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Organophosphate Triesters and Diester Degradation Products in Municipal Sludge from Wastewater Treatment Plants in China: Spatial Patterns and Ecological Implications

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Supporting Information

ABSTRACT: Little is known about the occurrences, distributions, sources, and potential risks of organophosphate (OP) triesters and diester degradation products in municipal sludge from wastewater treatment plants (WWTPs). In this study, we conducted the first nationwide survey to simultaneously determine a suite of 11 OP triesters and six diester degradation products in sludge from WWTPs across China. All OP triesters were detected and three diesters were identified for the first time in sludge samples. Total concentrations of OP triesters and diester degradation products were in the ranges of 43.9−2160 and 17.0−1300 ng (g of dry weight)$^{-1}$, respectively, indicating relatively low pollution levels in China compared with those of several developed countries. A distinct geographical variation of higher concentrations of OP triesters and diesters in East China than in Central and West China was observed, suggesting that regional levels of organophosphate esters are associated with the magnitudes of regional economic development. Source analysis revealed nonchlorinated OP diesters are mainly derived from degradation in WWTPs, while chlorinated OP diesters were largely sourced from outside WWTPs. The estimated total emission fluxes of OP triesters and diesters via land-application sludge in China were approximately 330 and 134 kg/year, respectively. Further risk assessment based on risk quotient values in sludge-applied soils indicated low to medium risks for most OP triesters and diesters except tris(methylphenyl) phosphate. The significant accumulation of OP triesters and widespread occurrence of diester degradation products in sludge raise environmental concerns about these contaminants.

INTRODUCTION

Organophosphate esters (OPEs) have been extensively used as flame retarding chemicals and as plasticizers and additives in plastics, lubricants, rubber products, electronic devices, textiles, furniture, food packaging, and hydraulic fluids.[1,2] Because polybrominated diphenyl ethers have been phased out, OPEs have become one of the most frequently used alternative flame retardants.[3] The annual global production of OPEs currently reaches approximately 200 kt,[4] with more than 70 kt being produced in China.[5] Western Europe, North America, and China are three major consumers of flame retardants, accounting for approximately 60% of global consumption.[6] The large amounts of OPEs produced and used worldwide have resulted in their widespread occurrence in various environmental matrices,[1−3,5,7−10] as well as in remote regions.[11] Depending on the ester linkage, OPEs can be categorized as aryl, nonchlorinated alkyl, chlorinated alkyl, and others.[12] Aryl- and nonchlorinated alkyl-OPEs with higher molecular weights are more hydrophobic, while chlorinated alkyl-OPEs are generally more water-soluble and resistant to degradation.[3] Chlorinated alkyl-OPEs, including tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), and tris(1,3-dichloroisopropyl) phosphate (TDCIPP), have attracted an increasing amount of attention because of their carcinogenicity and neurotoxicity.[13−15]

Organophosphate triesters can be rapidly enzyme-catalyzed and metabolized to diester metabolites in humans and animals.[3,10,16−26] These diester metabolites are more hydrophilic than triesters and are readily excreted in urine, which often function as biomarkers of exposure to OPEs.[17] OP diesters can also be generated via other degradation pathways such as microbial metabolism/biotransformation, base-catalyzed hydrolysis,[27] and photodegradation.[28] It should be emphasized that some OP diesters, such as diphenyl phosphate (DPHP), are more toxic than their parent compounds.[20] In cities, most released OP triesters and diester degradation products are commonly collected in sewer systems and

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accumulate in municipal wastewater treatment plants (WWTPs).[29−33] It has been reported that OP triesters were detected in influents of WWTPs at microgram per liter levels.[29−32,34,35] WWTPs are therefore considered as major sinks and perhaps degradation sites. Studies of the behavior of OPEs in WWTPs indicate that nonchlorinated alkyl- and aryl-OPEs can be partly degraded by activated sludge treatment,[12,29,31,32,34,36] while chlorinated alkyl-OPEs are poorly removed even during the advanced oxidation processes.[32] Most OPEs, particularly chlorinated alkyl-OPEs, ultimately end up in sludge.[31,32,36] Therefore, sludge is an excellent medium for tracing wastewater-derived OPEs and their degradation products locally.[37] However, until now, only limited studies have reported one or several selected OPEs in sludge at a regional level.[12,30,33,37−39] Among these studies, only two demonstrated the presence of both OP triesters and diesters in sludge.[12,33] Although OP triesters and diesters as emerging global contaminants in humans have been widely examined,[3,10,17−19,21−25] their co-occurrence, distributions, sources, and potential risks in abiotic matrices such as sludge on a large geographical scale remain unknown.

To fill the knowledge gap mentioned above, we conducted the first nationwide survey to simultaneously determine a suite of OP triesters and diester degradation products in sludge from WWTPs in 36 cities across China. The aims were (1) to examine the geographical distribution patterns and potential sources of currently used OP triesters and their diester degradation products, (2) to improve our understanding of the behavior and fate of the target compounds in WWTPs and the ambient environment, and (3) to evaluate the environmental emissions and potential ecological risks via land application of sludge in China.

■ MATERIALS AND METHODS

Chemicals and Materials. Eleven target OP triesters,[40] i.e., tris(propyl) phosphate (TPP), tris(butyl) phosphate (TNBP), tris(isobutyl) phosphate (TIBP), tris(2-butoxyethyl) phosphate (TBOEP), tris(2-ethylhexyl) phosphate (TEHP), TCEP, TCIPP, TDCIPP, tris(phenyl) phosphate (TPHP), tris(methylphenyl) phosphate (TMPP), and 2-ethylhexyl diphenyl phosphate (EHDPP), were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Six OP diesters, including di-*n*-butyl phosphate (DNBP) for parent TNBP, bis(2-butoxyethyl) phosphate (BBOEP) for parent TBOEP, bis(2-chloroethyl) phosphate (BCEP) for parent TCEP, bis(2-chloroisopropyl) phosphate (BCIPP) for parent TCIPP, bis(1,3-dichloroisopropyl) phosphate (BDCIPP) for parent TDCIPP, and diphenyl phosphate (DPHP) for parent TPHP, were studied. DNBP, BBOEP, BCEP, BCIPP, and BDCIPP were purchased from Toronto Research Chemicals (North York, ON), and DPHP was purchased from Tokyo Chemical Industry (Tokyo, Japan). Detailed information about their molecular formula/weight and physicochemical parameters is listed in Table S1. Internal standards TNBP-d_{27}, TDCIPP-d_{15}, TPHP-d_{15}, and DPHP-d_{10} were obtained from Cambridge Isotope Laboratories (Andover, MA). Stock solutions of the target analytes were prepared in acetonitrile and stored at −20 °C. Methanol, acetonitrile, ethyl acetate, and cyclohexane of high-performance liquid chromatography grade were acquired from Oceanpak (Gothenburg, Sweden).

Field Sampling. A total of 64 sewage sludge samples from WWTPs in 36 cities across China (Figure S1) were collected from October 2010 to May 2011. Details about the secondary treatment technologies, sewage sources, and treatment capacities for the WWTPs have been published previously[41] and are listed in Table S2. Freshly digested sludge (0.5−1.0 kg of wet weight) from a secondary clarifier in each WWTP was collected after the dewatering process. Wet sludge samples were packed in aluminum foil, sealed in ziplock bags, and transported immediately to the laboratory, where they were freeze-dried, homogenized, sieved through 100 mesh sieve, and then stored at −20 °C before being extracted.

Sample Extraction and Cleanup. The sample extraction procedure for OP triesters was adopted from previous studies with moderate modifications.[32,42] The procedure used to extract samples for OP diesters was different from that for triesters. Detailed sample extraction and cleanup procedures are presented in the Supporting Information.

Ultraperformance Liquid Chromatography−Tandem Mass Spectrometry (UPLC−MS/MS) Analysis. Analyte concentrations were measured using an ultraperformance liquid chromatograph (Nexera X2, Shimadzu) coupled to a tandem mass spectrometer (Triple Quad 5500 System, AB SCIEX) based on previously reported methods with some optimizations.[43−46] Detailed information with regard to UPLC and MS/MS parameters (Table S3) is given in the Supporting Information.

Quality Assurance and Quality Control. Strict quality controls were implemented to ensure accurate quantification of these target compounds. All glassware was soaked in a phosphate-free cleaning agent (decon90) for 12 h and then rinsed thoroughly with deionized water. After being carefully dried, the glassware was rinsed with solvent and then heated at 450 °C overnight prior to use. For the evaluation of extraction efficiency, sludge samples were randomly chosen for the fourth extraction after the first three extraction cycles, and the target compounds were undetected in the fourth extraction, which indicated high efficiencies of the first three extractions for sludge samples. One procedure blank sample was included in every batch of 10 samples to monitor the contamination of the blank. Most analytes in the blanks were under the limit of detection except TIBP and TPHP (Table S4), and therefore, the two OP triester concentrations were corrected by the blank.

Randomly selected sludge samples ($n = 6$) were fortified with known concentrations of OPEs (5−25 ng) for determination of the matrix effect (for details, see the Supporting Information).[12] The matrix effect was within 91−107%, and thus, the potential overestimation or underestimation of concentrations could be excluded. The matrix spike recovery was examined in a matrix spike sample and a matrix spike duplicate according to the U.S. Environmental Protection Agency (EPA) method.[47] Average matrix spike recoveries ($n = 6$) of target analytes and internal standards (IS) were between 67 and 99% and between 74 and 104%, respectively. Accuracy and precision were evaluated by fortification of samples ($n = 6$) with native and internal standards, and analysis of those samples through the entire procedure.[12] For accuracy, the deviations of IS-corrected quantitative results from the known values were ≤15%. For precision, the relative standard deviations (RSDs) in duplicate sample tests were ≤10%. Recoveries of TNBP-d_{27}, TDCIPP-d_{15}, TPHP-d_{15}, and DPHP-d_{10} in all field samples ($n = 64$) were 73 ± 6, 84 ± 17, 101 ± 10, and 78 ± 13%, respectively. The method quantification limits (MQLs) of the analytes were calculated as a signal-to-noise ratio of 10, which were from 0.09 ng g^{-1} (DPHP) to 3.76 ng g^{-1} (TCIPP). Detailed data are listed in Table S4. Concentrations below MQLs were replaced

Table 1. Descriptive Statistics of Concentrations (nanograms per gram of dry weight) of the Detected OP Triesters and Diester Degradation Products in Nationwide Municipal Sludge from China

analyte	DF[a] (%)	range	mean	median	P95[b]	AP[c] (%)
OP triesters						
TPP	76.6	<MQL−8.77	1.78	1.75	3.63	0.6
TNBP	100	2.97−430	24.7	14.5	45.6	8.2
TIBP	100	6.25−387	33.6	23.6	98.3	11.1
TBOEP	98.4	<MQL−350	39.7	15.0	148	13.1
TEHP	81.2	<MQL−272	21.3	11.9	54.4	7.0
TCEP	100	1.73−270	34.0	22.8	75.0	11.2
TCIPP	95.3	<MQL−645	43.8	27.0	109	14.4
TDCIPP	90.6	<MQL−85.9	10.4	7.38	28.0	3.4
TPHP	100	2.37−585	26.2	11.3	54.4	8.6
TMPP	100	3.77−624	39.4	21.0	92.6	13.0
EHDPP	93.8	<MQL−180	28.5	21.1	68.9	9.4
$\sum_{11}$OP triester	100	43.9−2.16 × 10^3	303	229	648	100
OP diesters						
DNBP	89.1	<MQL−406	30.1	12.6	94.2	24.5
BBOEP	100	0.48−50.6	8.30	3.86	33.2	6.8
BCEP	79.7	<MQL−287	29.1	18.4	68.1	23.7
BCIPP	95.3	<MQL−178	29.6	19.3	79.9	24.1
BDCIPP	32.8	<MQL−95.8	6.20	<MQL	18.6	5.0
DPHP	100	0.63−861	19.5	4.26	19.4	15.9
$\sum_6$OP diester	100	17.0−1.30 × 10^3	123	82.9	285	100

[a] Detection frequency. [b] The 95th percentile. [c] Averaged proportion in each group.

by half of the MQLs, and all data were log-transformed for statistical analysis using IBM SPSS Statistics 20.0 (IBM Corp.). Eight-point calibration curves were established in the range of 0.50−500 ng mL^{-1} with a regression coefficient (r^2) of >0.995.

Ecological Risk Assessment. The risk assessment in sludge-applied soils was performed using risk quotient (RQ) values, which are expressed as

$$\mathrm{RQ} = \frac{\mathrm{PEC_{soil}}}{\mathrm{PNEC_{soil}}}$$

where PNEC$_{\mathrm{soil}}$ is defined as the predicted no effect concentration on organisms and often derived from the no observed effect concentration (NOEC) in the laboratory. PEC$_{\mathrm{soil}}$ was estimated as the concentration of a contaminant in agricultural soil from one year after sludge-dose application.[48] The maximum probable risk of ecological effects was evaluated on the basis of the commonly recommended criteria: high risk ($\mathrm{RQ} \geq 1.0$), medium risk ($0.1 \leq \mathrm{RQ} < 1.0$), and low risk ($0.01 \leq \mathrm{RQ} < 0.1$).[48,49]

In this study, the PNEC$_{\mathrm{soil}}$ values for TCEP, TCIPP, TDCIPP, TPHP, TMPP, and EHDPP refer to the data from the European Commission,[6] while the PNEC$_{\mathrm{soil}}$ values for other OP triesters and diesters were estimated as a quotient of toxicologically relevant concentration LC$_{50}$ and an assessment factor (f) using the formula $\mathrm{PNEC_{soil}} = \mathrm{LC_{50}}/f$, where f was 1000.[50,51] For this purpose, the LC$_{50}$ for earthworm associated with TPP, TNBP, TIBP, TBOEP, TEHP, DNBP, BBOEP, BCEP, and DPHP was used for PNEC$_{\mathrm{soil}}$ calculation.[52]

The PEC$_{\mathrm{soil}}$ values in soils to which sludge had been applied were determined according to the European Commission Technical Guidance Document (TGD) on Risk Assessment:[48,50]

$$\mathrm{PEC_{soil}} = \frac{C_{\mathrm{sludge}} \times \mathrm{APPL_{sludge}}}{\mathrm{DEPTH_{soil}} \times \mathrm{RHO_{soil}}}$$

where C_{sludge} (grams per kilogram of dry weight) is the measured concentration of the target compound in sludge, APPL$_{\mathrm{sludge}}$ is the rate of application of dry sludge to agricultural soils (usually 0.50 kg m^{-2} year^{-1}), DEPTH$_{\mathrm{soil}}$ is the mixing depth (usually 0.20 m for agricultural soils), and RHO$_{\mathrm{soil}}$ is the bulk density of wet soil (usually 1.5 × 10^3 kg m^{-3} for agricultural soils).

RESULTS AND DISCUSSION

Concentrations, Spatial Distribution, and Composition Profiles of OP Triesters in Nationwide Sludge. All the target OPEs (triesters) were detected in most sludge samples (Table 1). The total concentration of 11 OPEs (the sum of which is designated as $\sum_{11}$OPE hereafter) ranged from 43.9 to 2160 ng [g of dry weight (dw)]$^{-1}$ with an average value of 303 ng (g of dw)$^{-1}$, indicating considerable variability among the WWTPs. The maximum and minimum concentrations of OPEs were found at WWTPs located in Zhejiang province of East China and Yunnan province of West China, respectively. The WWTPs under investigation mainly treat domestic wastewater or mixed domestic/industrial wastewater (Table S2). The highest $\sum_{11}$OPE concentration from East China may be attributed to the high industrial output in this region as corroborated by the large portion (70%) of industrial wastewater found in the WWTP influents. Sludge with predominant industrial inputs generally contained OPE levels higher than those of domestic sludge.[37] The national average concentration of sludge OP triesters in China was lower than that previously reported in two relatively more economically developed regions of China, i.e., 699 ng (g of dw)$^{-1}$ with a range of 204−4010 ng (g of dw)$^{-1}$ in Beijing[33] and 420 ng (g of dw)$^{-1}$ with a range of 96.7−1313 ng (g of dw)$^{-1}$ in the Pearl River Delta (PRD),[37] but higher than that found in Henan Province [mean of 170 ng (g of dw)$^{-1}$ and range of 38.6−508 ng (g of dw)$^{-1}$], which is a less developed region.[38]

Table 2. Pearson Correlation Matrix for Concentrations of OP Triesters in Sludge Samples[a]

	TPP	TNBP	TIBP	TBOEP	TEHP	TCEP	TCIPP	TDCIPP	TPHP	TMPP
TNBP	0.048									
TIBP	0.218	0.829[b]								
TBOEP	−0.145	0.300[c]	0.225							
TEHP	−0.183	0.169	0.131	0.344[b]						
TCEP	−0.052	0.390[b]	0.389[b]	0.168	0.146					
TCIPP	−0.079	0.340[b]	0.284[c]	0.159	0.295[c]	0.605[b]				
TDCIPP	−0.118	0.229	0.125	0.487[b]	0.679[b]	0.284[c]	0.481[b]			
TPHP	−0.012	0.510[b]	0.395[b]	0.519[b]	0.524[c]	0.356[b]	0.420[b]	0.682[b]		
TMPP	−0.150	0.425[b]	0.322[b]	0.280[c]	0.439[b]	0.311[c]	0.220	0.474[b]	0.555[b]	
EHDPP	−0.340	0.186	0.215	0.291[c]	0.265[c]	0.409[b]	0.196	0.193	0.169	0.265[c]

[a] Concentration correlation analysis was performed among all identified OP triesters after log-transformation. [b] Significant correlation at the $p < 0.01$ level. [c] Significant correlation at the $p < 0.05$ level.

Sludge $\sum_{11}$OPE concentrations in China were at least 10 times lower than those in Sweden [mean of 4239 ng (g of dw)$^{-1}$ and range of 620−6900 ng (g of dw)$^{-1}$],[31] Spain [mean of 4476 ng (g of dw)$^{-1}$ and range of 1185−13370 ng (g of dw)$^{-1}$],[32] Germany [only TCIPP detected over a range of 1000−20000 ng (g of dw)$^{-1}$],[30] and the United States [mean of 11800 ng (g of dw)$^{-1}$ and range of 4110−20200 ng (g of dw)$^{-1}$].[12] The relatively low levels of $\sum_{11}$OPE in China were consistent with the relatively low levels of consumption of OPEs in China compared with the levels of these developed countries. According to a report,[53] the amount of OPEs consumed in China accounted for only 4% of the global production in 2008, while Europe and the United States used 40 and 35%, respectively. These results implied that elevated sludge levels of $\sum_{11}$OPE in developed countries were likely associated with more widespread industrial activity together with greater consumption of OPEs, but the population density of the location of the WWTP was another potential factor.[54]

Of all target OP triesters, TNBP, TIBP, TCEP, TPHP, and TMPP were detected in all sludge samples, whereas TBOEP (98.4%), TCIPP (95.3%), EHDPP (93.8%), TDCIPP (90.6%), TEHP (81.2%), and TPP (76.6%) were partially detectable. In Sweden, Germany, and Spain,[30−32] EHDPP, TCIPP, TBOEP, and TEHP were the abundant compounds in sludge. Some previous studies in China indicated that the predominant compounds of OP triesters were TEHP and TMPP in Beijing,[33] TBOEP and TPHP in the Pearl River Delta,[37] and TCEP, TBOEP, and TCIPP in Henan Province.[38] In the study presented here, TIBP, TBOEP, TCEP, TCIPP, and TMPP made a comparable contribution (11.1−14.4%) (Table 1), which were identified as the dominant compounds. Generally, sludge samples from the same province or municipality were similar in their composition profiles of OPEs, but variations among different regions were observed (Figure S2). Differences in composition profiles of sludge OPEs between different regions in China and between China and other countries may be attributed to varying patterns of use.

There is still a lack of environmental data for OPEs in sludge among different countries worldwide. We compared individual OP triester concentrations with the reported data from Sweden, Spain, Canada, the United States, and Germany (Table S5). In the study presented here, TPP was detected in 49 of 64 samples at concentrations in the range of <MQL−8.77 ng (g of dw)$^{-1}$. The lowest concentration and percentage composition for TPP (Table 1) could be partly attributed to its low log K_{ow} and preferential partitioning in the aqueous phase, while the production volume, usage period, and stability were also related to the sludge TPP level. The concentrations of TNBP and TIBP in nationwide sludge samples from China were 2.97−430 and 6.25−387 ng (g of dw)$^{-1}$, respectively, comparable to those previously reported in Beijing and Henan Province[33,38] but lower than those detected in sludge from Sweden,[31] Spain,[32] and the PRD of China.[37] Similarly, two other alkyl-OPEs, TBOEP [<MQL−350 ng (g of dw)$^{-1}$] and TEHP [<MQL−272 ng (g of dw)$^{-1}$], also showed levels much lower than those found in Sweden,[31] Spain,[32] Canada,[55] and the United States.[12] For three hydrophilic chlorinated alkyl-OPEs, TCEP, TCIPP, and TDCIPP, accumulation in sludge was not a major mechanism of removal in WWTPs,[32] but their high detection frequencies (90.6−100%) in sludge were still observed in this study. The concentration of TCEP [1.73−270 ng (g of dw)$^{-1}$] was similar to those reported in Sweden[31] and Germany,[30] whereas sludge levels of TCIPP [<MQL−645 ng (g of dw)$^{-1}$] and TDCIPP [<MQL−85.9 ng (g of dw)$^{-1}$] were still much lower than those detected in Sweden, Spain, the United States, and Germany.[12,30−32] The aryl-OPEs, including TPHP, TMPP, and EHDPP, have relatively high log K_{ow} values (4.6−6.6) and can easily be adsorbed onto sludge. Concentrations of TPHP, TMPP, and EHDPP were in the ranges of 2.37−585, 3.77−624, and <MQL−180 ng (g of dw)$^{-1}$, respectively. Much lower levels of the three aryl-OPEs were also found upon comparison with those detected in Sweden, Spain, and the United States.[12,31,32] The consumption amount and usage pattern of OP triesters might be the major factors contributing to the nation-specific difference in the distribution of OP triesters in sludge.[12,53]

Pearson correlation analysis was performed on the log-transformed concentrations of OP triesters. Significant correlations (r = 0.265−0.829; $p < 0.05$) were found among all OP triesters except for TPP (Table 2), which could suggest some common sources and/or similar environmental fates. The nationwide spatial distribution patterns of chlorinated alkyl-OPE, aryl-OPE, nonchlorinated alkyl-OPE, and $\sum_{11}$OPE concentrations are shown in Figure 1A, while the stacked columns of $\sum_{11}$OPE in each province or municipality are presented in Figure S2. Higher concentrations of OPEs in East China, particularly in coastal regions, than in Central and West China can be visualized. Eastern provinces (e.g., Zhejiang and Guangdong) showed average sludge concentrations of total OPEs higher than those of central provinces (e.g., Hubei and Hunan) and western provinces (e.g., Yunnan and Gansu). Similar region-specific spatial distributions for alternative halogenated flame retardants (BFRs),[41] hydroxylated polybrominated diphenyl ethers,[56] and quaternary ammonium

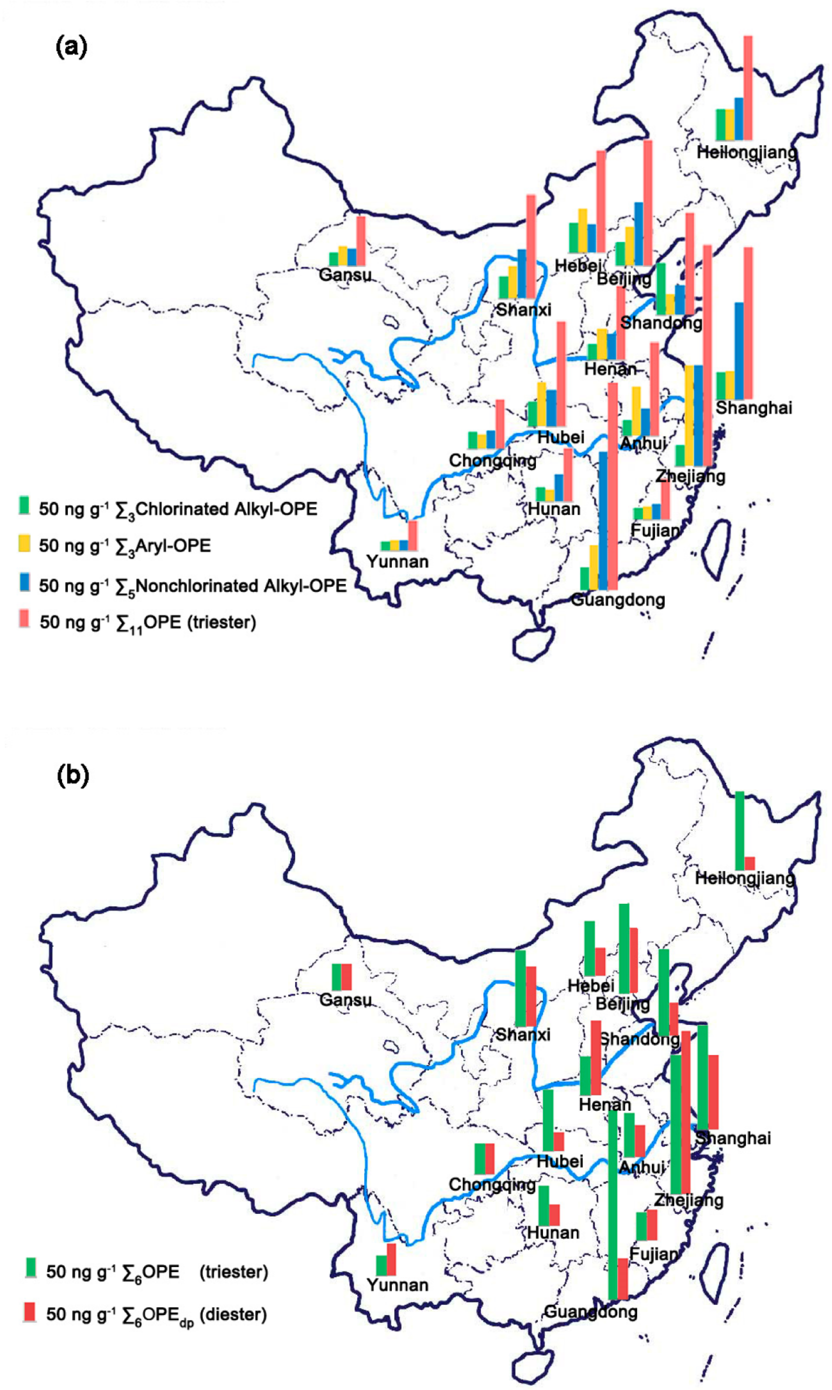

Figure 1. Spatial distribution patterns of (a) $\sum_3$chlorinated alkyl-OPE, $\sum_3$aryl-OPE, $\sum_5$nonchlorinated alkyl-OPE, and $\sum_{11}$OPE (triester) and (b) $\sum_6$OPE (TNBP, TBOEP, TCEP, TCIPP, TDCIPP, and TPHP) and their diester degradation products $\sum_6$OPE$_{dp}$ (DNBP, BBOEP, BCEP, BCIPP, BDCIPP, and DPHP) in sludge samples in China (mean concentrations are shown in each province or municipality).

compounds (QACs)[57] in Chinese sludge were also reported. As is well known, East China is a more economically developed region with a degree of industrialization and urbanization that is higher than those of Central China and West China, which is the major manufacturing base for electronic products, textiles, and plastic products in China. The relationship between the $\sum_{11}$OPE concentration of sludge and gross domestic product (GDP) in each province and municipality was analyzed (Figure S3). A significant positive correlation between $\sum_{11}$OPE and GDP was found ($r^2 = 0.40$; $p < 0.05$). Regions with higher GDP, especially in the production and consumption of products in the more economically developed regions, might increase the occurrence of these chemicals. The results indicate that variations in pollution levels of OPEs are closely associated with regional economic development levels. In a previous study, similar correlations were also reported between sludge concentrations of perfluoroalkyl substances (PFCs) and the GDP in selected Chinese cities.[54] In view of this, further monitoring and management efforts are desirable in developed regions to gauge potential risks from co-occurrence of multiple organic pollutants.

Concentrations, Spatial Distributions, and Composition Profiles of Diester Degradation Products in Nationwide Sludge. Organophosphate triesters can be rapidly metabolized in humans and animals in many studies.[3] We suspect that OP triesters can also been metabolized and/or transformed by microorganisms during active sludge treatment in WWTPs. Though the OP diesters as biomarkers of OP triester exposure have been largely investigated and reported in human urine samples worldwide, few studies have reported their widespread occurrence in municipal sludge. In the study presented here, six potential OP diester degradation products (DNBP, BBOEP, BCEP, BCIPP, BDCIPP, and DPHP, the sum of which is designated as $\sum_6\text{OPE}_{\text{dp}}$) were all identified in the sludge samples (Table 1). The concentration of $\sum_6\text{OPE}_{\text{dp}}$ varied from 17.0 to 1300 ng (g of dw)$^{-1}$ with a mean of 123 ng (g of dw)$^{-1}$. The large variability in $\sum_6\text{OPE}_{\text{dp}}$ in sludge of WWTPs nationwide indicated that multiple factors, including parent compound concentrations, degradation pathways, physicochemical properties, sewage sources, and biological treatment techniques, might affect the concentrations of OP diesters.

BBOEP and DPHP were detected in all sludge samples with mean concentrations of 8.3 ng (g of dw)$^{-1}$ [range of 0.48−50.6 ng (g of dw)$^{-1}$] and 19.5 ng (g of dw)$^{-1}$ [range of 0.63−861 ng (g of dw)$^{-1}$], respectively. DNBP was detected in 89.1% of the samples with a mean of 30.1 ng (g of dw)$^{-1}$ [range of <MQL−406 ng (g of dw)$^{-1}$]. Among three chlorinated OP diesters, BCEP and BCIPP were identified in sludge for the first time to the best of our knowledge. BCIPP, BCEP, and BDCIPP were detected in 95.3, 79.7, and 32.8% of the samples, respectively, and their mean concentrations were 29.6 ng (g of dw)$^{-1}$ [range of <MQL−178 ng (g of dw)$^{-1}$], 29.1 ng (g of dw)$^{-1}$ [range of <MQL−287 ng (g of dw)$^{-1}$], and 6.2 ng (g of dw)$^{-1}$ [range of <MQL−95.8 ng (g of dw)$^{-1}$], respectively. Of all identified OP diesters, DNBP, BCEP, and BCIPP contributed almost equally (23.7−24.5%) to $\sum_6\text{OPE}_{\text{dp}}$, which were found to be the predominant OP diesters in the current municipal sludge in China. For BCEP, BCIPP, and BBOEP, because of a lack of available data in the literature, there is no possibility for comparison of concentrations with those of other regions or countries at present. For DPHP, DNBP, and BDCIPP, the reported regional levels in Beijing from a previous study[33] were slightly lower than the national levels found in the study presented here.

Geographical distribution patterns of mean concentrations of six OP diester degradation products ($\sum_6\text{OPE}_{\text{dp}}$) and their parent compounds (TNBP, TBOEP, TCEP, TCIPP, TDCIPP, and TPHP, the sum of which is designated as $\sum_6\text{OPE}$) are shown in Figure 1B, while the stacked columns of six OP diesters and their distribution pattern in each province or municipality are listed in Figure S4. Similar to those of OP triesters, the mean concentrations of $\sum_6\text{OPE}_{\text{dp}}$ also decreased from eastern China toward central and western China, with the highest and lowest values observed in Zhejiang Province [408 ng (g of dw)$^{-1}$] and Heilongjiang Province [35.7 ng (g of dw)$^{-1}$], respectively. There was not much difference in $\sum_6\text{OPE}_{\text{dp}}$ concentrations between the central and western provinces of China. Similar composition profiles of OP diesters characterized by DNBP, BCEP, and BCIPP as the predominant compounds were observed among the provinces and municipalities (Figure S4). Pearson correlation analysis was performed on the log-transformed concentrations of OP diesters with a detection frequency of >50%. No significant correlations between OP diester concentrations in sludge were found except for DPHP versus DNBP and DPHP versus BBOEP (Table 3), implying that OP diester degradation products may have different sources and/or transport pathways in WWTPs. However, considering OP triesters having different transformation and/or degradation pathways in biota and the environment,[20] the linear correlation analysis presented below between OP triesters and diesters may be indicative of some OP diester formation not being the most important degradation pathway in WWTPs.

Table 3. Pearson Correlation Matrix for Concentrations of Major OP Diester Degradation Products[a]

	DNBP	BBOEP	BCEP	BCIPP
BBOEP	0.115			
BCEP	0.147	0.159		
BCIPP	0.085	0.225	0.019	
DPHP	0.469[b]	0.422[b]	0.081	−0.038

[a] Concentration correlation analysis was performed among emerging OP diester degradation products with a detection frequency above 50% after log-transformation. [b] Significant correlation at the p < 0.01 level.

Correlations between OP Triesters and Diester Degradation Products and Implication for Potential Sources. Because WWTPs receive influents from a variety of domestic and/or industrial wastewater input, OP diester degradation products in WWTPs may also come from excretion of human urine and feces and/or other pathways (e.g., photodegradation and hydrolysis) as well as biodegradation of their parent compounds during active sludge treatment.[27] To ascertain the potential sources of these OP diester degradation products, regression analyses between OP triesters and their diester degradation products were performed on the log-transformed concentrations both with a detection frequency of >50%. Strong linear correlations between the concentrations of TBOEP and BBOEP (r^2 = 0.49; p < 0.01) and TPHP and DPHP (r^2 = 0.51; p < 0.01) were observed in these sludge samples (Figure 2), but no significant correlations were found between the concentrations of TNBP and DNBP (r = 0.15; p > 0.05), TCEP and BCEP (r = −0.18; p > 0.05), and TCIPP and BCIPP (r = −0.045; p > 0.05). Because of the low detection frequency (32.8%) for BDCIPP, correlation analysis of BDCIPP and its parent TDCIPP was not conducted. These results indicated that BBOEP and DPHP in sludge may be mainly derived from biodegradation of their parent compounds

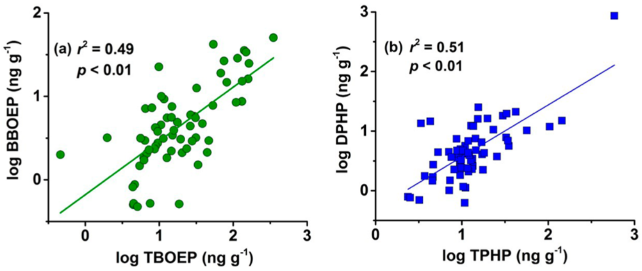

Figure 2. Significant correlations between log-transformed concentrations of OP triesters and diester degradation products in Chinese sewage sludge: (a) TBOEP and BBOEP and (b) TPHP and DPHP.

in WWTPs, but this was not the case for DNBP, BCEP, BCIPP, and BDCIPP.

The results presented above were further combined with the prediction models to diagnose the potential sources of diester degradation products in sludge. The behavior and fate of OPEs in typical WWTPs could partially be illustrated and predicted by their physicochemical properties. The estimated ultimate degradation half-life (BIOWIN3) and elimination fate (STPWIN32) of OPEs in wastewater treatment by EPI Suite version 4.11 (U.S. EPA)[52] are summarized in Table S6. Among the six OP diesters, only DNBP was documented to be industrially produced and used in plasticizers and metal extractants.[58] The mean concentration of DNBP in the study presented here was higher than that of TNBP. A recent mass balance analysis[36] also indicated that a high level of degradation during traditional sludge treatment can occur, coinciding with the predicted short degradation half-life of TNBP (Table S6). Hence, DNBP in sludge might have originated from both industrial sources and degradation of its parent compound (TNBP) in WWTPs, which also explains the lack of a significant correlation between DNBP and TNBP. TBOEP and TPHP also have short half-lives similar to that of TNBP (Table S6); thus, similar fast degradations are predicted. In fact, two previous studies[32,36] suggested that TBOEP and TPHP could be easily degraded by activated sludge treatments. The mean concentrations of BBOEP and DPHP were 21 and 74% of those of their parent compounds (TBOEP and TPHP), respectively, which can be explained by more rapid chemical hydrolysis of TPHP under general-pH conditions (6−9) in WWTPs.[27] The positive significant correlations between the two diesters and their triester parent compounds as mentioned above suggested that BBOEP and DPHP in sludge could mainly be derived from degradation of TBOEP and TPHP in WWTPs.

The chlorinated OP triesters (TCEP, TCIPP, and TDCIPP) are currently of most concern among the OPEs because of their high toxicity and possible health effects. The predicted degradation half-lives of TCEP, TCIPP, and TDCIPP are much longer than those of TNBP, TBOEP, and TPHP (Table S6), and therefore, these compounds are difficult to degrade in WWTPs. Actually, as the most recalcitrant OP triesters, TCEP, TCIPP, and TDCIPP showed poor degradation during conventional activated sludge treatment.[31,32] However, the widespread occurrences of BCEP and BCIPP as the predominant diester degradation products and the presence of BDCIPP in sludge indicate that the three chlorinated OP diesters could come from outside sources of WWTPs. Su et al.[27] recently reported that, in aqueous solutions, chlorinated OP triesters were stable at pH 7−11 but could be extensively degraded at pH 13 over a period of 35 days. Thus, some alkaline industrial wastewater could be a source of chlorinated diester degradation products to the WWTPs. The occurrence of chlorinated OP diesters has been widely reported in human urine,[3,10,17−19,21−23,26,44] which could be another source for the WWTPs. Consequently, some industrial wastewater and metabolic excretion of the exposed population around WWTPs could be the main sources of chlorinated OP diesters in sludge. The occurrence of BCEP, BCIPP, and BDCIPP was not mainly due to the degradation of parent compounds within WWTPs, which also can explain the lack of significant correlations between chlorinated diersters and their parent triesters in sludge. Further mass balance analysis is recommended to track and corroborate the sources by simultaneous determination of OP triesters and diesters into and out of WWTPs.[12] The widespread occurrences of BCEP, BCIPP, and BDCIPP at a national geographical scale should be of environmental concern.

Estimated National Emissions of OP Triesters and Diesters via Land-Application Sludge and Ecological Risk Assessment in Sludge-Amended Soils. In this study, 11 OP triesters and six diesters were positively identified in 64 sludge samples collected from nationwide WWTPs in China, suggesting the prevalent usage of OPEs and widespread occurrence of these anthropogenic contaminants. Compared with developed countries, China is currently not a major consumer but is one of the largest producers and exporters of OPEs in the world. It was documented that the production volume for OPEs has been ∼70 kt/year in recent years, with 15−20 kt/year consumed in the Chinese market.[5,59] According to the announcement from the Ministry of Environmental Protection of China, there were 4436 municipal WWTPs treating 135000 tons of wastewater on a daily basis in 2014.[60] The amount of sewage sludge generated is approximately 34 million t (at a moisture content of 80%) on an annual basis from the nationwide WWTPs in China.[61] On the basis of the latest statistical data,[62] sludge disposal in China generally includes landfilling (50%), land application (16%), incineration (10%), and producing building materials (9%), whereas untreated sludge accounts for 15% at present.

To evaluate the impact of the disposal of sludge on the environment, the nationwide annual emission fluxes of OP triesters and diesters were estimated on the basis of total sludge production volume and mean accumulation concentrations in sludge. The estimated emission fluxes were 2060 kg/year for $\sum_{11}$OPE and 836 kg/year for $\sum_{6}$OPE$_{dp}$. Of the three major categories of OPEs, the nonchlorinated alkyl-OPEs, aryl-OPEs, and chlorinated alkyl-OPEs accounted for 40, 31, and 29% of total emissions, respectively. Via comparison of the total annual accumulation (sum of OP triesters and diesters) in sludge to annual consumption volume in China, the leakage fraction of OPEs from the technosphere via municipal wastewater into sludge is 0.02%, which is comparable to that of alternative brominated flame retardants (BFRs) reported in our previous study.[41] This small fraction may be attributed to the relatively limited treatment rate of wastewater in China and large release with treated effluent.[36] Furthermore, the estimated environmental emission fluxes of 11 OP triesters and six diesters via land-application sludge in China are 330 and 134 kg/year, respectively. Until now, less has been known about the ultimate fate and environmental risks of these emerging chemicals in soils to which sludge had been applied.

The half-lives of OP triesters and diesters in soil, air, and water were estimated by EPI Suite version 4.11 (U.S. EPA),[52] and their overall persistence and transport potential in a multimedia evaluative environment were also predicted by the OECD Pov-LRTP Screening Tool.[63] As shown in Table S6, the half-lives in soils of chlorinated TCEP, TCIPP, and TDCIPP are obviously higher than those of TPHP and TMPP and much higher than those of TPP, TNBP, TIBP, TBOEP, TEHP, and EHDPP. Diesters BCEP and DPHP also show long half-lives, which are equal to those of TPHP and TMPP. The estimated half-lives of OP diesters are generally shorter than those of their parent triesters except for DPHP, which is more toxic than TPHP but has a half-life equal to that of TPHP. Furthermore, the predicted overall persistence and transport potential for TCEP, TCIPP, TDCIPP, TPHP, and TMPP are greater than for other OP triesters except for TEHP, which exhibits a shorter overall persistence but the highest transport potential. It was notable that BCEP and DPHP also have long persistence values and high transport potentials compared with those of other OP diesters and most triesters. TCEP, TCIPP, and TMPP are some of the identified dominant OP triesters, and BCEP and DPHP are OP triesters that are both highly abundant in sludge; their long persistence values and high transport potentials should raise environmental concerns about their ecological risk in soils to which sludge has been applied.

The risk assessment of all OP triesters and four diesters ($PNEC_{soil}$ values were unavailable for BCIPP and BDCIPP) in soils to which sludge had been applied was performed on the basis of risk quotient (RQ) values. The estimated risk quotients (RQs) of 11 OP triesters and four diesters are illustrated in Figure 3, and the $PNEC_{soil}$ (micrograms per kilogram) and PEC_{soil} (micrograms per kilogram) values of these pollutants are summarized in Table S7. A high risk in soils to which sludge had been applied was found for only TMPP. A potential medium risk was indicated for TEHP, TPHP, and EHDPP, as some of their RQ values were in the range of 0.1−1. In addition, low RQ values (<0.1) were found for other OP triesters and diesters, suggesting currently low ecological risks in soils after sludge fertilization in China. However, considering the much higher residual levels of OPEs in sludge in developed countries that consume more OPEs, we should pay greater attention to potentially high ecological risks in soils to which sludge has been applied in the future.

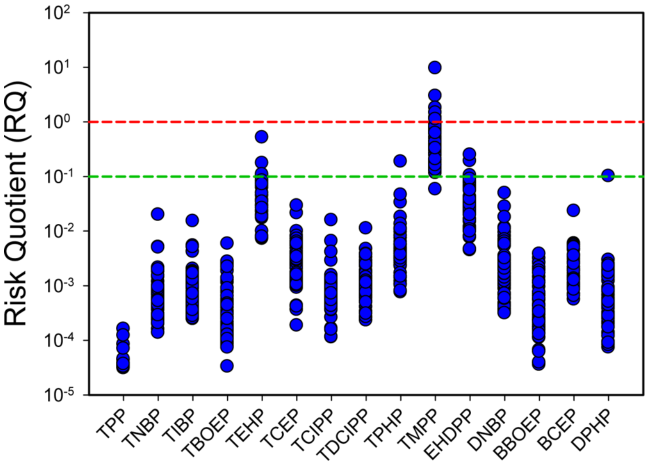

Figure 3. Estimated risk quotients (RQs) of 11 OP triesters and four diester degradation products in soils to which sludge had been applied. Red and green lines represent values of 1 and 0.1, respectively.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b04106.

> Additional information about sample extraction and cleanup, detailed information about target analytes and physicochemical parameters (Table S1), detailed information about WWTPs (Table S2), MS/MS parameters (Table S3), method validation (Table S4), comparison of concentrations between China and some developed countries (Table S5), predicted behavior and fate of OPEs in WWTPs and in the environment (Table S6), $PNEC_{soil}$ and PEC_{soil} values of analytes (Table S7), sampling map of WWTPs across China (Figure S1), average levels and composition profiles of OP triesters (Figure S2) and diesters (Figure S4) in each province or municipality, and correlation between sludge $\sum_{11}$OPE and GDP (Figure S3) (PDF)

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