Science of the Total Environment 636 (2018) 632–640

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Occurrence, distribution and risk assessment of organophosphate esters in surface water and sediment from a shallow freshwater Lake, China

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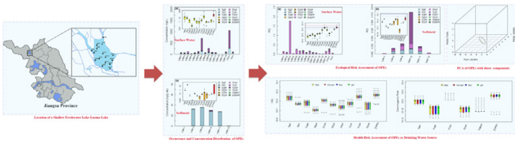
## HIGHLIGHTS

- Occurrence, distribution of OPEs in surface water and sediment from Luoma Lake were investigated.
- Ecological risks of organophosphate esters in surface water and sediment were assessed using RQ method.
- Human health safety of Luoma Lake as a drinking water source in the context of OPEs pollution was evaluated.
- During the process of health risk assessment, age and gender-specific intake of water were considered.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 25 January 2018
Received in revised form 23 April 2018
Accepted 24 April 2018
Available online xxxx

Editor: Kevin V. Thomas

*Keywords:*
Organophosphate esters
Luoma Lake
Ecological risk assessment
Surface water
Sediment

## ABSTRACT

Organophosphate esters (OPEs) are ubiquitous in the environment and pose a potential threat to ecosystem and human health. This study investigated the concentrations, distributions and risk of 12 OPEs in surface water and sediment from Luoma Lake, Fangting River and Yi River. Solid-phase extraction (SPE) method were used to extract OPEs from water samples, ultrasonic process and SPE method were used to extract OPEs from sediment samples, and the extracts were finally analyzed using the HPLC-MS/MS. The results revealed that the median and maximum concentrations of ΣOPEs were 73.9 and 1066 ng/L in surface water, and were 28.7 and 35.9 ng/g in sediment, respectively. Tris(2-chloroethyl) phosphate (TCEP) and trimethyl phosphate (TMP) were the most abundant OPEs in the surface water with median concentrations of 24.3 and 16.4 ng/L in Luoma Lake, respectively. Triethyl phosphate (TEP) was the most abundant OPE in the sediment with a median concentrations of 28.9 ng/g. However, tricresyl phosphate (TCrP) and ethylhexyl diphenyl phosphate (EHDPP) predominantly contributed to the ecological risk with respective median risk quotients 0.07 and 0.01 for surface water in Luoma Lake. TEP and TCrP were the most significant contributors to the ecological risk with respective median risk quotients of $6.4 \times 10^{-4}$ and $5.6 \times 10^{-4}$ for sediment. It was also found that inflowing Fangting River could be the major pollution source to Luoma Lake. The no-cancer and carcinogenic risks of OPEs were lower than the theoretical threshold of risk. The study found that the ecological and human health risks due to the exposure to OPEs were currently acceptable. In other words, the Luoma Lake was relatively safer to use as a drinking water source in urban areas in the context of OPEs pollution.

## 1. Introduction

As a major alternative for polybrominated diphenyl ethers (PBDEs), organophosphate esters (OPEs), are extensively used as flame

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https://doi.org/10.1016/j.scitotenv.2018.04.320
0048-9697/

retardants in plastics, textiles, electronic equipment, industrial materials and furniture, as antifoaming or anti-wear agents in lacquers, hydraulic fluids and floor polishing agents, and as non-ionic extractants in hydrometallurgy (Salamova et al., 2014; Shi et al., 2016; Yadav et al., 2017). Because of their widespread applications and weaker bond to the related products (Ding et al., 2015; van der Veen and de Boer, 2012), OPEs can be present in the surface water, groundwater, wastewater, sludge products, sediments, drinking water, and indoor and outdoor atmosphere. (Ding et al., 2015; Liang and Liu, 2016; Liang et al., 2018; Mizouchi et al., 2015; Salamova et al., 2014; Shi et al., 2016; Yadav et al., 2018; Yadav et al., 2017). Additionally, the OPEs and their metabolites have been detected in wildlife and human tissues (Ding et al., 2015; Guo et al., 2017).

Several toxicological studies have reported that different OPEs species can cause adverse effects on organisms. For example, tri(2-chloroethyl) phosphate (TCEP) had significant influences on the decrease of red blood cell cholinesterase activity, and disruption of thyroid endocrine system and neurotoxicity, while triphenyl phosphate (TPhP) was responsible for decreasing red blood cell cholinesterase activity, acetyl cholinesterase activity in cholinergic nerve synapses and human monocyte carboxylesterase activity, neurotoxicity, contact allergenic effects, and fertility. Similarly, tributoxyethyl phosphate (TBEP) also decreased red blood cell cholinesterase activity, whereas trimethyl phosphate (TMP) and triethyl phosphate (TEP) disrupted thyroid endocrine system through the activation of nuclear receptor (ATSDR, 2012; Ren et al., 2016; van der Veen and de Boer, 2012; Wang et al., 2014; Wei et al., 2015). TCEP and tris (1-chloro-2-propyl) phosphate (TCIPP) are even carcinogenic (van der Veen and de Boer, 2012; Wei et al., 2015; Yadav et al., 2018). Therefore, OPEs can cause significant threat to ecosystem and human health through diverse routes such as dermal contact, dust ingestion, inhalation, and dietary intake, due to the widespread occurrence of OPEs in the environment.

In recent years, several studies have investigated the occurrence, distribution, seasonal variation and fate of OPEs in water, soil and atmosphere environments (Cao et al., 2017; Guo et al., 2017; Liang et al., 2018; Wan et al., 2016; Wang et al., 2017; Yadav et al., 2017; Zhong et al., 2018). However, ecological and human risks associated with the use of OPEs contaminated shallow freshwater lake as a drinking water source have not been investigated. In particular no studies have investigated the occurrence, distribution and OPEs risk assessment in surface water and sediment of Luoma Lake, which is one of the four largest lakes in Jiangsu province, China (34°00′–34°14′N; 118°06′–118°18′E) and used for water supply, aquaculture, irrigation, navigation, and tourism. The average water depth and surface water area of Luoma Lake are 3.3 m and 260 km$^2$, respectively. It is a man-controlled, lightly eutrophic reservoir and a transfer station of South-to-North Water Transfer Project. Luoma Lake was once widely regarded as “clean water” before the establishment of factories (Feng et al., 2007; Liu et al., 2017; Yan et al., 2017).

The objective of this study was to generate new knowledge about the occurrence, and distribution characteristics of OPEs, and to conduct ecological and health risk assessment of OPEs in a shallow freshwater lake. Furthermore, the source identification of OPEs was investigated by correlation coefficient and principal component analysis (PCA), it was helpful to know pollution situation of OPEs in urban water supply sources. The OPEs concentrations in water and sediment samples were determined, and used to assess the risk according to the risk quotient (RQ) or hazard quotient (HQ) methods.

## 2. Materials and methods

### 2.1. Chemicals and reagents

The standards for TMP, TEP, TnBP, TBEP, TCPP, TDCP, TPhP, TCrP, TCEP, TEHP, TDBPP and EHDPP were purchased from J&K Chemical, Ltd. (St. Louis, MO, USA), while the internal standards for TnBP-d$_{27}$ and TPhP-d$_{15}$ were purchased from Cambridge Isotope Laboratories (Tewksbury, MA, USA). The solvents with HPLC grade and deionized water obtained from a Milli-Q water purification system (Millipore, Bedford, MA) were used in this study.

### 2.2. Sample collection

Sample collection was conducted according to the method described in our previous studies (Liu et al., 2017; Yan et al., 2017). Briefly, 16 surface water samples (depth: 0–1 m) and 6 sediment samples (depth: 0–0.1 m) were collected in November 2016. Among the water samples, 14 samples were obtained from Luoma Lake (LMH1-14), whereas the remaining two samples were obtained from two inflowing rivers, Yi River and Fangting River (YH1, and FTH1). The sediment samples (LMH1, 3, 9, 10, 11, and 12) were collected from the estuary, center and lake outlet. The sampling sites are shown in Fig. 1. The preserved samples were transported to the laboratory in pre-cleaned 2 L brown glass containers, and were immediately filtered through 0.45 μm × 50 mm glass fiber membranes (Membrane Solutions LLC., America). A Peterson grab sampler was used to collect sediment samples and stainless-steel containers were used to transport to laboratory, where they were freeze dried, ground, and sieved.

### 2.3. Sample treatment and analyses

The water samples (0.5 L) were spiked with 20 ng of TnBP-d$_{27}$ as surrogate and extracted using solid-phase extraction (SPE). After activated with 5 mL ethyl acetate, 5 mL methanol and 5 mL ultrapure water, Oasis HLB cartridges (500 mg, 6 mL, Waters) were passed through by filtrates at a flow rate of about 4 mL/min. Then, the cartridges were washed twice with 5 mL ethyl acetate at a flow rate of approximately 1 mL/min and were concentrated to about 200 μL with a gentle stream of nitrogen. The final extracts were spiked with 10 ng of TPhP-d$_{15}$ before analyzing using HPLC-MS/MS.

Sediment samples of 5 g each were spiked with 20 ng of TnBP-d$_{27}$ as surrogate, and then were extracted with 30 mL acetonitrile for 30 min using the ultrasonic process and centrifuged at 8000 rpm for 5 min. This process was performed twice. 60 mL extracts were then transferred into a flask and then concentrated to about 1 mL using a rotary evaporator, then the analytes were diluted to 100 mL with deionized water for further analysis. The same SPE method was used to extract OPEs from the water samples was employed for sediment samples.

The extracts were finally analyzed using the HPLC-MS/MS (LC-Agilent Technologies 1290 Infinity, MS-AB SCIEX QTRAP 4500; CA). Chromatographic analysis was performed with the ZORBAX Eclipse Plus C18 column (150 mm × 2.1 mm, 3.5 μm; Agilent) at a constant temperature of 30 °C, with the injection volume of 5 μL. 0.02% (V/V) formic acid (A) and methanol (B) was used as the mobile phases for the separation of analytes at a flow rate of 0.3 mL/min. The gradients with reference to A were 0 min 30% A, 8 min 30% A, 8 min 5% A, 16 min 5% A, and 20 min 30% A. The confirmation and quantification ions for each analyte in multiple reaction monitoring mode are given in Table S1 in Supplementary Information.

### 2.4. Quality assurance and quality control

Any plastic and rubber materials were avoided to minimize possible OPEs contamination of the samples during sampling, storage, transport, and extraction. Similar to our previous studies (Liu et al., 2017; Yan et al., 2017), strict protocols were established to ensure reliable results. Solvent blanks, standard and procedure blanks were simultaneously run in sequence to check for background contamination, peak identification and quantification. The quantification of OPEs was conducted using an internal standard method and the correlation coefficients ($R^2$) of the calibration curves were >0.994. Three spiked levels of two matrixes (Milli-Q water and fine black soil of China with almost no