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Occurrence, distribution, and potential affecting factors of organophosphate flame retardants in sewage sludge of wastewater treatment plants in Henan Province, Central China

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HIGHLIGHTS

- The levels of organophosphate esters (OPEs) in Henan province were lower than those of South China.
- Chlorinated OPEs were predominant in sewage sludge.
- Triphenyl phosphate (TPhP) level in sewage sludge depends on wastewater characteristics.
- The levels of OPEs in sewage sludge were independent of the total organic carbon (TOC) and solid retention time.

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ABSTRACT

Organophosphate esters (OPEs) are widely used as flame retardants. In this study, the occurrence and distribution of six OPEs were investigated in sewage sludge from 24 wastewater treatment plants (WWTPs) in 18 cities of Henan province, Central China. The results indicated that all target OPEs were detected in the sludge samples with the detection rate of 95.8%, except tris(dichloropropyl)phosphate (TDCP). The total concentration of the six OPEs ranged from 38.6 to 508 μg kg^{-1}. Tris(2-*chloroethyl*) phosphate (TCEP), tris(2-*butoxyethyl*)phosphate (TBEP), and tris(2-*chloroiso-propyl*)phosphate (TCPP) were found to be predominant, with concentrations ranging from 2.50 to 203, 1.60 to 383, and 6.70 −161 μg kg^{-1}, respectively. The potential factors affecting OPE levels in sewage sludge, such as wastewater source, sludge characteristics, operational conditions, treatment techniques, and total organic carbon (TOC) of sludge in WWTPs were investigated. The results indicated that the total concentration of OPEs in sewage sludge has no significant relationship with the individual parameters ($p > 0.05$). However, significant correlations were found between triphenyl phosphate (TPhP) level and treatment capacity ($R = 0.484$, $p < 0.05$), processing volume ($R = 0.495$, $p < 0.05$), and serving population ($R = 0.591$, $p < 0.05$). Furthermore, the relationship between treatment techniques and the total concentration of OPEs in sewage sludge was also investigated in this study, and the results illustrated that the levels of OPEs in sludge were independent of the solid retention time (SRT).

1. Introduction

In recent years, with the extensive use of flame retardants and plasticizers, organophosphate esters (OPEs) have regained recognitions and been regarded as a type of reemerging pollutants. While chlorinated OPEs such as tris(2-*chloroethyl*)phosphate (TCEP), tris(chloroisopropyl)phosphate (TCPP), and

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tris(dichloropropyl)phosphate (TDCP) are used as flame retardants, nonhalogenated OPEs such as tris(2-*butoxyethyl*)phosphate (TBEP), tributyl phosphate (TnBP), and triphenyl phosphate (TPhP) are mainly used as plasticizers, lubricants, antifoaming agents, and additives (Andresen et al., 2004). Because of the ban on the use of some polybrominated diphenyl ethers (PBDEs), mainly including penta-BDE, octa-BDE, and deca-BDE, in the European Union since 2008 (Betts, 2008), the use of OPEs as flame retardants has been increasing worldwide. Most OPEs have been regarded as high-production volume chemicals, with volumes exceeding 1000 t per year in Western Europe (Marklund et al., 2005; Stapleton et al., 2011).

As OPEs are not chemically bound to the appliances, these compounds can be released into the environment by volatilization, abrasion, and dissolution, and undergo long range atmospheric transportation (Reemtsma et al., 2008; Lai et al., 2015). Therefore, OPEs have been widely detected in the aquatic (Peverly et al., 2015; Zeng et al., 2014), terrestrial (Matsukami et al., 2015), and atmospheric environments (Mizouchi et al., 2015). There is an increased risk of exposure of OPEs to people, as previous studies have reported the presence of OPEs and their metabolites in human hair, nail (Liu et al., 2015; Cequier et al., 2015), and urine (Cequier et al., 2014). Extensive studies have already been conducted on the occurrence of OPEs, indicating that municipal wastewater from wastewater treatment plants (WWTPs) were the main contributors of OPEs to the aquatic environment (Fries and Puttmann, 2003, 2001). It was reported that the concentrations of OPEs were in the range of nanograms per liter to a few micrograms per liter in WWTP influents and effluents from different countries, such as South Korea (92–2620 ng L^{-1}) (Kim et al., 2007), Austria (20–900 ng L^{-1}) (Martinez-Carballo et al., 2007), Spain (20–3700 ng L^{-1}) (Rodil et al., 2009; Garcia-Lopez et al., 2008), Germany (25–62,000 ng L^{-1}) (Rodil et al., 2005; Bester, 2005; Quintana et al., 2006), and Sweden (40–3000 ng L^{-1}) (Marklund et al., 2005). Some OPEs, particularly hydrophobic OPEs, with low biodegradation and high bonding capacity to organic matters, are prone to be absorbed by organic compounds (Pang et al., 2013), which is considered as an important reason for the decrease of OPE concentrations in WWTP effluents (Bester, 2005; Marklund et al., 2005). Because of their high adsorption capacity onto sludge, the concentration of OPEs in sludge is relatively higher, in the range of micrograms per kilogram to a few milligrams per kilogram, such as in Sweden (2.2–4600 ng g^{-1}) (Marklund et al., 2005), Germany (1700–5100 ng g^{-1}) (Bester, 2005), Norway (3870–4810 ng g^{-1}) (Green et al., 2008), and South China (96.7–1312.9 μg kg^{-1}) (Zeng et al., 2014). The untreated sewage sludge directly discharged into the environment causes serious environmental problems. Thus, it is necessary to investigate the pollution due to OPEs in China. Henan province is located in Central China, which is the main grain-producing area, and the industrial sector has been developing fast in the recent years. This study aimed to investigate the occurrence and distribution of six common OPEs in the sewage sludge from 24 WWTPs in 18 cities of Henan province. It also assesses the potential factors affecting the levels of OPEs in sewage sludge in selected WWTPs. As the number of studies on pollution cause by OPEs in China is limited, this study helps to realize the pollution levels, occurrence, and distribution of OPEs, particularly in Central China.

2. Material and methods

2.1. Chemicals and reagents

Six organophosphates of flame retardant standard were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany): TCEP, TCPP, TDCP, TnBP, TPhP, and TBEP. Surrogate tri-*n*-butyl-d_{27} phosphate (TnBP-d_{27}, 98%) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Acetonitrile (ACN), ethyl acetate, and methanol were obtained from Fisher Scientific (Shanghai, China), and all solvents used in this study were of chromatographic grade. Ultrapure water (18.2 MΩ) was provided by Milli-Q Gradient system (Millipore, Bedford, MA, USA) in our laboratory. Individual OPE stock solutions (1000 mg L^{-1}) were prepared in ACN. The mixed stock solution containing 10 mg L^{-1} each of the six OPEs was prepared by diluting the stock solutions with water/ACN (50/50, v/v). All the stock solutions were stored in the dark at $4^{O}C$.

2.2. Sample collection

The sampling map and locations are shown in Fig. 1. A total of 24 sewage sludge samples were collected from different WWTPs in 18 cities in Henan province during the period of January to March 2015. Treatment technique, sewage sources, treatment capacity, serving population, and total organic carbon (TOC) values of sludge samples in each WWTP are summarized in Table S1.

The sludge samples collected in this study were dewatered ones, which were stored in glass bottles. They were stored at $-20^{O}C$ until analysis. The samples were then freeze-dried and ground fine. After sieved through 100 mesh, the sludge samples were stored in amber glass bottles until extraction. Glasswares were used in this study instead of plastic containers to avoid the interference of OPEs.

2.3. Sample pretreatment

The target OPEs were extracted using ultrasonic assistance according to the published procedures with minor modifications (Cao et al., 2012). In brief, 0.5 g of dry sludge from each sample was spiked with 10 μL of TnBP-d_{27} at 5 mg L^{-1} as surrogate and then extracted by ultrasonic assistance with 20 mL of ACN/water (25/75, v/v) at ambient temperature for 30 min. The extract was centrifuged at 9000 rpm and $20^{O}C$ for 15 min by using polytetrafluoroethylene (PTEF) centrifuge tube, and the supernatant was decanted into a 500 mL volumetric flask. This process was performed thrice and the combined extract was diluted to 500 mL by ultrapure water. Oasis HLB extraction cartridges (200 mg, 6 mL) were used for further separation and concentration. Before loading the water samples, the solid-phase extraction (SPE) cartridges were preconditioned with 4 mL of ACN and water sequentially. After loading, the cartridges were washed with 3 mL of water and dried with air for 10 min. The enriched analytes were eluted twice with 8 mL of ACN. After being concentrated to almost dryness with a gentle flow of N_2 using a nitrogen evaporator (Anpel, Shanghai, China), the resulting extract was subsequently diluted to approximately 500 μL with ACN/water (50/50, v/v), and an aliquot (10 μL) of the solution was injected into the high-performance liquid chromatography-electrospray ionization (HPLC–ESI) MS/MS (ACQUITY UPLC, Waters, USA) system for analysis. The detection parameters of the samples under study are shown in Table S2.

TOC was measured as the CO_2 content on acid-treated samples using a solid TOC analyzer (Shimadzu SSM-5000A, Japan). TOC concentration was calculated by the summation of organic and inorganic carbons.

2.4. Quantitation and quality control

Field blanks ($n = 4$), procedural blanks ($n = 4$), spiked blanks ($n = 4$), spiked matrix ($n = 4$), and replicate samples ($n = 7$) were analyzed with extraction to control contamination. In each spiked sample, 50- and 100-ng mixtures of six OPEs were added. All samples were spiked with TnBP-d27 as surrogate. TBEP and TnBP were not found in the blank; TPhP was found at the limited of