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Determination of 4-tert-octylphenol in surface water samples of Jinan in China by solid phase extraction coupled with GC-MS

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Abstract

Octylphenols, considered as xenoestrogens, mainly exist as 4-tert-octylphenol (OP) in aquatic environments. The high stability and accumulation of OP in aquatic systems have caused endocrine disruption. The OP in surface water in Jinan, China was analyzed by gas chromatography-mass spectrometry (GC-MS) coupled with solid phase extraction (SPE). Water samples were extracted by SPE on a cartridge system containing C-18 as sorbent. To increase sensitivity and selectivity, OP was derivatized to 4-tert-octyl-phenoxy silane. With the use of phenanthrene-d10 as internal standard, the detection limit based on signal-to-noise ratio ($S/N = 3$) was 0.06 ng/mL. The average recovery was from 84.67% to 109.7%. The precision of the method given as the relative standard deviations (RSD) was within the range 6.24%–12.96%. In the target water samples, the concentrations of OP were as follows: 15.88–71.24 ng/L for Jinxiuchuan Reservoir, 3.850–26.68 ng/L for the city moat, 6.930–41.56 ng/L for Daming Lake, 66.03–474.2 ng/L for Xiaoqing River, 14.66–17.72 ng/L for the Yellow River, and 10.60–26.43 ng/L for Queshan Reservoir. The Xiaoqing River was seriously polluted due to the discharge of wastewater from Jinan. Jinxiuchuan Reservoir had a higher concentration of OP compared with the Yellow River and Queshan Reservoir, which is ascribed to the surrounding human activities. These data are reported for the first time, providing strong support for the control of OP pollution in Jinan.

Key words: GC-MS; octylphenol; Jinan; solid phase extraction; derivatization; internal standard

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Introduction

4-tert-Octylphenol (OP), a kind of endocrine disrupting chemical, has been receiving increasing attention due to its widespread occurrence in the aquatic environment as a result of the discharge of its parent compounds, alkyl phenol polyethoxylates (APEO) (Tamagawa et al., 2006; Petrovic et al., 2002). OP has been shown to be the most estrogenic of the breakdown products of APEOs, and is up to 5 times more estrogenic than nonylphenol (Zhou, 2006; Jobling and Sumpter, 1993). Furthermore, OP can be concentrated by bioaccumulation along to the food chain and finally into animals and humans, causing greater harm. Because of its relatively high toxicity in aquatic organisms and long-term persistence in the environment, determination of the environmental concentration and distribution of OP is very important.

Recently, environmental OP contaminations have been reported in water and sediments (Loyo-Rosales et al., 2003), marine water (Famiglini et al., 2005), surface and drinking water (Kuch and Ballschmiter, 2001), an urban estuary (Sacks and Lohmann, 2011), healthcare facility wastewaters (Nagarnaik et al., 2010), infant food (Raecker et al., 2011) and human tissue (Lopez-Espinosa et al., 2009) all over the world. In particular, domestic OP contamination has been reported in many places in China. Yang et al. (2007) reported 130 ng/L OP in Qingdao Shilaoren seawater in Shandong Province. OP concentrations in the Haihe River and Bohai Bay were 18–56 ng/L and n.d.–14 ng/L, respectively (Shen et al., 2005). In surface sediment samples from the Pearl River and its adjacent branches in Guangzhou City, the OP concentration varied from 0.36 to 498.54 ng/g (dry weight) (Xu et al., 2007). Among the methods used in previous studies, the technique of gas chromatography-mass spectrometry (GC-MS) coupled with solid phase extraction (SPE) has been demonstrated to be reliable to determine OP concentrations in various samples (Ferguson et al., 2000; Jeannot et al.,

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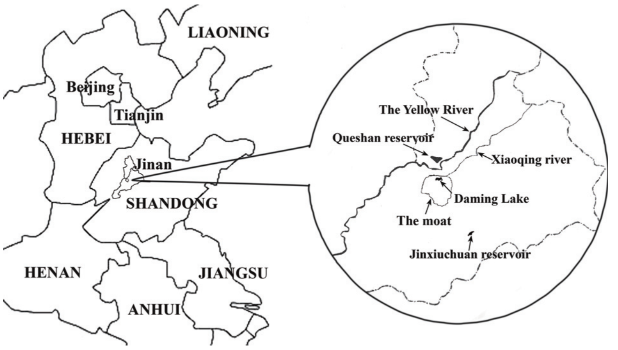

Fig. 1 Maps of water system of Jinan (Shandong Province, China).

2002; Kuklenyik et al., 2003; Ye et al., 2005).

Jinan, called the Spring City, is the capital of Shandong Province, China. The complex terrain, which is low in the north while high in the south, can be roughly divided into three zones (**Fig. 1**): the belt close to the Yellow River in the north, the central piedmont zone and the southern mountainous area. The limestone in the southern mountains is highly permeable. However, the north igneous rock is impermeable. Because of abundant rainfall in southern mountainous areas, water can infiltrate along the limestone fissures underground, and then flows along the topography towards the north where the water pressure increases due to the impermeable igneous rock in the north. Once a crack breaks out, a spring forms. This is the reason why springs are formed in Jinan.

Accordingly, the surface water system in Jinan mainly includes three sections: the Yellow River (Queshan Reservoir) and Xiaoqing River in the north, Daming Lake and the city moat system (including springs, for instance, Baotu Spring and Heihu Spring) in the center (downtown), and surface water in the southern mountainous area (Jinxiuchuan Reservoir) (**Figs. 1** and **S1**). There are two water paths for the surface water system. The first one is described as follows: water from the southern mountainous area feeds the springs in the city, forming the moat and flowing into Daming Lake. Then, water merges into the Xiaoqing River and flows away. The second path is the Yellow River, an important source of drinking water in Jinan City. However, there is no close relation between the river and other surface water in Jinan except that Queshan Reservoir uses water from the Yellow River.

So far in China, there are no relevant laws or regulations to restrict the use and discharge of APEOs in the environment. Importantly, little is known about the concentration of OP in surface water in Jinan City. It is of great significance to survey the distribution of OP in Jinan so as to assess the ecological risks of such chemicals. In this study, we determined for the first time the concentrations of OP in surface water samples in Jinan by GC-MS coupled with SPE. Before GC-MS analysis, OP was derivatized to 4-tert-octyl-phenoxy silane and phenanthrene-d10 was added as an internal standard.

1 Experimental

1.1 Reagents and standard solutions

OP standard, derivatization reagent (BSTFA+TMCS, 99:1) and internal standard phenanthrene-d10 were obtained from Sigma-Aldrich. Anhydrous sodium sulfate was made by baking sodium sulfate in a muffle furnace at 400°C for 4 hr.

OP standard stock solution (1.0 mg/mL) was prepared by dissolving 10.0 mg OP with 10.0 mL acetone. Working solutions of 10–1000 ng/mL OP were then prepared and used to generate calibration curves.

To prepare an internal standard stock solution (0.2 mg/mL), 1 mg of phenanthrene-d10 was dissolved with 5.0 mL of acetone. To obtain the working internal standard solution, 10.0 μL of the stock solution was added to the final sample vials to obtain the ultimate internal standard concentration of 4.0 μg/mL. Both the OP and internal standard stock solutions were stored in glass vials at 4°C in lightproof containers. Working solutions were freshly prepared each time from the stock solutions.

1.2 Sample collection and storage

Surface water samples were collected from 3–10 sites in Daming Lake, the city moat, the Xiaoqing River, Jinxiuchuan Reservoir, the Yellow River and Queshan Reservoir (**Fig. S1**), respectively. According to national guidance on sampling techniques from lakes and reservoirs (GB/T 14581-93, China), a 1.5-L water sample at each site was divided into three aliquots of 500.0 mL in plastic bottles which had been washed with ultra-purity water. Afterward, samples were placed in a refrigerator at 4°C to reduce the impact of microbial action.

1.3 Solid-phase extraction

All water samples were filtered through a filter paper, and then the pre-concentration step was performed. SPE with Agela Cleanert C-18 (500.0 mg, 3.0 mL) sorbent was used with a buffer device and an external AP-02B vacuum pump. The SPE cartridges were conditioned by 10.0 mL of methanol to wash away the impurities in the sorbent, and subsequently with 10.0 mL of ultra-purity water to activate the SPE column. A 500.0-mL of filtered samples were percolated through the SPE-cartridges at a flow rate of 5.0 mL/min. After pre-concentration, the C-18 cartridges were dried, and the elution was carried out using 10.0 mL acetone. Anhydrous sodium sulfate of 1.0 g was added to the eluent to remove the moisture. The extracts from SPE were evaporated to dryness in a gentle stream of N_2 at 55°C.

1.4 Derivatization and internal standard

The derivatization reagent 50.0 μL were added to the test vial containing extracts from SPE. Next, the vial was closed and placed at room temperature for 30 min. Then,