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A Nationwide Survey of 31 Organophosphate Esters in Sewage Sludge from the United States

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Abstract

Organophosphate esters (OPEs) are used as flame retardants and plasticizers in a wide range of consumer products. Nevertheless, studies on the occurrence and inventory of OPEs in sewage sludge are limited. In this study, 20 OP triesters and 11 diesters were measured in 75 archived sewage sludge samples collected from 67 wastewater treatment plants (WWTPs) across the United States (US). The median concentrations of $\sum_{20}$OP-triesters and $\sum_{11}$OP-diesters in sludge were 1,290 and 78.4 ng/g dry weight (dw), respectively. Sludge samples originating from the Western and Northeastern US contained higher concentrations of OP triesters than did those from the Midwestern and Southern US. Sludge samples from WWTPs with larger treatment capacity (>38 million liters per day) contained higher concentrations of OP diesters (p <0.05). OP diesters in sludge originated from two sources, triester degradation and direct inputs. Land application of sludge to US soils was estimated to result in annual mass inputs of 12,400–14,900 kg/year of OP triesters and 663–796 kg/year of OP diesters. A hazard assessment was performed for 14 OPEs found in sludge, which suggested a low level of risk from OPs at the current land application practices of sludge.

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Notes

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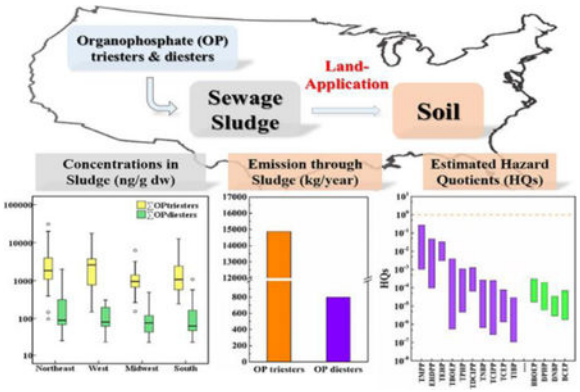

Keywords

Organophosphate esters; degradation; Sludge; Hazard Assessment; Emission

1. Introduction

Organophosphate (OP) triesters are widely used as flame retardants and plasticizers in many commercial products, including furniture, electronics, polyurethane foam (PUF), polyvinyl chloride (PVC), and in hydraulic fluids and lubricants (Cruz et al., 2015; van der Veen et al., 2012; Wei et al., 2015). The global production of OP triesters has increased in recent years, as these chemicals are deemed to be substitutes for brominated flame retardants (BFRs) (Wei et al., 2015). The global production of OPFRs was estimated at 680,000 metric tonnes in 2015 (Wang et al., 2015). Several recent studies have reported the occurrence of OP triesters in water (Kim et al., 2018; Kim et al., 2017), outdoor air (Castro-Jimenez et al., 2014; Rauert et al., 2018), indoor air (Hartmann et al., 2004; Vojta et al., 2017; Yadav et al., 2017), dust (Cao et al., 2014; Li et al., 2018), sediment (Wang et al., 2017; Giulivo et al., 2017; Yadav et al., 2018a), soil (Wang et al., 2018; Yadav et al., 2018b), and biota (Su et al., 2014), as well as in humans (Lu et al., 2017; Sun et al., 2018). Some OP triesters, especially chlorinated ones, possess carcinogenic and neurotoxic properties (Hou et al., 2016). Exposure to OP triesters is linked to reproductive and developmental toxicity (Behl et al., 2015), genotoxicity (Du et al., 2016), and endocrine disruption (Chen et al., 2015).

Wastewater treatment plants (WWTPs) are conduits for a variety of organic pollutants, including OP triesters that emanate from human activities. Studies have reported the occurrence of OP triesters in influents, effluents, and sewage sludge from WWTPs (Been et al., 2018; Cristale et al., 2016; Gao et al., 2016; Kim et al., 2017; Krzeminski et al., 2017). OP triesters can be hydrolyzed by microbial activities to yield OP diesters in the environment (Su et al., 2016). Human and animal studies have reported metabolic and enzymatic transformation of triesters to diesters (He et al., 2018; Hou et al., 2017; Hou et al., 2016). OP diesters are biomarkers of exposure to OP triesters, and the former have been measured in human urine (Carignan et al., 2017; He et al., 2018; Hoffman et al., 2017). In addition to the formation from triesters, some OP diesters can be emitted directly from their use in consumer products (Quintana et al., 2006). For example, bis(2-ethylhexyl) phosphate (BEHP), a biotransformation product or metabolite of tris(2-ethylhexyl) phosphate (TEHP),

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also is used as an extraction agent and an ingredient in surfactants (Lemire et al., 1986). OP triesters were not completely removed in WWTPs following advanced oxidation processes (Cristale et al., 2016; Liang et al., 2016). Low removal rates of OP triesters also were reported following aerobic composting of sewage sludge (Pang et al., 2018). Thus far, only a few studies have reported on the occurrence of OP triesters and diesters in sewage sludge from the US (Kim et al., 2017), European countries (Celano et al., 2014; Marklund et al., 2005), and China (Fu et al., 2017; Gao et al., 2016).

Land application of sewage sludge is an important pathway for OPs to enter into agricultural ecosystems. Limited studies have reported on the loading of OPFRs in soils through sludge application (Xue et al., 2015). The Targeted National Sewage Sludge Survey (TNSSS), a program developed by the U.S. Environmental Protection Agency to obtain national estimates of levels of emerging pollutants in sewage sludge to inform safe use and disposal options, collected sludge from 74 WWTPs with secondary treatment or better technology during the period 2006– 2007 (U.S. EPA 2009). Several studies have reported the occurrence of bisphenol analogs, perfluoroalkyl substances, and BFRs in these sludge samples (Venkatesan et al., 2013; Venkatesan et al., 2014a; Venkatesan et al., 2014b). However, no earlier studies have reported on the concentrations of OP di-and tri-esters in sewage sludge collected across the US. Here, we measured 20 OP triesters and 11 OP diesters in sludge samples, collected during the period of 2006–2007 by the TNSSS program, to investigate the occurrence and profiles of OP triesters and diesters; to estimate environmental emissions from land application of sludge; and to quantitatively assess potential ecological risks associated with disposal of sludge on soils.

2. Materials and methods

2.1 Target Chemicals

Twenty OP triesters, comprising alkyl compounds, were analyzed: trimethyl phosphate (TMP), triethyl phosphate (TEP), tri-propyl phosphate (TPP), tri-n-butyl phosphate (TNBP), tri-isobutyl phosphate (TIBP), tris(2-butoxyethyl) phosphate (TBOEP), and TEHP; chlorinated compounds (Cl-), namely, tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPPs), and tris(1,3-dichloro-2-propyl) phosphate (TDCIPP); aryl compounds, namely, triphenyl phosphate (TPHP), trimethylphenyl phosphate (TMPPs), 2-ethylhexyl diphenyl phosphate (EHDPP), cresyl diphenyl phosphate (CDPP), isodecyl diphenyl phosphate (IDDP), t-butylphenyl diphenyl phosphate (BPDP), and tris(p-tert-butylphenyl) phosphate (TBPHP); and oligomeric compounds, namely, resorcinol bis(diphenyl phosphate) (RDP), tetrakis(2-chloroethyl) dichloroisopentyl diphosphate (V6), and bisphenol A bis(diphenyl phosphate) (BDP). CDDP, IDDP, BPDP, and TBPHP are regarded as emerging aryl-OP triesters. Eleven OP diesters were analyzed: diethyl phosphate (DEP), dipropyl phosphate (DPRP), dibutyl phosphate (DIBP), diisobutyl phosphate (DNBP), bis(butoxyethyl) phosphate (BBOEP), BEHP, bis(2-chloroethyl) phosphate (BCEP), bis(1-chloro-2-propyl) phosphate (BCIPP), bis(1,3-dichloro-2-propyl) phosphate (BDCIPP), diphenyl phosphate (DPHP), and bis(methylphenyl) phosphate (BMPP). Deuterated compounds, TEP-d15, TMP-d9, TPP-d21, TNBP-d27, TEHP-d51, TCEP-d12, TCIPP-d18, TDCIPP-d15, TPHP-d15, DNBP-d18, DIBP-d14, BBOEP-d8, BEHP-d34,

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BCEP-d8, BCIPP-d12, BDCIPP-d10, DPHP-d10, and BMPP-d14 were used as surrogate standards. Detailed information on target chemicals and their physicochemical properties are presented in the Supplementary Information (SI) (Table S1).

2.2 Sample Collection

Sewage sludge samples (n = 75) were collected in 2006–2007 as a part of the TNSSS from 67 WWTPs deemed to be representative of the nation's then 3,337 WWTPs in 35 states (Table S2). Sampled WWTPs featured a treatment capacity of >3.8 million liters per day (MLD) and utilized secondary or better wastewater treatment technology (U.S. EPA 2009). Duplicate samples were collected at four WWTPs for quality assurance purposes, and at four facilities that produced two kinds of sludge by two different treatment technologies. A single sample was collected from the remaining 59 facilities. Frozen aliquots of samples archived in the National Sewage Sludge Repository (NSSR) of the Human Health Observatory (HHO) at Arizona State University (Venkatesan et al., 2015) were shipped to the Wadsworth Center, New York State Department of Health, Albany, New York, and stored at −20° C until further analysis.

2.3 Sample Preparation

For the extraction of OP triesters, freeze-dried sludge samples (0.1 g) were spiked with 10 ng each of labeled surrogate standard mixture, and extracted using acetonitrile (3 mL) with mechanical oscillation (1 h) followed by ultrasonication (30 min). Resultant extracts were centrifugated (3,510 *g*, 10 min) and transferred to a polypropylene (PP) tubes. The extraction procedure was repeated twice, and extracts were combined. Then the combined extracts were purified by Oasis HLB cartridges (60 mg, 3 cm^3; Waters, Milford, MA). The cartridges were preconditioned with 2.5 mL acetonitrile, loaded with the extracts (Fraction 1), and then eluted with 1.5 mL of acetonitrile (Fraction 2). The purified extracts (fractions 1 and 2) were collected and evaporated to near dryness and reconstituted with 200 μL of water/methanol (4/6; v/v) before analysis, using HPLC-MS/MS.

The extraction of OP diesters was slightly different from that for triesters. Freeze-dried sludge samples (0.15 g) were spiked with 10 ng each of labeled surrogate standard mixture, and extracted using acetonitrile with 5% acetic acid (v/v; 3 mL) with mechanical oscillation (1 h), followed by ultrasonication (30 min). Then the samples were centrifuged (3,510 *g*, 10 min) and the supernatant was transferred to a PP tube. The extraction procedure was repeated with acetone/hexane (1/1; v/v) with 5% acetic acid (v/v) (3 mL) and the extracts were combined. Combined extracts were evaporated to ~3 mL and transferred to acetonitrile. Then extracts were purified by Oasis HLB cartridges (60 mg, 3 cm^3; Waters, Milford, MA), using the same procedure as OP triesters, and the purified extracts were evaporated to nearly dryness and reconstituted with 200 μL of acetonitrile before HPLC-MS/MS analysis.

2.4 Instrumental Analysis

For the analysis of OP triesters, a high-performance liquid chromatography (HPLC, Agilent 1100 series; Agilent Technologies, Santa Clara, CA), coupled with electrospray triple quadrupole mass spectrometry (ESI-MS/MS, API 2000; Applied Biosystems, Foster City,

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CA), was used. A Betasil C_{18} column (100 mm × 2.1 mm, 5 μm; Thermo, Waltham, MA), connected to a Betasil C_{18} guard column (20 mm × 2.1 mm, 5 μm; Thermo), was used for the chromatographic separation of chemicals. HPLC-grade water with 0.1% acetic acid (v/v) (A), and methanol with 0.1% acetic acid (v/v) (B), were used as the mobile phase at a flow rate of 200 μL/min. The initial mobile phase flow was set at 60% B and held for 2 min; then increased linearly to 99% in 5.5 min and held for 9.5 min; followed by a decrease to 60% in 0.5 min; and then held for 7.5 min for equilibration. Electrospray positive ionization (ESI+) multiple reaction monitoring (MRM) modes were used for the identification and quantification of OP triesters.

For the analysis of OP diesters, the same instrument, as described above, was used. All target diesters were chromatographically separated by a HILIC column (100 mm × 2.1 mm, 2.6 μm; Phenomenex, Torrance, CA) connected to a Betasil C_{18} guard column (20 mm × 2.1 mm, 5 μm; Thermo, Waltham, MA). The mobile phase consisted of HPLC-grade water: methanol (2:3 v/v) with 10 mm ammonium acetate (A) and acetonitrile (B), at a flow rate of 200 μL/min. The mobile phase gradient started at 96.5% B. After a 2-min hold, B was decreased linearly to 88.5% for 1.5 min and further decreased to 86.0% for 3 min, held for 8.5 min, and then changed to the 96.5% B for 0.5 min and equilibrated for 9.5 min. Electrospray negative ionization (ESI-) MRM modes were used for the identification and quantification of OP diesters. Detailed information on MS/MS determination of OP triesters and diesters is presented in Tables S3 and S4.

2.5 Quality Assurance and Quality Control

A calibration curve, which ranged in concentrations from 0.05 to 100 ng/mL with regression coefficients >0.99, was used for the quantitation of target chemicals. The instrumental limits of quantitation (LOQs) were set at a signal-to-noise ratio of 10, at the lowest point of the calibration standard (Table S5). Recovery values for target chemicals from matrix-spiked samples were determined at 60.6–129% for OP triesters and 58.4–106% for OP diesters. Absolute recoveries of surrogate standards spiked into samples were 52.1–94.6% and 63.0–91.6% for OP triesters and diesters, respectively. All OP di-and tri-ester concentrations were corrected by the recoveries of surrogate standards spiked into each of the samples. Trace levels, ranging from 0.14 μg/L (TMPPs) to 3.66 μg/L (TNBP) for OP triesters, and from 0.45 μg/L (BBOEP) to 1.66 (DIBP) μg/L for OP diesters were found in procedural blanks. The concentrations in samples were reported after subtraction of blank values. For those analytes that were not found in procedural blanks, the method detection limits (MDLs) were calculated based on LOQs and sample volume taken for analysis. For those analytes that were present in procedural blanks, MDLs were calculated as three times the standard deviation (SD) of blank values and sample volume taken for analysis. MDLs ranged from 0.15 to 1.68 ng/g dw for OP triesters and from 0.02 to 1.38 ng/g dw for OP diesters. Detailed QA/QC data are presented in Table S5.

2.6 Data Analysis

Concentrations of OP triesters and diesters below the MDLs were assigned a value at 1/2 MDLs. OP triesters and diesters with detection frequencies below 50% were not included in the statistical analysis. The concentrations of TMPPs and TCIPPs were reported as the total

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concentrations of their isomers. The Spearman rank correlation analysis was conducted, using SPSS software (Version 22.0, SPSS Inc., Armonk, NY). The linear fittings were produced by Origin Pro 8.5 (Origin Lab Corporation, Northampton, MA).

Hazard quotient (*HQ*) values were used to assess potential risks of OPs in sludge-amended soils, using the following equation (eqn 1)

$$HQ = \frac{PEC_{soil}}{PNEC_{soil}} \quad (1)$$

where $PNEC_{soil}$ is the predicted no effect concentration of OPs in soil, and PEC_{soil} is the predicted soil concentration of OPs one year following sludge application (Fu et al., 2017; Gao et al., 2016). The potential risk is considerable for an OP when its HQ value is ≥ 1.

The European Commission (EC) reported *PNEC* values of TECP, TCIPPs and TDCPP in soil, based on the lowest effect concentrations in terrestrial biota. The *PNEC* values of TPHP, EHDPP, and TMPPs were based on an equilibrium partitioning model (Table S6) (European Commission 2011). For other OP triesters and diesters for which no $PNEC_{soil}$ values were available, we derived the values using the formula: LC_{50}/f, where LC_{50} is the lethal concentration (50%) for earthworm, and f is the assessment/uncertainty factor (1,000) (Table S6) (Fu et al., 2017). The $LC50$ *and* $PNEC_{soil}$ values were available for a limited number of OPs, and therefore HQs were calculated for only ten compounds.

The PEC_{soil} values for OPs in sludge-amended soils were estimated based on equation (2) from the EC Technical Guidance Document (TGD) on Risk Assessment (European Chemicals Bureau 2003):

$$PEC_{soil} = \frac{C_{sludge} \times APPL_{sludge}}{DEPTH_{soil} \times RHO_{soil}} \quad (2)$$

where C_{sludge} (g/kg dw) is the measured concentration of OP triesters and diesters in sludge, $APPL_{sludge}$ is the dry sludge application rate (0.50 kg/m^2/year), $DEPTH_{soil}$ is the mixing depth of soil (0.20 m), and RHO_{soil} is the bulk density of soil (1,500 kg/m^3).

3. Results and discussion

3.1 Concentrations of OP Di-and Tri-esters in Sludge

All aryl-and Cl-OP triesters were found at a detection frequency (DF) of 81–100% in 75 sludge samples (Table 1). Short chain alkyl-OP triesters, including TMP, TEP, TPP and TIBP, exhibited a lower DF of 1–56%, and the oligomeric OP triesters showed a DF of below 25%. All OP diesters, however, were detected at a high DF (85–100%), except for two Cl-OP diesters, BCEP and BCIPP, which showed a low DF of 62% and 32%, respectively (Table 2). Cl-OP triesters are more resistant to degradation (Regnery et al., 2010; Su et al., 2016) and are incompletely removed in WWTPs in comparison to aryl-and alkyl-OP

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triesters (Cristale et al., 2016; Liang et al., 2016; Yuan et al., 2015). This might explain the lower DF of Cl-OP diesters in sludge.

The median concentration of $\sum_{20}$OP-triesters in sludge was 1,290 ng/g dw (97.1–30,700 ng/g dw) (Table 1). The concentrations of OP triesters in sludge from the US, Germany, and Sweden were higher than those reported from China (Chen et al., 2009; Kim et al., 2017; Marklund et al., 2005) (Table S7), which suggests extensive use of these compounds in Europe and North America. TBOEP (580, not detectable [n.d.]–28,300 ng/g dw; median, range) was the most abundant OP triester in our sludge samples, followed by TEHP (170, 26.5–857 ng/g dw), TDCIPP (86.7, 5.18–328 ng/g dw), BPDP (40.2, 0.56–3,020 ng/g dw), and IDDP (31.0, n.d.–6,150 ng/g dw). Earlier studies have reported the predominance of TBOEP and TEHP in sludge from China (Gao et al., 2016; Kim et al., 2017). Similarly, high concentrations of TBOEP have been reported in WWTP influents from Australia (O'Brien et al., 2015). Sludge samples from Spain and Germany, however, showed 2–3 orders of magnitude higher concentrations of TCIPPs (Spain: 1,570 ng/g dw; Germany: 18,400 ng/g dw) (Celano et al., 2014; Chen et al., 2009), in comparison to the concentration found in this study (23.5 ng/g dw). International information on the environmental occurrence of aryl-OP triesters is limited to two studies that reported the occurrence of CDPP in sludge from China (n.d.−3.8 ng/g dw) (Gao et al., 2016; Liang et al., 2016). In our study, CDPP, IDDP, and BPDP were found in sludge at median concentrations of 3.81, 31.0, and 40.2 ng/g dw, respectively (DF: 88–100%). Occurrence of oligomeric OP triesters, BDP (2.06–5.82 ng/g dw) and RDP (0.44–3.45 ng/g dw), was reported in suspended solids from WWTPs in China (Liang et al., 2018), whereas these two compounds were not found in our sludge. The consumption of oligomeric OP triesters in the United States is <4,500 metric tonnes/year (van der Veen et al., 2012).

Few studies have reported on the occurrence of OP diesters in sludge from the United States and China (Fu et al., 2017; Gao et al., 2016; Kim et al., 2017) (Table S7). In our study, 11 OP diesters were measured in sewage sludge, and the median concentration of $\sum_{11}$OP-diesters was 78.4 (22.9–1,990 ng/g dw) (Table 2). A median $\sum_{6}$OP-diester concentration of 82.9 ng/g dw was reported in sludge from China (Fu et al., 2017), which was similar to the corresponding $\sum_{6}$OP-diester concentration in sludge from the US (62.1 ng/g dw). BBOEP (17.7, 3.21–219 ng/g dw; median, range), BEHP (7.31, n.d.–366 ng/g dw), and BDCIPP (9.48, n.d.–1,880 ng/g dw), were the major OP diesters found in our sludge, which is in accordance with high concentrations of parent OP triesters found in the sludge. An earlier study reported the occurrence of BDCIPP and DPHP at 397 and 40.5 ng/g dw, respectively (Kim et al., 2017), in sludge from New York, which is comparable to those measured in our study (arithmetic mean: BDCIPP 81.7 ng/g dw; DPHP 33.5 ng/g dw). Further, the concentrations of BCIPP, BCEP, and BEHP (median: 19.3, 18.4 and 86.5 ng/g dw, respectively) reported for sludge from China (Fu et al., 2017), were higher than those of the present study, whereas the concentrations of their corresponding parent OP triesters (TCIPPs, TCEP and TEHP) were similar in China and the United States. Variations in input sources and biological treatment techniques may explain the observed differences in concentrations and profiles of OPs between the two countries.

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3.2 Influence of Geographic Location and Treatment Capacity of WWTPs on OP Triesters and Diesters Concentrations in Sludge

The sludge samples were grouped based on the geographic location of WWTPs, into four regions: Northeastern, Midwestern, Southern, and Western United States. The concentrations of $\sum_{20}$OP triesters in sludge from the Western (median, range; 2,600, 149–17,600 ng/g dw) and Northeastern (1,840, 97.1–30,800 ng/g dw) United States were significantly higher than those from the Midwestern (1,060, 155–6,230 ng/g dw) and Southern (1,060, 245–12,600 ng/g dw) regions (Table S8). The most abundant OP triester, TBOEP, accounted for 40–60% of the $\sum_{20}$OP triester concentrations in all four regions (Figure 1). No significant difference was found in the concentrations of $\sum_{11}$OP-diesters in sludge among the four geographic regions (63.3–89.3 ng/g dw). BBOEP, BDCIPP, and BEHP collectively accounted for ~60% of $\sum_{11}$OP diester concentrations in sludge.

Information regarding the treatment capacity (in million liters per day; MLD) of WWTPs from which sludge had been collected, was available. Sludge samples were categorized on the basis of treatment capacity of WWTPs as: 3.8 < MLD < 38; 38 < MLD < 380; MLD ≥ 380. No significant difference was observed in the concentrations of $\sum_{20}$OP triesters in sludge collected from WWTPs with different treatment capacities ($p > 0.05$, Kruskal-Wallis H test) (Figure 2). For OP diesters, sludge samples from large WWTPs (i.e., MLD ≥ 380), contained $\sum_{11}$OP diester concentrations similar to those with medium capacities (i.e., 38 < MLD < 380). The median concentrations of $\sum_{11}$OP diesters in sludge collected from smaller WWTPs (i.e., 3.8 < MLD < 38), however, were significantly lower than those with higher treatment capacities ($p < 0.01$, Kruskal-Wallis H test). In general, larger WWTPs, that serve greater populations, contained higher OP diester concentrations in sludge than did those of smaller WWTPs. However, information on the identity of each WWTP was not available for further analysis. The high concentrations of OP diesters found in large WWTPs and of OP triesters in WWTPs from Western and Northeastern US may be related to population size, point sources, and sewage treatment types.

3.3 Correlation Between Organophosphate Triesters and Diesters

OP diesters are known to occur in human urine (Lu et al., 2017; Sun et al., 2018), representing a documented input of diesters to WWTPs through the domestic sewer system. Thus, the totality of OP diesters found in sludge may originate from two sources, direct release of human waste and degradation of the corresponding parent OP triesters during wastewater treatment (Cristale et al., 2016; Liang et al., 2016; Su et al., 2016). Correlations between concentrations of OP triesters and diesters in sludge were examined to reveal potential sources of diesters. The Spearman's rank correlation analysis suggested a weak but significant correlation between the concentrations of TBOEP and BBOEP ($Rho = 0.333$, $p < 0.01$) and TDCIPP and BDCIPP ($Rho = 0.386$, $p < 0.01$) (Table S9). Further, strong linear correlations of TBOEP and BBOEP ($r^2 = 0.35$, $p < 0.01$), TDCIPP and BDCIPP ($r^2 = 0.43$, $p < 0.01$), also were observed (Figure 3), which indicates that BBOEP and BDCIPP in sludge originated from the degradation of their parent OP triesters during activated sludge treatment. Spearman's rank correlations between the concentrations of TEHP and BEHP ($Rho = 0.145$, $p > 0.05$), TCEP and BCEP ($Rho = 0.028$; $p > 0.05$), and TCIPPs and BCIPP ($Rho = 0.091$, $p > 0.05$), however, were not significant. This suggests that, in addition to

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degradation of parent OP triesters, these diesters originate from direct loading contained in raw sewage arriving at the WWTPs. BEHP is known for its use as an extracting agent and raw material for surfactants (Lemire et al., 1986).

Further, a negative removal of TEHP was reported in WWTPs (Liang et al., 2016). Therefore, degradation rate of TEHP to BEHP in WWTPs is expected to be slow. Thus, the occurrence of BEHP in sludge indicates direct discharge from industrial sources or consumer products. Similar to BEHP, DNBP was reported to be used as a plasticizer and metal extractant (Quintana et al., 2006). The predicted half-life of DNBP was shorter as compared to all investigated OP diesters (Table S1). In addition, a high removal efficiency was reported for its parent compound, TNBP, in WWTPs (Cristale et al., 2016; Liang et al., 2016; Yuan et al., 2015). Therefore, both direct emission and degradation of TNBP are thought to be sources of DNBP in sludge. TMPPs is quickly transformed through activated sludge treatment (Liang et al., 2016), and TMPPs and TPHP were readily hydrolyzed in neutral to alkaline solution (Su et al., 2016). Therefore, BMPP measured in sludge originates from the degradation of TMPPs; a significant Spearman correlation between TMPPs and BMPP ($r = 0.342$, $p < 0.01$) in sludge confirms our finding. The chlorinated-OP triesters, TCEP and TCIPPs, are more resistant to degradation than are alkyl-and aryl-OP triesters (Su et al., 2016). A lower removal efficiency of TCEP and TCIPPs was reported in activated sludge treatment in WWTPs (Cristale et al., 2016; Liang et al., 2016). These results suggest that BCEP and BCIPP, the potential transformation products of TCEP and TCIPPs, originate from sources such as human urine (Chen et al., 2018; Dodson et al., 2014; Petropoulou et al., 2016; Romano et al., 2017).

3.4 Emission of Organophosphates from Sludge Application and Wastewater Discharge

An annual emission inventory of OP triesters and diesters from land application of sludge was calculated using as a basis the mean concentrations of OP triesters and diesters determined in this study, the annual sludge volume (dw) generated in the United States (6,513,586 metric tonnes in 2004), and the percentage of sludge applied on US land each year (50–60%) (Venkatesan et al., 2013). The annual emission inventory of $\sum_{20}$OP triesters through sludge was 24,800 kg/year, and the emission of $\sum_{20}$OP triesters through land application of sludge was 12,400–14,900 kg/year (Table 1). TBOEP was the largest contributor to OP triester emission (inventory: 11,400 kg/year; land application: 5,720–6,870 kg/year). The emission inventory for $\sum_{11}$OP diesters through sludge was 1,330 kg/year, of which 663–796 kg/year were emitted through land application of sludge (Table 2). The calculated environmental emission inventories of both $\sum_{20}$OP triesters and $\sum_{11}$OP diesters were higher than those reported for China through land application of sludge ($\sum_{11}$OP triesters 330 kg/year; $\sum_{6}$OP diesters: 134 kg/year) (Fu et al., 2017). Further, our emission estimates of $\sum_{20}$OP triesters were much higher than those reported for bisphenol analogs (1,659–2,034 kg/year) (Yu et al., 2015) and bisphenol A diglycidyl ethers (BADGEs) (1,350–1,560 kg/year) (Xue et al., 2015), measured in the same set of samples. Therefore, studies are needed to investigate the fate and environmental risks of OPs in sludge-amended soils.

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Based on the concentrations measured in sludge, and the predicted partitioning of OP di-and tri-esters and diesters between wastewater and sludge (Table S1), we estimated concentrations and emissions of these compounds through wastewater discharges. Oligomeric OP triester and BCIPP were not included in this calculation due to the lack of partitioning/adsorption data. The emission rates of $\sum_{17}$OP triesters and $\sum_{10}$OP diesters through wastewater discharges were 95,900 and 45,600 kg/year, respectively (Tables 1 and 2). Comparison of the emission of several OP triesters through WWTPs, with their annual production volume in 2006 (TCEP, 227–4,354 metric tonnes; TDCIPP, 4,500–22,700 metric tonnes; TPHP, 4,500–22,700 metric tonnes; TMPPs 454–4,500 metric tonnes) (van der Veen et al., 2012), showed that their emission via WWTPs was < 0.09% of the total production.

3.5 Hazard Assessment

A hazard assessment was performed for ten OP triesters and four OP diesters for sludge-amended soil (Figure 4). The hazard quotients for ten OP triesters were below 1 (HQs < 1). The highest HQ was only 0.26, found for TMPPs, suggesting low risk of OP triesters in sludge-applied soils. The HQ values for OP diesters in sludge-applied soils were 3–5 orders of magnitude lower than 1. The HQ values suggest that the current levels of OP triesters and diesters in sludge pose minimal risk to soil fauna following amendments.

The sludge samples analyzed in this study were archived for over 10 years and potential degradation of OP triesters and diesters at −20 °C during that period is not known. The hydrolysis rates of TPHP and TMPPs were <20% and of other OP triesters were <10%, at pH<9 after 35 days (Su et al., 2016). Estimated half-lives of OP triesters in sediments ranged from 74 to 3375 d (Table S1). Therefore, the concentrations and HQs values measured in this study should be interpreted with that caveat in mind.

4. Conclusions

Both OP triesters and diesters were found to be ubiquitous in sewage sludge collected from WWTPs across the United States in 2006/7. TBOEP and BBOEP were the dominant OPEs in sludge. Sludge from the Western and Northeastern United States showed a higher concentration of OP triesters than those from other geographic regions. Sludge from large WWTPs treating ≥380 MLD of sewage contained high concentrations of OP diesters. Strong linear correlations of TBOEP and BBOEP, and TDCIPP and BDCIPP, suggested that these diesters in sludge mainly originate from the degradation of parent triesters in WWTPs. This work constitutes the first US national survey of 31 OP esters. Further studies should focus on the occurrence and fate of OP triesters and diesters in contemporary sludge and receiving soils.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

- Organophosphate (OP) flame retardants are ubiquitous in sludge from the United States.
- TBOEP and BBOEP are the dominant OP esters found in sludge.
- Sludge from large WWTPs contained high concentrations of OP diesters.
- OP diesters in sludge originated from both triester degradation and direct inputs.

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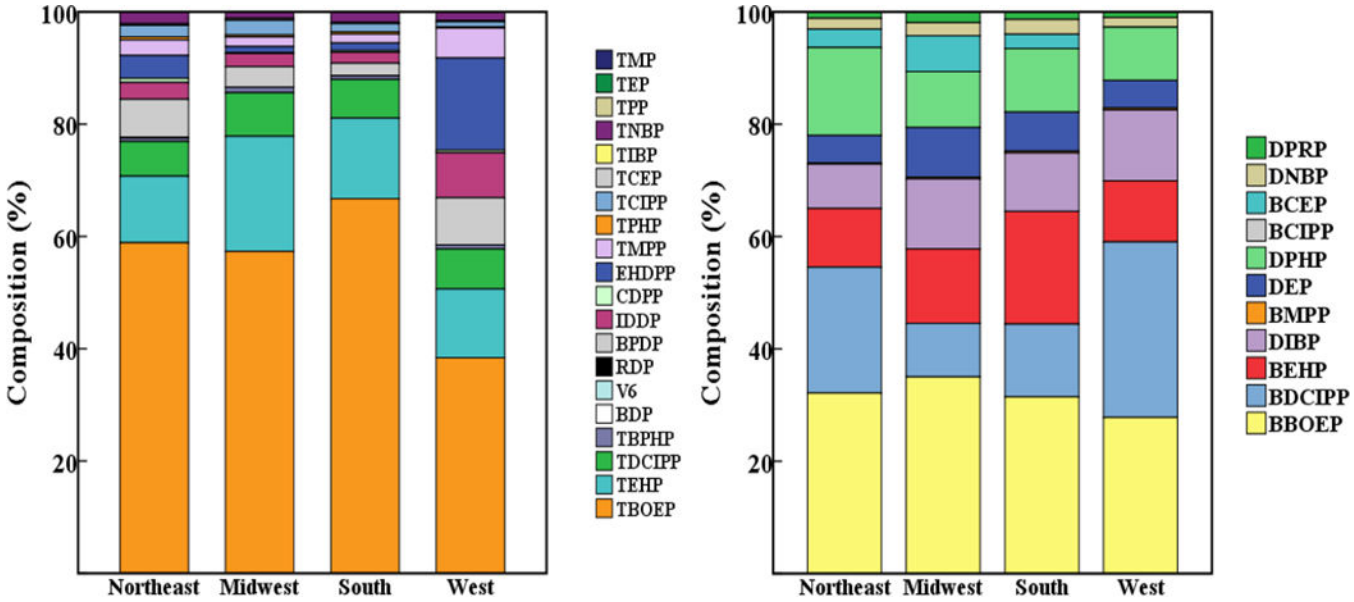

Figure 1.

Composition profile of organophosphate triesters (left panel) and diesters (right panel) in sewage sludge from four geographic regions of the United States.

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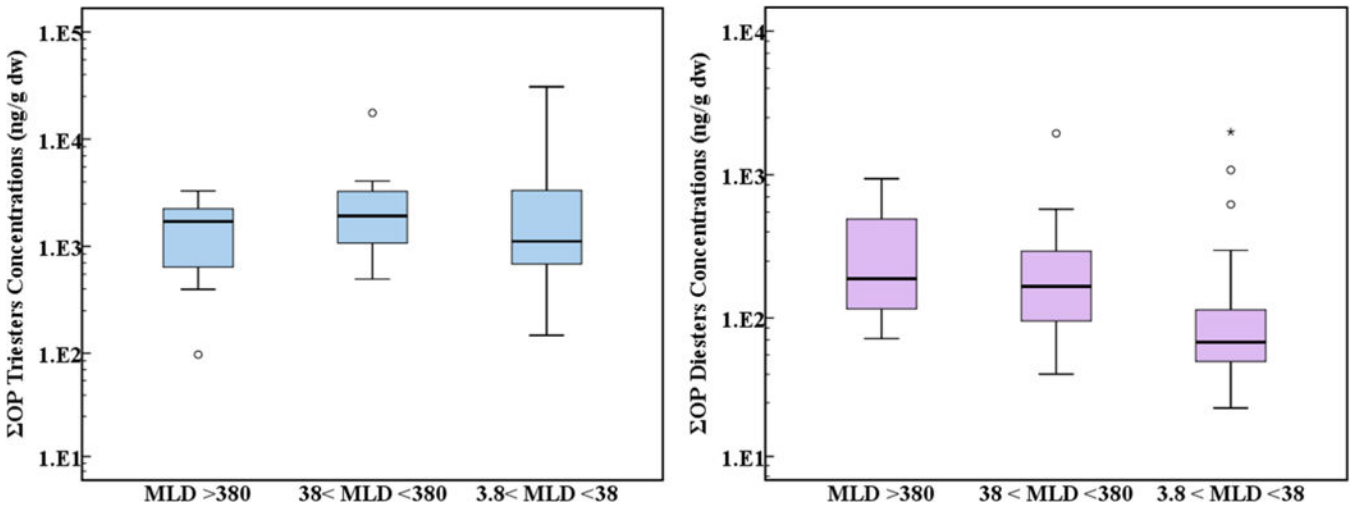

Figure 2.

Concentrations (ng/g dw) of organophosphate triesters and diesters in sewage sludge from the United States stratified by treatment capacity of wastewater treatment plants. MLD stands for million liters per day. The black horizontal line inside each box represents the median, the boxes represent the 25th and 75th percentiles of concentrations, whiskers represent a value of 1.5 standard deviations and dots represent outliers.

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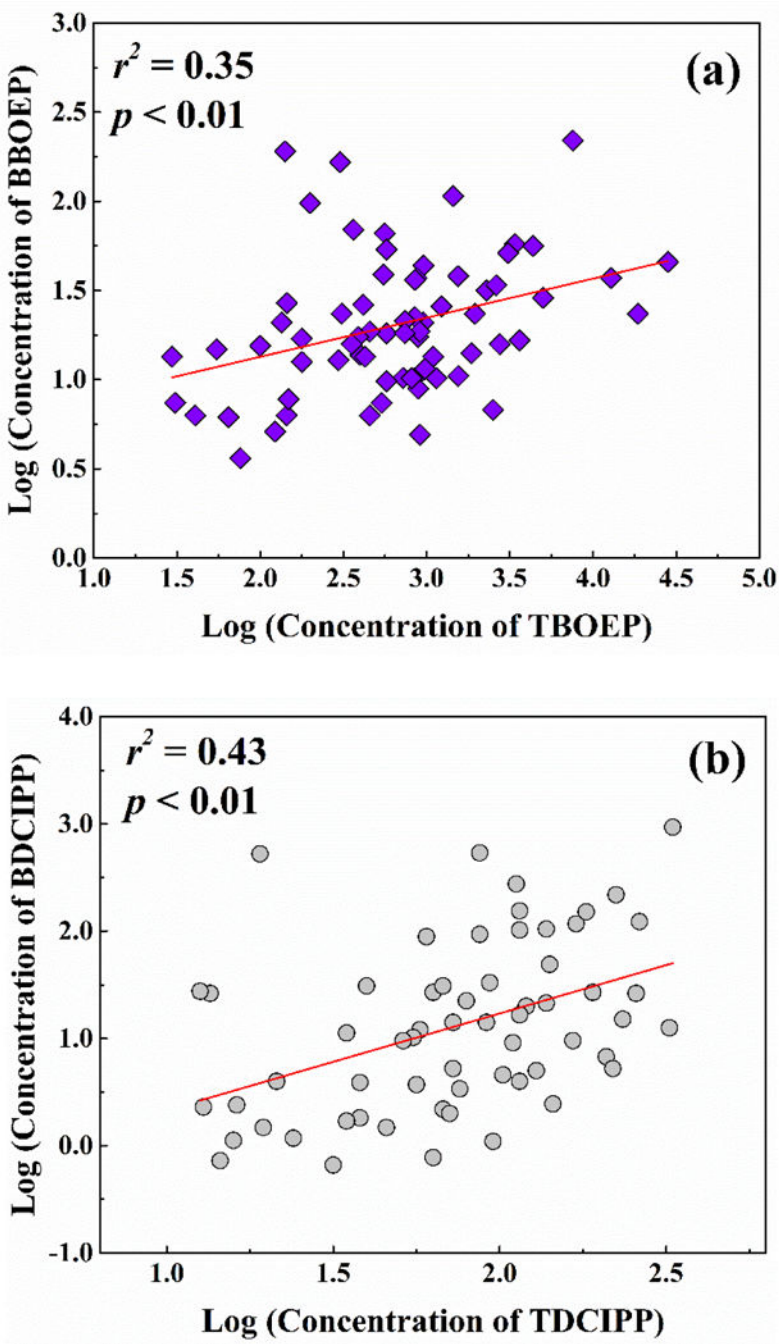

Figure 3.

Correlation between logarithm transformed concentrations between TBOEP and BBOEP (a), and TDCIPP and BDCIPP (b) in sewage sludge from the United States.

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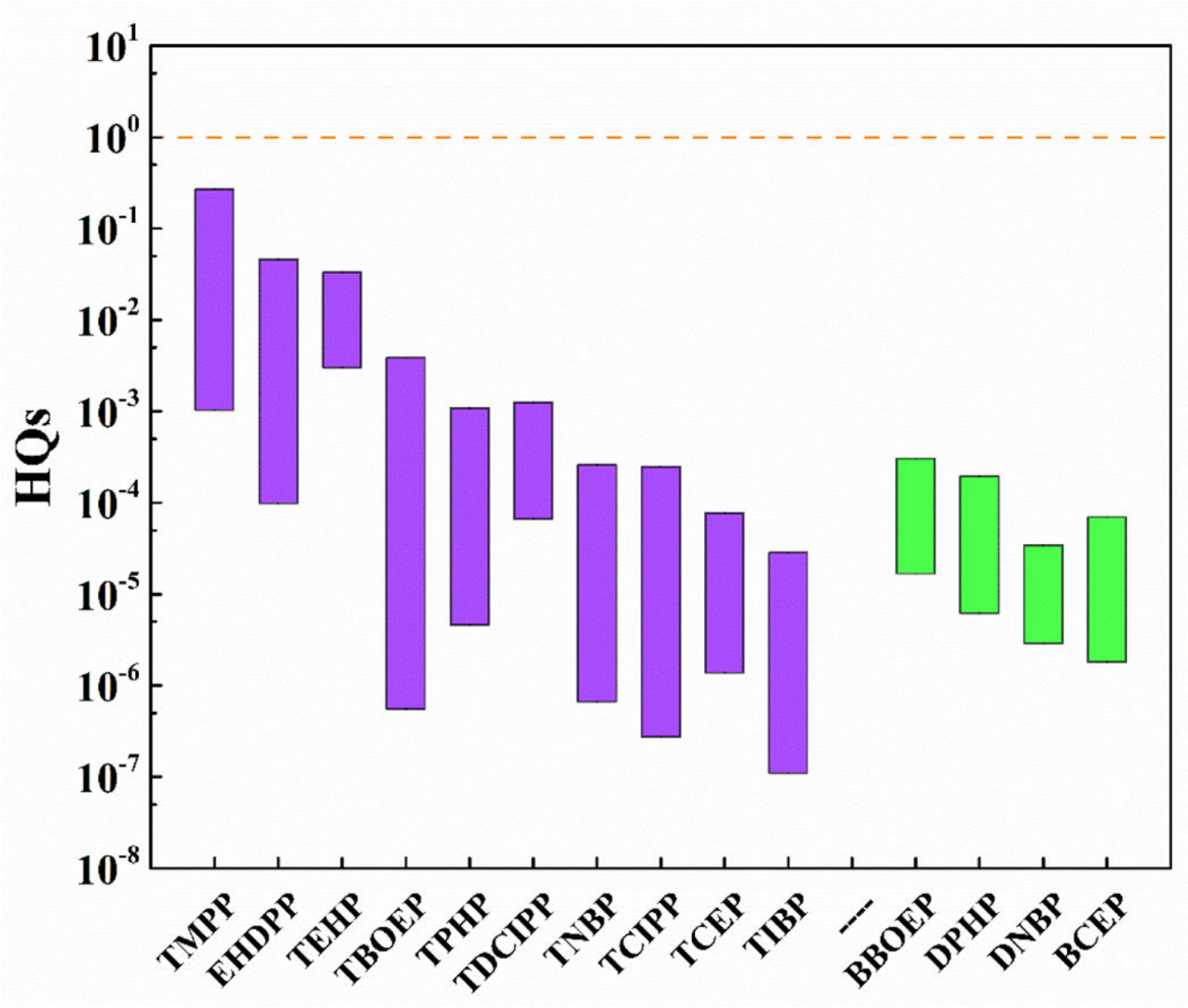

Figure 4.

Estimated hazard quotients (HQs) of major organophosphate triesters and diesters in soils amended with sludge from the United States. The top and bottom line of the column represent the HQs calculated for 5th and 95th percentile concentrations, and the dashed line represent the HQs=1.

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Table 1.

Concentrations and detection frequencies of organophosphate triesters in sewage sludge collected from the United States and the estimated emissions through land-application of sludge and WWTPs discharges.

OPFRs	Concentration (*n*=75; ng/g dw)				Emission through Sludge (kg/year)		Emission through WWTPs (kg/year)
	Mean	Median	Range	DF (%)	Emission Inventory	Land-application	
TMP	<MDL	n.d.	n.d.−5.80	13	1.06	0.53–0.64	60.1
TEP	8.50	0.52	n.d.−381	56	55.3	27.7–33.2	3100
TPP	<MDL	n.d.	n.d.-<MDL	1	0.04	0.02–0.02	1.90
TNBP	127	17.7	n.d.−6080	95	827	413–496	2780
TIBP	3.38	0.15	n.d.−30.7	56	22.0	11–13	144
TBOEP	1760	580	n.d.−28300	96	11400	5720–6870	57700
TEHP	199	170	26.5–857	100	1300	647–776	1390
TCEP	10.6	2.46	n.d.−317	93	69.3	35–42	3720
TCIPPs	61.7	23.5	n.d.−359	81	402	201–241	12300
TDCIPP	101	86.7	5.18–328	100	655	327–393	3920
TPHP	30.4	3.84	n.d.−1170	85	198	99–119	329
TMPPs	115	21.3	n.d.−2320	99	751	376–451	813
EHDPP	189	32.3	n.d.−4030	99	1200	617–741	1380
CDPP	23.3	3.81	n.d.−357	88	152	76–91	182
IDDP	243	31.0	n.d.−6150	99	6400	3190–3830	6860
BPDP	177	40.2	0.56–3020	100	1160	577–693	1240
RDP	<MDL	n.d.	n.d.−9.18	7	2.07	1.04–1.24	-
V6	0.71	n.d.	n.d.−6.36	23	4.64	2.32–2.79	-
BDP	<MDL	n.d.	n.d.−6.82	11	2.13	1.06–1.28	-
TBPHP	18.9	8.82	n.d.−168	92	123	61–74	2.22
∑OP triester	3070	1290	97.1–30700		24800	12400–14900	95900

*DF= detection frequency; n.d.= not detected; MDLs= method determination limits

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Table 2.

Concentrations and detection frequencies of organophosphate diesters in sewage sludge collected from the United States and the estimated emissions through land-application of sludge and WWTPs discharges.

OPFRs	Concentration (*n*=75; ng/g dw)				Emission through Sludge (kg/year)		Emission through WWTPs (kg/year)
	Mean	Median	Range	DF (%)	Emission Inventory	Land-application	
DEP	5.28	3.44	n.d.−50.6	96	34.4	17.2–20.6	1950
DPRP	1.12	0.68	n.d.−8.93	86	7.32	3.66–4.39	398
DNBP	1.99	1.20	<MDL-16.6	100	13.0	6.49–7.78	515
DIBP	10.3	5.27	2.13–130	100	67.2	33.6–40.3	2920
BBOEP	31.3	17.7	3.21–219	100	204	102–122	10400
BEHP	26.6	7.31	n.d.−366	97	173	86.6–104	189
BCEP	5.08	1.72	n.d.−26.2	62	33.1	16.5–19.8	1860
BCIPP	2.13	n.d.	n.d.−62.9	32	13.9	6.95–8.34	-
BDCIPP	81.7	9.48	n.d.−1880	89	532	266–319	22700
DPHP	33.5	5.47	0.93–1680	100	218	109–131	4680
BMPP	4.57	0.15	n.d.−305	85	29.8	14.9–17.9	105
∑OP diester	204	78.4	22.9–1990		1330	663–796	45600

*DF= detection frequency; n.d.= not detected; MDLs= method determination limit.