DISTRIBUTION AND CHARACTERISTIC OF PHENOLIC COMPOUNDS IN RIVERS AROUND BO SEA(CHINA)

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1. Introduction

Phenolic compounds such as Nonylphenol (NP) and Octylphenol (OP) which belonged to the group of non-ionic surfactants were widely used in agriculture, dyestuff industry and household applications as an important chemical raw material since 1950 and the usage amount were continue increasing since 1980s. These phenolic compounds enter the aquatic environment primarily through industrial and domestic wastewater with or without treatment due to their application characteristics [1]. Some research showed that phenolic compounds were suspected to be endocrine-disrupting chemicals (EDCs) [2, 3]. In recent years, scientists have been concerned for disrupting effects of phenolic compounds on reproductive and endocrine system. Some research found that phenolic compounds may cause death on aquatic organisms if the sewage contained these substances, and also have high toxicity in the human [4]. Furthermore, NP and OP had been identified as priority controlled hazardous substance for the potential carcinogenicity, deformity and mutation.

Many previous studies have devoted to the occurrence of phenolic compounds in the aquatic environment and most of them focused on their concentration levels in effluents [5, 6], river and coastal waters [7,8]. In China, the occurrence of phenolic compounds in some rivers had been reported, such as Haihe River [9]. However, little information can be available on phenolic compounds concentration levels in the north of China.

Bo Sea (37°07′–41°00′ N, 117°35′–121°10′ E), the largest inland sea of China, located in the north of China. In this study, we investigated the concentration and distribution of phenolic compounds in rivers around Bo Sea, which is important in assessing the impact of anthropogenic activities on the aquatic ecosystem.

2. Materials and methods

2.1 Reagents and chemical

Nonylphenol (NP), Bisphenol A (BPA), Octylphenol (OP), 2, 4-Dichlorophenol (2, 4-DCP), 4-Tert-octylphenol (POP), 4-Tert-butylphenol (PTBP), BPA-d16 were all of HPLC grade, which purchased from Sigma-Aldrich (St Louis, MO, USA). Methanol (HPLC grade) was from Merck (Darmstadt, Germany). Methylene chlorides, Acetonitrile, Ammonia water were all HPLC grade, which purchased from Tedia (Tedia Scientific, OH, USA). High purity water was prepared by a Milli-Q water purification system (Millipore, USA).

2.2 Sample collection

Water samples from rivers were collected in June 2009. The locations were selected to cover urban areas, rural areas and industrial regions. Sampling locations were shown in Fig.1. All samples were collected using a stainless steel bucket, and stored in 4L amber glass bottles. After collection, the samples were labeled and transported to the laboratory immediately and stored at 4°C before extraction. All the samples were acidified with HCl to pH 2-3.

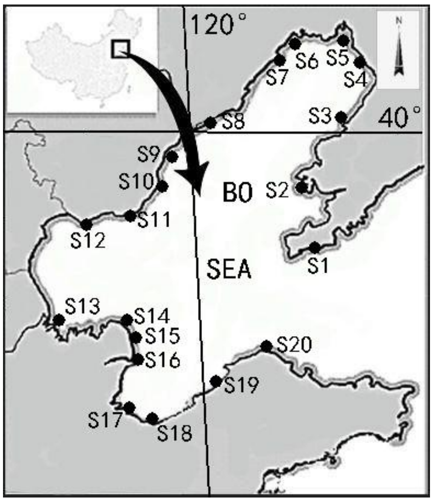

Fig.1sampling stations around the Bo Sea.

2.3 Analytical Methods

2.3.1 Sample preparation

Liquid–liquid extraction (LLE) was performed in this study. Water samples were filtered through 0.45 μm cellulose nitrate membrane to remove suspended particulate matter. 500 mL water sample which spiked with 100 μL 1 mg/L internal standard BPA-d_{16}, were extracted three times with 50 mL methylene chloride. Anhydrous sodium sulphate was added to the organic layer. The extraction were combined and dried in rotary vacuum evaporator at 40°C and then reach a final volume of 1.0 mL methanol. The solution was filtered with 0.2 μm syringe filter before injection to LC-MS/MS system.

2.3.2 HPLC-MS/MS analysis

The HPLC system was conducted using a Finnegan Surveyor (Thermo Electron, San Jose, CA, USA). Separation of phenolic compounds was achieved on a Waters Symmetry-C18 column (150mm× 2.1mm i.d., 3.5μm, USA). A binary mobile phase gradient with methanol (A) and 0.2% ammonia water (B) was used for analyte separation at a flow rate 0.2 mL/min. The elution gradient was linearly increased from 50%A to 80%A in 3 min, kept 1 min, then increased to 100%A in 1 min, kept 5 min, and then back to initial conditions in 2 min, kept 4 min.

In this study phenolic compounds were analyzed simultaneously with HPLC-MS/MS (Thermo Finnegan TSQ Quantum Discovery MAX), including NP, BPA, OP, 2, 4-DCP, POP and PTBP. All samples were detected in electro spray negative ionization mode. Typical MS settings were as follows: spray voltage, 3100 V; sheath gas pressure , 25 arbitrary units; auxiliary gas pressure, 8 arbitrary units; ion transfer capillary temperatures, 350°C; source CID, 10 V. Qualitative analysis of target compounds was accomplished at the basis of retention time and mass spectrum together in SRM model.

3. Results and discussion

NP, 2, 4-DCP and PTBP were detected in all samples, which suggested that these substances are ubiquitous in the rivers around Bo Sea. The total concentration were showed in fig.2, and the concentrations in station 10 and 20 were much higher than others.

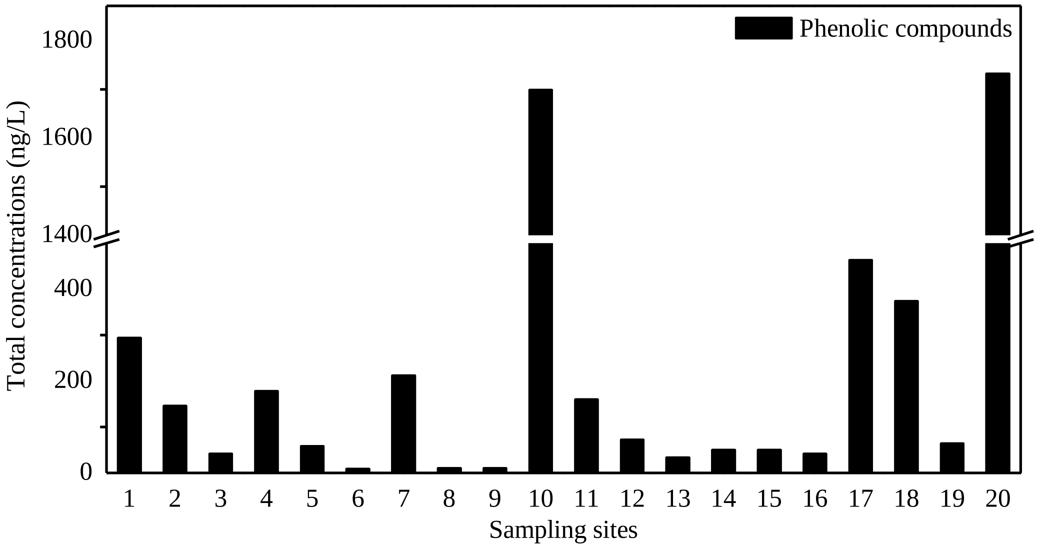

Fig.2. Total concentrations of Six phenol compounds

The NP concentration should not exceed 6.6 μg/L in freshwater and 1.7 μg/L in saltwater in the ‘‘chronic criteria recommendations” drafted by the Environmental Protection Agency (EPA) of USA. According to this criterion, the concentrations of NP in this study were all below 7.0 μg/L. The a largest permit concentration (MAC) for NP is 2 μg/L and an annual average (AA) concentration of NP is 0.3 μg/L, OP is 0.1μg/L in inland surface waters which set in 2008/105/EC. In this study, NP concentrations in all samples were below the MAC, and OP concentrations in samples were all belowAA except site 20, which is 1.307 μg/L.

The concentrations of NP were ranged from 110-640 ng/L in USA, 90-1582 ng/L in Korea [10], and 320-2760 ng/L in Singapore [11], which were higher than the concentrations around Bo sea. In China, there were some reports on the occurrence of phenolic compounds in rivers. In the Haihe River the concentration of NP was between 160-429 ng/L [9] and in Taiwan was from ND to 5100 ng/L[12], which were much higher than our results. However, the concentrations of NP in studied were much higher than those in eastern South China 20-40ng/L[1].

In this study, the highest concentration of BPA (1420.2 ng/L) was detected in site 10, which was higher than other rivers. The concentration of OP was 10-19 ng/L in Germany [13] and was 4.8-76.3 ng/L in Tama river[15]. The median concentration of BPA in the river around Bo sea was 95.19 ng/L was lower than it in the USA and Italy which were 140 ng/L and 145 ng/L[15,16]. Overall, the concentrations of BPA in rivers around Bo Sea were moderate.

The mean concentration of 2, 4-DCP was 25.8 ng/L in this study. And the highest concentration (211 ng/L) was found in site 7. 2, 4-DCP has been widely used as a chemical intermediate in the manufacture of herbicides, germicides, temporary soil sterilants, plant growth regulators, mothproofing agents, seed disinfectants and wood preservatives. In the Huaihe River the average concentration of 2, 4-DCP was 20.2 ng/L, which is lower than our results[17]. It reported by EPA that the acute and chronic toxicity to freshwater aquatic life occur at the concentration as low as 2,020 and 365 μg/L In this study, all concentration of 2, 4-DCP was below this criterion. Overall, the concentration of 2, 4-DCP in this area was low.

4. Acknowledgements

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