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Occurrence, distribution and risk assessment of estrogens in surface water, suspended particulate matter, and sediments of the Yangtze Estuary

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HIGHLIGHTS

- Estrogens were investigated along the Yangtze River Estuary over four seasons.
- Estrogen concentrations were the highest in January.
- Estrogens concentrations were regulated by organic carbon.
- Higher risk was found in the SPM and sediment compared to the water phase.

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ABSTRACT

The occurrence and distribution of six selected estrogen compounds were investigated in samples of surface water, suspended particulate matter (SPM), and sediment in the Yangtze Estuary and its coastal areas over four seasons. With the exception of 17α-ethinylestradiol (EE2), all estrogens were detected at least once in all three phases with bisphenol A (BPA) and estriol (E3) as the dominant estrogens in all phases. EE2 was not detected in any surface water samples. In addition, the highest total estrogen concentrations were found in January in all phases, which could be due to the low flow conditions and temperature during this season. A significant positive correlation was found between total estrogen concentrations and organic carbon (OC) contents, both in the water phase and solid phase (i.e. SPM and sediment), indicating the vital role played by OC. Based on a yeast estrogen screen (YES) bioassay, the higher estrogenic risk was found in the SPM and sediment phase when compared to the water phase. These results were confirmed by a risk assessment which revealed that the Yangtze Estuary was displayed a low to high risk over the seasons for all selected estrogens.

1. Introduction

Endocrine disrupting chemicals (EDCs) have received growing attention recently due to the endocrine disrupting effects on fish and other aquatic vertebrate species, even at concentrations as low as the ng L^{-1} level (Arnon et al., 2008; Guiguen et al., 2010; Walf et al., 2011; Goeppert et al., 2014), in which estrogen is an important class. Natural estrogens such as estrone (E1), 17β-estradiol (E2), and estriol (E3) mainly originate in the feces and urine of humans and livestock. Synthetic estrogens such as 17α-ethinylestradiol (EE2), 4-tert-octyphenol (OP), and bisphenol A (BPA) are used as contraceptives and industrial chemicals (Hanselman et al., 2006).

Owing to the physicochemical properties (e.g. solubility (S_W) and the octanol/water partition coefficient (K_{ow})), estrogens are only partially removed in wastewater treatment plants (WWTPs) and ultimately end up in ambient waters via effluent discharges and animal waste disposal (Stuart et al., 2012; Xu et al., 2012). Upon entering the water system, these compounds can be absorbed by aquatic organisms, and pose a severe threat to the

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whole ecosystem (Rhind et al., 2010; Zhang et al., in press; Nie et al., 2014a,b). Numerous studies in recent years have been performed on the occurrence, distribution and fate of estrogens in the aquatic environment (Zhang et al., 2010; Froehner et al., 2012; Rocha et al., 2013; Huang et al., 2013; Schultz et al., 2013).

Estuaries of large rivers are important interfaces between riverine and marine environments. They usually experience material fluxes that preserve a record of the drainage basin caused by either natural process or/and anthropogenic activities (Dong et al., 2014; Jiang et al., 2014). Yangtze Estuary, the largest estuary in Asia, receives a huge amount of sediment annually and has developed an extensive tidal flat along the estuarial area and coastal line. While the economy and population developed rapidly, the Yangtze Estuary has been subjected to significant human activities in recent decades. As a result, upstream runoff and sewage outfalls have introduced pollution into the Yangtze Estuary. Several studies have reported the detection of heavy metals (Dong et al., 2014), dichlorodiphenyltrichloroethanes (DDTs) (Liu et al., 2006), polycyclic aromatic hydrocarbons (PAHs) (Yang et al., 2008), pharmaceuticals (Yang et al., 2011a,b), and antibiotics (Yan et al., 2013) in the Yangtze Estuary. Until now, however, few study (Shi et al., 2014), to our knowledge has dealt comprehensively with estrogen residues in the Yangtze Estuary and its coastal area, especially in multiple phases.

The aim of the present study is to investigate the occurrence, distribution and risk assessment of the selected estrogens in different phases along the Yangtze Estuary and its coastal area. To explore the intrinsic association of estrogens among different phases, seasonal and spatial trends of estrogens in surface water, SPM, and sediments were studied at seven sampling sites over four seasons. The results are essential for pollution control and risk assessment in the Yangtze Estuary and its coastal areas.

2. Materials and methods

2.1. Chemicals and reagents

Standards for natural estrogens including E1, E2, and E3, as well as synthetic estrogens including EE2, OP, and BPA were purchased from Dr. Ehrenstorfer (GmbH, Germany), as well as the internal standards (E2-d_2 and BPA-d_{16}). The physicochemical properties of the selected estrogens including the molecular weight, formula, structure, $\log K_{ow}$ are shown in Table S1. A 10 mg L^{-1} standard mixture of each compound was prepared by diluting the stock solution (1000 mg L^{-1}) with methanol. All solvents used in the study were of HPLC grade. The derivatization reagent N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) was obtained from Sigma–Aldrich (St. Louis, USA). Neutral alumina and silica gel were pre-activated at 130 °C for 24 h and 48 h respectively, and deactivated by adding 10% ultra-pure water. All glassware, glass microfiber filters (GF/B, Whatman, Maidstone, UK), anhydrous sodium sulfate and quartz sand were baked in a muffle furnace at 400 °C for over 4 h.

2.2. Sample collection

Surface water and sediment samples were collected in intertidal mud flats at seven sampling sites along the Yangtze Estuary and its coastal areas in July 2011, October 2011, January 2012 and May 2012 (Fig. 1): Xupu (XP), Daxingang (DXG), Yinyang (YY), Bailonggang (BLG, the largest WWTP in Asia), Luchao (LC), Wusongkou (WSK, the junction of Huangpu River and Yangtze River), and Liuhekou (LHK, the junction of Liu River and Yangtze River). Water samples were stored in 50 L pre-cleaned stainless steel barrels, while sediments were covered with foil and collected in a valve bag. Once transported to the laboratory, the water samples were filtered immediately through glass fiber filters (1 μm, PAUL, USA) to obtain filtrates and SPM samples. All solid samples, including SPM and sediments, were stored at -20 °C and then freeze dried before use.

2.3. Sample treatment and analyses

Water samples were extracted and derivatized according to methods described in previous studies (Hibberd et al., 2009; Nie et al., 2014a,b). Briefly, water samples spiked with 100 ng internal standards were extracted through solid phase extraction (SPE). All Oasis HLB cartridges (Waters, USA) were pre-conditioned with 6 mL methanol and 10 mL ultra-pure water at a flow rate of 5–10 mL min^{-1}. Water samples were passed through the cartridges at a flow rate of 5–10 mL min^{-1}. After they were extracted, the target compounds were eluted with 10 mL methanol and dried under N_2. SPM and sediment samples were extracted using an accelerated solvent extractor (ASE 350, DIONEX, USA) by methanol. The extraction cell was loaded with a sample mixed with quartz sand above and two pieces of glass microfiber filters at the bottom, and extracted under 1500 psi at 60 °C in a static mode for 5 min. All extracted solutions spiked with 100 ng internal standards were concentrated to 1–1.5 mL by rotatory evaporation, and then cleaned by silica gel and neutral alumina columns which were pre-cleaned with methanol. The collected extraction was reduced and then completely dried under N_2. The estrogens were then derivatized with 50 μL pyridine and 50 μL BSTFA added into each vial with the dried extracts, and then the mixtures were activated at 65 °C for 30 min. After they were dried again, 100 μL of hexane was added to the vials before the GC–MS analysis.

The GC–MS (7890A/5975C, Agilent, USA) was equipped with a DB-5MS Ultra Inert polysiloxane polymer column (30 m × 0.25 mm × 0.25 μm), using the selective ion monitoring (SIM) mode. Helium was used as the carrier gas at a flow rate of 1.5 mL min^{-1}. The GC column temperature was programmed at an initial temperature of 100 °C (held for 1 min), and then increased to 260 °C at 15 °C min^{-1}, and further increased to 280 °C at 3 °C min^{-1} (held for 2 min). The typical chromatograms of a standard at 1 mg L^{-1} surface water and sediment sample are shown in Fig. S1. Quantification of the target compounds was conducted using internal standards. Limit of detection (LOD) and limit of quantification (LOQ) were 0.10–0.49 ng L^{-1} and 0.30–1.97 ng L^{-1} in aqueous samples, 0.15–0.44 ng g^{-1} and 0.93–3.15 ng g^{-1} in SPM and sediment samples, respectively, which had been reported in our earlier publication (Nie et al., 2014a,b). The recoveries of all estrogens ranged from 63.2% to 132.7% for the ultra-pure water sample (SD: 5.7–20.1%). No estrogens were detected in the controlled blank experiment. All experiments were conducted in triplicate.

2.4. Organic carbon analysis

The total organic carbon (TOC) concentration in sediments and SPMs was analyzed using elemental analysis (Vario EL, Elementar, Germany). The dissolved organic carbon (DOC) content in aqueous samples was detected by liquiTOC II (Elementar, Germany).

2.5. Estrogenic activity and risk assessment

To assess the potential risks of estrogenic activity to aquatic organisms, estradiol equivalents (EEQs) and risk quotients (RQ) were calculated.

2.5.1. Estradiol equivalents (EEQs)

The calculated EEQ (EEQ_{cal}) was extrapolated from the concentrations of the analyzed target compounds using the following equation:

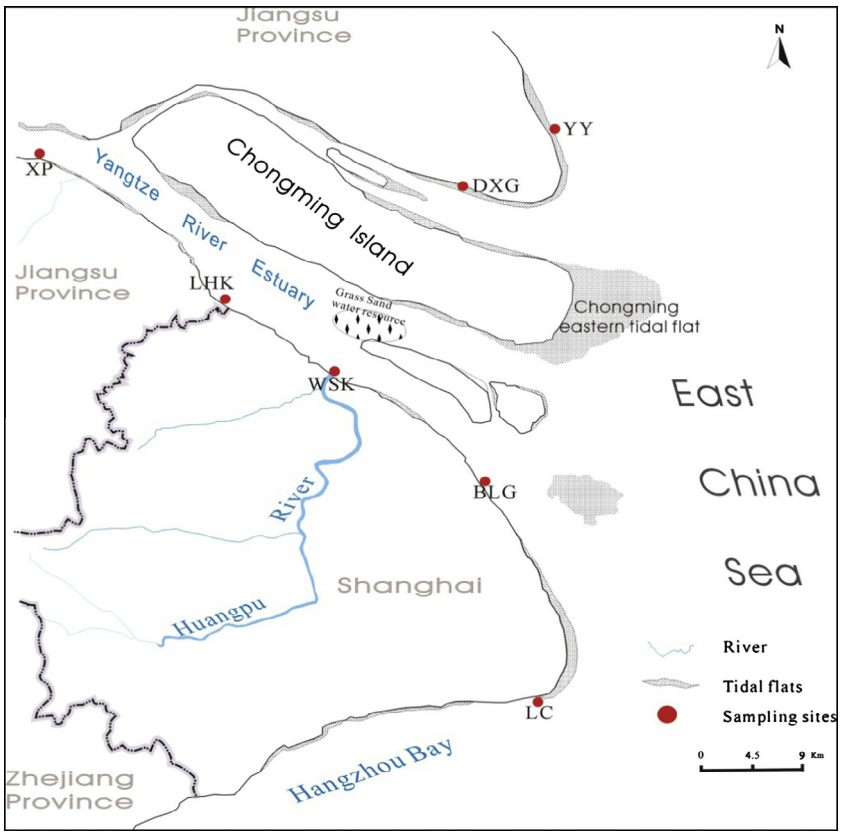

Fig. 1. Sampling sites along the Yangtze Estuary and its coastal area.

$$EEQ_{cal} = \sum EEQ_i = \sum (C_i \times EEF_i) \quad (1)$$

where EEQ_i is the EEQ value of the selected compound *i*, C_i is the relative potency of the selected compound *i*, and EEF_i is the estrogenic equivalent factor relative to E2. The EEF values of E1, E2, E3, EE2, OP, and BPA were 0.25, 1, 5.9×10^{-3}, 1.25, 4.5×10^{-6} and 1.2×10^{-4}, respectively, which were derived from yeast estrogen screen (YES) assay results (Beck et al., 2006).

2.5.2. Risk quotient (RQ)

RQ is the ratio between a measured environmental concentration (MEC) and a predicted no effect concentration (PNEC), as described in equation (2):

$$RQ = MEC/PNEC \quad (2)$$

The PNEC value is often derived from the chronic (i.e. no observed effect concentrations, NOECs) or acute toxicity data (EC50) when chronic data were unavailable (EMEA, 2006). Note however, for a certain compound, that several NOECs have been generated for the same or different endpoints, as well as the age of the species (Wright-Walters et al., 2011). An estrogen might also trigger observable effects at extremely high or low doses, but almost no effect at moderate doses (Lemos et al., 2009). In this study, therefore, different acute and chronic toxicity data from the EPA ECOTOX database of multiple species were acquired to build the species sensitivity distribution (SSD) curve (see Table S2). For the same species with different toxicity data, the lowest concentration was chosen. Among all models, the log–logistic or log-normal distribution often best fit the toxicity data (Caldwell et al., 2008). Based on the best fit distribution, an HC_5 was derived from an SSD of each compound, which means that 95% of the species would not display any adverse estrogenic effect associated with this concentration. In the present study, the calculated HC_5 values were 3.70 ng L^{-1}, 0.58 ng L^{-1}, 50.97 ng L^{-1}, 2.65 ng L^{-1} and 128.53 ng L^{-1} for E1, E2, E3, OP and BPA, respectively (Fig. S2). No HC_5 value of EE2 was determined due to its low detected concentration in surface water (below LOQ; see details in the following discussions). Then PNEC values were defined as the hazardous concentration values for 5% of the species (HC_5) (Zhao et al., 2011).

In addition, estrogens with relatively high hydrophobic characteristics might be assessed as low risk for aquatic organisms, but these estrogens could accumulate in sediments. In general, substances with a $\log K_{ow}$ value $\geqslant 3$ were likely to be absorbed into sediment (SETAC, 1993). Due to the absence of a reliable test in sediments, an equilibrium partitioning method was used based on the assumptions that sediments contain dwelling organisms, and that water column organisms are equally sensitive to the selected estrogens. The PNEC of sediment was quoted from a European technical guidance document (TGD) using equation (3) (EC TGD, 2003):

$$PNEC_{sed} = K_p \times PNEC_{wat} \times 1000/RHO_{SPM} \quad (3)$$

where $PNEC_{sed}$ and $PNEC_{wat}$ are the PNEC in the sediment and aquatic phase, respectively; K_p is the SPM–water partition coefficient calculated according to TGD (L L^{-1}); and RHO_{SPM} is the bulk density of SPM (1150 g L^{-1}) from TGD.

3. Results and discussions

3.1. Occurrence of estrogens in surface water

Measured concentrations of the selected six estrogens in filtered water samples are shown in Fig. 2. EE2 was not detected in any water sample during the four sampling campaigns, while

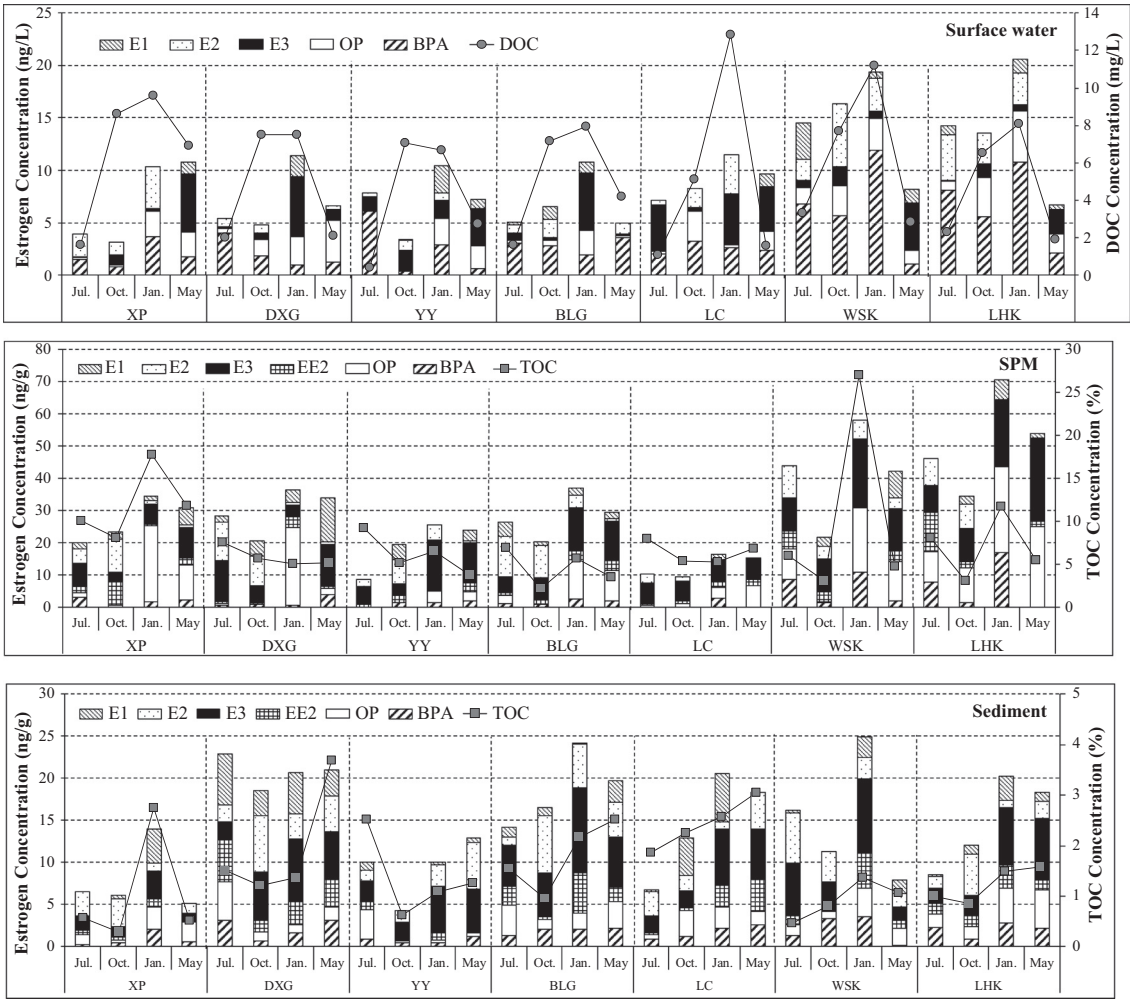

Fig. 2. Concentrations of estrogens in surface water, SPM and sediments of the Yangtze Estuary over the four seasons.

E3, OP, and BPA were most frequently detected, and were detected in all seasons. The total estrogen concentration ranged from 3.92 ng L^{-1} to 14.54 ng L^{-1} in July, from 3.22 ng L^{-1} to 16.36 ng L^{-1} in October, from 10.42 ng L^{-1} to 20.61 ng L^{-1} in January, and from 5.03 ng L^{-1} to 10.77 ng L^{-1} in May. In general, the concentration of synthetic estrogens in the study area was slightly higher than that of the natural estrogens. BPA was the dominant estrogen contributing 8.53–77.99% of the total estrogen concentration, and the highest concentration of BPA was found at the WSK site in January 2011 (11.96 ng L^{-1}). E3 followed as the secondary most common compound, accounting for 1.01–61.18% in the study area.

The Huangpu River, originates from the Tai Lake and finally enters into the Yangtze Estuary, where BPA and E3 were also observed to be the dominant estrogens, with higher detection frequencies and concentrations in surface water samples (Nie et al., 2014a,b). BPA is widely used in manufacturing of chemical products such as digital media (typically CDs and DVDs), reusable bottles, glazing, and sealants. (Huang et al., 2012; Daskalaki et al., 2013), and is inefficiently removed by bacteria in WWTPs (Richardson, 2009). As the metabolite of E1 and E2, E3 is more stable and reaches its peak during the pregnant of mammal, which might result in its relatively high detection frequency and concentration in the environment (Arcand-Hoy et al., 1998).

Additionally, the overall estrogen concentration in January was the highest of the four seasons (Fig. 2). Numerous previous studies have reported that the higher EOC concentrations were usually found in the dry season, which could attributed to lower dilution of the wastewater inputs, and cold temperature inhibiting bacterial activity (Kim and Carlson, 2007; Yang et al., 2011a,b; Yan et al., 2013). However, the lowest total estrogen concentration was not constant during the year at different sampling sites. For example, the lowest total estrogen concentrations were found in the north branch of the Yangtze Estuary (DXG and XP) in October. However in May, the lowest total estrogen concentrations were observed in the south branch (BLG, LHK and WSK). This might result from the different application pattern of these estrogens, and highly complex and dynamic environmental conditions in the Yangtze Estuary. Although a seasonal trend was shown in total estrogen concentrations, no obvious seasonal trend was found for individual compounds. Moreover, the highest DOC concentrations were also observed in January (Fig. 2), and a significant correlation was found between DOC contents and estrogen concentrations ($R = 0.41$, $P = 0.032$) (Fig. 3), confirming the results of previous studies (Yan et al., 2013; Nie et al., 2014a,b). This indicates the vital role played by DOC in controlling estrogen behaviors in an estuarial environment.

Except for May 2012, the highest total estrogen concentrations for the other seasons were found at the WSK and LHK sites, where tributaries (i.e. Liu River and Huangpu River) flowed into the Yangtze River. A similar trend was observed in the spatial distribution of antibiotics in the Yangtze Estuary (Yan et al., 2013). In spite of being influenced greatly by WWTP, however, the estrogen

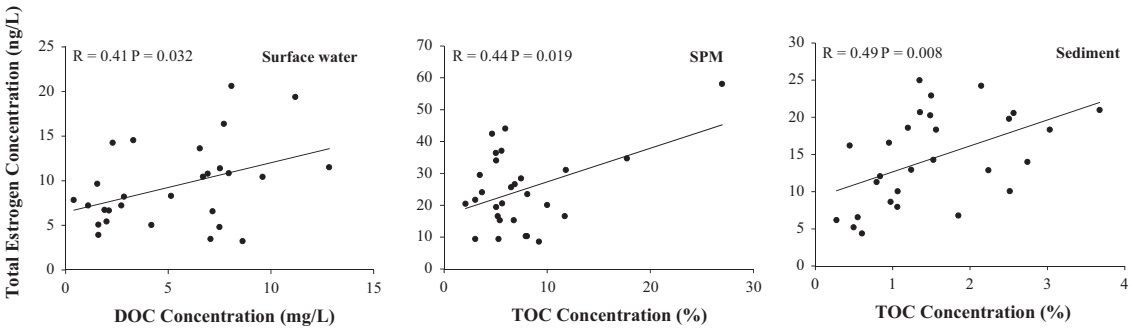

Fig. 3. Correlation between total estrogen concentrations and DOC/TOC concentration.

Table 1
The logK_{oc} values between SPM and water phase.

		E1	E2	E3	OP	BPA
2011.7	Min.	–	1.91	2.26	1.20	0.74
	Med.	–	2.87	3.43	2.24	1.44
	Max.	3.37	3.37	3.99	3.13	2.33
2011.10	Min.	–	2.12	2.57	1.41	1.31
	Med.	–	3.00	3.25	1.91	1.86
	Max.	3.88	3.45	4.08	2.50	2.77
2012.1	Min.	–	–	2.08	1.78	1.35
	Med.	–	–	2.94	2.72	1.87
	Max.	2.61	2.98	3.28	3.43	2.38
2012.5	Min.	–	–	2.15	2.01	1.27
	Med.	2.01	–	2.80	2.71	2.21
	Max.	3.14	2.59	3.45	4.22	2.94
Literature		2.45–3.34	3.10–4.01	2.13–2.62	3.54–5.18	2.50–6.60

concentration at the BLG site was not very high, demonstrating that the removal efficiency was relatively high for estrogens when compared to antibiotics (Yan et al., 2013). It was confirmed in the literature that the removal efficiency is approximately 71% for BPA and 40–50% for antibiotics (Deblonde et al., 2011).

3.2. Occurrence of estrogens in SPM

SPM is ubiquitous, distributed in all aquatic environments, and important in terms of its effect on the sorption of organic contaminants (Ra et al., 2008; Yang et al., 2011a,b). All selected estrogens were found in most sampling sites, with the exception of EE2, which was absent in surface water samples. In the SPM phase, the average total estrogen concentrations for all the sampling sites were 26.30 ng g^{-1} in July, 21.36 ng g^{-1} in October, 39.86 ng g^{-1} in January, and 32.89 ng g^{-1} in May. E3 was the most abundant estrogen at most sites, with a contribution ranging from 9.48% to 66.13%. Similar seasonal and spatial distributions were also observed in the SPM phase, the highest estrogen concentrations were detected in January, and at the junction of rivers (i.e. WSK and LHK sites) (Fig. 2). Moreover, TOC concentrations in the SPM phase were also significantly correlated to total estrogen concentrations ($R = 0.44$, $P = 0.019$) (Fig. 3).

Sorption behavior is a key process controlling the transport and fate of estrogens in the aquatic environment, as is organic carbon content. Therefore, the organic carbon normalized sorption coefficient of estrogens between the SPM and the water phase (K_{oc}, L kg^{-1}) was calculated according to equation (4):

$$K_{oc} \times f_{oc} = C_s/C_w \quad (4)$$

where C_s and C_w are the estrogen concentrations in SPM and the aqueous phase, respectively, and f_{oc} is the fraction of TOC in SPM. The results are shown in Table 1. The calculated logK_{oc} values were highly variable, ranging from 2.08 to 4.08 for E3, from 1.20 to 4.22 for OP, and from 0.74 to 2.94 for BPA. Such variability is likely attributed to SPM–water interactions, differences in SPM properties, and environmental conditions such as temperature, salinity and water flow rate. The average logK_{oc} values generally decreased according to the following order: E3 > E2 > OP > BPA, and were relatively stable over the seasons. These values were within the ranges previously observed in other parts of the world (Table 1) (Campbell et al. 2006; Duong et al. 2010).

The detection of estrogen concentrations in both SPM and aqueous phases allowed us to calculate a mass balance for total estrogen between these two phases in the estuarine system. As shown in Fig. S3, the SPM phase contributed 15.97–65.81% in July, 23.57–63.23% in October, 20.50–53.99% in January, and 17.65–88.38% in May. Therefore, a considerable percentage of estrogens was still concentrated in the aqueous phase, which could be attributed to the high sorption capability of colloids to organic contaminants in water (Yang et al., 2011a,b; Duan et al., 2013).

3.3. Occurrence of estrogens in sediments

Estrogens absorbed onto the SPM phase could settle out to become a part of the streambed sediments. These will either be deposited temporarily on the streambed, or will be flushed out as suspended load (Su et al., 2014). Compared to estrogen concentrations in SPM, the estrogen levels in sediment were 1–6 times lower. A similar distribution pattern in SPM and sediment was also found in the distribution of pharmaceuticals in the Yangtze Estuary (2–5 times higher in SPM phase) (Yang et al., 2011a,b). In this study, the total estrogen concentrations in sediments ranged from 6.54–22.91 ng g^{-1} in July, 4.36–18.58 ng g^{-1} in October,

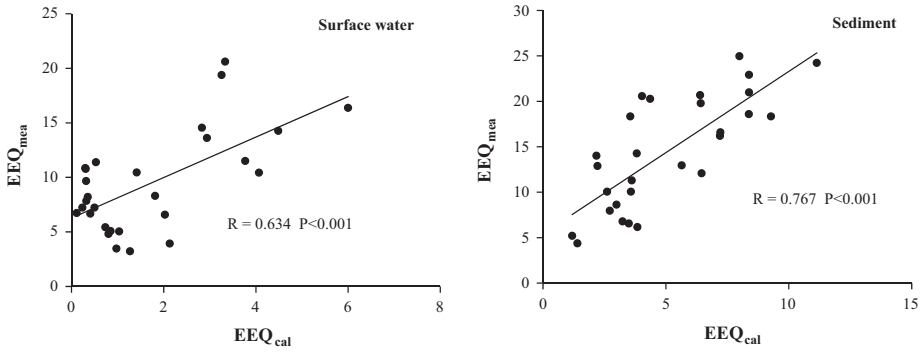

Fig. 4. Plots of measured total estrogen concentrations versus EEQ_{cal} in surface water and sediments.

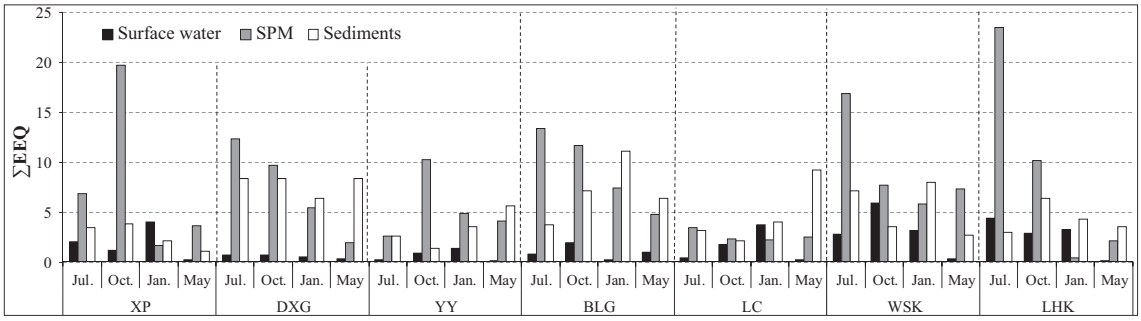

Fig. 5. Calculated EEQ values of selected compounds in Yangtze Estuary over the four seasons.

10.04–24.96 ng g^{-1} in January, and 5.19–20.97 ng g^{-1} in May (Fig. 2). Similar to the SPM, E3 was still the most abundant compound in sediment with an average contribution of 25.87–36.89% over the four seasons. E2 followed, contributing 12.28–35.49% to the total estrogen. While the largest estrogen contributors remained constant throughout the year, the lowest contributors varied by season.

The estrogen concentrations in this study were in the range of those in Pearl River Delta (Gong et al., 2011) and Yangtze River Delta (Shi et al., 2013). Excluding DXG and YY sites, the highest estrogen concentration also was found in January (Fig. 2), while the estrogen concentrations in sediment were also related to the TOC content ($R = 0.49$, $P = 0.008$) (Fig. 3). No significant spatial distribution, however, was found in sediments which might be due to the relatively low concentration compared to SPM phase.

3.4. Estrogenic activity

The measured estrogenicity (EEQ_{mea}) in surface water, calculated as the summation of each estrogen detected from GC–MS, correlated significantly with the calculated estrogenicity (EEQ_{cal}) derived from the YES bioassay ($R = 0.634$, $P < 0.001$) (Fig. 4), which was consistent with previous studies (Wang et al., 2011; Jiang et al., 2012; Zhang et al., in press). This corroborated that the selected estrogens accounted for the majority of the estrogenicity in the Yangtze Estuary. Moreover, as found in these studies, the EEQ_{cal} values in the present study were also lower than EEQ_{mea}, which could be explained by the unknown antagonists and agonistic in the water samples (Tanaka et al., 2001; Witters et al., 2001). A similar trend was also found in sediments ($R = 0.767$, $P < 0.001$) (Fig. 4), although no obvious correlation was found between EEQ_{mea} and EEQ_{cal} for SPM. Among all compounds, E2 and EE2 showed higher EEQ_{cal} in all phases, even reaching a proportion of 99%, revealing that the primary estrogenic activity was induced by E2 and EE2 in spite of their low EEQ_{mea}. In general, the EEQ_{cal} in SPM was relatively high, followed by sediments, which might be attributed to the higher K_{ow} values of these compounds (Fig. 5). Among all phases, the highest EEQ_{cal} value of 23.53 ng L^{-1} was observed in the SPM at the HLK site in July 2011. Excluding surface water samples at some sites, the EEQ_{cal} values were all above the PNEC values of E2 (0.58 ng L^{-1}), indicating that the aquatic environments in the Yangtze Estuary might cause estrogenic effects on the aquatic organisms. Specifically, more attention needs to be paid to the SPM and sediments.

3.5. Risk assessment

The potential estrogenic activity risk in the Yangtze Estuary was assessed by ranking the RQ. The common risk ranking criteria are as follows: $0.01 < RQ < 0.1$ is considered low risk, $0.1 < RQ < 1$ is considered medium risk, and $RQ > 1$ is considered high risk (Hernando et al., 2006). Fig. 6 showed the RQ value-distribution of selected estrogens for both the aquatic phase and the sediment phase over one year in the Yangtze Estuary. The RQ values of all estrogens in both surface water and sediments declined according to the following order: E2 > OP > E1 > E3 > BPA. In surface water, generally, most of the sampling sites displayed low to medium risk for most of the sensitive aquatic organisms (95%) in the Yangtze Estuary in all seasons. However, the RQ values of E2 at all sampling sites in July and October of 2011 were relatively high (>1), as well as at some sites in other seasons, which was consistent with the data of estrogenic activity. OP was followed by E2 with RQ values between 0.1 and 1, which posed a medium risk to the organisms. While in the sediment phase, overall, most sampling sites displayed a variation from low to high risk over the seasons. Among all compounds, the RQ values of E2 and OP were higher, which were at high risk level at most of the sampling sites in all seasons. E1 and E3 were followed and posed low to medium risk to the

Fig. 6. ERA of estrogens discharged into receiving waters from the four seasons.

aquatic organisms. Although the detected concentrations of BPA were higher than other compounds, the RQ values of BPA were the lowest both in surface water and sediment.

4. Conclusions

In the present study, the occurrence and distribution of six selected estrogens were investigated using GC–MS along the Yangtze Estuary and its coastal area over four seasons. Samples of surface water, SPM and sediment all contained E3 as the most abundant compound in all phases. The seasonal distribution results showed that the highest total estrogen concentration was found in January 2011, however no single trend was found for the individual compounds. Furthermore, a significant positive correlation was observed between the total estrogen concentrations and OC content in all phases, indicating the important role played by OC. Additionally, E2 and EE2 contributed more to the estrogenic activity compared to all other compounds both in surface water and sediment, and it was also confirmed by the risk assessment which applied a species sensitivity distribution (SSD) based on EPA ECOTOX database. Results revealed that most of the sampling sites displayed a low to high risk for the selected estrogens. However, because the chemical-related effects on the organisms in the real aquatic system are exposed to a mixture of estrogens rather than to a single chemical, more recent studies focus on the combined effects of multiple chemicals in aquatic organisms. Accordingly, further work is needed to determine the occurrence and distribution of estrogens in multi-phases, and the combined effects of estrogens to the ecosystems and human health.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2015.01.021.

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