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Baseline

# Regional distribution of halogenated organophosphate flame retardants in seawater samples from three coastal cities in China

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ABSTRACT

Thirteen samples of seawater were collected from Yellow Sea and East China Sea near Qingdao, Lianyungang, and Xiamen, China. They were analyzed for halogenated organophosphorus flame retardants (OPFRs). The compounds selected for detection were Tris(2-chloroethyl) phosphate (TCEP), Tris(2-chloroisopropyl) phosphate (TCPP), Tris (1,3-dichloro-2-propyl) phosphate (TDCPP), and Tris(2,3-dibromopropyl) phosphate (TDBPP). The total concentrations ranged from 91.87 to 1392 ng/L and the mean concentrations of these four chemicals were 134.44, 84.12, 109.28, and 96.70 ng/L, respectively. TCEP exhibited the highest concentrations, although concentrations of TCPP and TDCPP were also fairly high in Lianyungang and Xiamen. Generally, Lianyungang was the most heavily polluted district, with very high concentrations of TCEP at LYG-2 (550.54 ng/L) and LYG-4 (617.92 ng/L). The main sources of halogenated OPFRs were municipal and industrial effluents of wastewater treatment plants in the nearby economic and industrial zones.

Flame retardants are produced and used in various commercial products to reduce the flammability of plastics, textiles, foams, furniture and other materials made from synthetic polymers (Fries and Puttmann, 2001). Halogenated OPs are typically preferred for use as flame retardants rather than non-halogenated OPs (Cao et al., 2012). The reports which shows that organophosphate esters (OPs) have been widely used as flame retardants and plasticizers first appeared in 1970s (Saeger et al., 1979; Sheldon and Hites, 1978). At present, penta- and octabrominated diphenyl ethers (PBDEs) are being banned or phased out owing to their persistence, bioaccumulation, and toxicity (Moeller et al., 2012); accordingly, the use of organophosphate esters as alternative flame retardants has increased dramatically to meet flammability standards and commercial needs (Kawagoshi et al., 2002). For example, the estimated annual consumption of OPFRs was nearly twice that of all brominated flame retardants (BFRs) in Western Europe (Reemtsma et al., 2008), increasing from 83,000 t/yr in 2001 to approximately 91,000 t/yr in 2006 (EFRA, http://www.cefic-efra.com). In 2007, the production of OPFRs accounted for 20% of the world market (EFRA, http://www.cefic-efra.com) and more than 70,000 t of OPs were produced in China (Wang et al., 2010).

Halogenated OPFRs, which are applied primarily as flame retardants, are highly persistent in the environment (Andresen et al., 2004; Regnery and Puettmann, 2010) and are frequently detected as primary pollutants (Cao et al., 2012; Möller et al., 2012; Stapleton et al., 2009a; Stapleton et al., 2011; van der Veen and de Boer, 2012). Chlorinated OPFRs' carcinogenicity and toxicity were identified to be associated with human health risks (van der Veen and de Boer, 2012). The highly brominated TDBPP (Tris(2,3-dibromopropyl) phosphate) was banned from use in children's pajamas in the late 1970s because of its mutagenic and carcinogenic properties (Dodson et al., 2012). Previous studies have also reported their wide distribution in various environmental media, including indoor air and dust (Ali et al., 2012; Dodson et al., 2012; Reemtsma et al., 2008; Salthammer et al., 2003; Stapleton et al., 2009b; Van den Eede et al., 2012), surface water and groundwater (Andresen et al., 2004; Bacaloni et al., 2007; Fries and Puttmann, 2001; García-López et al., 2007; Martinez-Carballo et al., 2007; Regnery and Puettmann, 2010; Regnery et al., 2011; Wang et al., 2011), wastewater (García-López et al., 2007; Rodil et al., 2005), drinking water (Li et al., 2014), sediment and soil (Cao et al., 2012; Fries and Mihajlovic, 2011; Mihajlović et al., 2011), rain and snow (Regnery and Püttmann, 2009), and even biosamples (Schindler et al., 2009; Sundkvist et al., 2010). However, few studies have described their distribution in marine

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systems; in fact, OPFRs have only been reported previously for the North Sea, where concentrations of TCPP (Tris(2-chloroisopropyl) phosphate), TCEP (Tris(2-chloroethyl) phosphate), and TDCPP (Tris(1,3-dichloro-2-propyl) were found to be 70–300 ng/L, 22–140 ng/L, and 10–15 ng/L, respectively (Andresen et al., 2007; Weigel et al., 2005).

In the present study, the occurrence and distribution of four of the most widely used types of halogenated organophosphates: TCEP, TCPP, TDCPP and TDBPP were investigated based on 13 seawater samples from three coastal cities: Lianyungang, Qingdao, and Xiamen, which are located along the coast from north to south (Fig. 1). Lianyungang and Qingdao are located close to the Yellow Sea, whereas Xiamen lies adjacent to the East China Sea. Many developing and developed cities, including some economic and industrial zones are located in those areas which are inhabited by millions of people. In addition, the two big seas serve as habitats for many marine fish and plants, so pollution in the seawater may pose threat to people through direct contact and dietary exposure. To our knowledge, this is the first report describing the occurrence of OPFRs in seawater areas of China, so the results present in the paper can help to understand the pollution situation and regional distribution of OPFRs around the sea area along the three coastal cities. And the results can also help to Support information for future risk evaluation.

Samples were collected from 2 stations in Qingdao (QD-1 and QD-2), 6 stations in Lianyungang (LYG-1, LYG-2, LYG-3, LYG-4, LYG-5, and LYG-6), and 5 stations in Xiamen (XM-1, XM-2, XM-3, XM-4, and XM-5) (Fig. 1). At each sampling station, a 1 L sample of water was collected in a polypropylene bottle. All samples were stored at 4 °C until pre-treatment within 24 h.

Before extraction, we spike 500 ml seawater samples with 50 ng $d_{27}$-TBP as a surrogate standard, and ENVI-18 (Supelco, 1 g, 6 mL) cartridges were sequentially activated and conditioned with 15 mL n-hexane, 15 mL dichloromethane, 15 mL acetonitrile, and 15 mL Milli-Q water. All of the water samples were then passed through the cartridges at a flow rate of about 5 mL/min. After the samples were loaded, the cartridges were dried under nitrogen and stored in a desiccator before elution. The analytes were eluted with acetonitrile 3 times (3 mL each time). The eluents were concentrated in a rotary evaporator, reduced to dryness under a gentle stream of nitrogen, and then dissolved in 0.5 mL methanol. The sample solution was then transferred to a vial for instrument analysis.

OPFR analysis was performed using a Waters ACQUITY UPLC system equipped with a Waters ACQUITY TQD triple quadrupole mass spectrometer (Waters, Milford, MA, USA). The liquid chromatography (LC) system was equipped with a Waters Xterra® BEH phenyl column (2.1 × 100 mm, 1.7 μm particle size; Waters) at a column temperature of 40 °C. The mobile phases consisted of deionized water (A) and acetonitrile (B), both spiked with 0.1% formic acid (v/v). The mobile phase flow rate was 0.4 mL/min and the following gradient was employed: 5% B linearly ramped to 100% B over 8 min and linearly decreased to 5% B over 1 min, then held for 1 min. A 10 μL aliquot of the sample was injected into the LC system.

The mass spectrometry (MS)/MS system was equipped with an electrospray ionization probe operated in positive mode. The nebulizing and collision gases were high purity nitrogen and argon, respectively. The multiple reaction monitoring (MRM) mode was used for detection and quantification of OPFRs using the most abundant parent and daughter ions for individual OPFR. Other parameters were optimized as follows: capillary voltage, 4.01 eV; source temperature, 100 °C; probe temperature, 300 °C; cone gas flow, 150 L/h; and desolvation gas flow, 700 L/h. The compound-dependent operation parameters and MRM transitions are listed

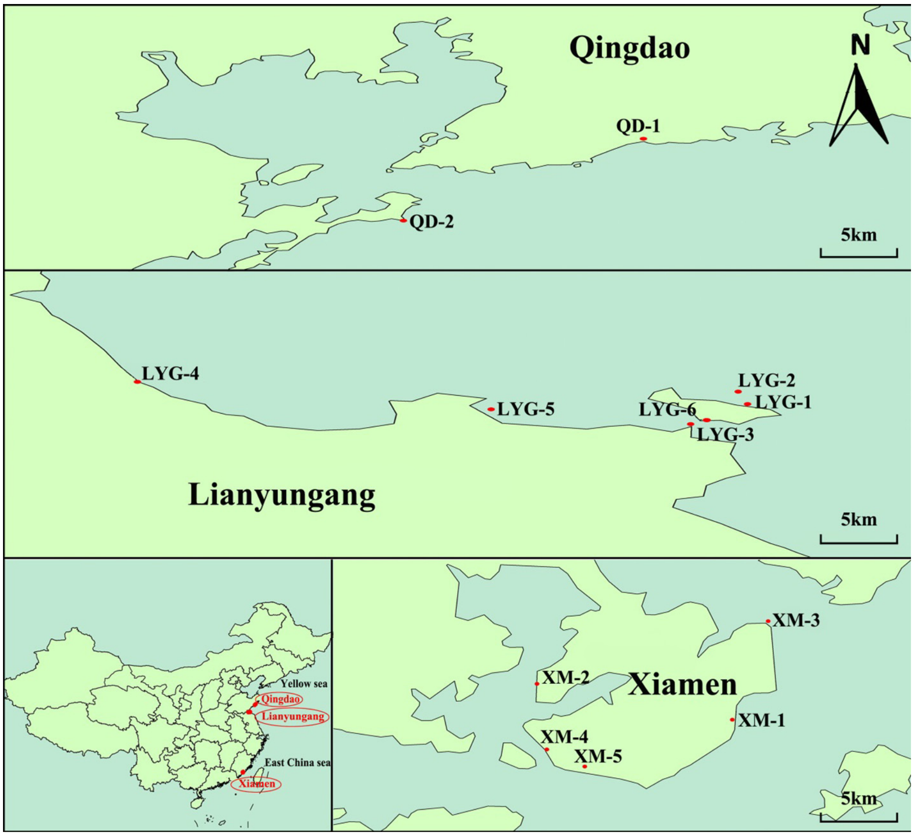

**Fig. 1.** The three cities selected and their respective sampling stations in China.