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Spatial distribution, temporal variation and risks of parabens and their chlorinated derivatives in urban surface water in Beijing, China

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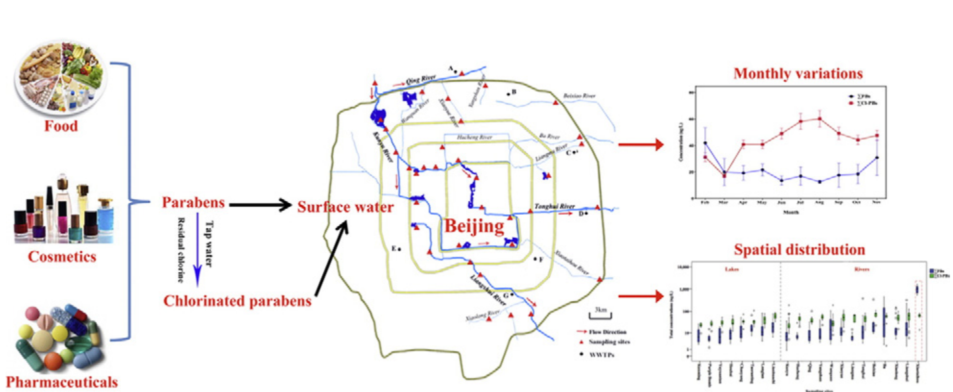
HIGHLIGHTS

- Parabens and chlorinated parabens are ubiquitous in surface water in Beijing.
- Octylparaben with longer chain was firstly detected in surface water.
- Untreated sewage discharge was the main source of parabens in river.
- Parabens exhibited a different seasonal variation from chlorinated derivatives.
- The risks of target compounds are negligible at environmentally relevant levels.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence and distribution of 13 target compounds, including eight parabens, four chlorinated parabens and *p*-hydroxybenzoic acid (PHBA), were detected in surface water samples at 35 sampling sites in the Beijing River system, China. The surface water samples were collected from the main rivers and lakes in the urban area monthly from July 2013 to June 2014 (except the frozen period). Laboratory analyses revealed that parabens were ubiquitous in the surface water of Beijing. PHBA was the predominant compound in the surface water samples, with the average concentration of 239 ng L^{-1}, followed by the total amount of chlorinated parabens (average 50.1 ng/L) and parabens (average 44.3 ng/L). It is noteworthy that octylparaben with longer chain was firstly detected in the surface water. Significant difference was observed for paraben concentrations from different sampling sites, and the highest level of parabens was found in the Xiaotaihou River, which was mainly due to the untreated sewage discharge. Seasonal variation of target compounds in the urban surface water was also studied, and parabens exhibited a different temporal variation from chlorinated derivatives. A combination of factors including high residual chlorine level and water temperature as well as intense ultraviolet radiation might enhance the persistence of chlorinated parabens in chlorinated water during the wet season. Risk assessment showed that parabens and their chlorinated derivatives are not likely to produce biological effects on aquatic ecosystems at current levels in the surface water of Beijing.

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1. Introduction

Parabens, alkyl and aryl esters of *p*-hydroxybenzoic acid (PHBA), are extensively used as preservatives in cosmetics, food, pharmaceuticals and industrial products (Gorga et al., 2013; Guo and Kannan, 2013; Liao and Kannan, 2014). These compounds were traditionally considered as ideal preservatives because of their low toxicity, chemical stability, wide spectrum of antibacterial activity, and low production costs (Haman et al., 2015; Soni et al., 2005). However, more and more studies have demonstrated that parabens are an emerging group of endocrine-disrupting chemicals, which may modulate or disrupt the endocrine system to affect the reproductive system, cause immune dysfunction, and produce developmental and behavioral disorders (Kang et al., 2013; Karpuzoglu et al., 2013; Meeker et al., 2011; Oishi, 2002; Piao et al., 2014; Soni et al., 2005). In addition, several studies have reported that parabens were associated with breast cancer etiology, and lead to a potential increase in breast cancer incidence (Darbre et al., 2004; Darbre and Harvey, 2014; Harvey, 2004). Moreover, conventional toxicity tests also show that parabens were toxic to aquatic organisms, such as algae, invertebrate and fish (Bazin et al., 2010; Dobbins et al., 2009; Yamamoto et al., 2011).

As one of the most common preservatives, large amounts of parabens are continuously released into the environment via domestic and industrial wastewater. Although parabens are readily biodegradable, most of them can be replaced by ongoing wide use, leading their pseudo-persistence in the environment. Due to their undesirable effects on human health and aquatic organisms, the occurrence and behavior of parabens in the aquatic environment have been receiving particular attention (Alvarez-Rivera et al., 2014). Until now, limited research has been conducted regarding the occurrence of parabens in surface water, such as the Ebro River in Spain (Gorga et al., 2013), Taff River in UK (Kasprzyk-Hordern et al., 2008), Glatt River in Switzerland (Jonkers et al., 2009), urban streams in Tokushima and Osaka, Japan (Kimura et al., 2014) as well as Pearl River in China (Peng et al., 2008), indicating their ubiquitous distribution in aquatic environment at ng/L to μg/L level (Bledzka et al., 2014). However, most of them were mainly concentrated on the improvement of analytical methods, and only a single sampling campaign was performed in one or several rivers, making the robustness of their conclusions to be compromised. Additionally, due to the lack of standards, limited data was available on the presence of chlorinated parabens in surface water, which are considerably more stable in environment and more toxic to aquatic organisms than their corresponding parent parabens (Bledzka et al., 2014; Terasaki et al., 2009b). Moreover, there are relatively few studies on PHBA, the main metabolite and hydrolysis product of all parabens, in surface water (Blanco et al., 2009). Nevertheless, chlorinated parabens and PHBA may be two noteworthy ways of the introduction of parabens into the aquatic environment (Haman et al., 2015). In order to better understand the behavior of parabens in surface water, the chlorinated derivatives and metabolite should be simultaneously determined (Terasaki et al., 2009b).

Beijing, the capital of China, is one of the most populous cities in the world, with a huge population of 20.693 million in 2012 (Wang et al., 2015). Owing to the large population, the consumption of various productions containing parabens is expected to be massive in this densely populated city. It is reported that large quantities of domestic sewage (about 3.3 million tons per day) were produced from residential areas. However, only 83% of wastewater was treated in the wastewater treatment plants (WWTPs), and the rest is directly discharged into the waterbody (Dai et al., 2015). Although parabens can be effectively removed during conventional sewage treatments (>90%) (Gonzalez-Marino et al., 2011; Jonkers et al., 2009; Ramirez et al., 2012), a small percentage of parabens can still be observed in effluents and may reach the aquatic environment (Li et al., 2015). Consequently, the urban rivers and lakes in Beijing would suffer serious parabens contamination. However, no earlier studies have reported the occurrence of parebens in urban surface waters in Beijing, China.

In this study, 13 target compounds, including eight parabens, PHBA, and four chlorinated derivatives, were simultaneously determined in 350 surface water samples collected from urban rivers and lakes in Beijing. The objectives of the research are to investigate the occurrence, spatial and temporal variations of parabens in urban surface waters, search possible sources of parabens in the aquatic environment, and evaluate the potential risks of these compounds to aquatic organisms. To our best knowledge, this is the first study demonstrating the ubiquitous occurrence of parabens and their chlorinated derivatives in surface water in China.

2. Materials and methods

2.1. Standards and reagents

The methanol and acetonitrile from Fisher Scientific (Pittsburgh, PA, USA) are all of HPLC grade; ammonium acetate (99%) was purchased from Alfa Aesar (Ward Hill, MA). All purity water (>18.2 $M\Omega \cdot cm^{-1}$) was prepared with Milli-Q Advantage A10 system (Millipore, USA).

Chemical standards of p-Hydroxybenzoic acid (PHBA, 100%), Methyl paraben (MeP, 97.5%), Ethyl paraben (EtP, 99.0%), Propyl paraben (PrP, 99.3%), Butyl paraben (BuP, 100%), Pentyl Paraben (PeP, 98.0%), Heptyl paraben (HeP, 99.0%), Benzyl paraben (BzP, 100%), Octyl paraben (OcP, 98.0%), Methyl 3-chloro-4-hydroxybenzoate (3-Cl-MeP, 98.0%), Methyl 3,5-dichloro-4-hydroxybenzoate (3,5-2Cl-MeP, 98.0%), Ethyl 3-chloro-4-hydroxybenzoate (3-Cl-EtP, 97.0%) and Ethyl 3,5-dichloro-4-hydroxybenzoate (3,5-2Cl-EtP, 98.0%) were purchased from AccuStandard Inc. (New Haven, CT, USA).

The following isotopically labeled compounds were used as surrogate standards (500.0 μg/L in methanol): p-Hydroxybenzoic acid-d_4 (PHBA-d_4), Methyl Paraben-d_4 (MeP-d_4), Ethyl Paraben-d_5 (EtP-d_5), Propyl Paraben-d_7 (PrP-d_7), Paraben-d_9 (BuP-d_9) and Benzyl Paraben-d_9 (BzP-d_7), which were purchased from Toronto Research Chemicals (Oakville, ON, Canada). Information on physicochemical properties of the target parabens is provided in Table S1 in the Supplementary materials.

2.2. Sample collection

The study area is sited in the urban of Beijing (Fig. 1). Monthly sampling campaigns were performed at 35 sampling sites in the Beijing River system from July 2013 to June 2014 (except January and December in frozen period). Of which, sites R1-R8 were located in the Kunyu River, R9-R11 were located in the Tonghui River, R22-R25 were located in the Liangshui River, R26-R27 were situated in the Xiaolong River, and R13-R17 were situated in the Qing River and its tributaries. The rest of sampling sites located at Xiaotaihou River (R21), Liangma River (R20), Ba River (R19), Beixiao River (R18), and Hucheng River (R12). Eight lakes were also selected as the target sampling sites, including Kunming Lake (L1), Purple Bambo Lake (L2),Houhai Lake (L3), Yuyuantan Lake (L4), Taoranting Lake (L5), Longtan Lake (L6), Chaoyang Park Lake (L7), and Lianhuachi Lake (L8).

Most of the riverbeds were reinforced with concrete and periodically dredged, so only water samples were collected in this study. A total of 350 surface water samples were obtained in 10 sampling campaigns. All of the surface water samples were collected in 1-L polypropylene bottles rinsed with water and methanol. Immediately after being transported to the laboratory, the samples were stored at 4 °C and pretreated as soon as possible.

2.3. Sample preparation and analysis

Target compounds were extracted from water samples using AutoTrace SPE 280 (Dionex, USA) with an Oasis HLB cartridge (6 mL, 200 mg; Waters, USA), as described in our previous study with some