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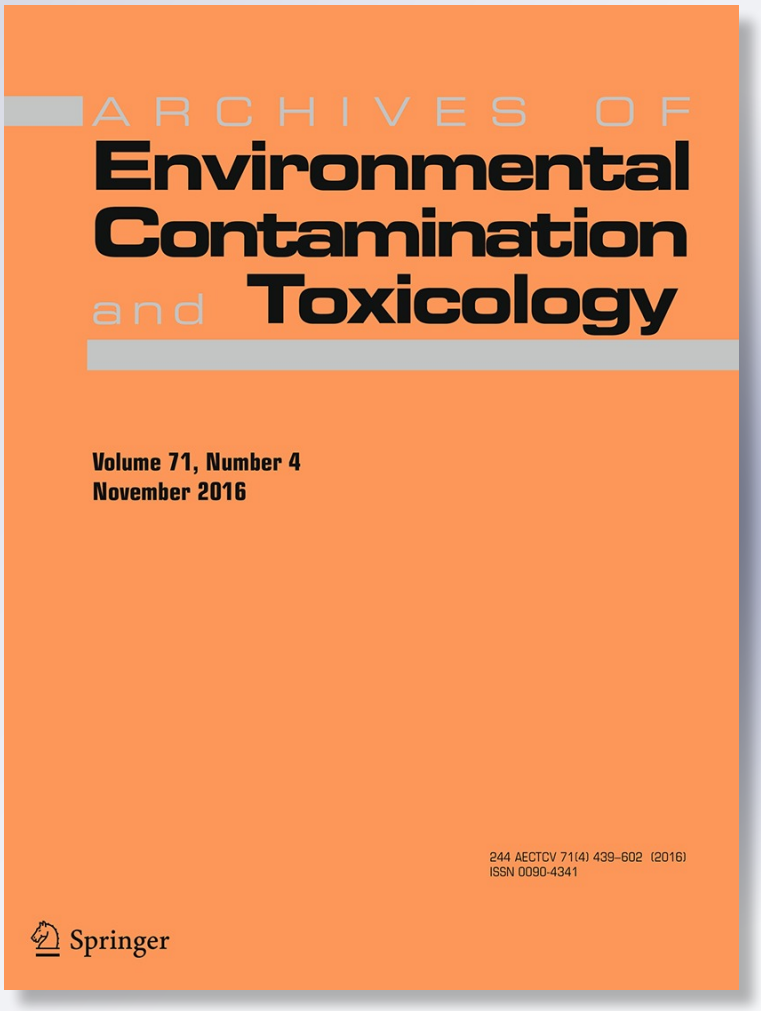

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Monitoring of Endocrine-Disrupting Compounds in Surface Water and Sediments of the Three Gorges Reservoir Region, China

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Abstract Occurrence and distribution of eight selected endocrine-disrupting compounds (EDCs), including estrone (E1), 17α-ethinylestradiol (EE2), 17α-estradiol (αE2), 17β-estradiol (βE2), estriol (E3), bisphenol A (BPA), 4-nonylphenol (NP), and 4-octylphenol (OP), were investigated in surface water and sediments of the Three Gorges Reservoir region (TGRR). The mean concentrations of E1, αE2, βE2, E3, EE2, BPA, NP, and OP were 10.3, 3.3, 3.7, 17.2, 7.8, 26.6, 10.8, and 32.3 ng L^{-1} respectively in surface water and 2.6, 4.1, 7.7, 2.4, 11.8, 17.4, 5.0, and 5.3 ng g^{-1} dry weight (dw) respectively in sediments. BPA, NP, and OP were the main EDCs in both media. Distributions of EDCs in surface water and sediments varied significantly in space but not synchronously. The higher EDCs abundance was found in the upstream water of the TGRR. EDCs concentrations in sediments had no correlations with those in water and the total organic carbon content in sediments. EDCs presented low to high risks in the water, and steroidal estrogens were the main contributors to the total estrogenic activities.

Endocrine-disrupting compounds (EDCs) are a series of exogenous compounds, including pesticides, industrial chemicals, pharmaceuticals, naturally occurring hormones, which may result in disorder of endocrine systems, development and reproduction problems, and even cancer, in wildlife, and humans (Jenkins et al. 2012; Migliarini et al. 2011). EDCs enter into the aquatic environment mainly through wastewater discharge and surface water runoff (Esteban et al. 2014; Pal et al. 2010). Even at low concentrations, EDCs can cause adverse effects on aquatic organisms, such as infertility, feminization, and anomalies of reproductive organ (Pal et al. 2010; Schlenk 2008), which consequently do harm to the population persistence of aquatic species (Mills and Chichester 2005). Humans also suffer potential impairments due to exposure to EDCs through food chains and water sources (Campbell et al. 2006). Therefore, it is essential to monitor the pollution levels of EDCs in water to protect the aquatic ecosystem.

The Three Gorges Dam is the greatest water project to date ever built in the world, located in the upstream of the Yangtze River, the largest river in China. The Three Gorges Reservoir was formed after the completion of the dam in 2009, covering a water surface area of 1080 km^2 along the Yangtze River from Jiangjin District, Chongqing City to Yichang City, Hubei Province. The region surrounding the reservoir is known as the Three Gorges Reservoir region (TGRR) (Zhang and Lou 2011). However, with rapid development of agriculture, industrialization, and urbanization in this region, million tons of polluted agricultural runoff, industrial wastewater, and domestic sewage are discharged into the reservoir, seriously threatening the ecological health of aquatic environment in this region (Tullos 2009; Zhang and Lou 2011). Toxic inorganic or/and organic pollutants, such as heavy metals (Han et al. 2015; Wang et al. 2012a), organochlorine pesticides (Liu

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et al. 2015; Wang et al. 2009), polychlorinated biphenyls, and polybrominated diphenyl (Ge et al. 2014; Wang et al. 2009), were successively reported in the TGRR, posing various kinds of risks to the aquatic organisms and humans along the reservoir. However, very limited information is available regarding contamination status of EDCs in this huge reservoir region.

According to their origins, EDCs can be divided into two groups. Natural estrogens, such as estrone, 17β-estradiol, estriol, and their metabolites, are primarily from human and animal excretion (Young et al. 2002). Synthetic estrogens, such as 17α-ethinylestradiol, is widely applied in oral contraceptives, whereas bisphenol A and 4-nonylphenol are important industrial chemicals (Zhang et al. 2015a). In this study, eight estrogens, including four natural estrogens [estrone (E1), 17α-estradiol (αE2), 17β-estradiol (βE2), and estriol (E3)] and four synthetic estrogens [17α-ethinylestradiol (EE2), bisphenol A (BPA), 4-nonylphenol (NP), and 4-octylphenol (OP)] were selected for investigation. These compounds are marked by high bioactivity, ubiquitous distribution, and persistence (Zhang et al. 2015a) and present the most frequently discovered EDCs in waters of China (Jiang et al. 2012; Lu et al. 2010). The purpose of this study was to investigate the occurrence, spatial distribution, and risk assessment of the selected EDCs in surface water and sediments of the TGRR, with the hope of providing useful information for water protection and estrogen control in this region.

Materials and Methods

Chemicals and Materials

The eight target EDCs, including E1, αE2, βE2, E3, EE2, BPA, NP, and OP, were purchased from Sigma-Aldrich (USA). Standard solutions of target compounds were prepared in methanol (1 mg L^{-1}) and stored in refrigerator (−20 °C). Dichloromethane, methanol, and acetonitrile were all of HPLC grade and obtained from Fisher Scientific (USA). Oasis hydrophilic lipophilic balance (HLB) cartridges (500 mg, 6 mL) for solid phase extraction (SPE) were from Waters Corporation (USA). Glass fiber filters (pore size 0.45 μm) were from Whatman (Maidstone, UK) and were baked at 450 °C for at least 4 h before use.

Sampling Sites and Sample Collection

Sampling work was performed along the TGRR (29°16′–32°25′N, 106°–111°50′E, from Jiangjin District, Chongqing City to Zigui County, Yichang City) in August 2015. A total of 14 sampling sites were selected and located by the global position system (GPS) (Fig. 1). At each site, 1 L of surface water (0–15 cm) was collected and stored in a precleaned, amber glass bottle. To inhibit the development of microorganisms, 0.5 g of sodium azide was added into each water sample immediately after collection. Approximately 100 g of surface sediment sample (0–10 cm) was collected at each site using a precleaned, stainless steel grab sampler and placed into a polytetrafluoroethylene bag. Samples were stored at 4 °C and transported to the laboratory for analysis with the shortest time possible.

Sample Preparation and Extraction

Water samples were filtered through the prebaked filters (0.45 μm) to remove the insoluble particles and extracted with the SPE method. Briefly, 1 L of the filtered water was passed through an Oasis HLB cartridge that was pretreated with 5 mL of dichloromethane (DCM), 5 mL of methanol, and 5 mL of ultrapure water. After loading, the HLB cartridge was washed with 10 mL of ultrapure water and dried under vacuum for approximately 2 h. The analytes were eluted with methanol and blown to dryness under gentle nitrogen flow. Finally, each extract was reconstituted with 100 μL of acetonitrile and filtered through a 0.22-μm filter before instrumental analysis. Sediment samples were freeze-dried, homogenized, and passed through a 60-mesh standard sieve and stored at −20 °C until extraction. Treatment and extraction of sediment samples were performed with the ultrasonic assisted solvent extraction and SPE method. Briefly, 5 g of sediment in dry weight (dw) was thoroughly mixed with 25 mL of solvent (methanol/DCM, 1:1) and extracted with ultrasonic assistance for 20 min. Then, the mixture was centrifuged and the supernatant was collected. The extraction process was repeated for three times, and the extracts were combined and concentrated to 5 mL via rotary evaporation and dissolved in 500 mL of ultrapure water for SPE as mentioned above.

Instrumental Analysis

Qualitative and quantitative analysis of target EDCs in water and sediment samples was performed with liquid chromatograph–mass spectrometry using atmospheric pressure chemical ionization (LC–MS, Thermo Fisher Scientific). Total organic carbon content (TOC, %) for the sediments was determined with the TOC-VARIO elemental analyzer.

Quality Assurance and Quality Control

A series of measures were taken to validate the quantification process of EDCs. Surrogate standard (17β-E2-D_2) was spiked in all the samples to test the recovery, which ranged from 78 to 116 % after analysis. The average

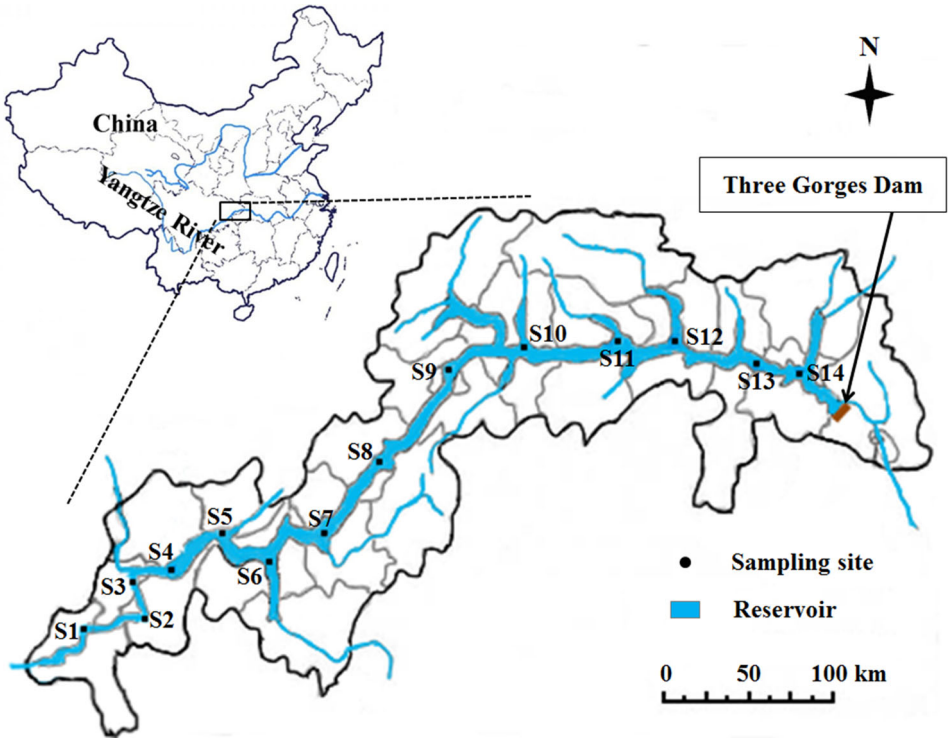

Fig. 1 Locations of sampling sites in the TGRR

recoveries of target EDCs were in range of 70–105 %. A solvent blank and a matrix blank were analyzed for every ten samples to check the possibility of background contamination. No analytes were detected in the blanks. The calibration curves obtained for the target compounds were linear between the limit of detection (LOD) and 5 μg L^{-1}, with correlation coefficients (R^2) higher than 0.99 in all cases. The LODs of EDCs were defined as three times of the signal-to-noise ratio (S/N). LODs for E1, αE2, βE2, E3, EE2, BPA, NP, and OP were 0.5, 0.2, 0.2, 0.3, 0.2, 0.2, 1.7, and 0.3 ng L^{-1} respectively in surface water, and were 0.8, 0.3, 0.9, 1.1, 0.7, 0.8, 1.5, and 0.5 ng g^{-1} dw respectively in sediments. Not detected (nd) was used to indicate non-detects and treated as zero in the statistical analysis. All of the results were corrected with the recovery.

Risk Assessment

The total estrogenic activity in each sample was expressed as estradiol equivalency quotient (EEQ), which was calculated with the following equation: $EEQ = \sum C_i \times EEF_i$, where C_i was the concentration of individual EDCs and EEF was its respective estradiol equivalency factor relative to βE2. The EEF values of E1, αE2, βE2, E3, EE2, BPA, NP, and OP were 0.01, 0.03, 1, 0.3, 1.25, 0.00003, 0.00008 and 0.00011, respectively, which were derived from the human breast cancer cell proliferation assay (E-Screen) results (Yang et al. 2015; Zhang et al. 2015a).

Statistical Analysis

Statistical analysis was carried out by the SAS/PC 9.3 (SAS Institute Inc., USA). Pearson correlation analysis was employed to investigate the relationships between concentrations of EDCs in sediments and surface water, and the correlations of EDCs concentrations with TOC content in sediments. A p value <0.05 was considered statistically significant.

Results and Discussion

Profiles of EDCs in Surface Water and Sediments of the TGRR

The eight target EDCs were detected in surface water and sediments from the TGRR (Table 1). In water samples, βE2 was found with the highest detection frequency (100 %), followed by BPA (92.9 %), OP (71.4 %), NP (71.4 %), and αE2 (71.4 %). Concentrations of the eight tested EDCs ranged from nd to 120.0 ng L^{-1}. OP was found with the highest mean concentration at 32.3 ng L^{-1}, followed by BPA at 26.6 ng L^{-1}, whereas αE2 and βE2 had the least mean concentrations at 3.3 and 3.7 ng L^{-1}, respectively. Total concentrations of the eight target compounds (∑8EDCs) varied from 22.0 to 197.4 ng L^{-1} for the water samples. In surface water of the TGRR, concentrations of E1, αE2, E3, EE2, and OP were in range of

Table 1 Concentrations of eight target compounds in surface water (ng L^{-1}) and sediments (ng g^{-1} dw) of the TGRR

Compounds	Sites														Range	Mean	DF (%)
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14			
Surface water																	
E1	21	10	nd	41.0	nd	52.3	nd	nd	20.0	nd	nd	nd	nd	nd	nd–52.3	10.3	35.7
αE2	1.5	13.1	3.7	8.3	6.0	3.5	nd	nd	6.8	nd	1.6	1.1	1.3	nd	nd–13.1	3.3	71.4
βE2	1.3	0.7	1.1	2.8	1.1	8.1	5.4	6.9	7.6	10.0	3.3	1.2	1.2	0.1	0.1–10.0	3.7	100
E3	nd	22.5	81.6	60.8	nd	40.6	nd	nd	nd	nd	nd	nd	nd	35.5	nd–81.6	17.2	35.7
EE2	32.0	nd	23.3	18.1	nd	nd	nd	nd	35.3	nd	nd	nd	nd	nd	nd–35.3	7.8	28.6
BPA	14.9	33.3	50.1	16.9	21.5	44.2	20.1	38.7	23.5	20.7	35.7	nd	14.8	37.5	nd–50.1	26.6	92.9
NP	6.3	8.0	16.7	33.3	nd	14.9	4.6	nd	16.9	11.5	nd	19.7	nd	18.6	nd–33.3	10.8	71.4
OP	120.0	53.2	20.1	16.3	76.4	11.4	nd	nd	67.4	11.0	nd	nd	57.4	18.7	nd–120.0	32.3	71.4
∑8EDCs	197.0	140.8	196.7	197.4	105.0	175.0	30.1	45.6	177.5	53.2	40.6	22.0	74.7	110.4	22.0–197.4	111.9	
Sediment																	
E1	nd	8.1	nd	6.8	9.1	2.9	nd	nd	nd	3.4	nd	nd	6.8	nd	nd–9.1	2.6	42.9
αE2	8.8	3.9	nd	14.8	9.1	nd	nd	nd	17.0	nd	3.8	nd	nd	nd	nd–17.0	4.1	42.9
βE2	5.2	2.1	11.1	13.7	5.2	6.9	4.2	nd	17.2	13.8	nd	7.1	9.7	12.1	nd–17.2	7.7	85.7
E3	nd	2.8	1.0	1.3	9.5	1.2	4.3	1.0	4.2	nd	2.2	0.7	3.8	1.0	nd–9.5	2.4	85.7
EE2	3.0	1.8	10.2	22.0	2.8	nd	37.6	5.6	16.8	15.1	34.3	12.9	3.4	nd	nd–37.6	11.8	85.7
BPA	9.1	41.1	4.7	14.4	38.3	6.4	4.8	6.9	10.1	13.7	24.7	32.7	25.8	11.6	4.7–41.1	17.4	100
NP	nd	0.7	7.3	nd	8.5	7.6	6.2	5.2	6.3	8.0	6.7	4.6	5.8	2.8	nd–8.5	5.0	85.7
OP	6.6	1.5	3.5	0.7	1.3	2.8	10.9	4.4	nd	10.2	6.4	6.3	12.4	6.6	nd–12.4	5.3	92.9
∑8EDCs	32.7	62.0	37.8	73.8	83.8	27.7	68.2	23.0	71.5	64.3	78.1	64.2	67.6	34.2	23.0–83.8	56.4	

nd not detected, *DF* detection frequency, *∑8EDCs* total concentrations of the eight target EDCs

nd to 52.3, nd to 13.1, nd to 81.6, nd to 35.3, and nd to 120.0 ng L^{-1}, respectively, much higher than those reported in the literature (Table 2). The concentration range of βE2 was between 0.1 and 10.0 ng L^{-1} in the studied water, roughly in line with those in the rivers of Germany (Hintemann et al. 2006) but lower than those in waters from England (Hibberd et al. 2009) and America (Benotti et al. 2008) and higher than those in the Pearl River (Yu et al. 2011) and the Yellow River (Wang et al. 2012b). BPA and NP, as two widely applied industry materials, ultimately end up in aquatic environments via discharge of domestic and industrial wastewater (Luo et al. 2014). The maximum concentrations of BPA and NP in the TGRR were 50.1 and 33.3 ng L^{-1}, respectively, both presenting relatively lower levels than those reported in the literature.

In the sediments of the TGRR, concentrations of the eight target EDCs varied from nd to 41.1 ng g^{-1} dw, with BPA having the highest mean concentration at 17.4 ng g^{-1} dw, followed by E3 at 11.8 ng g^{-1} dw (Table 1). ∑8EDCs of sediments ranged between 23.0 and 83.8 ng g^{-1} dw, with a mean value at 56.4 ng g^{-1} dw. BPA was the most frequently detected compound (100 %), followed by OP (92.9 %), and NP (85.7 %). Compared with steroid estrogens, BPA, NP, and OP presented significantly higher levels in both surface water and sediment samples, which corresponded to their wide application in industrial products and household wares, such as plastics, food packaging, thermal receipts, and dental sealants (Rochester 2013; Zhang et al. 2015a). Except for E1 and EE2, all the other three steroid estrogens (αE2, E3 and βE2) had 85.7 % of detection frequencies. Overall, concentrations of the five steroidal estrogens, including E1, αE2, E3, βE2, and EE2 in sediments of the TGRR were close to or higher than those in the literature (Table 2). BPA was found with a concentration range of 4.7–41.1 ng g^{-1} dw in the studied sediments, higher than that reported in America (Stuart et al. 2005), but lower than those detected in the Elbe River, Germany

Table 2 Comparisons of concentration ranges of eight target chemicals in water (ng L^{-1}) and sediments (ng g^{-1} dw) between the TGRR and other places in the world

	China			Korea	England	Germany	America	Australia
	TGRR	Pearl River	Yellow River					
Surface water								
E1	nd–52.3	3.2–12	nd–15.6	nd–18	0.6–14.3		nd–0.9	nd–4.6
αE2	nd–13.1	nd–6.5						
βE2	0.1–10.0	nd–0.42	nd–2.3		3.1–21.4	nd–9.2	nd–17	nd–1.2
E3	nd–81.6	nd–0.37						nd–1.9
EE2	nd–35.3	1.3–4.2			nd–1.5	nd–1	nd–1.4	nd–0.33
BPA	nd–50.1	228–625	12.5–171.5		nd–69.3	nd–776	nd–14	nd–600
NP	nd–33.3	234–437	165.8–1187.6	9.7–928	nd–4.4	nd–221	nd–130	nd–890
OP	nd–120.0		2.4–14.5	nd–25	nd–37.6	nd–17		nd–41
Sediment								
E1	nd–9.1		nd–8.0		nd–5.8	nd–0.2	0.3–0.6	
αE2	nd–17.0							
βE2	nd–9.5	nd–4.12	nd–4.1		nd–11.2	nd–0.2	0.16–0.45	
E3	nd–37.6							
EE2	nd–17.0				nd	nd–0.2		
BPA	4.7–41.1	18.3–148			7.7–56.1	10–379	nd–30	
NP	nd–8.5	533–5500	16.6–203.8	92–557	nd–11.0	24–428	122–3200	20–2830
OP	nd–12.4	1.8–51.2	2.4–14.5		4.7–31.3	2.4–25		
Reference	This study	(Yu et al. 2011; Zhao et al. 2011)	(Wang et al. 2012b)	(Li et al. 2008; Yoon et al. 2010)	(Hibberd et al. 2009)	(Heemken et al. 2001; Hintemann et al. 2006)	(Benotti et al. 2008; Schlenk et al. 2005; Stuart et al. 2005)	(Hohenblum et al. 2004; Micić and Hofmann 2009)

nd not detected

(Heemken et al. 2001), the River Medway, UK (Hibberd et al. 2009), and the Pearl River, China (Zhao et al. 2011). Concentrations of NP and OP ranged from nd to 8.5 and nd to 12.4 ng g^{-1} dw respectively in sediments of the TGRR, both lower than those reported in the literature.

Spatial Distribution of EDCs in Surface Water and Sediments of the TGRR

Abundance of EDCs varied significantly in the TGRR (Table 1). Interestingly, higher abundance and detection frequencies of the target EDCs were found in the upstream of the TGRR. αE2, βE2, BPA, and OP were quantified in all the water samples from S1 to S6. Except for βE2, average concentrations of E1, αE2, E3, EE2, BPA, NP, and OP in the region between S1 and S6 were 20.7, 6.0, 34.3, 12.2, 30.1, 13.2, and 49.6 ng L^{-1}, respectively, significantly higher than the mean levels of corresponding compounds for all the sampling sites. In addition, the mean value of ∑8EDCs from S1 to S6 was 168.6 ng L^{-1}, approximately 1.5 times of that for the whole TGRR. Especially, S3 and S4, located in the metropolitan areas of Chongqing Municipality, were found with the highest ∑8EDCs at 196.7 and 197.4 ng L^{-1}, respectively. This implied certain correlations might exist between EDCs abundance and anthropogenic factors (Zhang et al. 2015a), because these sites are all marked by large population density and booming economy. As a commonly used component in oral contraceptives, EE2 is more likely present in effluents from wastewater treatment plants (WWTPs) in populous areas and ends up in surface water via wastewater discharge and runoff (Zhang et al. 2015a). In the past years, concentrated animal feeding operations have gained great development in the TGRR (Zhang et al. 2015b). However, due to lack of pollution prevention facilities, livestock excrement from most of large-scale breeding farms is discharged into the water body directly (Zhang et al. 2015b), which could be an important contributor to high levels of E1, αE2, βE2, and E3 in upstream water of the TGRR, because these livestock farms were increasingly concentrated around populous districts. Human is another producer of natural estrogens, while sewage discharge from WWTPs is the major way for these compounds to enter into the aquatic environment (Zhang et al. 2015a). Notably, the high abundance of BPA, NP, and OP in TGRR were probably attributed to the wide application of these synthetic chemicals in industries (Miller and Staples 2005). Compared with other sources, discharge of household and industrial wastewater is considered as a main cause of the presence of BPA, NP, and OP in surface water (Luo et al. 2014). The eight target EDCs are widely produced naturally or industrially by humans and enter into the aquatic system via various ways, such as surface runoff, discharge of domestic and industrial wastewater, effluent from WWTPs, which consequently increase the possibility of environmental pollution in water (Luo et al. 2014; Zhang et al. 2015a). There was a close relationship between the tested compounds and the presence of anthropogenic activities near the sampling point. Therefore, the characteristics of population and anthropogenic activities along the TGRR played a key role in the spatial variation of EDCs in surface water of the reservoir.

Although EDCs in the water body can be absorbed by sediments and move back into the water column by mobilization (Campbell et al. 2006; Johnson et al. 1998), variation of the EDCs levels in sediments and surface water was not consistent in the TGRR. Compared with that in the surface water, distribution of the tested chemicals in sediments was relatively more balanced. Except that E1 and αE2 concentrated in the upstream, the other compounds were widely distributed in sediments of the TGRR. The ∑8EDCs of sediments ranged from 23.0 to 83.8 ng g^{-1} dw and presented a wave distribution as a whole (Table 1). To explore the relationships between EDCs in surface water and sediments, βE2, BPA, OP, and NP, as four frequently detected compounds in both media, were selected for Pearson correlation analysis. As shown in Fig. S1, all the p values in the analysis were greater than 0.2, implying that no significant correlations were found between EDCs in surface water and sediments of the TGRR. Similar results were found in Honghu Lake and East Dongting Lake, China (Yang et al. 2015), and Anoia River and Cardener River, Spain (Petrovic et al. 2002). The target EDCs are all poorly soluble in water, and their water solubility strongly depends on parameters of water, such as existence of dissolved organic matter, ionic strength, pH, temperature, and pressure (Silva et al. 2012). As a result of their hydrophobic properties, these compounds tend to partition with solid phase (Zhang et al. 2015a). In this study, the detection frequency of EE2 in sediments was higher than that in surface water, which probably resulted from its greater potential to sorb to sediments (Young et al. 2002). Due to the large surface area and richness in organic materials, the fine and suspended sediments can absorb large amount of EDCs from water (Ying et al. 2002) and serve as the vector to take them away with the help of water flow. Sinking of these EDCs-loaded sediments can aggravate the pollution levels of the receiving riverbed. In the TGRR, the interception of the Three Gorges Dam changes the flow velocity of the Yangtze River, as a result of which suspended sediments with various sizes and contamination levels may sink in different reaches in this region. Besides, the high water flow in flood season can stir the fine sediments and carry them away (Wang et al. 2012b). These might be factors accounting for the distribution inconsistence of EDCs levels in surface water and sediments of the TGRR.

Sorption capability and distribution of contaminants in sediments are affected by sediment properties, such as particle size distribution, and the organic carbon content (Cornelissen et al. 2005; Lai et al. 2000). Many EDCs have moderate to high log Koc values and usually end up in organic complexes of sediments rather than remain soluble (Campbell et al. 2006). TOC, therefore, may affect the levels of EDCs in sediments. Pearson correlation analysis was employed to investigate the relationship between the TOC content and concentrations of four frequently detected EDCs (including βE2, EE2, BPA, and OP) in sediments (Fig. S2). No significant correlations were found between TOC content and concentrations of the selected EDCs in sediments of the TGRR. Similar results were reported in the East Dongting Lake (Yang et al. 2015) and the Yellow River, China (Wang et al. 2012b). However, studies in Aire, Calder and Thames Rivers, UK (Johnson et al. 1998) and Beitang, Dadu and Yongding New Rivers in Tianjin, China (Lei et al. 2009) presented an opposite case. Although the organic carbon is considered as an important factor affecting the sorption of estrogens to sediments (Lai et al. 2000), the distribution and partitioning of these chemicals are determined by their physicochemical properties and site-specific environmental conditions (Ying et al. 2002), such as sediment texture (Wang et al. 2012b), salinity (Lai et al. 2000), microorganisms (Zhang et al. 2015a), and so on.

Risk Assessment

The presence of EDCs in the aquatic environment can cause adverse endocrine effects to the aquatic organisms, such as vitellogenin induction, feminization, imposex, and histological and reproductive problems (Young et al. 2002). Predicting the estrogenic activity of EDCs mixtures is essential to evaluate potential risks of these compounds to the aquatic ecosystem, because aquatic wildlife in reality is exposed to complex combinations of chemicals. Estrogenic compounds have the capacity to act together in an additive manner and their combined effects can be accurately predicted by concentration addition (Brian et al. 2005). Based on the concentration addition model, calculated EEQ is widely applied to assess the mixture effects of estrogens (Nie et al. 2015; Wang et al. 2012b; Zhao et al. 2011). Its validity has been demonstrated in vitro or vivo, using assays, such as the recombinant yeast estrogen screen (rYES) (Jiang et al. 2012; Wang et al. 2012b; Zhao et al. 2011), the human breast cancer cell proliferation assay (E-Screen) (Payne et al. 2001), and introduction of vitellogenin (VTG) in juvenile rainbow trout (Thorpe et al. 2005). In the present study, total estrogenic activities of the eight target EDCs in surface water for each site were evaluated by the calculated EEQ, which was expressed as the summation of estrogenic contributions of eight target EDCs by multiplying their corresponding estradiol equivalency factors (EEFs) with chemical concentrations. The EEQ values in water samples from the TGRR were in range of 1.2–52.1 ng L^{-1}, with 42.9 % of the sampling sites having EEQ values greater than 10 ng L^{-1} (Fig. 2). As proposed by the Environment Agency of UK, the predicted no-effect concentration (PNEC) and lowest observable effect concentration (LOEC) for βE2 were 1 and 10 ng L^{-1}, respectively (Gross-Sorokin et al. 2005; Young et al. 2002). Based on this criterion, aquatic organisms in the TGRR were predicted to be at a low to high risk of endocrine disruption. It also was reported that aquatic organisms in Nanjing section (Lu et al. 2010; Song et al. 2011) and the estuary (Nie et al. 2015) of the Yangtze River suffered from impairment of their reproductive physiology due to long-term or chronic exposure to environmental estrogens. Considering their ubiquitous existence in the Yangtze River basin (Li et al. 2015), estrogenic compounds might be an important contributor to the decline in fish population (Wang et al. 2014). However, there are hundreds or even thousands of classes of EDCs in the aquatic environment, many of which may not yet be discovered (Campbell et al. 2006). In addition, the mixture of various kinds of synthetic and natural organic compounds may interact with each other, resulting in synergistic, agonistic, or antagonistic effects to the exposed aquatic organisms (Wang et al. 2014). Thus, prediction of the overall risk posed in real exposure situations can be more complex than that expected on the basis of the effects assessment of the measured compounds.

To explore the individual contributions of the eight target EDCs to the total estrogenic activities, their contribution rates for the EEQ values were calculated (Fig. 3). βE2 was found with the highest contribution rate (1.35–99.98 %, mean value at 53.75 %), followed by E3

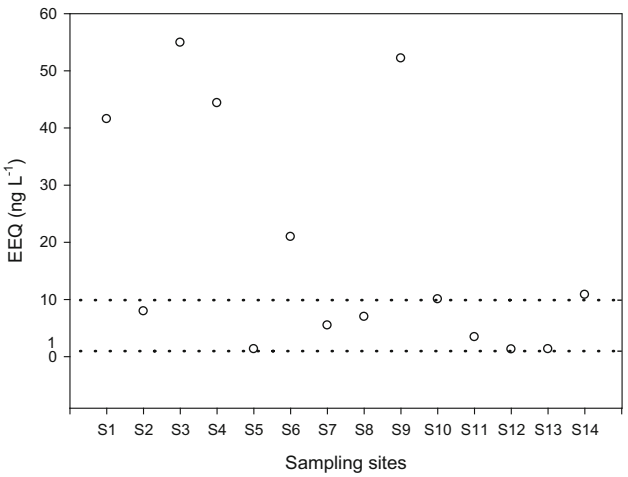

Fig. 2 EEQ values for the surface water of the TGRR

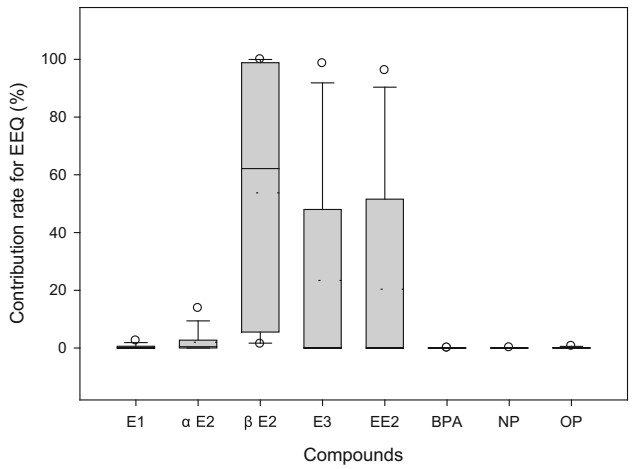

Fig. 3 Individual contribution rates (%) of the eight target EDCs to EEQs. The *solid horizontal lines* from *top* to *bottom* indicated max values, 75th percentiles, median, 25th percentiles, min values, respectively. The *dashed horizontal lines* indicated mean values. The *circles* outside the *boxes* represented outliers

(0–98.61 %, mean value at 23.41 %), and EE2 (0–96.22 %, mean value at 20.35 %). The contribution rates for αE2 and E1 ranged from 0 to 13.77 % (mean value at 1.97 %) and 0 to 2.5 % (mean value at 0.40 %). Of the total estrogenic activities, 99.88 % were contributed by the steroidal estrogenic chemicals, which thereby were the main contributors to the environmental risks of estrogens in water. Although widely detected with high levels in surface water of the TGRR, the three xenoestrogens, BPA, NP, and OP, due to their low EEFs, did not greatly contribute to the estrogenic potencies in this region. Effective measures should be taken to reduce the discharge of sewage containing estrogenic chemicals into the water body of the TGRR to protect aquatic organisms in this region.

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