



# Occurrence of phthalic acid esters in source waters: a nationwide survey in China during the period of 2009–2012



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## ABSTRACT

The first nationwide survey of six phthalic acid esters (PAEs) (diethyl phthalate (DEP); dimethyl phthalate (DMP); di-n-butyl phthalate (DBP); butyl benzyl phthalate (BBP); bis(2-ethylhexyl) phthalate (DEHP); di-n-octyl phthalate (DnOP)) in source waters was conducted in China. The results showed these PAEs were ubiquitous in source waters. DBP and DEHP were the most frequently detected with high concentrations ranging nd–1.52 µg/L and nd–6.35 µg/L, respectively. These PAEs concentrations (except DBP) in surface water (rivers, lakes and reservoirs) were generally higher than those in groundwater; DBP had high concentrations in groundwater in Northeast China (Liao River Basin) and North China (Hai River Basin). Their concentrations in the northern regions were generally higher than those in the southern and eastern regions; particularly, in North China. Three short-chain PAEs (DMP, DEP and DBP) were detected with high concentrations in Hai River Basin, Pearl River Basin and Yellow River Basin.

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## 1. Introduction

Since 1930, phthalic acid esters (PAEs) have been widely used as plasticizers that are added to polymers for increasing the plasticity and toughness of consumer products and industrial products (Latini, 2005), including cosmetics, personal care products, cleaning products, medical devices, food packages, vinyl toys, etc ([www.toxtown.nlm.nih.gov](http://www.toxtown.nlm.nih.gov)). Some PAEs have been proved to possess reproductive and developmental toxicities to animals (Howdeshell et al., 2008; Kondo et al., 2006; Lovekamp-Swan and Davis, 2003), and are suspected of endocrine disrupting effects on humans (Latini, 2005; Lyche et al., 2009; Matsumoto et al., 2008). Therefore, some countries have limited the usage of PAEs (EC, 2003; EC, 2005; PRC-NS, 2008). In spite of this restriction, worldwide annual consumption of PAEs has been steady for 20 years (Peijnenburg and Struijs, 2006) and approximately 5 million tons was used in 2010 (Guo et al., 2012). PAEs are readily released to the environment during the production, usage and final disposal of plastic consumer products and industrial products because they are not chemically bound to polymers. In addition, these pollutants are refractory to biodegradation in the environment by microorganisms, leading to

their widespread presence in the environment (Abdel daiem et al., 2012). Therefore, due to the high consumption, the continuous release to the environment and their resistance to microbial decomposition, many PAEs are found to be ubiquitously present in water, air and food (Fierens et al., 2012; Kang et al., 2012; Kolpin et al., 2002).

In China, over one million tons of PAEs is consumed per year (Zhang, 2004), accounting for one-fifth of the global consumption, leading to massive release of PAEs to the environment. Thus, there is an urgent need to investigate the levels of PAEs in the environmental media in China. The water environment is a major sink of PAEs, receiving the wastewater effluent, landfill leachate and atmospheric precipitation, and various PAEs have been detected in rivers, lakes, reservoirs and groundwater in China (Chen et al., 2012; Wang et al., 2006; Zeng et al., 2009; Zhang et al., 2009). However, there has been no systematic monitoring of occurrence of PAEs at a national scale for identifying their potential risk levels. In China the Environmental Quality Standards for Surface Water (PRC-NS, 2002) and Standards for Drinking Water Quality (PRC-NS, 2006) have regulated the limit values for two PAEs (DEHP = 8 µg/L and DBP = 3 µg/L) and three PAEs (DEHP = 8 µg/L, DBP = 3 µg/L and DEP = 300 µg/L), respectively. The nationwide monitoring data is not available to provide the information to the policy makers when deciding whether to modify the current standards or set new standards for other PAEs. Thus, supported by the Ministry of

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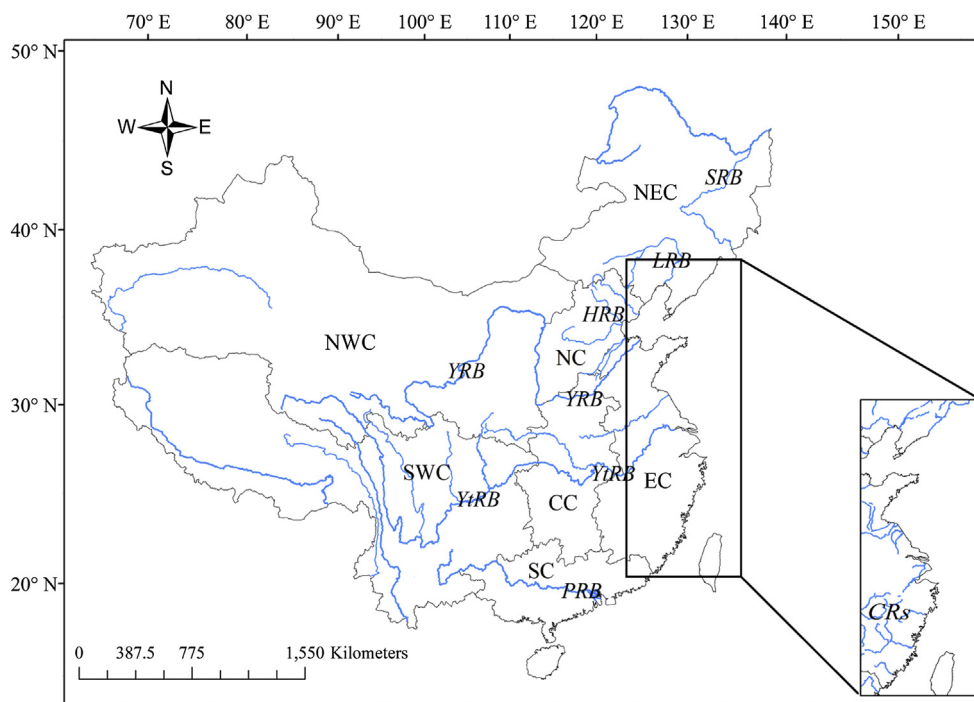


Fig. 1. Sampling locations of surface- and ground-source waters in China. The region in the box exhibits those coastal rivers (CRs).

Housing and Urban-Rural Development of the People's Republic of China (MOHURD), the first nationwide survey of PAEs contamination in major drinking water sources was conducted across seven geographical zones and seven major river basins in China from 2009 to 2012.

Currently, more than 20 types of PAEs have been found in the environment (Abdel daiem et al., 2012), six of which (DMP, DEP, DBP, BBP, DEHP and DnOP) are in the list of priority pollutants of the US Environmental Protection Agency (Keith and Telliard, 1979), four of which (DBP, DnOP, DEHP and BBP) are in the list of priority pollutant of the European Communities (EC, 1994; EC, 1995; EC, 1997), and three of which (DEP, DBP and DEHP) are in the Environmental Quality Standards for Surface Water (PRC-NS, 2002) and Standards for Drinking Water Quality in China (PRC-NS, 2006). In this study, six PAEs (DMP, DEP, DBP, BBP, DEHP and DnOP) were selected to represent the pollutant levels of PAEs in source waters in China.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Two kinds of EPA PAEs Mix (200 mg/L each component in methanol and 2000 mg/L each component in n-hexane) containing DMP, DEP, DBP, BBP, DnOP and DEHP and the internal standard deuterated bis (2-ethylhexyl) phthalate (DEHP-d<sub>4</sub>) were purchased from Sigma–Aldrich (Bellefonte, PA, USA). Stock solutions of the six PAEs were prepared in HPLC-grade methanol (4 mg/L) and HPLC-grade n-hexane (40 mg/L) and stored at  $-20^{\circ}\text{C}$ . Working standard solutions (10–2000  $\mu\text{g/L}$ ) in n-hexane for direct injection calibration were prepared by serial dilution of the stock solutions and stored at  $4^{\circ}\text{C}$ . Standard solutions in methanol were also prepared for the recovery experiment and stored at  $4^{\circ}\text{C}$ . The organic solvents used in this experiment, including methanol, diethyl ether and n-hexane, were HPLC grade and obtained from Mallinckrodt Baker, USA.

### 2.2. Sampling location and sampling methods

Groundwater and surface water (including river, reservoir and lake water) used for drinking water were targeted in this nationwide survey. The survey of the six PAEs was conducted over the period of December 2009–May 2012 across the seven geographical zones in China: Northeast China (NEC) including Heilongjiang

Province, Jilin Province, Liaoning Province and the eastern region of Inner Mongolia; North China (NC) including Beijing City, Tianjin City, Hebei Province, Shanxi Province and the western region of Inner Mongolia; Northwest China (NWC) including Shānxī Province, Gansu Province, Qinghai Province, Ningxia Hui Autonomous Region and Xinjiang Uygur Autonomous Region; Southwest China (SWC) including Chongqing City, Sichuan Province, Yunnan Province, Guizhou Province and Tibet Autonomous Region; South China (SC) including Guangdong Province, Guangxi Province and Hainan Province; East China (EC) including Shanghai City, Jiangsu Province, Zhejiang Province, Fujian Province, Shandong Province, Anhui Province and Jiangxi Province; Central China (CC) including Henan Province, Hubei Province and Hunan Province (Fig. 1). Meanwhile, this survey covered the national seven major river basins (Hai River Basin, HRB; Liao River Basin, LRB; Songhua River Basin, SRB; Yellow River Basin, YRB; Yangtze River Basin, YtRB; Pearl River Basin, PRB; and Coastal Rivers, CRs) (Fig. 1).

152 water samples including 18 groundwater samples, 64 river water samples and 70 lake and reservoir water samples were taken during two sampling campaigns, in which 80 water samples were taken from December 2009 to March 2011, and the others were taken from August 2011 to May 2012. In the second sampling campaign, 39 water samples were taken at the same sampling sites with the first sampling campaign; 33 water samples were taken at those sampling sites different from the first sampling sites, because some drinking water treatment plants permanently or temporarily changed their water sources. PAEs concentrations in surface water were closely related to seasonal variation; due to the large-scale sampling geographical scope, during the two sampling campaigns, the intensive sampling in each geographical zone were preferentially performed in the same seasons primarily considering to the cost effectively and smoothly complete each sampling campaign in around one year. The specific sampling period of each sampling site was described in Table S1, which shows that the sampling period mainly varied with the geographical zones. The source water samples were collected in Teflon-capped amber glass bottles from each sampling site, and delivered under cooled conditions ( $4^{\circ}\text{C}$  in cooling boxes) to the laboratory immediately for further pretreatment and analysis.

### 2.3. Sample pretreatment

Before extraction, 1 L water sample was passed through glass fiber filters (GF/F, 0.7- $\mu\text{m}$  pore size, Whatman) to remove particulate matter, and then stored in pre-cleaned amber glass bottles. Solid-phase extraction (SPE) with an Oasis HLB cartridge (3 mL, 200 mg, Waters) was conducted to extract the six compounds from the water samples. The HLB cartridge was preconditioned with 5 mL of methanol/diethyl ether (5/95, v/v), 5 mL of methanol and 10 mL of Milli-Q water. The filtered water sample was passed through the HLB cartridge at a flow rate of 5–8 mL/min under a vacuum. When the extraction was completed, the cartridge was dried under a vacuum. The cartridge was then eluted with 6 mL of methanol/diethyl ether (5/95,

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