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Occurrence, distribution and seasonal variation of organophosphate flame retardants and plasticizers in urban surface water in Beijing, China

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ABSTRACT

The occurrence, spatial distribution and seasonal variation of 14 organophosphate esters (OPEs) were investigated in urban surface water (river and lake water) from July 2013 to June 2014 in Beijing, China. Sewage influent and effluent samples, as well as rainwater and road runoff samples were also analyzed as the potential sources of OPEs in surface water. Tris(2-chloro-1-methylethyl) phosphate (TCPP) and tris(2-chloroethyl) phosphate (TCEP) were the most abundant OPEs with the average concentrations of 291 ng L^{-1} and 219 ng L^{-1}, respectively. Relatively high concentrations of OPEs were detected in rivers located at southern and eastern urban of Beijing, which was probably attributed to the treated and untreated sewage discharge. Besides, higher levels of OPEs were observed in urban surface water in the summer, and the wet deposition (rainfall) was confirmed to be an important factor for this observation. Risk assessment showed low or medium risk of OPEs for the organisms (algae, crustacean and fish).
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1. Introduction

As the major replacement for polybrominated diphenyl ethers (PBDEs), organophosphate esters (OPEs) are utilized as flame retardants in a large variety of consumer products such as plastics, textiles, electronic equipment, industrial materials and furniture (Reemtsma et al., 2008; Yang et al., 2014). Chlorinated-OPEs are the predominant compounds for this application (Reemtsma et al., 2008). Apart from being used as flame retardants, OPEs are also applied as plasticizers, antifoaming or anti-wear agents in lacquers, hydraulic fluids, floor polishing agents, and non-ionic extractants in hydrometallurgy (Marklund et al., 2005a, b; Salamova et al., 2014a). In general, there is a considerable variation in the physical and chemical properties of OPEs. As shown in Table S1, these chemicals exhibit a wide range of logKow values (from −0.65 to 9.49). Additionally, OPEs can be classified as semi-volatile compounds with Henry's law constant values ranged from 2.92×10^{-10} to 1.98×10^{-8} atm m^3 mol^{-1} (Wensing et al., 2005). Although the atmospheric half-lives of OPEs are below 2 days (from <1 to 21.3 h), their occurrence in precipitation in the North Sea atmosphere and Arctic, indicates that they can undergo long range atmospheric transport (LRAT) (Möller et al., 2012; Shoeib et al., 2014).

Considering that OPEs are generally not chemically bonded to materials, these compounds could be slowly released into surrounding environment by volatilization, leaching and abrasion (Yang et al., 2014). According to previous reports, several OPEs have been detected in the aquatic (Cristale et al., 2013a; Martinez-Carballo et al., 2007; Venier et al., 2014), terrestrial (David and Seiber, 1999; Fries and Mihajlovic, 2011; Mihajlovic and Fries, 2012), and atmospheric environment (Möller et al., 2012; Möller et al., 2011; Salamova et al., 2014b). Additionally, potential adverse effects of OPEs to the ecosystem and human health have also been pointed out in previous studies (Kim et al., 2011; Meeker et al., 2013; Reemtsma et al., 2008). The reports associated with human exposure have demonstrated the reduction of sperm counts and hormone levels due to the exposure to TPhP and TDCP (Meeker and Stapleton, 2010). TCEP and TDCP are considered as carcinogens and potential neurotoxicants (Cequier et al., 2015; Salamova et al., 2014a), and may cause acute or chronic adverse effects to aquatic

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organisms (Cristale et al., 2013a; Kim et al., 2011). TCPP is also a suspected carcinogen (Reemtsma et al., 2008), and TnBP has neurotoxic properties after chronic exposure (Reemtsma et al., 2008). TPhP and 2-ethylhexyl diphenyl phosphate (EHDPP) reveal potentially bioaccumulative and toxic role to aquatic ecosystem (Kim et al., 2011; Sundkvist et al., 2010).

The occurrence and fate of OPEs in aquatic environment is of concern since these compounds can massively reach surface water from industrial and domestic sewage discharge (Fries and Puttmann, 2003; Martinez-Carballo et al., 2007) and atmosphere deposition (Bacaloni et al., 2008; Möller et al., 2011; Regnery and Püttmann, 2009). The discharge of industrial and domestic sewage is considered as the major source of OPEs in surface water (Reemtsma et al., 2008). Some alkyl-OPEs such as trimethyl phosphate (TMP) and triethyl phosphate (TEP), have been well removed in sewage treatment plants (STPs), whereas the chlorinated-OPEs are not subjected to the significant removal, which are, thus, discharged with effluents into rivers (Bester, 2005; Marklund et al., 2005a; Meyer and Bester, 2004). Besides, atmosphere deposition has been pointed to be another important source of OPEs in surface water environment (Möller et al., 2011; Regnery and Püttmann, 2009). The OPEs at levels from ng L^{-1} to μg L^{-1} have been detected in many rivers in Germany (Andresen et al., 2004; Fries and Puttmann, 2001, 2003; Regnery and Puttmann, 2010), Aire River in UK (Cristale et al., 2013a), volcanic lakes in Italy (Bacaloni et al., 2008), and rivers in Austria (Martinez-Carballo et al., 2007), as well several rivers in China (Wang et al., 2015, 2014, 2011).

Considering the widely application of OPEs in buildings, vehicles, electronics and plastics, more consumption of these compounds was expected in urban city, especially in large city with a dense population, and the urban surface water may suffer serious contamination of OPEs. So far, only one study focused on the occurrence and distribution of OPEs in urban surface water from Germany (Regnery and Puttmann, 2010), hence, more information should be collected to fill our knowledge gaps of the occurrence and distribution of OPEs in urban surface water from densely populated cities. Moreover, temporal variation of OPEs in aquatic environment should be further investigated since the seasonal trend was uncertain in previous studies (Bacaloni et al., 2008; Regnery and Puttmann, 2010).

According to the data from European flame retardants association (EFRA), China is one of the most flame retardants-consuming countries, accounting for approximately 20% of global consumption (EFRA, 2012). It is estimated that the annual yield of OPEs had reached 70,000 tons in 2007 and was predicted to increase by 15% annually in China (Wei et al., 2015). Accordingly, their universal usages may lead to widespread pollution of OPEs in China.

Beijing is one of the most populated and developed cities in China, with total dimension of 16410.54 km^2 and a huge population of 21.516 million. The aim of this study was to investigate the occurrence and distribution of OPEs in urban surface water from densely populated city. To this end, levels of 14 OPEs in surface water covering almost the whole urban of Beijing, China were studied. Besides, spatial distribution and seasonal variation from July 2013 to June 2014 of the target compounds in surface water were also investigated. Additionally, sewage influent and effluent, rainwater and road runoff samples were collected and analyzed as the potential sources of OPEs in surface water. Finally, environmental risk of OPEs in surface water was evaluated to explore the impact of these chemicals on aquatic organisms.

2. Materials and methods

2.1. Materials and reagents

Seven alkyl phosphates, including TMP, TEP, TnBP, tri-iso-butyl phosphate (TiBP), TBEP, tripropyl phosphate (TPrP) and tri(2-ethylhexyl) phosphate (TEHP), and three chlorinated alkyl phosphates (TCEP, TCPP and TDCP), and four aryl phosphates, including TPhP, tri-m-cresyl phosphate (TCrP), cresyl diphenyl phosphate (CDPP) and EHDPP, were obtained from Dr. Ehrenstorfer GmbH (Germany) as target OPEs, and detailed information was listed in Table S1 (Supplementary material). TMP-d_9, TEP-d_{15} and TPrP-d_{21} obtained from C/D/N Isotopes Inc. (USA), TnBP-d_{27} and TPhP-d_{15} purchased from Cambridge Isotope Laboratories (UK), and TCPP-d_{18} supported by Toronto Research Chemicals Inc. (Canada) were used as internal standards (IS). HPLC grade acetonitrile and dichloromethane (DCM) were provided by Fisher Scientific (USA). Ultrapure water (18.3 MΩ) was produced by a Milli-Q Gradient system (Millipore, Bedford, USA).

Individual stock solution with the concentration of 1000 mg L^{-1} was prepared in acetonitrile, and mixed stock solution containing all analytes was prepared in acetonitrile at the concentration of 10 mg L^{-1}. All stock solutions were kept in a −20 °C refrigerator. Calibration solutions (0.05–1000 μg L^{-1}) used in routine application were prepared in acetonitrile/water (4:6).

2.2. Sampling

2.2.1. Urban surface water

River and lake water samples were collected at 34 sampling sites in the urban of Beijing monthly from July 2013 to June 2014 (except December 2013 and January 2014 in frozen period). A total of 340 water samples (surface layer, 0.2 m depth) were obtained in 10 sampling campaigns. In order to fully understand the occurrence of OPEs in surface water in Beijing, all of the major rivers and lakes in the urban areas are included in this study. As shown in Fig. 1, the samples L1-L8 were collected from lakes in various parks. The sampling sites R1-R8 belong to Chang River, and sampling sites R9-R11 belong to Tonghui River, while the samples R12-R17 were collected from Liangshui River and its tributaries, and samples R18-R21 were collected from Qing River and its tributaries. The rest sampling sites R22-R26 were located at Beixiao River, Xiba River, Liangma River, Baijialou Sewer and Xiaotaihou River, respectively.

2.2.2. Wastewater

Additionally, seven STPs (A-G) in the urban of Beijing were also marked in Fig. 1. Influent and effluent water samples were collected as 24 h composite samples by using automatic samplers with sampling interval of 2 h from STP A in October 2013. The plant employs conventional activated sludge treatments to remove biologically degradable organic materials, and the secondary effluent was discharged into the Qing River.

2.2.3. Rain water

A total of 10 rain water samples were collected from June to August 2013 using a stainless steel box (area 1 m^2, height 30 cm) placed at monitoring station in Beijing teaching botanical garden. This sampling site located in the central urban of Beijing, which near the sampling site L4.

2.2.4. Road runoff water

A total of 43 road runoff samples were collected at 5 sampling sites at the main road of Beijing (the 2nd ringroad, 3rd ringroad and 4th ringroad) from June to August 2013. On each occasion, one composite road runoff sample was obtained using a 40-L stainless steel container below the road storm sewer from each site.

All of water samples were collected in glass bottles (500 mL) rinsed with methanol and dried in advance. Immediately after being transported to the laboratory, the samples were stored at 4 °C and treated by SPE within two days. Before SPE procedure, water

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