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A passive sampling method for assessing the occurrence and risk of organophosphate flame retardants in aquatic environments

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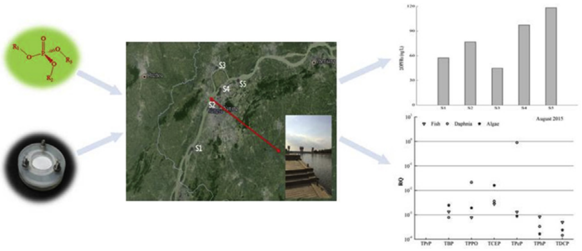
HIGHLIGHTS

- POCIS sampling rates were determined for 7 OPFRs.
- The effect of water flow rate made a primary role in sampling rates.
- Field sampling rate was significantly higher than that in the laboratory.
- POCIS were deployed in the Yangtze River, China.
- Tripentyl phosphate (TPeP) caused high risk to daphnia.

GRAPHICAL ABSTRACT



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ABSTRACT

A modified polar organic chemical integrative sampler (m-POCIS) was used to determine the occurrence of and risk posed by organophosphate flame retardants (OPFRs) in the Yangtze River in Nanjing. Laboratory calibrations were performed to determine sampling rates (R_s) in different situations. R_s values increased with the flow rate, but the effect of dissolved organic matter (DOM) on R_s was relatively small. The validation of R_s in the m-POCIS for 15 days at the Yangtze River in 2015 showed that the R_s values for most of the test compounds are considerably larger than those obtained in the laboratory. The aqueous concentrations of OPFRs were estimated by using R_s values obtained in the field. OPFRs were widely distributed in the Yangtze River, with total concentrations as determined by the m-POCIS ranging from 44.95 ng/L to 118.38 ng/L. These suggest their widespread use and persistence in the river. This study also provided a protocol for the assessment of risk posed by OPFRs. It showed that tripentyl phosphate (TPeP) could pose medium risk to daphnia in the Yangtze River.

1. Introduction

In recent years, organophosphate flame retardants (OPFRs), which are ubiquitous organic pollutants, have been detected in all compartments of the environment because of their extensive use in industrial and other products (Solbu et al., 2007; Chen et al., 2012; Brandsma et al., 2013; Gao et al., 2013). OPFRs are normally used as additives, their extensive use is due to their specific properties of the flame retardance, insulation and low smoke generation as well as the gradual disenablement of polybrominated flame retardants. They can easily leach into the environment via volatilization, abrasion, and dissolution. Conventional water treatment using plastic materials hardly remove OPFRs. Tris(2-chloroethyl) phosphate (TCEP), tris(1,3-dichloroisopropyl)phosphate (TDCP) have been detected in raw water and in effluents from treatment plants producing drinking water (Stackelberg et al., 2004). A

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comprehensive analysis of drinking water in China found that total OPFR concentrations in tap water range from 85.1 ng/L to 325 ng/L (Li et al., 2014). Total OPFR concentrations in 40 rivers draining into the Bohai Sea in northern China range from 9.6 ng/L to 1549 ng/L, with an average of 300 ng/L (Wang et al., 2015). Moreover, a growing number of toxicological studies have revealed that several OPFRs may cause adverse effects in organisms. TDCP was identified to have neurotoxic properties in PC12 cells (Dishaw et al., 2011) and also caused reproductive and developmental toxicity in zebrafish (Liu et al., 2013). In addition, OPFRs have been suggested to be associated with certain effects on human health, such as mucosal irritation (Kanazawa et al., 2010). Thus, there is an urgent need for continuous monitoring of OPFRs in the environment.

Conventional methods of screening for OPFRs rely on water analysis of grab samples from aquatic environments. However, these methods are influenced by factors such as accidental spills and seasonal variation. They are also characterized by low operating efficiency, limitation to instantaneous water concentrations, and their inability to provide time-weighted average (TWA) concentrations. In contrast, passive samplers, emerging tools for water sampling, conveniently obtain analyte concentrations based off kinetic variables and chemical accumulation in the sampler in situ and enable determination of the TWA concentration of water contaminants over long sampling periods. Various designs of passive sampling devices (PSDs) for sampling of aquatic organic pollutants with different polarities exist, including semipermeable membrane devices (SPMD), the Empore disk (ED), solid-phase micro extraction (SPME) (Ouyang et al., 2007; Koelmans et al., 2010; Harman et al., 2011). However, several researches indicated that these PSDs usually are used for absorbing hydrophobic rather than polar hydrophilic organics (Martin et al., 2003; Petty et al., 2004; Harman et al., 2008).

In the present study, we used the modified polar organic chemical integrative sampler (m-POCIS) for the integrated monitoring of OPFRs. This technique has been widely used in detecting polar organic compounds such as endocrine disrupting chemicals (EDCs) (Alvarez et al., 2005; Vermeirssen et al., 2005), pharmaceutical and personal care products (PPCPs) (Petty et al., 2004; Togola and Budzinski, 2007), perfluorinated compounds (PFCs) (Alvarez et al., 2007; Kaserzon et al., 2013; Ma et al., 2015), as well as polar pesticides and herbicides (Thomatou et al., 2011) in aquatic environments such as surface water, sewage effluents, and sediment interstitial water. Calculation of TWA concentrations over a specified duration are performed by using a consistent sampling rate (R_S) with continuous exposure to the hydrodynamic environment. However, R_S depends on experimental hydrodynamic conditions such as pH, dissolved organic matter (DOM) concentration, biofouling, temperature, and salinity (Harman et al., 2012; Kaserzon et al., 2013; Shi et al., 2014). Although on the basis of critical reviews by Harman et al., (2012) and Ibrahim et al., (2013), it indicated that R_S values calculated from laboratory experiments are different from those obtained in the field, few standard data on R_S values coincide in different effects, which could not be satisfied with a wide range of compounds.

The aim of the present study was to optimize and validate the monitoring of OPFRs in drinking water sources using a m-POCIS. First, we evaluated the effects of pH, DOM concentration, and flow rates/turbulence on the R_S values of the sampling device in the laboratory and in the field. The m-POCIS was subsequently used to sample drinking water and to determine TWA concentrations of target compounds in the sample through the validated R_S value (for the Yangtze River in Nanjing). Finally, a preliminary ecological risk assessment of drinking water sources was performed on the basis of the measured concentrations of OPFRs to understand the risks they pose to sensitive organisms.

2. Materials and methods

2.1. Chemicals and materials

The standards for the target organophosphates were tripropyl phosphate (TPrP), tributyl phosphate (TBP), tris(2-chloroethyl) phosphate (TCEP), tripentylphosphate (TPeP), tris(1,3-dichloroisopropyl)phosphate (TDCP), triphenyl phosphate (TPhP), triphenylphosphine oxide (TPPO) (Dr. Ehrenstorfer, Germany). Deuterated tributyl phosphate (d_{27}-TBP, 98%–99%; C/D/N Isotopes, Canada) was used as an internal standard. Methanol (HPLC grade) and acetone (HPLC grade) were purchased from Merck Company (USA). Humic acid was obtained from Sigma Aldrich Trading Co., Ltd. (China). Stock solutions in methanol (1.0 g/L) of the individual compounds and internal standard were prepared. From the stock solution of the individual standards, a 50.0 mg/L working solution of all compounds was prepared by dilution with methanol. All standard solutions were stored at −20 °C. Ultrapure water was produced by a water purification system (Sichuan Ulupure Ultrapure Technology Company, China).

The PSD was composed of 200 mg of sorbent packed between two pieces of microporous polyether sulfone (PES) membranes (0.45 μm pore size, 47 mm diameter, 140 μm thickness; Lu Na Sheng Bio Technology Company, China). Different from the commercially-available POCIS with a PES membrane with a 0.1 μm pore size, the PSD was then called modified POCIS (m-POCIS). The sorbent was removed from Oasis HLB (35 cc, 6 g) solid-phase extraction (SPE) cartridges (Waters Corporation, USA). The sorbent was pooled and then washed with acetone, methanol, and ultrapure water before use. All components of the m-POCIS were washed with ultrapure water, immersed in methanol, dried, and then wrapped with cleaned aluminum foil.

2.2. Laboratory calibration of the m-POCIS and calculation of R_S

2.2.1. Effect of flow rate/turbulence on R_S calibration

The m-POCIS was calibrated for OPFRs by using a static-renewal experimental design, including a stirring batch experiment carried out in 2 L glassware and a 60 L flow-through channel system. In this experiment, m-POCISs ($n = 2$) were suspended and immersed in the glassware that was washed with methanol before use. The glassware contained 2 L ultrapure water ($\text{pH} = 7$) in a temperature-controlled chamber (20 °C). The water was spiked with a solution of OPFRs at a concentration of 1.0 μg/L. Stirring was done magnetically at a speed of 400 rpm to simulate turbulent conditions in water. All bottles were covered with aluminum foil to reduce exposure to light and to minimize volatilization. To maintain the concentration of compounds constantly, the water was replenished daily and 1 mL water was collected and analyzed for OPFRs after equilibration. Sampling was carried out for 15 days. The samplers were removed from the glassware at staggered consecutive design intervals (1 × 2, 2, 4 × 2, 7 × 2, 8, and 15 days; Table S1). The devices were washed with ultrapure water, wrapped in aluminum foil, and stored at −20 °C until extraction.

To determine the effect of water flow rates on the R_S, m-POCISs were exposed to a constant concentration 1.0 μg/L in a flow-through channel system. The system consisted of two separate water channels, two submerged pumps, and a 60 L tank, which was shielded from ambient light. Flow velocities in the channel systems were 1.6 and 9.6 cm/s. Tap water was spiked with a methanol solution containing seven OPFRs, and the resulting solution was mixed well to achieve a nominal concentration of 1.0 μg/L. The system was operated for 24 h before m-POCIS exposure to allow establishment of steady-state concentrations of OPFRs in the tank. The temperature of the water in the system was kept at 20 ± 1 °C,