



Environmental estrogens in a drinking water reservoir area in Shanghai: Occurrence, colloidal contribution and risk assessment



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HIGHLIGHTS

- AFOs were the potentially important source for estrogens in the river.
- A positive correlation between estrogen and OC concentrations was found.
- Aquatic colloids, often neglected, showed strong sorption of estrogens.
- Colloids could be transported from AFOs waste water into the river.
- Estrogens could pose risk on the aquatic organisms in the study area.

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ABSTRACT

The occurrence and multi-phase distribution of six environmental estrogen compounds were investigated in a drinking water reservoir area by analyzing estrogens in suspended particulate matter (SPM), filtrate (conventional dissolved phase, <1 μm), permeate (truly soluble phase, <1 kDa) and retentate (colloidal phase, 1 kDa to 1 μm). The estrogen concentrations at different sites occurred in the following order: animal feed operation (AFO) wastewater-affected streams > tributaries > main stream channel. Correlation analysis showed that organic carbon (OC) contents had significantly positive correlations with environmental estrogens in filtrate, SPM and colloidal phases, respectively, indicating the important role played by OC. Aquatic colloids, often neglected, showed a much higher sorption capability of environmental estrogens compared to SPM. Similar K_{oc} values in three types of sampling sites showed that colloids could be transported from AFO wastewater to tributaries and further into the main river channel. Mass balance calculations showed that 14.5–68.4% of OP, 4.5–32.1% of BPA, 2.0–58.4% of E1, 8.36–72.0% of E2, 0–20.6% of EE2, 3.4–62.7% of E3 and 8.3–36.1% of total estrogens were associated with colloidal fractions, suggesting that the colloids could act as a significant sink for environmental estrogens. Risk assessment demonstrated that the occurrence of environmental estrogens might pose a risk to aquatic organisms in the study area.

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1. Introduction

Environmental estrogens, including natural and synthetic estrogens, have attracted increasing attention in the scientific community because there is a possibility of adverse effects on the reproductive system in humans and aquatic organisms via disruption of normal endocrine function (Jobling et al., 2006; Schilirò et al., 2009). Long-term exposure of sensitive species of fish to low concentrations of estrogens (at ng/L

levels) could result in biological changes, decreased reproductive success and alterations in species composition (Garcia-Reyero et al., 2005; Arnon et al., 2008). Furthermore, the increasing incidences of cancer and decreasing reproductive fitness in humans are thought to be caused by exposure to estrogenic compounds, including steroidal and phenolic compounds, especially via drinking water (Carlsen et al., 1995; Daston et al., 1997). Besides of waste water treatment plants (WWTP) (Khanal et al., 2006), livestock (Chen et al., 2010; Ciparis et al., 2012) and aquaculture (Kolodziej et al., 2004) discharges were significant nonpoint sources of environmental estrogens. Natural estrogens, such as estrone (E1), E2, estrilol (E3) and their metabolites are mainly excreted by humans, livestock and aquaculture with feces and urine (Hanselman et al., 2003; Kolodziej et al., 2004). Many estrogen drugs, especially synthetic estrogens, such as 17α-ethinylestradiol

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(EE2), are widely used in human daily life and veterinary therapy (Liu et al., 2012). In addition, synthetic chemicals showing estrogen-like activity in animals, include products associated with plastics, such as bisphenol A (BPA) and products associated with surfactants, such as 4-tert-octylphenol (OP). The occurrence and distribution of these environmental estrogens have been widely reported in surface water (Chang et al., 2009; Wang et al., 2011; Wang et al., 2012), groundwater (Arnon et al., 2008; Bartelt-Hunt et al., 2011), soil and sediment (Lei et al., 2009; Wang et al., 2011). However, colloids, defined as particles in sizes from 1 nm to 1 μm with a wide variety of chemical compositions, origins and physicochemical properties (Braga et al., 2005; Lead and Wilkinson, 2006), are often neglected in the studies on the behavior and fate of contaminants in aquatic systems. These fine particles are often arbitrarily attributed to the “dissolved” phase and are poorly characterized (Wilding et al., 2005; Pokrovsky et al., 2010). Limited studies on colloidal sorption of EDCs in the laboratory showed that colloidal particles are stronger sorbents for environmental estrogens than other environmental matrices, such as sediment and SPM (Bowman et al., 2002; Zhou et al., 2007). Thus, they likely play an important role in regulating the transportation and fate of these contaminants in aquatic systems (Yang et al., 2011).

As one of the most important drinking water reservoirs, the upper Huangpu River supplies more than 50% of the drinking water in Shanghai. Water quality in this area is attracting great environmental, health and safety concern. With high-speed urbanization and intensive human activities, the occurrence of contaminants like heavy metals (Zhang, 2007), polycyclic aromatic hydrocarbons (Liu et al., 2009), and antibiotics (Jiang et al., 2011) has been reported. However, up to now, no study has comprehensively dealt with environmental estrogens in the drinking water reservoir of upper Huangpu River. Effluent from animal fee operations (AFOs), including hennery, swine, beef cattle and dairy cow operations has been identified as potential sources of estrogens in this study area. The present study focuses on the occurrence, multi-phase distribution and risk assessment of six environmental estrogens in the drinking water reservoir of upper Huangpu River. To determine the intrinsic association of estrogen compounds among different phases, water samples were separated to SPM, filtrate, colloidal and soluble phases using a validated cross-flow ultrafiltration (CFUF) system. Such knowledge was essential to assess the multi-phase fate and potential risks of environmental estrogen compounds in such a drinking water reservoir area.

2. Materials and methods

2.1. Reagents and chemicals

Environmental estrogen standards, including OP, BPA, E1, E2, EE2 and E3, were purchased from Dr. Ehrenstorfer (GmbH, Germany). The physical and chemical characteristics of estrogens are shown in Table S1, in the Supplementary material. Deuterated estrogens including bisphenol A-d16 (BPA-d16) and 17 β -estradiol-d2 (E2-d2) were used as internal standards. A 10 mg/L mixture of working standards containing each compound was prepared by diluting the stock solution (1000 mg/L) with methanol. All standard solutions were stored at $-10\text{ }^{\circ}\text{C}$. N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) for GC derivatization, was obtained from Sigma-Aldrich (St. Louis, USA). Unless otherwise indicated, chemicals used in the analysis were high performance liquid chromatography (HPLC) grade. All glassware used in the experiment was washed and heated at $450\text{ }^{\circ}\text{C}$ for 4 h prior to use.

2.2. Sample collection

The Huangpu River is the largest river in Shanghai in terms of total length (114 km) and annual average flux (316 m^3/s) (Xu et al., 2008). It originates from the Tai Lake and flows northeast through Shanghai

into the Yangtze Estuary with a basin area of 24,000 km^2 . As the most important drinking water reservoir for nearly 20 million people in Shanghai, the upper stream of Huangpu River played a key role in supplying water for living, industry and irrigation. Many animal feeding operations are located in the upper reaches of the river, which are thought to be significant sources of organic pollutants in the study area. In order to understand the occurrence and behavior of environmental estrogens in the river system, water samples were taken along the upper Huangpu River in August 2011 (Fig. 1), among which six sampling sites (M1 to M6) were located in the mainstream of the river, and five sites (T1 to T5) were located at the mouth of five main tributaries to the main river channel. Among them, M2, M6 and T1 were water intakes for municipal water utilities. Samples were also taken from receiving streams (downstream 2–5 m) impacted by AFO wastewater discharges, including poultry, swine, beef cattle and dairy cow operations (A1 to A4). Sample details are listed in Table S2, in the Supplementary material. Surface water samples were collected from bridges or boats by stainless buckets and were stored in 50 L stainless steel barrels. Both buckets and barrels were first cleaned by acetone, deionized water and Milli-Q water. Once transported to the laboratory, all water samples were filtered through ashed 1 μm glass filters (Pall, USA) to obtain SPM and filtrate fractions within 15 h. All treated water samples were stored in pre-cleaned amber glass bottles.

2.3. Colloidal isolation

Filtered water samples (conventionally dissolved phase, $<1\text{ }\mu\text{m}$) were further processed using a CFUF system (Pellicon System, Millipore, USA) to obtain permeates (truly soluble phase) and retentates (concentrated colloidal solution). The CFUF system consisted of a Millipore 1 kDa regenerated cellulose Pellicon 2 PLAC ultrafiltration membrane (surface area 0.5 m^2) with a concentration factor (*cf*) of 25. In the present study, filtrate fractions are defined as $<1\text{ }\mu\text{m}$, permeate is $<1\text{ kDa}$, and retentate is the colloidal suspension where colloids are defined as particles between 1 kDa and 1 μm .

The concentrations of each environmental estrogen and organic carbon (*C_c*) in colloidal phase could be estimated from the concentrations in the permeate (*C_p*) and retentate (*C_r*) and the *cf* as follows:

$$C_c = \frac{C_r - C_p}{cf} \quad (1)$$

The *cf* values could be calculated according to Eq. (2):

$$cf = \frac{V_p + V_r}{V_r} \quad (2)$$

where *V_p* and *V_r* were the permeate and retentate volumes, respectively.

2.4. Sample treatment

Water samples were processed and analyzed by using a modified method from Hibberd et al. (2009). Briefly, 100 ng internal standards were spiked into duplicate aqueous samples (filtrates, retentates and permeates) before the solid phase extraction (SPE). After Oasis HLB cartridges (Waters, USA) were conditioned with 10 mL of methanol and 15 mL of ultrapure water, aqueous samples were passed through the cartridges at a flow rate of 5–10 mL/min. The cartridges were washed with 15 mL of ultrapure water and dried by vacuum. Subsequently, 15 mL of methanol was used to elute the analytes from the SPE cartridges, and then reduced to 1 mL under a gentle stream of high purity N_2 .

SPM samples were freeze-dried and extracted by methanol using an accelerated solvent extractor (ASE 350, Dionex, USA) in duplicate. The samples were extracted under 1500 psi at $60\text{ }^{\circ}\text{C}$ with a static time of 5 min for 3 cycles. The extraction (approximately 60 mL) was

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