



## Spatio-temporal distributions and the ecological and health risks of phthalate esters (PAEs) in the surface water of a large, shallow Chinese lake



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### HIGHLIGHTS

- Monthly variation in PAEs was first investigated in a large Chinese shallow lake.
- Ecological and health risks with uncertainty were determined.
- PAEs with low and high level of carbon would be from different sources.
- DnBP predominated within PAE congeners and posed a much greater ecological risks.
- The studied PAE congeners posed little health risks to the nearby citizens.

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### ABSTRACT

The spatio-temporal distributions and the ecological and health risks of PAEs in surface water of Lake Chaohu, the fifth largest lake in China, were studied based on the monthly monitoring of six PAE congeners from May 2010 to April 2011. The annual total concentration of the six PAE congeners ( $\Sigma_6$ PAE) in the surface water ranged from 0.467 to 17.953  $\mu\text{g L}^{-1}$ , with the average value of  $4.042 \pm 3.929 \mu\text{g L}^{-1}$ . The di-n-butyl phthalate (DnBP) that dominated the  $\Sigma_6$ PAE at 65.8% was found at its highest and lowest levels in the western lake (TX) and eastern drinking water source area (JC), respectively. The temporal distributions of  $\Sigma_6$ PAE showed that the highest and lowest levels were observed in September 2010 and June 2010, respectively. The different relationships between the runoff and the PAEs with low and high levels of carbon might suggest their different sources. The DnBP had much greater ecological risks than the other studied PAE congeners as indicated by its potential affected fractions (PAFs) and the margin of safety (MOS10). The PAE congeners studied posed little health risk to the nearby male and female citizens.

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### 1. Introduction

Phthalate esters (PAEs) account for approximately 92% of the produced plasticizers and dominate the production and consumption of plasticizers worldwide (Rahman and Brazel, 2004). In 2004, nearly 6 million tons of PAEs were produced and consumed worldwide (Xie et al., 2007). In China, 1.3 million tons of PAEs, mainly di(2-ethylhexyl) phthalate (DEHP) and di-n-butyl phthalate (DnBP), are produced and consumed. Thirty-one percent of PAEs, primarily DEHP, are imported (CPCIA, 2009). Previous studies have shown that PAEs are endocrine-disrupting chemicals (EDCs) as indicated by developmental and behavioral abnormalities after extensive exposure

to PAEs; also, the alkyl chain length and the hydroxylation of PAEs significantly affected the binding to estrogen receptors and peroxisome proliferator-activated receptors (Harris et al., 1997; Jobling et al., 1995; Moore, 2000; Okamoto et al., 2011). PAEs such as diethyl phthalate (DEP) and DnBP can alter the human serum albumin's conformational structure (Zhou et al., 2012). Extensive exposure to PAEs will increase the risks to human reproductive development.

In aquatic ecosystems, PAEs hydrolyze at slow rates with half-lives ranging from approximately 3 years for dimethyl phthalate (DMP) to 2000 years for DEHP (Wolfe et al., 1980). The PAE photo-oxidation process is also relatively slow with half-lives ranging from 2.4 to 12 years for DEP and DnBP and 0.12 to 1.5 years for DEHP (Howard, 1991). Nevertheless, biodegradation plays a critical role in the fate of PAEs, and mixed microbial populations can completely mineralize PAEs (Kurane, 1986). Studies have indicated that aerobic degradation rates are up to 10 times faster than anaerobic degradation rates. The PAE degradation rates ranged from days to weeks (Yuan et al.,

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2002). Low- and mid-molecular-weight PAEs (DMP, DnBP and butylbenzyl phthalate (BBP)) did not seem to demonstrate significant biomagnification or biodilution, while high-molecular-weight PAEs (DEHP and di-n-octyl phthalate (DnOP)) showed significant biodilution (Mackintosh et al., 2004) due to their desorption and degradation in the ecosystem (Mackintosh et al., 2006). The main source of PAEs is water from streams or other surface runoff followed by atmospheric deposition and the discharge from wastewater treatment plants (Fauser et al., 2009).

Due to the physicochemical properties and biogeochemical cycling of PAEs, they are detected in various media. The water phase is very important in aquatic ecosystems, and PAEs have been detected in this phase in Europe, the United States, and Japan (Clark et al., 2003; Dargnat et al., 2009; Peijnenburg and Struijs, 2006; Vitali et al., 1997). The PAEs in the surface water of large rivers, including the Yellow River and Yangtze Rivers, and large and urban lakes in China have been monitored over the past five years (He et al., 2011; Sha et al., 2007; Wang et al., 2008; Yang et al., 2009; Zeng et al., 2008, 2009). DnBP and DEHP have been detected at very high levels worldwide, and concentrations of DEP, BBP and DnOP in the domestic water are lower than in Western countries.

The ubiquity and the slow hydrolysis and photolysis rate of PAEs determine their potential accumulation in aquatic organism communities and has drawn scientific interest, particularly with regard to the toxicity and ecotoxicity of PAEs for aquatic microorganisms, algae, invertebrates, and fish in freshwater or saltwater (Staples et al., 1997). The acute toxicities of DMP, DEP, DnBP, and BBP for aquatic organisms were 29–337 mg L<sup>-1</sup>, 10.3–131 mg L<sup>-1</sup>, 0.35–6.29 mg L<sup>-1</sup>, and 0.21–5.3 mg L<sup>-1</sup>, respectively, and the toxicity of PAEs increases with increasing alkyl chain length. Although PAEs present a potential health risk to human beings, water treatment processes have been shown to purify 90% of phthalates. Additional PAEs can be removed by boiling the water (Shi et al., 2012). Urban populations have clean water because of advanced water treatment facilities, but rural populations that drink lake and well water with little treatment have a high hazardous risk from PAEs as do aquatic organisms in natural ecosystems (Yang et al., 2012). Therefore, it is necessary to assess the ecological and health risks of PAEs regularly. A number of ecotoxicity tests have been performed to provide suitable amounts of data for risk evaluations (Adams et al., 1995; Staples et al., 1997, 2011). The predicted no-effect concentrations (PNECs) calculated by methods adopted by the US EPA (United States Environmental Protection Agency) and the Netherlands showed that PAEs did not pose a ubiquitous threat to aquatic organisms in North American and Western European surface waters (Staples et al., 2000). A hazard quotient (HQ) method was applied to assess the PAEs' aquatic ecological risk, which did not exceed the criterion in Thailand and posed little ecological risk to aquatic organisms in the river basin in Chongqing, China (Luo et al., 2009; Sirivithayapakorn and Thuyviang, 2010).

Lake Chaohu (117.18°–117.50° E, 31.25°–31.42° N), a shallow freshwater lake that is located in East China, has a subtropical monsoon climate and is one of the five largest freshwater lakes in China, had a yearly average water level of 8.37 m and a reservoir capacity of 1.72–3.23 billion cubic meters. The lake has suffered from serious eutrophication (major pollution from the total nitrogen and total phosphorus) in the last decades. Moreover, various persistent toxic substances have been detected in recent years (Li et al., 2010; Xu et al., 1999, 2001; Zhang et al., 2007). Although the surface water PAE concentrations in Lake Chaohu have been reported in recent years (Yang et al., 2009), their temporal variation and potential ecological and health risks are still unknown. The objectives of the present study are (1) to perform a monthly investigation into the PAE occurrence and composition in the Lake Chaohu surface waters, (2) to ascertain the temporal and spatial variation of PAEs in the surface water and (3) to evaluate the ecological and health risks of PAEs in the surface water.

## 2. Materials and methods

### 2.1. Reagents and materials

Methanol (pesticide grade) and n-hexane (high-performance liquid chromatography grade (HEX, HPLCG)), which were used for the activation of the SPE column, and dichloromethane (DCM, HPLCG), which was used for elution, were purchased from Tedia Co. Inc., Fairfield, Ohio, USA. A PAE stock standard mixture was prepared by diluting n-hexane with a commercial 6 PAE standard mixture (Accustandard Inc., New Haven, Connecticut, USA), which included 1000 µg mL<sup>-1</sup> each of DMP, DEP, DnBP, BBP, DEHP, and DnOP. The working standard solution was prepared by diluting the stock standard with n-hexane. One hundred micrograms per milliliter each of surrogate standard (SS) (3,4,5,6,d4-DnBP) and internal standards (ISs) (3,4,5,6,d4-DEP and 3,4,5,6,d4-DnOP) were acquired from Accustandard Inc., New Haven, Connecticut, USA. A solid phase extraction (SPE) device and C18 SPE cartridges (ENVI-18, 6 mL, 500 mg) were purchased from Supelco Co., Bellefonte, Pennsylvania, USA. Granular anhydrous sodium sulfate (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and glass fiber membranes wrapped with aluminum foil were heated at 650 °C and 450 °C, respectively, in a furnace for 6 h and were stored in a sealed desiccator until they were used. All glassware was cleaned in an ultrasonic cleaner (KQ-500B, Kunshan Ultrasonic Instrument, Kunshan, China) and was heated at 450 °C for 6 h.

### 2.2. Sampling and preprocessing

A total of 44 samples were collected from 3 to 4 sampling sites monthly from May 2010 to April 2011 (Fig. 1). The sample site TX, located in the northwestern region of Lake Chaohu, was once the drinking water source for the citizens of Hefei City, which is the capital of the Anhui Province, but was replaced because of eutrophication. The sample site JC, located in the northeastern region of Lake Chaohu, currently provides the water for the Chaohu City waterworks. The sample site ZM is located at a scenic location. The sample site MS is located near Lake Chaohu's center island, which divides the lake.

Ten liters of water were collected at a 0.5 m depth (representative of the mixed water columns) of the lake from each sampling site. After shaking and mixing, a 1-L aliquot of each sample was filtered through a 0.45-µm glass fiber filter using a filtration device consisting of a peristaltic pump (BT-001, Baoding Longer Precision Pump Co., Ltd., China) and a filter plate with a diameter of 142 mm. Several drops of concentrated sulfuric acid were added into the dissolved phase of the water samples to adjust the pH to 2. The samples were then passed through an SPE cartridge containing an octadecyl silane-bonded silica (ODS) C18 filler, which had been cleaned twice with 5 mL of a DCM:HEX (1:1) mixture, activated by 6 mL of methanol, and finally washed using 10 mL of ultrapure water. During the activation and washing with the ultrapure water, the liquid level remained tangent to the filler to keep the C18 wet. After extracting the target compounds from the water, the SPE cartridges were blown dry using the SPE device, wrapped with aluminum foil, and stored in desiccators.

### 2.3. Elution and GC/MS analyzing

Ten milliliters of a DCM:HEX (1:1) mixture (2 repetitions of 5 mL) were used to elute the C18 SPE cartridge, which was jointed to an anhydrous sodium sulfate (5 g) cartridge. The extracts were concentrated to approximately 1 mL in an eggplant-shaped flask using a vacuum rotary evaporator (N1100 V-WD, Tokyo Rikakikai Co., Ltd., Japan) at a temperature below 38 °C. The IS was added to the flask. The samples were sealed in vials and stored at -20 °C before analysis.

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