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## Occurrence, distribution and risk assessment of suspected endocrine-disrupting chemicals in surface water and suspended particulate matter of Yangtze River (Nanjing section)



Yan-Hua Liu<sup>a,1</sup>, Sheng-Hu Zhang<sup>b,1</sup>, Gui-Xiang Ji<sup>b</sup>, Sheng-Min Wu<sup>b</sup>, Rui-Xin Guo<sup>a</sup>, Jie Cheng<sup>c</sup>, Zheng-Yu Yan<sup>a,\*</sup>, Jian-Qiu Chen<sup>a,\*</sup>

<sup>a</sup> Key laboratory of Drug Quality Control and Pharmacovigilance (Ministry of Education) & School of Science, China Pharmaceutical University, Nanjing 211198, China

<sup>b</sup> Nanjing Institute of Environmental Sciences, Ministry of Environmental Protection, Nanjing 210042, China <sup>c</sup> Second Institute of Oceanography, State Oceanic Administration, Hangzhou 310013, China

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#### ABSTRACT

The occurrence and distribution of eight selected endocrine-disrupting chemicals were investigated in samples of surface water and suspended particulate matter (SPM) in Nanjing section of Yangtze River over a year (the flow period, the wet period and the dry period). All target compounds were detected at least once in surface water with 4-tert-butylphenol (4-TBP), nonyphenol (NP) and bisphenol A (BPA) as the dominant compounds, with concentrations in the range of 225–1121 ng/L, 1.4–858 ng/L and 1.7–563 ng/L, respectively. Except for December, all selected compounds for the other sampling times were not found in all sampling points. NP (mean concentration 69.8  $\mu$ g/g) and BPA (mean concentration 51.8  $\mu$ g/g) were also the dominant estrogens in SPM. In addition, the highest total compounds concentrations were found in December in both phases, which could be due to the low flow conditions and temperature during this season. Meanwhile, a significant positive correlation was found between the total compounds concentrations in the water phase and those in SPM phase. Risk assessment based on the calculated risk quotients (RQ) showed that low and moderate risk for the aquatic environment from presence of the target compounds at all sampling points with exception of 4-TBP and NP which might pose a high risk to aquatic organisms.

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#### 1. Introduction

The existence of endocrine-disrupting chemicals (EDCs) in the aquatic environment has attracted increasing attention from environmental scientist because of its adverse effects on normal reproductive functions of aquatic organisms and human by disrupting endogenous hormones (Diamanti-Kandarakis et al., 2009; Goeppert et al., 2014; Huang et al., 2012; Kortenkamp, 2007; Walf et al., 2011; Wu et al., 2015). Many recent studies have shown that the frequent occurrence of cancerous tumors, obesity and impaired reproductive function in humans are thought to be caused by exposure to EDCs via drinking contaminated water (Chen et al., 2013; Huang et al., 2012; Ma et al., 2014; Michałowicz, 2014; Wu et al., 2015). Furthermore, it has been confirmed that EDCs exposure levels are also one of important factors related to the

\* Corresponding authors.

*E-mail addresses:* yanzhengyujiang@126.com (Z.-Y. Yan), cjqer@163.com (J.-Q. Chen).

<sup>1</sup> These authors contributed equally.

http://dx.doi.org/10.1016/j.ecoenv.2016.09.035 0147-6513/© 2016 Elsevier Inc. All rights reserved. structural changes of ecosystem, alterations in species composition (Arnon et al., 2008; Nie et al., 2014) and quantity reduced of hydrobiological species (Leonard et al., 2014; Pawlowski et al., 2004). Among these groups of chemicals, phenolic xenoestrogens (e.g. alkylphenols, bisphenol A and tetrabromobisphenol A) deserve particular attention as they have moderately estrogenic potency and massive usage (Gong et al., 2011). Due to their estrogenic activity, several compounds belonging to alkylphenols have been included in diverse list of priority contaminants. More specifically, nonylphenols (NPs) and octylphenols (OPs) have been listed as priority hazardous substances in the field of water policy by the European Community Water Framework (Directive, 2000/ 60/EC and the final European Union decision No. 2455/2001/EC).

With the wide use of these compounds in agriculture, industry, livestock agriculture and modern medicine areas, they inevitably enter the aquatic environment via different routes, e.g., releasing during the production and manufacturing process (Liu et al., 2016b; Luo et al., 2015), direct discharging through pesticide application (Banjac et al., 2015), leachate from landfills (Meier et al., 2007) and waste water treatment plants (WWTP) (Khanal et al.,



Fig. 1. Location of Yangtze River of Nanjing Section and distribution of sampling points.

2006; Ko et al., 2007). Upon entering the water system, these compounds can be adsorbed by aquatic organisms, and pose a severe threat to the whole ecosystem (Meier et al., 2007; Song et al., 2014). Numerous studies in recent years have been performed on the occurrence, distribution, and fate of these environmental contaminants in the aquatic environment (Chen et al., 2013; Duan et al., 2014; Liu et al., 2015b; McAvoy et al., 2016; Nie et al., 2014; Singare, 2016; Staniszewska et al., 2015).

Yangtze River is one of the two major rivers of the East China Sea (ECS). It originates from the Qinghai Tibetan Plateau flowing eastward for more than 6300 km, and drains an area of more than  $1.94 \times 10^{6}$  km<sup>2</sup> before finally discharging into the ECS with abundant fishery resources of 123 fish species (Liu et al., 2007). The Nanjing section locates in the lower reaches of Yangtze River and is the major drinking water source for Nanjing residents in Jiangsu province, China (Hu et al., 2013). While the economy and population developed rapidly, Nanjing section of Yangtze River has been subjected to significant human activities in recent decades. It was reported that about 30 industrial chemical plants were built at the lower reaches of Yangtze River and EDCs in upstream of Yangtze River have been reported to harshly affect the water quality and pose a high environmental risk to the local aquatic organisms (Shi et al., 2009). As a result, sewage outfall and upstream runoff have introduced pollution into the Nanjing section of Yangtze River. Several studies have reported the detection of alkylphenols, bisphenol A and tetrabromobisphenol A in the Yangtze River (Adeleye et al., 2016; Liu et al., 2015b; Shi et al., 2014a; Shi et al., 2014b). Due to their hydrophobic nature, these compounds in the river water tend to be associated with suspended particulate matter that played an important role in the processes controlling the transport and fate (Patrolecco et al., 2010). While the importance of SPM in assessing chemical quality status has already been acknowledged in European legislation (Directive, 2000), which makes it compulsory to monitor organic chemical pollutants in surface water. Until now, however, few studies, to our knowledge, have dealt comprehensively with these compounds residues in the Nanjing section of Yangtze River,

especially in suspended particulate matter (Lu et al., 2010; Song et al., 2010). Thus, it is necessary to monitor the occurrence of EDCs in multiple phases and systematically evaluate their ecological risk to provide systemic guide for risk assessment of Yangtze River (Nanjing section). The objectives of this study were (i) to study the occurrence and distribution of these chemicals in surface water and SPM of Nanjing section of the target section; (ii) to explore the seasonal and spatial trends of these chemicals in surface water and SPM; (iii) to assess the potential environmental risk of selected chemicals in Nanjing section of Yangtze River.

#### 2. Materials and methods

#### 2.1. Chemicals and reagents

Standard for all chemicals including 4-tert-Octylphenol (OP), nonyphenol (NP), Bisphenol A (BPA), Tetrabromobisphenol A (TBBPA), 4-tert-Butylphenol (4-TBP), 4-Butylphenol (4-BP), 4-Hexylphenol (4-HP) and 2,4-Di-tert-amylphenol (2,4-DTAP) were purchased from Sigma-Aldrich (St. Louis, USA). Detailed substance information for all the target chemicals is listed in Table S1. All the solvents used in this study were of high-performance liquid chromatography (HPLC) grade.

#### 2.2. Sample collection

Surface water and suspended particulate matter samples (0.5 m under water) were collected at fourteen sampling points along Nanjing section of Yangtze River (Fig. 1) in April 2014 (the flow period), August 2014 (the wet period) and December 2014 (the dry period). And the detail information about the fourteen sampling points was shown in Table S2. Water samples were stored in 2 L pre-cleaned brown glass bottle, while suspended particulate matters were covered with foil and collected in a valve bag after filtrating surface water samples with 0.45  $\mu$ m glass filter membranes (Membrane Solutions LLC., America). Once transported to

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