Occurrence and distribution of organophosphate triesters and diesters in sludge from sewage treatment plants of Beijing, China

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HIGHLIGHTS

- Organophosphate (OP) triesters are flame retardants of emerging concern.
- Repeated samples of sewage sludge were taken from eight different STPs 2008–2014.
- OP di- and triesters were simultaneously detected in sludge for the first time.
- Potential risks of OP triesters in sludge were identified.

GRAPHICAL ABSTRACT

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ABSTRACT

The occurrence and distribution of 14 organophosphate (OP) triesters and 5 diesters were investigated in sludge from eight sewage treatment plants (STPs) in Beijing, China, during 2008–2014. Tri(2-ethylhexyl) phosphate (TEHP) and tri-m-cresyl phosphate (TCrP) were the predominant triesters with the average concentration of 233–137 µg/kg, respectively. Also, the polar and hydrophilic trimethyl phosphate (TMP) and triethyl phosphate (TEP) were detected in 19% and 74% of sludge samples, respectively. Three of five diesters were detected in sludge samples, and di(2-ethylhexyl) phosphate (DEHP) revealed the highest average concentration of 96.0 µg/kg, followed by diphenyl phosphate (DHP), 18.0 µg/kg. The levels of OP triesters in sludge varied with the compositions of the sewage and treatment capacity of STPs, as well as the adjacent sources. In comparison with that in the former years, relatively higher concentration of total OP triesters in sludge was observed in 2014, which is consistent with the rapid growth in consumption of these chemicals in China. Finally, environmental risk assessment indicated potential harmful effects of OP triesters on soil microorganisms after sludge landfill or fertilization.

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1. Introduction

Organophosphate (OP) triesters are extensively used as flaming retardants and plasticizers in many products such as building materials, cables, insulation materials, electronic goods, furniture and textiles (Reemtsma et al., 2008; Brandsma et al., 2013). In addition, some of them are also used as anti-wear additives or extreme pressure agents in hydraulic fluids and lubricants, and non-ionic extractants in hydrometallurgy as well as anti-foaming agents in floor polishing (Reemtsma et al., 2008; Salamova et al., 2014). As the restriction on the application of polybrominated diphenyl ethers (PBDEs), global consumption of OP triesters has increased sharply in recent years (Reemtsma et al., 2008; Wei et al., 2015). The consumption of OP triesters only as flame retardants is approximately 91,000 t in 2006 in Western Europe, which reveals an increase by 7% compared with that in 2005 (Reemtsma et al., 2008). In 2011, phosphorus flame retardants reveal the rapid increase in market when compared with brominated flame retardants in Europe (EFRA, 2012). According to the data from European Flame Retardants Association (EFRA), China, North America and Western Europe are the highest consumption countries and regions for flame retardants, accounting for approximately 60% of global consumption (EFRA, 2012). According to the reports, the annual yield of organophosphate flame retardants reaches up to 70,000 t in 2007 with the predicted increase by 15% annually in China (Wei et al., 2015).

Previous studies have suggested that several OP triesters can be harmful to human and ecological health. For instance, the occurrence of triphenyl phosphate (TPhP) in dust has been reported to be associated with the decrease of human sperm concentration (Meeker and Stapleton, 2010). Tri(2-chloroethyl) phosphate (TCEP) and tri-*n*-butyl phosphate (TnBP) are reported to have neurotoxic properties after chronic exposure (Yang et al., 2014). TCEP and tris(1,3-dichloro-2-propyl) phosphate (TDCP) have been proven to be carcinogenic (Brandsma et al., 2014; Wang et al., 2015), while tri(2-chloroisopropyl) phosphate (TCPP) and tributoxylethyl phosphate (TBEP) are also suspected as carcinogens (Brandsma et al., 2014; Venier et al., 2014; Wang et al., 2015). Additionally, chlorinated alkyl phosphates are considered as persistent pollutants due to their resistance to degradation (Kawagoshi et al., 2002; Meyer and Bester, 2004; Bollmann et al., 2012; Gao et al., 2013).

So far, many of these contaminants have been detected in wastewater (Marklund et al., 2005a; Martinez-Carballo et al., 2007), surface water (Regnery and Puttmann, 2010; Bollmann et al., 2012; Cristale et al., 2013; Wang et al., 2015) and drinking water (Stackelberg et al., 2004; Andresen and Bester, 2006), as well as soil (Fries and Mihajlovic, 2011; Mihajlovic and Fries, 2012) and dust samples (Kim et al., 2013; Abdallah and Covaci, 2014; Zheng et al., 2015). It has been reported that several OP triesters cannot be completely eliminated in municipal sewage treatment plants (STPs) (Meyer and Bester, 2004; Marklund et al., 2005a), and then are discharged into receiving rivers and soil subjected to reclaimed water irrigation or sludge treatment. Therefore, STPs may play a significant role in the life cycle of this family of chemicals since they act as sink and point source for the environment. In STPs, the absorption of activated sludge is one of effective ways to remove OP triesters from wastewater, suggesting that sludge may serve as an important reservoir of these compounds, especially for hydrophobic ones. Up to now, several OP triesters, including TCPP, TCEP, TBEP and TnBP, have been determined at $\mu\text{g/L}$ levels in influents and effluents of STPs (Paxeus, 1996; Meyer and Bester, 2004; Bester, 2005; Marklund et al., 2005a; Martinez-Carballo et al., 2007). However, only limited studies have demonstrated the levels of OP triesters in sewage sludge (Bester, 2005; Marklund et al., 2005a; Cristale and Lacorte, 2013; Zeng et al., 2014).

In addition, investigations of STP influents and effluents have suggested that some triesters may be biodegraded into diesters during sewage treatment processes (Reemtsma et al., 2008). In addition, several diesters, particularly di-*n*-butyl phosphate (DnBP) and di(2-ethylhexyl) phosphate (DEHP), are often employed as ionic extractants in

hydrometallurgy or plasticizers (Quintana et al., 2006). In order to thoroughly identify the fate of OP triesters in STPs, the studies regarding to the occurrence of both OP triesters and diesters in sludge are needed. According to our current knowledge, there have no studies on the concentrations of both OP triesters and diesters in sludge from multiple STPs; usually only OP triesters in one or a few of STPs with a single sampling campaign have been studied. Therefore, it is worthwhile to get more information on OP triesters and diesters to fill our knowledge gaps of the fate of OP triesters in STPs.

Beijing is one of the most populated and developed cities in China, with total dimension of 16,410.54 km^2 and a huge population of 21.516 million. There is mature sewage treatment system in this high-density city, which contains 9 STPs in the central urban area with the sewage treatment capacity of 2,560,000 m^3/d and the sludge amount of 2500 t/d in 2010 (Xing et al., 2012). The aim of this study is to investigate the occurrence and distribution of both OP triesters and diesters in sewage sludge. In the present study, the levels of 14 OP triesters and 5 diesters were determined in sewage sludge from eight STPs in Beijing, China. The concentration among different STPs and temporal variation of these compounds were studied. Meanwhile, environmental risks of OP triesters in sewage sludge were assessed. According to our knowledge, this is the first study focusing on both OP triesters and diesters in sewage sludge, and it will greatly contribute to understand the fate of OP triesters in STPs.

2. Experimental

2.1. Chemicals and materials

OP triesters: TMP, TEP, TCEP, TCPP, TDCP, TBEP, TnBP, TiBP, TPhP, TPrP, TCrP, CDPP, EHDPP and TEHP were obtained from Dr. Ehrenstorfer GmbH (Germany), and detailed information on their names and molecular weights was listed in Table S1 (Supplementary material). Internal standards (IS): TMP- d_9 , TEP- d_{15} and TPrP- d_{21} were purchased from C/D/N Isotopes Inc. (USA), and TnBP- d_{27} and TPhP- d_{15} were obtained from Cambridge Isotope Laboratories (UK). Individual stock solution with the concentration of 1000 mg/L was prepared in acetonitrile. Mixed stock solution containing all analytes was also prepared in acetonitrile at the concentrations of 10 mg/L. All stock solutions were kept in a -20°C refrigerator.

OP diesters: BDCPP, DnBP, DPhP and DEHP, as well BDCPP- d_{10} and DPhP- d_{10} were purchased from Toronto Research Chemicals (TRC, Canada). The standard of DiBP was not commercially available and obtained by chemical synthesis. The detailed information about the synthetic process of DiBP was listed in the Supplementary material. Individual stock solutions were prepared in methanol and mixed stock solutions containing all analytes were prepared in methanol at the concentration of 10 mg/L. All stock solutions were kept in a -20°C refrigerator.

Dichloromethane (DCM), acetonitrile and methanol (HPLC grade) were provided by Fisher Scientific (USA), and ammonium acetate was bought from Alfa Aesar (USA). Ultrapure water (18.3 M Ω) produced with a Milli-Q Gradient system (Millipore, Bedford, USA) was used.

2.2. Samples

A total of 43 anaerobically digested sludge samples after filter pressing (50–60% water content) were collected from eight STPs (A–H) in Beijing at five individual time points (January 15, May 28 and September 24 in 2008, October 15 in 2009, May 13 in 2010, and April 10 in 2014). The sampling sites were shown in Fig. S1 (Supplementary material). These sludge samples were collected in polyethylene bags and immediately freeze-dried after being delivered to the laboratory. The sludge was ground and sieved to smaller than 0.44 mm, and then stored at -20°C until analysis.

The eight STPs have different treatment capacities (average daily flow from 0.01 to 1.0 million m³/d) and serve different numbers of residents. All STPs employ activated sludge process to remove biologically degradable organic materials. Details associated with STPs were listed in Table 1.

2.3. Sample preparation

OP triesters: Totally 0.1 g of dry sludge samples was weighed, and 10 ng of IS were added in sludge samples. After mixing and aging for 24 h, the samples were extracted through shaking for 12 h with 10 mL of acetonitrile, and then centrifuged at 4000 r/min. The extract was concentrated to 1 mL at 37 °C under a stream of N₂, diluted to approximately 50 mL with ultrapure water, and then purified using SPE technology with ENVI-18 cartridges (6 mL, 500 mg; Supelco). ENVI-18 cartridges were conditioned with 5 mL of acetonitrile and 5 mL of ultrapure water sequentially. Then, 50 mL of samples were passed through the cartridges at a flow rate of 4 mL/min. After that, the cartridges were rinsed with 10 mL of ultrapure water, dried for 30 min, and finally eluted with 6 mL of 25% DCM in acetonitrile. The eluent was finally condensed to approximately 0.4 mL at 37 °C under a stream of N₂ and diluted to a final volume of 1 mL with ultrapure water.

OP diesters: Totally 0.1 g of dry sludge samples was weighed, and 50 ng of DPHP-d₁₀ and 500 ng of BDCPP-d₁₀ were added in sludge samples. After mixing and aging for 24 h, the samples were subjected to ultrasonic extraction with 4 mL of methanol for 20 min, and then centrifugation at 4000 r/min. Then, the extraction process was repeated twice. The extract was combined and condensed to 1 mL at 37 °C under a stream of N₂, diluted to approximately 50 mL with ultrapure water, and then purified using SPE technology with HLB cartridges (6 mL, 200 mg; Waters). HLB cartridges were conditioned with 5 mL of methanol and 5 mL of ultrapure water sequentially. Then, 50 mL of samples were passed through the cartridges at a flow rate of 4 mL/min. After that, the cartridges were rinsed with 10 mL of ultrapure water, dried for 30 min, and finally eluted with 6 mL of methanol. The eluent was finally condensed to approximately 0.5 mL at 37 °C under a stream of N₂ and diluted to a final volume of 1 mL with ultrapure water.

Total organic carbon (TOC) of sludge was measured as CO₂ in acid-treated samples with a Solid TOC Analyzer (O.I. Analytical Co., USA).

2.4. LC–MS/MS analysis

Analytes were separated using a high-performance liquid chromatography system equipped with an Ultimate 3000 pump and autosampler (ThermoFisher, USA). A triple-quadrupole mass spectrometer (API 3200; Applied Biosystems/MDS SCIEX, USA) was connected with HPLC for the determination of analytes.

Table 1

The information of eight STPs involved in this study.

STPs	Treatment techniques	Sewage source	Treatment capacity (10 ⁴ m ³ /d)	Inhabitants (10 ⁴)	HRT (h)	SRT (d)
A	AAO	dom/ind	100	240	9	10–12
B	MBR	dom/ind	10	40	6–7	5.2
C	AAO	dom	4	10	9.7	10
D	OD	dom/ind	20	48	8–11	10.2–18
E	AAO	dom	55	81.4	13.5	12.2–17
F	SBR	dom	8	18	7	11
G	AAO	dom	60	192	12.5	12
H	SBR	dom	1	5	–	–

AAO: anaerobic–anoxic–oxic; MBR: membrane bio-reactor; OD: oxidation ditch; SBR: sequencing batch reactor.

OP triesters: Acclaim Mixed-Mode HILIC-1 column (2.1 mm × 150 mm, 5.0 μm; Thermo, USA) with the binary mobile phase of pure water (A) and acetonitrile (B) was used for the analysis of OP triesters. The column temperature was kept at 25 °C and an injection volume of 15 μL was used. The Mixed-Mode HILIC-1 column was performed at a flow rate of 0.25 mL/min and the gradient was set as follows: the initial 40% B was maintained for 1.0 min; then increased linearly to 60% in 4 min; followed by an increase to 100% B in 3 min and held for 7 min. Finally, the gradient was returned to the initial conditions of 40% B in 0.2 min and held for 6.8 min to allow for equilibration. The electrospray ionization was operated in a positive ion mode with the ion spray voltage of 5.0 kV, source temperature of 600 °C, collision gas pressure of 0.02 MPa and curtain gas of 0.14 MPa. Individual MS/MS parameters for each compound were shown in Table S2.

OP diesters: Luna Phenyl-Hexyl column (2.0 mm × 150 mm, 5.0 μm; Phenomenex, USA) with the binary mobile phase of 50 mM ammonium acetate in water (A) and 100% methanol (B) was used for the analysis of OP triesters. In addition to the column temperature of 25 °C and injection volume of 15 μL, the column was performed at a flow rate of 0.2 mL/min and the gradient was set as follows: the initial 50% B was increased linearly to 100% in 1 min and held for 10 min; then the gradient was returned to the initial conditions of 50% B in 0.5 min and held for 8.5 min to allow for equilibration. The electrospray ionization was operated in a negative ion mode with the ion spray voltage of –4.5 kV, source temperature of 500 °C, collision gas pressure of 0.02 MPa and curtain gas of 0.07 MPa. Individual MS/MS parameters for each compound were shown in Table S2.

2.5. Quantitation and quality control

OP triesters: The calibration curve was prepared within a wide range of concentrations to reveal strong linearity ($R = 0.9874–0.9985$). The limits of detection (LODs) defined as the lowest concentration with a signal-to-noise ratio (S/N) of 3 were 0.41–24.7 μg/kg (dry weight, dw) for sludge samples. Recovery rates of OP triesters for sludge samples ranged from 59.4% to 113.9%, with the relative standard deviations (RSD) of 1.2–19.5%. Detailed information was listed in Table S3.

OP diesters: The calibration curve was also prepared within a wide range of concentrations to reveal strong linearity ($R = 0.9931–0.9948$). The limits of detection (LODs) were 0.03–5.45 μg/kg (dw) for sludge samples. Recovery rates of OP triesters ranged from 60.6% to 105.3%, with the relative standard deviations (RSD) of 4.5–10.5%. Detailed information was listed in Table S3.

In view of the wide distribution of OP triesters in dust, plastics and glass, all equipment and containers were rinsed with methanol and water before use to avoid analytical interference and/or cross contamination. Additionally, procedural blanks were analyzed to control laboratory contamination. A 10 μg/L standard was set as the quality control, which was checked every 10 injections to ensure analysis stability and verify calibration.

2.6. Risk characterization

Ecotoxicological risk of OP triesters in sewage sludge was evaluated by risk quotient values (RQs) (Li et al., 2012; Cristale et al., 2013). RQ value of each compound in sewage sludge was calculated using following formula: $RQ = MEC/PNEC$, where MEC is the measured environmental concentration in sludge, and PNEC is the predicted no effect concentration (EC, 2011).

In risk assessment studies, common criteria for risk levels were established by interpreting RQ values: low risk (RQ value from 0.01 to 0.1), medium risk (RQ value between 0.1 and 1) and high risk (RQ value higher than 1) (Hernando et al., 2006; Van Doorslaer et al., 2014; Venier et al., 2014).

3. Results and discussion

3.1. Levels of OP triesters in sludge

Thirteen OP triesters except TPrP were detected in sewage sludge from STPs in Beijing, and this is the first time for the quantification of TEHP, TCrP, CDPP, TMP and TEP in sludge samples. As shown in Table 2, the total concentration of OP triesters ranged in 204–4101 µg/kg (dw) and 128–2563 µg/kg (wet weight, ww), respectively. Compared to brominated flame retardants, the sum of OP triesters in our study was higher than that of PBDEs detected in sewage sludge from China (5.1–1114.9 µg/kg, dw) (Wang et al., 2007), Sweden (nd–450 µg/kg, ww) (Oberg et al., 2002) and Germany (142–2491 µg/kg, dw) (Knoth et al., 2007).

In this study, TEHP, TCrP and TBEP were the most abundant analytes in sludge samples with the detection frequency of 100%, accounting for an average of 64.6% of the sum of OP triesters in sludge samples. TEHP and TCrP were rarely detected in wastewater samples (Marklund et al., 2005a; Martinez-Carballo et al., 2007), so their high levels in sludge may be explained by their strong absorption tendency, which can be deduced from their high values of Log_{K_{ow}} (9.49 and 5.11, respectively). In addition, TCPP, TBEP, EHDPP and TnBP are reported to be the dominant compounds in sludge in previous studies (Bester, 2005; Marklund et al., 2005a; Green et al., 2008; Cristale and Lacorte, 2013). Thus, the high levels of TEHP and TCrP in sludge from STPs in Beijing may also result from the different use patterns in regions.

In the present study, the concentrations ranged from 46.0 to 1200 µg/kg for TEHP, from 3.7 to 3550 µg/kg for TCrP, and from 6.3 to 281.4 µg/kg for TBEP, respectively. The level of TCrP in sludge from STPs in Beijing was higher than that detected in STPs in the south of China (LOQ–265.0 µg/kg) (Zeng et al., 2014). While the TBEP concentration in our study was lower than that detected in Swedish STPs (<5.1–1900 µg/kg) (Marklund et al., 2005a) and in STPs in the south of China (25.1–783.7 µg/kg) (Zeng et al., 2014).

The concentrations of TnBP (1.2–285.9 µg/kg) and TiBP (<LOD–473.7 µg/kg) in our study were similar to those detected in STPs in Norway (TnBP: 69–270; TiBP: 52–81 µg/kg) (Green et al., 2008), but much lower than those detected in sludge from Swedish STPs (TnBP: 39–850; TiBP: 27–2700 µg/kg) (Marklund et al., 2005a) and from STPs in the south of China (TnBP: 7.1–804.9 µg/kg) (Zeng et al., 2014). The concentrations of TPhP (4.4–66.8 µg/kg) and EHDPP (<LOD–139 µg/kg) in this study were also much lower than those detected in previous studies in Sweden (Marklund et al., 2005a), Norway (Green et al., 2008) and south of China (Zeng et al., 2014).

Table 2
Concentrations of OP triesters determined in sewage sludge from STPs of Beijing, China (µg/kg).

Analytes	Dry weight (dw)				Wet weight (ww)				Fre. (%)
	Max.	Min.	Mean	Med.	Max.	Min.	Mean	Med.	
TMP	10.0	<LOD	1.20	<LOD	6.30	<LOD	0.80	<LOD	19
TEP	366	<LOD	22.2	4.60	229	<LOD	13.9	2.90	74
TPrP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0
TCEP	208	<LOD	22.4	17.9	130	<LOD	14.0	11.2	58
TPhP	66.8	4.40	25.0	21.6	41.7	2.80	15.6	13.5	100
TCPP	378	<LOD	50.1	<LOD	236	<LOD	31.3	<LOD	49
CDPP	29.3	<LOD	5.60	3.80	18.3	<LOD	3.50	2.40	93
EHDPP	139	<LOD	24.0	21.4	86.9	<LOD	15.0	13.4	63
TCrP	3550	3.70	137	30.0	2219	2.30	85.6	18.8	100
TBEP	281	6.30	90.0	64.9	176	3.90	56.2	40.6	100
TDGP	63.3	<LOD	14.4	15.7	39.6	<LOD	9.00	9.80	53
TEHP	1200	46.0	232	166	750	28.7	145	104	100
TnBP	286	1.20	29.6	17.4	179	0.70	18.5	10.9	100
TiBP	474	<LOD	17.7	4.40	296	<LOD	11.1	2.80	86
Total	4100	204	699	521	2563	127	437	326	100

<LOD: concentration below the limit of detection.

The concentrations of <LOD–208.3, <LOD–378.0 and <LOD–63.3 µg/kg were determined for TCEP, TCPP and TDCP, respectively, with the detection frequency lower than 60% in this study. Similar level of TCEP has been reported in sewage sludge from Swedish STPs (6.6–110 µg/kg) (Marklund et al., 2005a), whereas the levels of TCPP and TDCP in our study were much lower than those in STPs from Sweden (TCPP: 61–1900; TDCP: 3.3–260; µg/kg) (Marklund et al., 2005a), Germany (TCPP: 1000–20,000 µg/kg) (Bester, 2005), Norway (TCPP: 650–944; TDCP: 110–330 µg/kg) (Green et al., 2008) and Spain (TCPP: 600–2900; TDCP: 92.0–600 µg/kg) (Cristale and Lacorte, 2013; Wei et al., 2015). However, concentrations of chlorinated OP triesters in this study were slightly higher than those found in STPs in the south of China (Zeng et al., 2014).

In our study, the polar and hydrophilic OP triesters, TMP and TEP, were detected in 19% and 74% of sludge samples, with the concentration of <LOD–10 and <LOD–366 µg/kg, respectively. It has been previously demonstrated that the hydrophobicity of OP triesters dominated their adsorption on carbon nano tube (CNT) (Yan and Jing, 2014). The presence of TMP and TEP in sludge samples in our study suggested that other mechanisms except hydrophobic effects could also play an important role for the adsorption of these chemicals onto sludge.

3.2. Concentrations of OP triesters from different STPs and temporal variation

As illustrated in Fig. 1, there was no significant difference in total levels of OP triesters from STP A to STP G ($p > 0.05$). While elevated total concentration was observed at STP H, which was one order of magnitude higher than other STPs. Besides, the compositions of OP triesters in this STP were different from others, considering that TCrP and TEP accounted for significantly higher proportion at STP H (Fig. 1). Additionally, significantly positive correlations between TCrP and TEP levels in sludge samples were observed ($r = 0.645$, $p < 0.01$), suggesting their similar sources. TCrP and TEP can be used as plasticizers in polyvinylchloride, and TCrP is also widely used in hydraulic fluids, cutting oils, and transmission fluids (Schindler et al., 2013; Wei et al., 2015). TCrP has previously been detected in snow samples from an airport and road intersection (9.9 µg/kg) (Marklund et al., 2005b). Based on our knowledge, STP H was one of STPs with the smallest treatment capacity (10,000 m³/d), and located in an industrial area near a railway

Fig. 1. Comparison of OP triester concentration in sludge from different STPs.

station in Beijing. Therefore, the unusually high level of OP triesters in STP H, especially TCrP, is probably related to the wastewater of railway station and nearby industries. The maximum concentration of TBEP was detected at STP A, the biggest STP with the treatment capacity of $1 \times 10^6 \text{ m}^3/\text{d}$ and the serviced population of 2.4 million. TBEP is usually used as an ingredient in floor waxes and floor Polish, and has been reported as the most abundant OP triester in indoor dust (Marklund et al., 2003). Therefore, TBEP may be likely to reach STPs via cleaning water from buildings, and reveal higher concentration in the STP with greater treatment capacity, especially for domestic sewage.

In the present study, temporal variation of OP triesters in sludge during four sampling years was statistically analyzed as box-and-whisker plots (Fig. 2). The result showed a gradual increase in total levels of OP triesters in sludge from 2008 to 2014. Additionally, the concentrations of TEHP, CDPP, TnBP and TiBP were also increased with years. This may be attributed to the increased consumption of OP triesters in recent years in China. On account of the strengthening of fire protection safety in public places in China and the global trends of non-halogen fire retardants, the production of OP triesters reveals the rapid increase with an expected growth rate of more than 15% (Ou, 2011). In contrast, the concentrations of TCrP and TBEP exhibit the gradual decrease over time, which may be explained by the change in usage patterns in materials, while the concentration of TPhP fluctuates with time and no clear trend can be observed.

3.3. OP diesters in sludge

In this study, DEHP and DPhP were detected in 100% of sludge samples at the concentration of 11.2–275 and 5.18–96.4 $\mu\text{g}/\text{kg}$ (dw), respectively (Table 3). In contrast, DnBP was only detected in 20.9% of samples at the concentration of <LOD–15.7 $\mu\text{g}/\text{kg}$ (dw), and DiBP and BDCPP were not detected in any samples. This result was consistent with a previous study showing the highest level of DEHP in untreated wastewater, while the concentrations of DnBP and DPhP were about 1 or 2 orders of magnitude lower than that of DEHP (Quintana et al., 2006).

Among five OP diesters, only DEHP and DnBP are industrially produced and used as metal extracts, plasticizers, and in the textile industry (Quintana et al., 2006). Poor biodegradation of TEHP into DEHP was observed in the laboratory biodegradation test (Quintana et al., 2006). Thus, the high concentration of DEHP in sludge may be not originated from the biodegradation of TEHP, but from the consumption of DEHP-containing products. In contrast, complete primary degradation of TnBP in experiments has been previously observed (Quintana et al.,

Table 3

Concentrations of OP diesters in sewage sludge ($\mu\text{g}/\text{kg}$).

Concentrations		BDCPP	DPhP	DnBP	DiBP	DEHP
Dry weight (dw)	Max.	<LOD	96.4	15.7	<LOD	275
	Min.	<LOD	5.18	<LOD	<LOD	11.2
	Mean	<LOD	18.0	1.60	<LOD	96.0
	Med.	<LOD	15.2	<LOD	<LOD	86.5
Wet weight (ww)	Max.	<LOD	60.3	9.81	<LOD	172
	Min.	<LOD	3.24	<LOD	<LOD	7.02
	Mean	<LOD	11.2	1.00	<LOD	60.0
	Med.	<LOD	9.50	<LOD	<LOD	54.0
Fre. (%)		0	100	20.9	0	100

<LOD: concentration below the limit of detection.

2006); hence, the presence of DnBP in sludge could originate from both technical products and the biodegradation of corresponding triester. Besides, DiBP, DPhP and BDCPP tend to generate as biodegradation intermediates of parent triesters (Quintana et al., 2006). The absence of BDCPP in sludge is probably attributed to the poor biodegradation of chlorinated OP triesters, which is almost no removal during conventional sewage treatment process (Marklund et al., 2005a). Considering that generally higher levels of TiBP than TPhP are measured in the influent of STPs (Meyer and Bester, 2004), the absence of DiBP in sludge is surprising in this study. This result could be explained by two factors. First, the biodegradation of TiBP has been previously observed to be significantly slow and totally 16 days are required for the complete removal of TiBP (Quintana et al., 2006), while the sludge retention time (SRT) is usually 10–15 days in STPs in this study. Thus, in the process of sewage treatment, the formation of DiBP from TiBP may be limited by the slow degradation rate. Secondly, DiBP is more likely to be retained in aqueous phase in comparison with DPhP, which can be deduced from their parents' values of $\text{Log}K_{ow}$ (TiBP: 3.60; TPhP: 4.59).

The high detection frequency of DPhP in sludge in this study may be explained by the fast degradation from TPhP to DPhP (Quintana et al., 2006). Furthermore, DPhP is completely removed from wastewater samples within 10 days, and no monoester (MPhP) could be detected during biodegradation (Quintana et al., 2006). So the high level of DPhP in sludge samples in this study indicated that the removal of DPhP in wastewater is presumably due to the absorption onto sludge rather than the degradation into monoester. As shown in Fig. 3, the DPhP/TPhP ratios in sludge varied in STPs, and the STP C showed relatively lower DPhP/TPhP ratio and TOC content. Also, statistical analysis

Fig. 2. Temporal variation of OP triesters in sludge from 2008 to 2014.

Fig. 3. Variation of the DPhP/TPHP ratio and TOC content in sludge.

showed a positive correlation between DPhP/TPHP ratio and TOC content in sludge ($r = 0.131$, $p > 0.05$), suggesting that TOC may be one of important factors for the degradation of TPHP. In the future, it is worthwhile to obtain more information to understand the degradation of OP triesters in STPs.

3.4. Ecotoxicological risk assessment

Landfill has been widely used for sludge disposal in China (Ouyang et al., 2005) and sludge-composting technology has also been applied sometimes (Wang et al., 2010). It is estimated that approximately 65% of mechanical dewatered sewage sludge in China is disposed in landfill (Zhan et al., 2014). However, this management strategy represents an additional entry route for pollutants into the terrestrial environment, and then produces harmful effects on microorganisms.

RQ values of OP diesters in sewage sludge can be calculated using the maximum concentrations measured as MEC values, and using the $PNEC_{\text{sediment}}$ as $PNEC_{\text{sludge}}$ values. The $PNEC$ values of TPHP, TCEP, EHDPP, TCrP, TCPP, TDCP and CDPP in sediment and soil (EC, 2011), and RQ values of these compounds in sludge were summarized in Table 4. High environmental risk in sewage sludge was obtained for

Table 4
The risk quotient values (RQs) of seven OP triesters in sludge.

Analytes	$PNEC_{\text{sediment}}$	$PNEC_{\text{soil}}$	MEC_{max}	RQ_{sludge}
TPHP	160	130	41.7	0.26
TCEP	NA	386	130	NA
EHDPP	37.3	30.2	86.9	2.33
TCrP	3.3	2.7	2219	672
TCPP	2920	1700	236	0.08
TDCP	180	320	39.6	0.22
CDPP	74	59	18.3	0.25

$PNEC$: predicted non-effect concentrations, $\mu\text{g/kg}$ (EC, 2011); MEC_{max} : the maximum measured concentration in sludge, $\mu\text{g/kg}$, ww; NA: not available.

TCrP (RQ value: 672) and EHDPP (RQ value: 2.33). Besides, medium risk was indicated for TPHP (RQ value: 0.26), TDCP (RQ value: 0.22) and CDPP (RQ value: 0.25), as their RQ values were determined between 0.1 and 1. In addition, low RQ value of 0.08 was determined for TCPP, suggesting its low environmental risk in sewage sludge. Moreover, the maximum concentrations of TCrP (2219 $\mu\text{g/kg}$, ww) and EHDPP (86.9 $\mu\text{g/kg}$, ww) in sludge were higher than the corresponding $PNEC$ values (2.7 and 30.2 $\mu\text{g/kg}$, ww, respectively) in soil, suggesting potential harmful effects of TCrP and EHDPP on microorganisms in soil after sludge landfill or fertilization. Therefore, environmental exposure assessment of OP diesters from sewage sludge to soil needs to be further investigated.

4. Conclusion

In the present work, a total of 13 OP triesters and 3 diesters were detected in sludge samples from eight STPs in Beijing, China. TEHP and TCrP were the predominant triesters, and DEHP and DPhP were the most abundant diesters in sludge samples. The presence of hydrophilic triesters (TMP and TEP) in sludge samples indicated that besides hydrophobic effects, other mechanisms probably play an important role in the absorption of OP triesters in sludge. The levels of OP triesters in sewage sludge varied among different STPs, and the highest concentration was determined in the smallest STP (H), which may be due to possible point sources. In addition, the total concentration of OP triesters in sewage sludge showed an increasing trend from 2008 to 2014, which could be explained by their increasing application in China. Finally, high environmental risks were obtained for TCrP and EHDPP in sewage sludge, and they also present potential harmful effect on soil microorganisms after sludge landfill and fertilization. Further investigations of exposure assessment from sewage sludge to soil are highly needed in the future.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2015.11.094>.

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