



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 17 α -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.

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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; Goepfert et al., 2014), in which estrogen is an

important class. Natural estrogens such as estrone (E1), 17 β -estradiol (E2), and estriol (E3) mainly originate in the feces and urine of humans and livestock. Synthetic estrogens such as 17 α -ethinylestradiol (EE2), 4-tert-octylphenol (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-d₂ and BPA-d₁₆). 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 N₂. 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 N₂. 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:

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