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Distribution and potential ecological risk of 50 phenolic compounds in three rivers in Tianjin, China ☆

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ABSTRACT

Phenolic compounds widely exist in the surface water of many countries; however, few studies have simultaneously analyzed and evaluated broad-spectrum phenolic compounds in various components of the water environment. Therefore this study analyzed the distribution and potential ecological risk of 50 phenolic compounds in the surface water, sediment and suspended particulate matter of three important rivers in Tianjin, the main heavy industry city with high pollution in China. The qualitative results show that phenolic pollution existed extensively in the three rivers and the kinds of phenolic compounds in the water were relatively higher than in both sediment and suspended particulate matter. The quantitative results show that the phenolic pollution in the wet-season samples was serious than dry-season samples. Meanwhile, total concentrations of phenolic compounds in three components from the Dagu Drainage River (DDR) were all much higher than those in the Beitang Drainage River (BDR) and Yongdingxin River (YDXR). The highest total concentrations of phenolic compounds in three components all appeared in wet-season samples in DDR, and the highest total concentration was 1354 μg/L in surface water, 719 μg/kg dw in suspended particulate matter and 2937 μg/kg dw in sediment, respectively. The ecological risk of phenolic compounds in surface water was evaluated using the quotient method, and phenolic compounds with risk quotient (RQ) > 1 (RQ > 0.3 for YDXR) were identified as priority pollutants. Five kinds of phenolic compounds were identified as priority phenolic compounds in BDR, and the order of risk was 2-cresol > 2,4-xylenol > 2-sec-butylphenol > 2-naphthol > 3-cresol. Six kinds of phenolic compounds were identified as priority phenolic compounds in DDR, and the order of risk was 2-naphthol > p-chloro-m-xylenol > 4-cresol > 3-cresol > 2,4-xylenol > 2,3,6-Trimethylphenol. In YDXR, only phenol, 2-naphthol and 2,4-xylenol were identified as priority phenolic compounds.

1. Introduction

Phenolic compounds can arise from natural substance degradation, industrial activities and agricultural practices; as a result, a large number of phenolic compounds have been introduced into water environment. Phenolic compounds have been detected in the rivers of many countries, such as Spain, Australia, Germany and Albania (Jáuregui and Galceran, 1997; Jennings et al., 1996; Piperidou et al., 1996; Schmidt-Bäumler et al., 1999; Bolz et al., 2001). In China, much research also has examined the occurrence of phenolic compounds and found them to be ubiquitous in the Chinese rivers (Jin et al., 2004; Wang et al., 2013; Wu et al., 2013; Gao et al., 2008). Owing to their adverse effects on human health and their toxicity, persistence and bioaccumulation in animals and plants (Davì and Gnudi, 1999), the occurrence of phenolic compounds in water environment has become an issue of international concern.

Previous relevant studies on the Chinese water environment of river focused on a limited number of regulated phenolic

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compounds such as BPA, nonylphenol and 2,4-chlorophenol, owing to the well-known adverse effects of these compounds on aquatic organisms and humans. The distribution of a large number of other potentially harmful phenolic compounds has not received sufficient attention. Nevertheless, many studies on the water environment in other countries have found that many kinds of un-regulated phenolic compounds which can pose potential adverse effects to aquatic organisms and human health as well as regulated phenolic compounds are also common contaminants. According to the previous relevant studies of our group, we also found some un-regulated phenolic compounds in the surface water of lake and effluent from sewage treatment plant (STP) of China (Zhong et al., 2010, 2012). In order to evaluate the harm of phenolic compounds comprehensively, a study on the distribution and ecological risk of broad-spectrum phenolic compounds in the Chinese water environment is therefore of considerable importance.

Tianjin is located in northern China near Beijing and adjacent to the Bohai Sea. It is one of the four municipalities directly under the Central Government and is an important commercial and industrial center in China. In our previous studies in 2012, we simultaneously identified and determined the concentrations of fifty different phenolic compounds in sewage water and effluents of five STP in Tianjin. Seventeen different phenolic compounds were found in sewage and five —including two regulated phenols (phenol and 2,4,6-trichlorophenol) and three un-regulated phenols (2-chlorophenol, 2,5-dichlorophenol and 2,4-dichloro-3-ethyl-6-nitrophenol) —were identified in effluents. Chemical components in sewage effluent are among the critical factors that determine the quality of receiving waters and the potential of such waters for use and recycling of reclaimed water. Dagu Drainage River (DDR), Beitang Drainage River (BDR) and Yongdingxin River (YDXR) are three primary drainage rivers in Tianjin. The phenolic compounds exist in effluent of five STPs will be imported into these three drainage rivers. It is therefore necessary to analyze the contamination status and ecological risk associated with phenolic compounds present in the three rivers. On the other hand, drainage rivers not only receive effluent of STP, but also transport most of the domestic, industrial and agricultural wastewater from the Tianjin area (Liu et al., 2007; Song et al., 2006). Hence, a large number of other potentially harmful un-regulated phenolic compounds perhaps will be introduced. It is therefore a matter of urgency to investigate the distribution of broad-spectrum phenolic compounds in these three rivers and then to assess potential hazards associated with any phenolic compound that may be found. With an objective to evaluate the distribution and ecological risk of phenolic compounds comprehensively, the study described herein included 50 phenolic compounds (Table 1 in Zhong et al., 2017) owing to their widespread usage and potential impact on the health of animals and humans.

Furthermore, previous relevant studies only focused on water samples or sediment samples. There are no relevant studies that have analyzed surface water samples, sediment samples and suspended particulate matter samples simultaneously. Organic contaminants in aquatic systems may exist in several forms, including the free dissolved phase, adsorbed to suspended particulate matter (SPM), and associated with surface sediments. Knowledge on partitioning of pollutants in aquatic systems will assist in estimating their mobility, toxicity and associated risks. Thus, the present study consisted of a broad-spectrum analysis of river samples to gain comprehensive understanding of the concentration ranges of the 50 phenolic compounds in surface water samples, sediment samples and SPM samples simultaneously.

In this context, the objectives of the present study were as follows: 1) To identify and quantify the concentration of a wide range of phenolic compounds in surface water, sediment and SPM samples from three rivers in Tianjin, and 2) To assess potential hazards associated with phenolic compounds present in the three rivers.

2. Materials and methods

2.1. Sampling

Sample collection locations (Fig. 1) were identified using a global positioning system. Thirty-seven sample locations were situated in three rivers. Sample locations b1–b7 were situated in BDR, d1–d16 were located in DDR and y1–y14 were located in YDXR. Thirty-seven surface water samples, thirty-seven SPM samples and thirty-six sediment samples (excluding b6) were collected in the wet season. Twenty-nine surface water samples, SPM samples and sediment samples were collected in dry season (excluding b3, d2, d4, d6, d9-d11, d14). Three sub-samples were collected for each sample type at each location. The sub-samples for a given sample type were mixed thoroughly into composite samples for analysis to reduce the effect of possible random variation in contaminant concentrations.

2.2. Preparation and analytical procedure

The information of 50 phenolic compounds were list in Table 1 in Zhong et al. (2017). The chemicals and materials used to treat and analyze samples, the detailed methods for preparing water samples and analytical procedures have been published elsewhere (Zhong et al., 2010, 2011, 2012). In this paper, we only showed the information in brief in supporting information (SI). This method is simple and fast, which could identify and quantify 50 kinds of phenolic compounds simultaneously. By using this method, phenolic compounds can be detected at the ng/L level in environmental samples.

The method for preparing sediment and SPM samples were described concisely as follow: 1) each sediment sample of 5 g was spiked with the surrogate standards and Soxhlet-extracted for 48 h with 200 mL DCM using sufficient copper sheets to remove Sulphur; 2) each SPM sample was ultrasonically extracted after separated from water and freeze-dried. The detailed method for preparing sediment and SPM samples were list in SI.

2.3. Quality assurance/quality control (QA/QC)

The methods for QA/QC have been published elsewhere (Zhong et al., 2010, 2011, 2012). The same method was used in this study. The reliability of the preparation method had been evaluated by parallel, blank and matrix spike experiment. No phenolic compound was identified from the blank samples. In this study, one in ten samples was selected as matrix spike sample to verify the recoveries of analytes. Ten typical phenolic compounds (phenol, 2-cresol, 3-cresol, 2-chlorophenols, 2,6-dichlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol) were selected as representative phenolic compounds, because they can represent of the 50 phenolic compounds in terms of polarity, substituent positions, substituent number and substituent groups. The instrument limits of quantification (LOQ) of 50 phenolic compounds ranged from 0.7 to 87.7 pg which is consistent with our previous studies (Zhong et al., 2010, 2011, 2012). The matrix spike recoveries for ten typical phenolic compounds in surface water, sediment and SPM samples ranged from 68.3% to 114.8%, 56.61%–125% and 58.2%–88.7%, respectively. The RSD% for three kinds of samples ranged from 2.12% to 13.6% for water samples, from 4.41% to 11.7% for sediment samples and from 5.24% to 12.3% for SPM samples.