDCs in source water from the cities located at the downstream of the watershed is relatively higher. The EDCs of the water sources from Jiangsu Province (Suzhou, Wuxi, Xuzhou, Yancheng) seem to have lower concentrations than that from the other areas, possibly due to better management for pollution.

Correlation Analysis Between Selected EDCs in the Studied Source Water

Correlation analysis is a useful method to provide the interesting information on the sources and pathways of

Table 4 Concentrations (mean or range) of selected EDCs from other places in China (ng/L)

Location	DMP	DEP	BBP	DBP	NP	BPA	EE2	E1	References
Beijing City					10–349.6	30.2–82.7			Wang et al. (2006), Jin (2004)
Xiliu River (Guangdong)	–	–	–	–	<30	70–150	–	–	Li et al. (2010)
Upstream of Huangpu River (Shanghai City)	–	–	–	–	–	86	1.27	12.9	Nie (2012)
Minhang (Shanghai City)	–	<710	–	370–17,700	170–3520	<1380	–	–	Xu (2005)
Yellow River (Lanzhou reach)	–	–	–	3640	–	–	–	–	Dong et al. (2010)
Songhua River	33–1775	102–5760	–	123,300–163,800	55–1261	22–64	7–16	26–65	Shao and Ma (2008), Shao et al. (2008)
Chang and Jialing River (Chongqing reach)	–	–	–	9480	–	–	–	–	Tain et al. (2003)
Three Gorges Reservoir	–	70–126	–	83–221	–				Xu et al.(2007)
Yangshupu (Shanghai City)	124,000	385,000	–	4210	–	26,000	–	–	Li (2006)
Suzhou City	8	81	287	–	3760–46,700	19–147			Zhang (2011), Chen (2013), Zhang (2012)
Changzhou City	56	33	348	–	–	–	–	–	Zhang (2011)
Wuxi City	30	62	24	–	–	–	–	–	Zhang (2011)
Xuzhou City	<1	8	<1	–	–	–	–	–	Zhang (2011)
Yancheng City	64	64	38	–	–	–	–	–	Zhang (2011)
Nanchang City	–	–	–	10–16	–	13–18	–	–	Yan et al. (2007)
Yangtze River Delta	0.06–239.32	0.48–84.12	0.16–196.81	0.08–315.93					Shi et al. (2012)
Liuxi Reservoir					22.5–25.1	2.30–2.69			Peng et al. (2017)
This study	<310	25–310	76–1351	431–1299	739–2960	215–627	0.023–0.107	<0.174	
Environmental levels	–	2.90 + E07[a]	–	3,000[b]	6,600[a]	10,000[c]	–	3.00[d]	

– No date

[a]USEPA

[b]Ministry of Environmental Protection of the People's Republic of China

[c]Former Soviet Union

[d]British Environmental Protection Agency

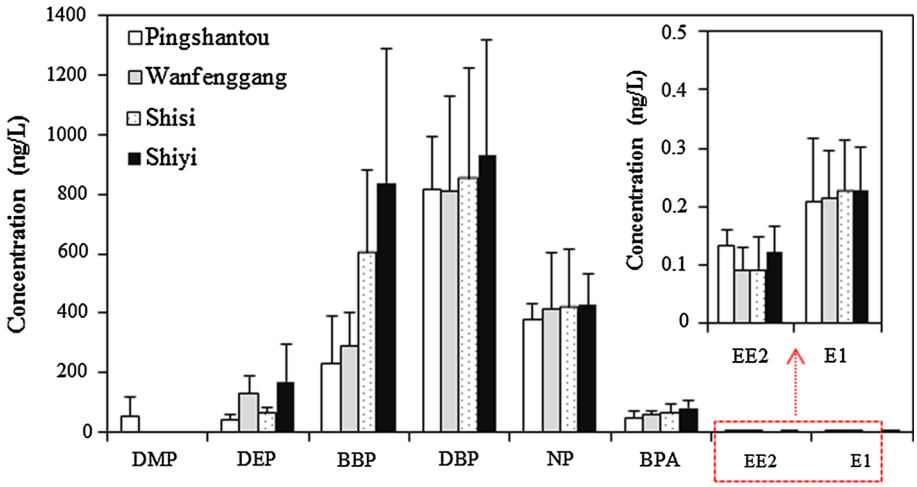

Fig. 4 Variation of pollutant concentration from the upstream to downstream of Huai River

chemicals based on the assumption that if the compounds come from the same source(s) they are correlated with amounts (Peng et al. 2008; Yoon et al. 2010). In this paper, Pearson Correlation Analysis, which is performed using SPSS (Version 20.0), is employed and the result is summarized in Table 5.

DEP showed a significant relation with four compounds (BBP, DBP, NP, and BPA), BBP with four (DEP, DBP, BPA, and E1), DBP with six (DEP, BBP, NP, BPA, EE2, and E1), NP with five (DEP, DBP, BPA, EE2, and E1), BPA with six (DEP, BBP, DBP, NP, EE2, and E1), EE2 with four (DBP, NP, BPA, and E1) and E1 with five (BBP, DBP, NP, BPA, and EE2), respectively. This result suggests that at least four compounds could appear in same source; and DEP-BP-DBP, NP-BPA, and EE2-E1 might have the same sources, respectively. However, NP was not related to BBP, EE2 was not to BEP and BBP, and E1 was not related to DEP, respectively. Therefore, the source of NP was different from that of BBP, EE2 different from that of BEP, and BBP and E1 was different from that of DEP.

EDCs in water bodies are originally from wastewater, pharmaceuticals, agricultural fertilizers and pesticides, and wastes of human and animals. Considering the use of selected EDCs in life and industry, the surroundings of each water source as well as the environment between the water sources in the studied area, it can be concluded that the DMP only present in Pingshantou water source was possibly from the effluents of domestic sewage treatment plants and the direct discharge of domestic sewage (small scale) and runoff from agricultural area, DEP effluents of industrial wastewater treatment plants, BBP and DBP effluents of industrial wastewater treatment plants and domestic sewage treatment plants, NP and BPA effluents of industrial wastewater treatment plants and domestic sewage treatment plants, as well as the discharge from agricultural area and EE2 and E2 were from the effluents of pharmaceutical wastewater treatment plants and domestic sewage treatment plants and the direct discharge of domestic sewage (small scale), respectively.

Table 5 Correlation among selected EDCs in the investigated source water

	DMP	DEP	BBP	DBP	NP	BPA	EE2	E1
DMP	1							
DEP		1						
BBP		0.670**	1					
DBP		0.612**	0.639**	1				
NP		0.530*	0.484	0.877**	1			
BPA		0.674**	0.603**	0.634**	0.706**	1		
EE2		0.506	0.422	0.557*	0.548*	0.705**	1	
E1		0.492	0.542*	0.740**	0.771**	0.761**	0.795**	1

* Correlation is significant at the 0.05 level (1-tailed)

** Correlation is significant at the 0.05 level (2-tailed)

Table 6 Ambient severity of EDCs in investigated source water

Compound	MEG (ng/L)		Pingshantou		Wanfenggang		Shisi		Shiyi	
	Health	Ecology	AS_H	AS_E	AS_H	AS_E	AS_H	AS_E	AS_H	AS_E
DMP	7.00E+04	3.00E+04	<1	<1	<1	<1	<1	<1	<1	<1
DEP	7.00E+04	3.00E+04	<1	<1	<1	<1	<1	<1	<1	<1
BBP	1.30E+06	5.00E+07	<1	<1	<1	<1	<1	<1	<1	<1
DBP	7.00E+04	3.00E+04	<1	<1	<1	<1	<1	<1	<1	<1
NP	–	–	–	–	–	–	–	–	–	–
BPA	–	–	–	–	–	–	–	–	–	–
EE2	–	–	–	–	–	–	–	–	–	–
E1	–	–	–	–	–	–	–	–	–	–

Table 7 RQ of EDCs in investigated source water

	Allowable concentration (ng/L)	Minimum concentration (ng/L)	Maximum concentration (ng/L)	$RQ_{bcs} < 1$	$RQ_{bcs} > 1$	$RQ_{wcs} < 1$	$RQ_{wcs} > 1$
DMP	–	nd	130				
DEP	2.90 + E07[a]	25	31	●		●	
BBP	–	76	1351				
DBP	7.00 + E04[a]/3.00 + E03[b]	431	1299	●		●	
NP	6.60 + E03[b]	215	627	●		●	
BPA	1.00 + E04[c]	23	107	●		●	
EE2	–	nd	0.174				
E1	3.00[d]	0.143	0.334	●		●	

– No date

[a]USEPA

[b]Ministry of Environmental Protection of the People's Republic of China

[c]Former Soviet Union

[d]British Environmental Protection Agency

Risk Assessment

Health and ecological ambient severity in Huai River (Huainan section) were calculated to evaluate the potential adverse effects from exposure to selected compounds. It has been documented that the TAS for human and ecological health were in the range of 0.15–0.52 for Taihu Lake (Pan and Xie 1994). The human and ecological health risk due to exposure organic pollutants from surface water in Shijiazhuang city were less than 1, with the maximum TAS value 0.80 (Pei and Su 2000). In addition, the ranges of TAS for human and ecological health were found to be 0.13–0.39 and 0.17–0.79 respectively for Liuxihe Reservoir, which supply the drinking water for 60% inhabitants of Guangzhou City (Liu et al. 2013). The calculated TAS of this study is shown in Table 6. The TAS values both for human health risk human and ecological health risk of EDCs in the source water from the Huai River (Huainan section) were less than 1, wherein the highest for human health risk were 1.86E−03 for DMP, 4.43E−03 for DEP, 1.04E−03 for BBP, and 1.86E−02 for DBP. The highest for ecological health risk were 4.33E−03 for DMP, 1.03E−02 for DEP, 2.70E−05 for BBP, and 4.33E−02 for DBP. It is suggested that TAS of source water from the Huai River (Huainan section) were lower than the highest value of healthy severity. The water may pose little or no threat to humans potentially, which also was considered relatively safe from an ecological perspective. Moreover, the highest TAS appearing in the upstream followed by midstream and downstream for each water source; therefore, it is recommended to draw water from downstream of the each water source.

The RQs of EDCs were summarized in Table 7 as estimated for local residents in the Huai River (Huainan section). The RQ analysis was conducted only on the pollutants whose corresponding health guidelines were available. The calculated RQs for most analyses were smaller than unity under both worst-case and best-case scenarios, suggesting that these pollutants posed little or no threat to the health of local consumers.

Due to the lack of native reference values, in China, USEPA reference values have been used commonly to

purse the environmental risk of EDCs (Gao et al. 2011; Liu et al. 2014; Li et al. 2015). However, the targeted (suggested) concentration of pollutants from the USEPA may not be completely applicable in China (Wei et al. 2006). For one thing, population susceptibilities (age, immune status, etc.) are greatly related to the adverse health outcome from exposure to contaminants (Fung et al. 2005; Liu et al. 2014), whereas the way and level of exposure are different between Chinese and American. The structures of aquatic ecosystem of between China and America also are inconsistent. These differences may result in different dose–effect on human and ecological system. Therefore, more studies should be performed and different methods should be employed under different applicable conditions. In addition, to provide more recommendations, the genetic data as well the variation of EDCs level as the source water flows to the water plants will be investigated in a future study.

Conclusions

This study investigated the concentration, distribution, and human and ecological health risk of eight EDCs in the source water of Huai River (Huainan section). The studied water sources had been associated with notable levels of EDCs, especially for BBP, DBP, and NP. However, as the water of Huai River went through Huainan City, some EDCs were continuously discharged into Huai River. EDCs in Huai River (Huainan section) posed little or no threat to the health of local consumers and ecological environment. It is a good strategy to draw water from downstream of the each water source, considering the overall decreased threat to the human health and ecological risk with water flow direction for each water source. The rapid economic development of Huainan City had resulted in obvious environmental impacts on the water quality of the Huai River; special attention needs to be paid to diminish the inputs external source of EDCs to avoid the deterioration of water quality of source water. Specifically, more efficient management should be taken to eliminate the input of EDCs, which is not only from the area in the upper reach of water source but also from the runoff and unorganized discharge of home sewage around the water source. Reduction strategies for EDCs also should be designed effectively in a further study on the removal of EDCs both in water plants and wastewater treatment plants.

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