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Distribution and bioaccumulation of endocrine disrupting chemicals in water, sediment and fishes in a shallow Chinese freshwater lake: Implications for ecological and human health risks

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ABSTRACT

The occurrence, distribution and bioaccumulation of six endocrine disrupting compounds (EDCs) were investigated in water, sediment and biota samples from Luoma Lake, a shallow Chinese freshwater lake. Total concentrations of Σphenolic EDCs were much higher than Σestrogens EDCs in both waters and sediments. There were not obvious differences on the concentrations of target compounds [except nonylphenol (NP)] in upstream, lake and downstream locations, these may be suggested that they were mainly affected by non-point discharges in this area. However, the high concentration of NP in water may be associated with the discharge of rural domestic wastewater without thorough treatment. Furthermore, concentrations of NP were about 2–3 order magnitude higher than those of OP in both water and sediment compartments. Relatively higher bioaccumulation factors (BAF) were obtained for DES and EE2. Ecological risk assessment revealed greater risk of NP in surface water, which may pose a serious threat to aquatic ecosystems. The estrogen equivalent concentration (EEQ) of male were higher than those in female, and occurred in the order of city > rural-urban > countryside.

1. Introduction

Endocrine disrupting chemicals (EDC) are defined as “an exogenous agent that interferes with synthesis, secretion, transport, metabolism, binding action, or elimination of natural blood borne hormones that are present in the body and are responsible for homeostasis, reproduction, and developmental process (Diamanti-Kandarakis et al., 2009).” With progress of research on these chemicals, they are classified into natural and synthetic chemicals (Gorga et al., 2015). In 2013, the publications in World Health Organization (WHO) and United Nations Environment Programme (UNEP) concluded that EDCs can induce endocrine disorders of wildlife and humans (WHO, 2012). In fall 2015, Second Scientific Statement on EDC (EDC-2) drew conclusions about the strength of evidence between EDC exposures and obesity, diabetes and cardiovascular disease; female reproductive disorders; male reproductive disorders; hormone-sensitive cancers; thyroid conditions; and neurodevelopment and neuroendocrine effects (Gore et al., 2015).

EDCs have attracted global attention, because they can enter the most vulnerable ecosystem, aquatic environment, by different routes, including direct discharge of industrial and domestic wastewaters, discharge of wastewater treatment plants (WWTPs) effluents, agricultural drains to streams and rivers and overland flow after rainfall events (Gorga et al., 2015; Liao and Kannan, 2014; Lu et al., 2015; McAvoy et al., 2015; Ying et al., 2002; Zhang et al., 2015). Among the natural estrogens, 17β-estradiol (E2) is the most powerful estrogenic hormone and plays a major role in the complex mechanism of ovarian cycle in female (Guo et al., 2015; Rao et al., 2015). It excreted by both humans and livestock and deposited into river systems via WWTPs effluents (Zhang et al., 2008). The most potent man-made EDCs are 17α-ethynylestradiol (EE2) and diethylstilbestrol (DES). EE2 is an orally bioactive estrogen, and is one of the most commonly used medications for humans as well as livestock and aquaculture activity (Aris et al., 2014). It has become a widespread problem in the environment due to its high estrogenic potency (Esteban et al., 2014a). DES is a drug used in treating female canine incontinence stemming from poor sphincter control (Zhang et al., 2014). In addition, phenolic EDCs, including bisphenol A (BPA), nonylphenol (NP), and 4-tert-octylphenol (OP), are used in commercial products and industrial goods, such as thermal

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paper, detergents, and the production of plastics (Klosterhaus et al., 2013; Liao and Kannan, 2014). EDCs have been found ubiquitous in the aquatic environment, such as water, sediment, biota, etc (Alvarez-Munoz et al., 2015; Jakimska et al., 2013; Liu et al., 2011; Luigi et al., 2015; Nie et al., 2015; Yang et al., 2015; Zhang et al., 2014). However, limited studies have focused on the occurrence and bioaccumulation of EDCs in both surface water, sediment and biota three compartments, especially in China (Klosterhaus et al., 2013; Pojana et al., 2007; Salgueiro-González et al., 2015).

Luoma Lake is the fourth largest freshwater lake in Jiangsu province, China (34°00'–34°14'N; 118°06'–118°18'E). It has an average water depth of 3.3 m and a surface water area of 260 km^2. The lake is located on the east route of the South-to-North Water Diversion Project (SNWDP), which is designed to ease water challenges in Northern China and thus contribute to socioeconomic development (Ren et al., 2007, 2015). Therefore, Luoma Lake is water diversion project with the main function of retain the water, and with comprehensive functions like water supply, aquaculture, irrigation, navigation, and tourism. Many villages and several factories were located in Fangting River, Yi River and Luoma lake flow major regions, a large quantity of living sewage water and industrial waste water enter this river by direct or indirect emission, which have become the main potential sources of EDCs in Luoma Lake (Shen et al., 2013; Zhang and Cui, 2012). Polycyclic aromatic hydrocarbons (PAHs) and heavy metal contaminations were previously studied in the sediments of this area (Chen et al., 2013; Liu et al., 2012c). However, few studies, to our knowledge have investigated the distribution of EDCs in Luoma Lake. Thus, it is necessary to determine the concentrations of EDCs in aquatic environment which can provide scientific-based guidance for the management of risk. The objectives of this study were (1) to clarify the occurrence and distribution of EDCs (E2, EE2, DES, BPA, NP and OP) in surface water, sediment, and biota of Luoma Lake; (2) to estimate the bioaccumulation of these chemicals in biota, and (3) to assess their potential the ecological risk and health in the lake.

2. Materials and methods

2.1. Sample collection

A total of twenty-two water samples (100–150 cm) (one sample per point) were taken from Loma Lake region during April of 2016. At fourteen sampling points located in the Loma Lake, four samples were collected in two inflowing rivers (Yi River; Fangting River), the other four points corresponded to the outflowing rivers (south of Zhongyun River; Xinyi River, through Zhangshan Lock) (Fig. 1). Water samples were preserved in 2 L brown glass containers bottles that had been precleaned and transported to the laboratory, where they were filtered immediately through 0.45 μm × 50 mm glass fiber filters (0.45 μm). pH, temperature (T), water transparency (WT) and dissolved oxygen (DO) of water samples were shown in Table S1 (supplementary material). There are many sands and gravels in the riverbed, only six sediment samples (one sample per point) were collected in Luoma Lake with a Peterson grab sampler. The sediments were wrapped into stainless steel containers, freeze dried, ground, sieved and stored at −20 °C for further extraction. Two dominant fish species (Grass Carp and Lateolabrax japonicus) were bought immediately after they were caught from local fishers. Biota samples were immediately placed in coolers with ice, transported to the laboratory freeze-dried and stored at −20 °C for further extraction.

2.2. Reagents and standards

Pure standards of the target compounds E2, EE2, DES, BPA, NP and OP were purchased from J & K Chemical, Ltd. (St. Louis, MO, USA). Detailed substance information for all the target compounds is summarized in Table S2. Methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). Ammonia (25%) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All organic solvents used in this study were HPLC grade. Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA). Stock solutions of all target chemicals at concentrations of 1 g/L prepared in methanol were stored at 4 °C.

2.3. Sample treatment and analyses

The method of pretreatment for water samples was based on our previous studies (Ding et al., 2014). Briefly, water samples (1 L) were extracted by solid-phase extraction (SPE). All Oasis HLB cartridges (500 mg, 6 mL, Waters) were conditioned with 5 mL methanol and 5 mL ultrapure water. Filtrates were then passed through the cartridges at a flow rate of about 5 mL/min. Following extraction, the analytes were eluted with 10 mL methanol after drying for 30 min, and the solution was then concentrated to 1 mL under a gentle stream of N2.

Ten gram of each sediment samples were extracted by ultrasonic extraction and amended with a mixture solvent of 40 mL hexane-chloromethane (v/v = 1:4), then extracted for 30 min and centrifuged at 8000 rpm for 5 min. The extract was then added into a flask and concentrated to dry, after which it was redissolved into 1 mL of methanol. Next, 99 mL of ultrapure water were added to the solution for further cleanup by SPE. The procedures were similar to that in water samples.

The fish muscle was collected after removing internal organs, bones and skin. Only fish muscle was collected for chemical analysis. Ten gram of homogenized fish samples were stored in glass bottles, mixed with anhydrous sodium sulfate and then extracted by ultrasonic extraction and amended with a mixture solvent of methanol-acetone (v/v = 1:1). The extraction was repeated twice with total 25 mL solvent and then combined the extract. The extract was then added into a flask and concentrated to almost 0.5 mL, Next, 100 mL of ultrapure water were added to the solution for further cleanup by SPE. The procedures were similar to that in water samples.

The extracts were finally analyzed by HPLC-MS/MS (LC-Agilent Technologies 1290 Infinity, MS-AB SCIEX QTRAP 4500; CA), after which chromatographic analysis was performed with a ZORBAX Eclipse Plus C18 column (2.1 mm × 150 mm, 3.5 μm; Agilent). The column was maintained at 30 °C, and the injection volume was 2 μL. Gradient elution programs are presented in Table S3A. The mass spectrometer was operated in negative electrospray ionization and in multiple reaction monitoring mode. The typical mass spectrometric conditions are provided in Table S3B.

2.4. Quality assurance and quality control

To ensure reliable results, a strict protocol was established. In all sample preparation procedures (including sample collection), plastic material and detergents were discarded to avoid contamination and blank problems. Furthermore, glassware was carefully washed with acetone, Milli-Qwater and methanol prior to use. The analytical method was evaluated under optimized conditions in terms of linearity, relative standard deviations, method quantification limits (MQLs), and recoveries. For water, sediment and biota samples, relative recoveries varied from 74.6% to 101.3% (RSD < 3%), from 74.0% to 101.2% (RSD < 3%) and from 72.8% to 87.4% (RSD < 6%), respectively. The MQLs for each compound ranged from 2 to 5 ng/L in water, 0.2–1.0 ng/g in sediments, and 0.2–1.0 ng/g in biota. Detailed method performance parameters are summarized in Table S4.

2.5. Statistical analyses

The correlation coefficient between the target EDCs were evaluated by Pearson's test. Linear regression was used to evaluate the relationship of the individual EDCs concentrations in water and sediment. The