



# Application of fully automatic hollow fiber liquid phase microextraction to assess the distribution of organophosphate esters in the Pearl River Estuaries



Xiaowei Wang<sup>a</sup>, Yingqian He<sup>b</sup>, Li Lin<sup>b</sup>, Feng Zeng<sup>c</sup>, Tiangang Luan<sup>a,b,\*</sup>

<sup>a</sup> MOE Key Laboratory of Aquatic Product Safety, School of Marine Sciences, Sun Yat-sen University, Guangzhou 510275, PR China

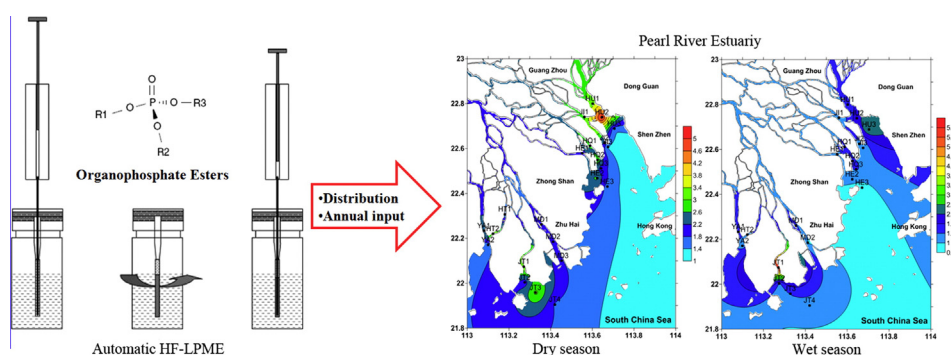
<sup>b</sup> School of Life Sciences, Sun Yat-Sen University, Guangzhou 510275, PR China

<sup>c</sup> School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, PR China

## HIGHLIGHTS

- Automatic HF-LPME coupled with GC–MS was developed to determine OPEs in seawaters.
- Parameters that affect the proposed method were optimized.
- Distribution of OPEs in seawaters of the Pearl River Estuary was investigated.
- Spatial interpolation method was selected to estimate OPEs in the unsampled area.
- Annual input of OPEs of the Pearl River Estuaries was calculated.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Organophosphate esters (OPEs) are widespread organic pollutants that could be detected in various environmental matrices. In this study, a sample pretreatment method was developed for the determination of 9 OPEs by automatic hollow fiber-liquid phase microextraction (HF-LPME) coupled with gas chromatography–mass spectrometry (GC–MS). High sensitivity of OPEs could be achieved after optimization of several important parameters with the limits of detection (LODs) ranging from 2.6 to 120 ng L<sup>-1</sup> for different individual OPEs, and the relative standard deviations (RSDs) ranged from 2.1% to 10.4%. Acceptable recoveries were observed and the proposed method was then successfully applied to determine OPEs in seawaters collected from 23 sampling sites of the Pearl River Estuaries in dry and wet seasons, respectively. All of the OPEs could be detected, except tris(2-ethylhexyl) phosphate (TEHP). The total concentrations of 9 OPEs in seawaters were ranging from 2.04 (Hemen) to 3.12 (Humen) µg L<sup>-1</sup> in the dry season and from 1.08 (Hemen) to 2.50 (Jitimen) µg L<sup>-1</sup> in the wet season. By using spatial interpolation method of ordinary kriging, the most polluted area of ΣOPEs was found in Humen in the dry season, while it was Jitimen in the wet season. Moreover, the annual input of ΣOPEs discharged via eight estuaries ranged from 384 tons (Jitimen) to 1225 tons (Modaomen), and the total annual input was 5694 tons.

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\* Corresponding author at: MOE Key Laboratory of Aquatic Product Safety, School of Marine Sciences, Sun Yat-sen University, Guangzhou 510275, PR China. Tel.: +86 20 84112958; fax: +86 20 84112199.

E-mail address: [cesltg@mail.sysu.edu.cn](mailto:cesltg@mail.sysu.edu.cn) (T. Luan).

## 1. Introduction

Organophosphate esters (OPEs) are man-made industrial chemicals being applied as flame retardants, plasticizers, antifoaming agents and

hydraulic fluids (Marklund et al., 2003). They have been extensively used worldwide for several decades in large scales with an annual global consumption volume of 209,000 tons reported for 2004. Since polybrominated diphenyl ethers have been restricted in the early 2000s and the penta-BDE and octa-BDE mixtures have been finally included in the Stockholm Convention list on Persistent Organic Pollutants, they might be replaced directly by certain organophosphate flame retardants in some applications. The general production and usage of organophosphate esters are expected to increase in the future (Reemtsma et al., 2008).

In most applications, OPEs are used additively in the material allowing them to easily leach out of the material into the environment via volatilization, abrasion, and dissolution. Reports on the occurrence of OPEs in water and air have increased continuously over the past decade (Reemtsma et al., 2008). Since 1980, OPEs have already been detected in surface waters and groundwater (Ishikawa et al., 1985) influenced by wastewater (Fries and Puttmann, 2003) and drinking water (Stackelberg et al., 2004) as well as in sediments (Garcia-Lopez et al., 2009), snow (Regnery and Puttmann, 2009), and outdoor air and dust (Quintana et al., 2007). They have also been found in effluents of municipal wastewater treatment plants (Marklund et al., 2005), where they are received via the sewage system from households, industrial sites, and stormwater drainage. Especially, the chlorinated ones such as tris-(2-chloro-1-methylethyl)-phosphate (TCPP), tris-(2-chloro-1-chloromethylethyl)-phosphate (TDCEP) and tris-(2-chloroethyl)-phosphate (TCEP) might be considered as persistent pollutants since they are not effectively removed in conventional urban wastewater treatment plants (Meyer and Bester, 2004; Andresen and Bester, 2006), the pollutants could therefore transport into surface and drinking water supply sources. Based on the growing usage of OPEs, more and more attentions have been paid for their distribution in the environment and toxicity to ecosystem. Moreover, OPEs had been included in European lists of aquatic priority substances as well.

The Pearl River Delta (PRD) is one of the most developed and populated regions in China, connecting the Pearl River Estuary (PRE) and South China Sea (SCS) via eight major estuaries. The annual mean temperature is 14–22 °C and the annual precipitation is 1200–2200 mm<sup>3</sup> (Ni et al., 2008). As a result, riverine runoff is an important route to transport contaminants to global oceans. However, no study has been conducted to address this issue so far. Much more information is therefore needed to understand the fate of these pollutants which is critical for risk assessment as the PRE is one of the most polluted area in the world.

Traditionally, liquid–liquid extraction (LLE) (Andresen et al., 2004; Andresen and Bester, 2006) and solid-phase extraction (SPE) (Rodil et al., 2005; Bacaloni et al., 2007) have been the most often employed sample pretreatment techniques for OPE determination in aqueous samples. Despite their widespread use, those methods are tedious, involved with multistage operation and consume large amounts of organic solvents. In recent years, miniaturized scale sample preparation techniques have been developed and applied to determine OPEs in different matrices, such as solid phase microextraction (SPME) (Rodriguez et al., 2006), dispersive liquid–liquid microextraction (DLLME) (Garcia-Lopez et al., 2007), membrane-assisted solvent extraction (MASE) (Quintana and Reemtsma, 2006) as well as microporous membrane liquid–liquid extraction (MMLLE) (Garcia-Lopez et al., 2008). However, those reported methods were labor-intensive and might cause poor analytical reproducibility as they carried out by manual operations.

Liquid phase microextraction (LPME) is introduced in the mid-late 1990s as a miniaturization of LLE, in which a small organic droplet of immiscible solvent was suspended on the tip of a micro-syringe needle and acted as the extraction phase (Jeannot and Cantwell, 1996). However, the organic droplet sometimes is unstable and could cause loss of the analytes, so that hollow fiber liquid phase microextraction (HF-LPME) was developed by using a porous hollow fiber to stabilize and protect the extracting solvent (Pedersen-Bjergaard and Rasmussen, 2008).

HF-LPME has been widely applied in the fields of environmental and pharmaceutical analysis in recent years (Muller et al., 2003; Jiang et al., 2005). Several studies had reported the automation for HF-LPME techniques (Hou et al., 2003; Muller et al., 2003; Jiang et al., 2005; Ouyang and Pawliszyn, 2006), but no automatic HF-LPME had been developed to analyze OPEs in aqueous samples yet.

In this study, an automatic HF-LPME procedure coupled with gas chromatography–mass spectrometry (GC–MS) was therefore introduced for the determination of OPEs in seawater samples. After optimization of several important parameters and evaluation of the proposed method, OPEs in duplicate seawater samples were analyzed from 23 sampling sites of the Pearl River Estuary in the dry season and the wet season, respectively. Based on the obtained data, the distribution of OPEs in the sampling sites and the unsampled area was thus interpolated by the method of ordinary kriging, and the annual input of OPEs from the PRE to the coastal ocean was determined as well.

## 2. Experiment

### 2.1. Material and reagents

Tris(2-ethylhexyl) phosphate (TEHP, 97.0%), tris(2-chloroethyl) phosphate (TCEP, 97.0%), triphenylphosphine oxide (TPPO, 98.0%), tri-*iso*-propyl phosphate (TiPrP, 98.0%), tributyl phosphate (TBP, 99.0%), and triphenylphosphate (TPHP, ≥98.0%) were acquired from Sigma-Aldrich (St. Louis, MO, USA). 2-Ethylhexyl diphenyl phosphate (EHDPP, 87.0%), tris(2-chloroisopropyl) phosphate (TCPP, 99.5%), and tris(2-chloro-1-(chloromethyl)ethyl) phosphate (TDCEP, 97.0%) were from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The surrogate standard [2H27]-tri-*n*-butyl phosphate (TnPrP, 99.0%) was acquired from Cambridge Isotope Laboratories (Woburn, MA). Full names, abbreviations and octanol–water partition coefficients of all standards are showed in Table 1. Analytical grade dichloromethane, ethyl acetate, *n*-hexane, toluene, 1-octanol, cyclo-hexane and sodium chloride were supplied by Guangzhou Chemical Reagent Factory. The polyvinylidene difluoride hydrophobic (PVDF) hollow fiber (200 μm wall thickness, 1.2 mm internal diameter, 0.2 μm pore size and 85% porosity) was purchased from Tianjin Polytechnic University (Tianjin, China). The polypropylene (PP) hollow fiber (200 μm wall thickness, 1.2 mm internal diameter, 0.2 μm pore size and 70% porosity) was made by Membrana (Wuppertal, Germany). Ten microliter screw vials with magnetic crimp caps and PTFE coated silicone septa (Supelco, Oakville, Canada) were used for the automated analysis. Ultrapure water was obtained by a Millipore purification system (Billerica, USA).

### 2.2. Preparation of standard solutions and sample collection

Surrogate standard solution (10 g L<sup>-1</sup>), and stock solution (1.0 g L<sup>-1</sup> for each analyte) with a mixture of 9 individual standards were all prepared in acetone. Fresh working solutions were prepared by the dilution with an appropriate amount of pure water (with the concentrations ranged from 0.01 μg L<sup>-1</sup>–10 μg L<sup>-1</sup>) or seawater and spiked with surrogate standard of 0.5 μg L<sup>-1</sup> before extraction.

Sampling was designed to evaluate the distribution of OPEs in the eight estuaries of the Pearl River including Humen (HU), Jiaomen (JI), Hongqimen (HQ), Hemen (HE), Modaomen (MD), Jitimen (JT), Yamen (YA) and Hutiaomen (HT). Therefore, 23 seawater samples (surface layer, 0.5 m depth) were collected during one tidal cycle twice in December 2011 (dry season) and May 2012 (wet season), and the sampling sites were displayed in Fig. 4. All of the seawater samples were analyzed directly using the fully automatic HF-LPME method after being spiked with surrogate standard without further filtration.

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