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Polybrominated diphenyl ethers and their alternatives in soil cores from a typical flame-retardant production park: Vertical distribution and potential influencing factors^{\star}

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ABSTRACT

With the prohibition on the production and use of polybrominated diphenyl ethers (PBDEs), decabromodiphenyl ethane (DBDPE) and organophosphate flame retardants (OPFRs) have emerged as their alternatives. However, the vertical transport and associated influencing factors of these chemicals into soil are not clearly understood. To clarify the vertical distribution of the pollutants and related influencing factors, surface soil and soil core samples were collected at a depth in the range of 0.10–5.00 m in a typical 20-year-old flame-retardant production park and surrounding area. PBDEs and DBDPE show a clear point source distribution around the production park with their central concentrations up to 2.88×10^4 and 8.46×10^4 ng/g, respectively. OPFRs are mainly found in residential areas. The production conversion of PBDEs to DBDPE has obvious environmental characteristics. The vertical distribution revealed that most of the pollutants have penetrated into the soil 5.00 m or even deeper. The median concentrations of deca-BDE and DBDPE reached 50.9 and 9.85×10^3 ng/g, respectively, even at a depth of 5.00 m. Soil organic matter plays a crucial role in determining the vertical distribution, while soil clay particles have a greater impact on the high molecular weight and/or highly brominated compounds.

1. Introduction

Brominated flame retardants (BFRs) are frequently used in various plastic materials for domestic and industrial applications to delay ignition or self-extinguish combustion (Bevington et al., 2022; McGrath et al., 2017). Due to their extensive production and usage, as well as their irregular disposal, these chemicals have been ubiquitously detected in atmospheric, soil, and aquatic environments (Chen and Ma, 2021; Lee et al., 2020; Ruan et al., 2019; Yadav et al., 2018), and even in the human body and other organisms (Klinčić et al., 2020; Ma et al., 2020; Wang et al., 2021a,b; Zhao et al., 2021). Since the early 1900s, several traditional flame retardants have been included in the control list of

persistent organic pollutants by the United Nations Environment Program, such as α -, β -, and γ -hexabromocyclododecane in 2013 (Cao et al., 2018) and commercial polybrominated (penta-, octa-, and deca-) biphenyl ethers (PBDEs) in 2009 and 2017 (Abbasi et al., 2019).

These regulations have created a potential market for alternatives. For example, the cumulative production of decabromodiphenyl ethane (DBDPE) in China was estimated to have reached 230 kilotons in the decade from 2006 to 2016, an increase of 182% (Shen et al., 2019). Furthermore, since 2012, DBDPE has surpassed PBDEs in terms of the market share, and the gap has been widening year by year (Shen et al., 2019). For organophosphorus flame retardants (OPFRs), another alternative, their production has skyrocketed nearly 99-fold over eight years

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from 2011 to 2018 (Zhang et al., 2022a,b). China is the main producer and user of OPFRs, and the total production increased by 40% from 150 tons in 2014 to 210 tons in 2018 (He et al., 2021). Nevertheless, these alternatives have also proven to be environmentally unfriendly (Chen and Ma, 2021; Wang et al., 2019; Wang et al., 2023; Xue et al., 2022).

Soil is important environmental matrix and functions as both a sink and secondary source in the atmospheric migration of persistent organic pollutants (An et al., 2023; Tian et al., 2023). To date, most studies have focused on the two-dimensional spatial distribution of pollutants in urban, farmland, and industry soil samples (Oloruntoba et al., 2021; Zapata-Corella et al., 2023). BFRs and their alternatives typically exhibit a point-source distribution pattern centered on a specific area (Ge et al., 2020; Li et al., 2016; McGrath et al., 2018; Yue et al., 2022). However, the vertical migration of these chemicals in soil and the main influencing factors have received limited research attention, although there were some studies on their leaching and degradation through soil on a laboratory scale (Akortia and Okonkwo, 2022; Badea et al., 2013; Liao et al., 2020). For example, highly hydrophobic polychlorinated dibenzo-p-dioxins and dibenzofurans can infiltrate soil at depths ranging from 4 to 17 m (Grant et al., 2015). Chlorinated paraffins can also effectively penetrate to depths of 45-70 cm below ground, and their less chlorinated or short chain congeners are more transportable (Huang et al., 2016; Xu et al., 2023; Zeng et al., 2011). However, there is a lack of research on the behavioral patterns of flame retardants, such as DBDPE and OPFRs, in soil cores in actual sites, although there has been a report on PBDEs from an electronic waste dismantling site (Cheng et al., 2014).

Soil organic matter (SOM) and soil clay particles play crucial roles in the distribution and composition of organic pollutants in soil by influencing the adsorption-desorption process (Liu et al., 2008; Yuan et al., 2012). SOM has been recognized as the main factor controlling the partitioning of hydrophobic organic pollutants in natural soils (Alvarez-Esmorís et al., 2021; Liu et al., 2011; Zhu et al., 2018). In contrast, for soils with a low organic matter content, the inorganic soil components may have a more important role in adsorption and desorption processes (Badea et al., 2013). Soil clay particles (particle size $<2 \mu m$) are closely related to the adsorption and compositional patterns of PBDE fractions in soil (Yuan et al., 2012). However, these results are largely based on studies of surface soil samples, which make it unclear whether they can be used to explain the distribution and transport of BFRs and their alternatives in soil cores (Akortia et al., 2019; Liu et al., 2008). For instance, in soil cores, correlations or non-correlations between certain chemicals, such as short/long chain chlorinated paraffins and PBDE congeners, and soil organic constituents have been found, although such relationships are not always consistent under different environmental conditions (Cheng et al., 2014; Zeng et al., 2011). Therefore, the effects of SOM and soil particles on the vertical distribution and transport of BFRs and their alternatives in soil are of concern.

Furthermore, the vertical transport behavior of the alternatives of PBDEs in soils has not been well-studied, and whether it differs from traditional flame retardants is still unknown. Therefore, the main objectives of our study were to investigate the spatial distribution and vertical transportation of BFRs and their alternatives, including PBDEs, DBDPE, and OPFRs, in soil samples inside and outside a flame-retardant production park as well as the associated influencing factors, such as SOM and soil particle size. This study not only provides a deeper understanding of the enrichment pattern of these compounds in different depth layers of the soil cores, but also offers an important data basis for *in situ* soil remediation required for the relocation of related flame-retardant production parks.

2. Materials and methods

2.1. Reagents and materials

Standards of 20 PBDE congeners and DBDPE were purchased from

AccuStandard, Inc. (New Haven, CT, USA), in which three types of OPFR compounds including 3 alkyl-OPFRs (tripropyl phosphate, TPrP; tris(2ethylhexyl) phosphate, TEHP; tris(2-butoxyethyl) phosphate, TBEP), four Cl-OPFRs (tris(2-chloroethyl) phosphate, TCEP; tris(chloropropyl) phosphate, TCPP; tris(2-chloropropyl) phosphate, T(2-C)PP; tris(1,3dichloro-2-propyl) phosphate, TDCP), and five aryl-OPFRs (triphenyl phosphate, TPhP; 2-ethylhexyl diphenyl phosphate, EHDPP; tri-m-cresyl phosphate, *m*-TCP; tri-*p*-cresyl phosphate, *p*-TCP; tri-*o*-cresyl phosphate, o-TCP) were also provided. ¹³C₁₂-PCB141 was used as a surrogate standard, as well as $^{13}\mathrm{C}_{12}\text{-}\mathrm{PCB208}$ and three deuterated OPFRs (D_{12}\text{-} TCEP, D₁₅-TPhP, and D₂₇-TBP (tributyl phosphate)) as internal standards, which were obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). All solvents (high-performance liquid chromatography grade) (iso-octane, n-hexane, dichloromethane, and ethyl acetate), and Florisil solid phase extraction (SPE) cartridges (1 g/6 mL) were purchased from CNW Technologies (Dusseldorf, Germany). Copper scraps for desulfurization provided by Aladdin (Shanghai, China) were handled using dilute hydrochloric acid (1 M) to remove the oxide film prior to the sample pre-treatment step.

2.2. Study area and sample collection

Shouguang, located in Bohai Bay, is the largest production base of brominated flame retardants in China (Chen et al., 2023; Shen et al., 2019). Convenient meteorological conditions in the coastal area make it an important source of emissions in North China (Lin et al., 2015). A large variety of flame retardants and their derivatives have been found in water, soil, gas, sediments, and organisms as a result of its long production history (Deng et al., 2016; Li et al., 2015; Li et al., 2016; Yu et al., 2022; Zhao et al., 2010). The studied production park is located in the flame-retardant manufacturing base, and there are no other factories of the same type in the sampling area. The park primarily produces brominated flame retardants, and has two production workshops for decabromodiphenyl ether (BDE209, which has been in production for 20 years), three industrial bromine production lines, a large-scale decabromodiphenyl ethane production project, and multiple production lines for other products, such as bromotrigine and bromopropane. The geographical location and sampling range of the study area are shown in Fig. S1.

In the present study, seven undisturbed soil columns (0.1–5.0 m deep) situated close to the plant's manufacturing and storage facilities were taken within the production plant (Table S2), and two soil columns were located in residential and agricultural areas, which were 1 and 2 km away from the plant, respectively. Each intact soil core was collected using a gasoline powered portable impact drilling rig (QTZ-2 model, Lanchuang Machinery Equipment Co., Ltd., Jining, China) and cut into 5–10 cm pieces using a solvent-cleaned scraper. In addition, a total of 22 surface soil samples (0–10.0 cm) were collected around the production plant, and one of them was from a flower bed located next to the office area (Table S2). All of the surface samples were collected based on a grid scheme within a 3×3 km² area, and each of them was a mixture of five sub-samples. All of the collected surface soil and soil core samples were transported to our laboratory in an ice-box.

2.3. Sample preparation and pre-treatment

After removing impurities, such as stones and plant roots, the samples were freeze-dried for 24 h and ground. The final soil samples were passed through a 100-mesh stainless steel sieve and stored in a brown reagent bottle at -20 °C prior to use.

A 0.5 g soil sample was added into a Teflon centrifuge tube. After being spiked with the surrogate standards (13 C-PCB141, D₁₂-TCEP, D₁₅-TPhP, and D₂₇-TBP), 10 mL of a mixture of ethyl acetate, dichloromethane, and n-hexane [1:2:2 (v/v)] was added as the extractant. Vortex and ultrasonic extraction was carried out for 1 and 10 min, respectively, and the mixture was then centrifugated for 10 min at 4000 rpm. The supernatant was collected and the residue re-extracted as described beforehand for two cycles. The combined supernatant was left overnight with activated copper scraps added to desulphurize the sample. The solution was concentrated to approximately 1 mL using a rotary evaporator, and the resulting sample was purified using a Florisil SPE cartridge, which was successively pre-cleaned using 6 mL of ethyl acetate, 12 mL of dichloromethane, and 12 mL of *n*-hexane. The target compounds were eluted using 10 mL of a mixture comprised of ethyl acetate and dichloromethane (1:1, v/v). The sample was further concentrated under nitrogen steam and transferred into an autosampler vial. Finally, ¹³C-PCB208 was added as an internal standard and 50 µL of *iso*-octane added. The final sample was stored at -20 °C until instrumental analysis.

2.4. Instrumental analysis

Determination of the PBDEs and DBDPE was carried out using gas chromatography-mass spectrometry (GC-MS) (7890B/5977B, Agilent, USA) with a DB-5HT capillary column (15 m \times 0.25 mm, 0.1 µm, Agilent, USA) used for chromatographic separation. The oven temperature was initially set at 80 °C and maintained for 0.5 min, then increased to 310 °C at 20 °C/min, and maintained for 3 min. 1 µL of sample was injected and gasified in the inlet at 280 °C. High-purity helium was used as the carrier gas at a constant flow rate of 1 mL/min. The ion fragments of the target contaminants were analyzed in selected ion monitoring mode with a negative chemical ionization source and quadrupole, which were set at 200 and 150 °C, respectively. Methane was selected as the reaction gas in the chemical ionization process.

The quantification of the OPFRs was performed using gas chromatography coupled with triple quadrupole tandem mass spectrometry (7890B–7000C, Agilent, USA). A DB-5MS capillary column (30 m \times 0.25 mm, 0.25 µm, Agilent, USA) was used to separate the chemicals. The oven temperature was programmed as follows: The initial temperature was set at 80 °C (maintained for 1 min) and increased to 200 °C at 10 °C/min, then increased to 280 °C at 5 °C/min, and to 300 °C at 10 °C/min (maintained for 5 min) successively. The oven temperature was finally increased to 315 °C at 20 °C/min and the temperature was held for 1 min. The flow rate of the carrier gas, injection volume, and inlet temperature were the same as those used for the determination of the PBDEs and DBDPE. An electron ionization source (70 eV) was used and the temperature was set at 230 °C. The parent ions and fragment ions of each compound under multiple reaction monitoring mode are listed in Table S1.

2.5. Soil organic matter and particle size analysis

The SOM of the soil core samples was analyzed using the ignition loss method (Zhang et al., 2014a,b). Briefly, a soil sample was placed in a high-temperature (450 °C) baked porcelain crucible and left overnight in an electric drying oven at 105 °C to remove moisture. After cooling to room temperature in a drying dish, the sample was first weighed, and then, burned in a muffle furnace at 450 °C for 3 h, cooled to room temperature in a drying dish, and weighed for the second time. The amount of organic matter in each sample was calculated using the weight difference. The determination of each sample was conducted three times to ensure the accuracy of the data.

Freeze-dried soil core samples were homogenized (not ground) in a mortar and then passed through a 2 mm sieve to remove large debris such as gravel prior to the particle size distribution of the soil particles being measured (Vdović et al., 2019). The particle size distribution was then measured using a laser diffraction particle size analyzer (Mastersizer 3000, Malvern Instruments Ltd.) with ultrapure water used as the dispersant at a particle refractive index of 1.50 and absorptivity of 0.10, and the results of three parallel tests with weighted residuals within 1% were averaged and used as the final results. The types of soil samples were identified by the percentage of sand (50–2000 μ m), silt (2–50 μ m),

and clay (<2 μ m), according to the soil particle size classification standard issued by U.S. Department of Agriculture (Sangster et al., 2015).

2.6. Quality assurance and quality control

Each batch of experiments consisted of 10 soil samples, one spiked matrix, and one procedure blank. The concentration of target compounds in each procedure blank was not higher than 5% of the actual sample. The spiked matrix was used to check the recovery efficiency of each batch of experiments and the concentrations of the target compounds in all of the actual samples were recovery-corrected. The recoveries of the PBDEs, DBDPE, and OPFRs were 83.6–127%, 83.5–126%, and 64.8–99.4%, respectively. The linear regression coefficient of each of the calibration curves obtained for quantification was >0.99. The limit of detection (LOD) and limit of quantification (LOQ) were calculated using three and ten times the signal-to-noise ratio of each compound, and their respective ranges were 0.01–1.69 and 0.03–5.63 ng/g, respectively, which are listed in Table S1.

2.7. Calculation and statistical analysis

To investigate the point source effect of the diffusion of semi-volatile organic pollutants, a radial dilution model, which has been widely used in the literature (Li et al., 2016; Li et al., 2017; Ling et al., 2022; McDonald and Hites, 2003), was utilized in the present study, and its expression determined as follows:

$C(r) = a_0 r^{a_1}$

where *r* is the distance between the sampling point and point source, *C* (*r*) is the concentration corresponding to the point, and a_0 and a_1 are the fitting coefficients, which are provided in Table S5.

Any concentration below the LOD was denoted as not detected (n.d.). When it was higher than the LOD yet lower than the LOQ, it was denoted 1/2 LOQ (>50%) or 1/4 LOQ (<50%) depending on the detection frequency. In addition, the concentration was expressed as the dry weight unless otherwise specified. SPSS software (IBM, USA) was used for statistical analysis. Due to the non-normal distribution of the data, Kruskal-Wallis *H* tests and Spearman analysis were employed to assess the difference and correlation due to the abnormal distribution data set. And statistical plots are plotted using median values rather than means unless otherwise stated. The threshold of statistical significance was set at *p* < 0.05. The Kriging interpolation method was used in the drawing of the contour plots on Surfer (Golden Software, USA).

3. Results and discussion

3.1. Occurrence and spatial distribution of the target chemicals

The concentrations of the PBDEs, DBDPE, and OPFRs in the surface soils of the production park and surrounding areas are shown in Table S3. The median concentration of PBDEs (BDE209 accounted for 82.9%) reached up to 2.25 \times 10³ ng/g, which was equivalent to or slightly higher than those reported in similar studies (Table S4). This could be related to the Chinese government's limits on the production and use of technical Deca-BDE since 2017, which has also caused the widespread manufacturing and use of DBDPE as an alternative to PBDEs. The median concentration of DBDPE was found to be 2.24×10^3 ng/g, which was one to two orders of magnitude higher than the levels reported in a recent study conducted in Shouguang (Li et al., 2016; Yu et al., 2022). In addition, the mean concentration of DBDPE (9.93×10^3 ng/g) was more than twice that of the PBDEs (4.52×10^3 ng/g), which was consistent with the results detected in the local atmosphere and particulate matter in the same year (Ren et al., 2023). Similarly, a higher proportion of DBDPE relative to PBDEs was observed in other regions.

The ratios of DBDPE/BDE209 in sediment from an electronic waste dismantling site in East China was observed to be as high as 5.6 (Ling et al., 2021). This trend is expected to keep expanding after technical Deca-BDE is entirely banned in China by the end of 2023 (Chen et al., 2023). Comparatively, the median concentration of \sum_{12} OPFRs (sum concentrations of OPFRs) was only 7.12 ng/g, which was lower than or comparable to most reported in similar studies (Table S4). The low concentration and abundance were consistent with the fact that OPFRs are not produced in this production park.

The spatial distribution of the target chemicals shows that both the PBDEs and DBDPE display typical point source distribution characteristics surrounding the production park with their central concentrations reaching up to 2.88×10^4 and 8.46×10^4 ng/g, respectively (Fig. 1). The



Fig. 1. Spatial distributions of DBDPE (A), PBDEs (B), and OPFRs (C) in the surface soil sample of the production park and surrounding area.

large-scale production of PBDEs in the past and its legacy in the surrounding sites, as well as the sharp increase in DBDPE production in recent years, contribute to this situation. Additionally, a tendency for the distribution of PBDEs and DBDPE to disperse from the park towards the residential areas located in the northeast direction has been observed. However, the meteorological data show that the dominant wind direction in study area is south-southeast throughout the year, which is not consistent with the actual dispersion trend of PBDEs and DBDPE, and cannot well explain the phenomenon that the concentration of OPFRs is low in the park but high in the residential area. Consequently, it was deduced that residential areas are a secondary source for PBDEs and DBDPE, with a greater influence on pollutant distribution than the potential factor of wind direction. And this infer can be supported by the concentration distribution of OPFRs not produced in the park.

A radial dilution model was used to study the point source effect of the diffusion of these chemicals and the results shown in Fig. 2 and Table S5. The concentrations of DBDPE and the PBDEs decline exponentially as the distance increases. The fitting curve indices obtained for DBDPE and the PBDEs with distance were -1.48 and -2.95, respectively. The higher absolute values of the indices of the PBDE congeners indicate that their concentrations were more rapidly decreased in the soil surrounding the production park and also characterized by more pronounced point-source contamination. In addition, BDE206, 207, 208, and 209 achieve higher R² values than their low brominated congeners. This can be explained by the fact that the highly brominated congeners were more likely to combine with particulate matter and deposit close to the emission source, exhibiting point source pollution characteristics, whereas low brominated congeners are easier to distribute in the gas phase and have higher volatility and mobility (de Wit et al., 2010; Ling et al., 2022), which was aggravated by the serious fine particle pollution in the production park (Ren et al., 2023). Individual congeners such as BDE71, 99, and 154 do not match the model well, pointing to the possibility of additional emission sources. Considering the high concentration and highly concentrated distribution pattern of the PBDEs and DBDPE at the source sites. The investigation of their vertical transportation was necessary.

3.2. Vertical distribution of the targets in the soil core samples

The vertical distribution of the target substances in the soil core samples were investigated to further understand the penetration and transport characteristics of the chemicals through the soil (Table S6–S8).



Fig. 2. Radial dilution model fitting between the concentration of DBDPE or PBDEs and their distance from the production park.

In the soil core samples obtained from the production park, the concentration of \sum_{20} PBDEs ranged from 54.3 to 5.80 × 10⁴ ng/g with BDE209 being 17.9 to 3.31 × 10⁴ ng/g. Meanwhile, the concentration of DBDPE ranged from 203 to 5.87 × 10⁵ ng/g. In general, the concentration of chemicals in the soil decreases exponentially with depth (Hollander et al., 2007). However, even at a depth of 5.00 m in the soil core samples, the median concentrations of BDE209 and DBDPE still reached up to 50.9 ng/g and 9.85 × 10³ ng/g, respectively. Moreover, their median concentrations reached 6.96 × 10³ ng/g and 1.58 × 10⁵ ng/g in the shallow soil samples (0.10 m), respectively. This highlights the severity of soil contamination in the production park due to the long production history of these chemicals.

When compared with the residential and agricultural regions, the soil core samples in the production park had much higher levels of the PBDEs and DBDPE (Fig. 3). The concentrations of the PBDEs and DBDPE decline rapidly by two to three orders of magnitude with increasing depth in both the production park and the other two regions, as well as the trend remaining essentially the same at the different sampling points. The median concentrations of the PBDEs in residential and agricultural areas decreased from 96.9 to 741 ng/g at a depth of 0.1 m-2.13 and 2.41 ng/g at a depth of 5.0 m, and DBDPE decreased from 647 to 5.99×10^4 ng/g to n.d. and 28.6 ng/g, respectively. Meanwhile, there was a certain degree of fluctuation rather than a monotonic decrease in the process of concentration decreasing with the increase of sampling depth, which may be related to the heterogeneity of soil and its intricate physical and chemical properties. Among the different brominated congeners, the concentrations of octa-, nona-, and deca-BDE (BDE209) decrease significantly with depth (p < 0.05), whereas none of the other PBDE congeners were (p > 0.05), despite of the fact that a definite decreasing tendency was observed (Fig. S2). DBDPE exhibits a similar attenuation trend as the highly brominated PBDEs (p < 0.05). These results indicate that the higher brominated PBDE congeners and DBDPE may have been subjected to stronger soil retention during downward infiltration.

In contrast, different from PBDEs and DBDPE, while similar to the



Fig. 3. Vertical distributions of PBDEs, DBDPE, and OPFRs in soil cores.

distribution characteristics in the surface soils, the OPFRs were found at higher concentrations in the residential areas, while they were only found in extremely low concentrations at a depth of less than 1.50 m in the production park and not detected at deeper depths (Fig. 3). The concentrations of the OPFRs in the production park hardly changed with depth. Even in the residential areas, the most abundant areas, they did not decrease significantly. Although obvious changes in their concentrations were observed in the agricultural areas, they were only decreased by approximately an order of magnitude. This phenomenon may be caused by a variety of factors, such as soil conditions and the unique properties of the compounds themselves, and more details was discussed in the following sections.

3.3. Composition characteristics in soil core samples

In the present study, BDE209, the primary congener in PBDEs, exhibits a drop in abundance from 59.9% to 17.9% with increasing depth in the production park, while the other congeners exhibit opposite tendencies with the abundance increasing the greatest by 18.1% for \sum_{5} hexa-hepta BDEs (Fig. S3). In the agricultural and residential areas at some distance from the production park, the abundances of the low brominated congeners were still low (0%-10.3%) and essentially unchanged with depth. However, there was a relationship between BDE209 and nona-BDEs, in which "as one falls, another rises". This could be a result of the PBDEs being continuously introduced into the soil in the production park at a rate greater than their degradation. A certain degree of fluctuation in the pollutant inputs due to variable meteorological conditions in the coastal area may be a main reason for this result, while farming and urban human activities may also partially contribute to these findings. In addition, there was a significant positive correlation among each of the PBDE congeners (p < 0.05), and the smaller the difference in the bromine number between the two congeners, the greater the correlation coefficient, indicating that the progressive debromination of the PBDEs in the production park soil samples occurred (Fig. S4).

For the OPFRs, their concentrations at the production park sites were very low, and many substances were not detected or were near the LOD. It is not meaningful to use this concentration to discuss the composition profiles of the OPFRs. Therefore, only the differences in the composition of the OPFRs (classified by Cl, alkyl, and aryl groups) among the production park, residential, and agricultural areas have been discussed in the present study. The abundance of Cl-OPFRs in the production park, residential, and agricultural areas were 87.5, 97.2, and 100%, respectively. Alkyl- and aryl-OPFRs only account for less than 15%, or even not detected. On the one hand, such composition characteristics may be determined by the emission sources. In the surface soil sample with the highest concentrations in the residential areas, the composition of Cl-, alkyl-, and aryl-OPFRs was 87.1, 7.6, and 5.3%, respectively, which was the proportion closest to the original emission in theory. On the other hand, Cl-OPFRs rarely undergo direct photolysis during their transportation from the emission source to other regions via the atmosphere (Tian et al., 2023), and when it is stored in the soil, its photoactivity toward •OH is far lower than that of alkyl- and aryl-OPFRs (Zhang et al., 2022a,b), so as to minimize its photolysis rate. Therefore, a higher abundance was observed.

3.4. Influence of environmental media on the vertical distribution of OPFRs

In the present study, the SOM contents show a trend of increasing (0.10–1.00 m) and then decreasing (1.00–5.00 m) (Fig. S5A), although it typically decreases with increasing soil depth, as reported in the literature (Cheng et al., 2014). The main type of soil in the upper part of the production park is sandy loam, while the parts with a depth of more than 1.50 m were mainly loamy sand and sand grains with large particle size, which may make the soil less effective in blocking the downward

transport of pollutants (Fig. S5B and Fig. S5C).

To investigate the influence of the SOM and soil clay particle contents on the concentrations of the target substances, the correlations between the chemicals and these factors were analyzed (Fig. 4). In the



Fig. 4. Linear regression of SOM with PBDEs (A), DBDPE (B), and OPFRs (C).

present study, the absolute value of the regression slope was used as an indicator of the effect of associated variable on the distribution of the target chemicals. Regression analysis was conducted on the total concentrations of the 12 OPFRs, due to the concentrations of the individual OPFRs in some of the samples being less than the LOD. Fig. 4 shows all of the PBDEs and DBDPE shows significant positive correlations with the SOM (p < 0.01), whereas the OPFRs were negatively correlated. The results suggest that SOM may play a crucial role in determining the distribution of the target compounds. However, only hexa-BDEs and highly brominated PBDEs and DBDPE correlated with the soil clay particle content (Table S9), which indicates that soil clay particles had a greater impact on the adsorption of high molecular weight and/or highly brominated organic compounds.

It is worth noting that the strong correlation in the above results cannot be explained by the fact that the target chemicals were only retained through the partition of organic matter or soil particles to the soil environment. On one hand, soil is a complex and uneven aggregate, rather than a discrete mixture of organic and inorganic phases. In addition to quantity of soil particles, the structure and properties of the SOM and soil particles, as well as the degree of aging of pollutants in soil, can also affect the adsorption-desorption process and thus lead to varied distribution characteristics (Carmo et al., 2000; Olshansky et al., 2011). On the other hand, the contents of SOM and soil clay in the present study area were at relatively low levels. When the SOM content drops below a certain threshold, the contribution of SOM to pollutant adsorption may lose its dominance, and this threshold needs to be determined based on a substance-specific basis (Cheng et al., 2021). More importantly, the nature of the target compounds should be fully considered.

3.5. Influence of physicochemical properties on the vertical distribution

To further understand the factors influencing on the vertical distribution of the target compounds in the soil samples, the relationship between their hydrophobicity and distribution was analyzed. It was shown that the regression slopes of hexa-deca BDE concentrations with SOM or clay were significantly (p < 0.05) and highly significantly (p < 0.01) correlated with their K_{OW} , respectively, and increased by 1.53 and 1.70 upon increasing K_{OW} (Fig. 5). However, tri-penta BDEs did not show such a correlation (p > 0.05). The strong correlation indicates that PBDEs with higher K_{OW} values are more susceptible to the influence of SOM and the soil clay particle distribution within a specific range. Interestingly, although DBDPE has the largest K_{OW} value, it did not show a stronger response to SOM and soil clay particles when compared with the other PBDEs.

Degradation and transport should also be considered as contributors to the distribution and composition of the target substances in the soil core samples. In the present study, the concentrations of the majority of the PBDE congeners were lower at a depth of 0.10 m than at a depth of 0.30 m (Table S6). A similar phenomenon has also been observed in the literature. In a study on the transport of PBDEs in biosolids-amended soils, the rate of decrease in the total PBDEs in the uppermost soil (0-0.05 m) was almost two orders of magnitude higher than the rate of increase in the lower soil (0.05-0.20 m) over the course of a year, suggesting that effects such as photo-degradation and/or volatilization may be significant in the upper soil layer (Gorgy et al., 2013). To our knowledge, various degradations of traditional and new flame retardants in surface soil, mainly by photolysis, have been widely observed although it is usually based on the speculation of environmental test results (Dong et al., 2014; Paliya et al., 2022; Wang et al., 2021a,b; Zhang et al., 2014a,b). Moreover, a research study has shown that only contaminants on the soil surface may be susceptible to photodegradation due to the stringent requirements for ultraviolet energy (Zhang et al., 2021). Therefore, the photodegradation of the target compounds in surface soil may contribute to the composition of PBDEs. And it has also been reported that light avoidance and anaerobiosis greatly reduce the potential for microbial degradation (Wong et al.,



Fig. 5. Slope of the regression of compounds on SOM and soil clay particle contents versus Log K_{OW} .

2012). The degradation of the target compounds may be minimal in anaerobic, dark, and undisturbed deep soil environments when compared to the long-term, sustained, and high-intensity input of the chemicals into production park soils (Sahu et al., 2021; Tian et al., 2023). Therefore, the low brominated PBDE congeners in the soil core samples are more likely to originate from the various forms of degradation of BDE209 in the surface soil, while the fraction originating from its *in situ* degradation is probably rather limited.

For PBDEs, DBDPE, and OPFRs, although some of their highly hydrophobic congeners were tightly adsorbed on SOM and soil particles, the differences in their concentration and composition in the soil core samples at different depths provide evidence of downward transport (Chou et al., 2019; Zeng et al., 2011). The ratio of the concentration of the compounds in each soil layer to the uppermost soil layer (relative abundance) was used to compare their transport capacities. The faster the percentage decreases with depth, the easier it is for the compound to adsorb into soil, and the poorer its transport capacity. In the present study, the transport trends in the production park soil profiles can be clearly divided into two parts (Fig. 6). The percentage of each compound decreases sharply in the 0.10–1.50 m depth soil profile, indicating that this soil layer has very strong blocking properties. BDE209 and nona-BDEs decrease the fastest showing their weak transport capacity,



Fig. 6. Proportions of the compounds at different depths relative to the 0.10 m soil profile.

in contrast to the slight decline of OPFRs, which was consistent with the distinctive nature of OPFRs found earlier. In the soil profile at 1.50–5.00 m, the decrease in the target substances was slow and the OPFRs even showed a slight upward trend, indicating that they have a strong transport capacity considering the relatively high hydrophilicity of OPFRs. Therefore, the possibility of groundwater pollution caused by these chemicals should be considered. Overall, the lower brominated congeners were found to be more permeable, while surprisingly DBDPE did not show weaker permeability when compared to the other compounds, although it is the most brominated chemical as BDE209. Unfortunately, due to the lack of research on the leaching behavior of DBDPE in soil, this phenomenon cannot be reasonably explained for the time being. The present results suggest that the differences in the structure and properties of the target compounds may also be important factors affecting their vertical distribution.

4. Conclusions

This study aimed at clarifying the spatial and vertical distribution patterns and compositional characteristics of flame retardants, and to investigate the transport process and potential influencing factors in the soil core samples. To do so, surface soils were collected in an area centered on a flame-retardant production park, and nine soil cores of 0.10-5.00 m depth were collected within the park and the surrounding area. Our results showed that the main contributor to soil pollution in the flame-retardant manufacturing park and surrounding area has been gradually replaced by DBDPE instead of PBDEs, due to the prohibition of the latter. The distribution patterns of the two types of chemicals showed typical park-centered point source characteristics, while OPFRs mainly originated from human activities in residential areas. The vertical concentration distribution and composition indicated that most of the chemicals penetrated into the soil 5.00 m or even deeper below ground. Compounds with larger K_{OW} are more susceptible to the partitioning effects of SOM and soil clay particles, as well as being subject to stronger blocking effects from the soil during downward transport. Lower brominated PBDEs in the soil core samples more likely originate from surface soil degradation and migration, with limited in situ origin. However, the distinctive behavior of DBDPE needs to be explored in future studies.

Supporting information

Supplementary data associated with this article can be found in Figs. S1–S5 and Tables S1–S9.

CRediT authorship contribution statement

Chifei Bai: Writing - original draft, Methodology, Data curation.

Xiang Ge: Writing – original draft, Methodology, Data curation. Zhaofa Huang: Methodology. Zenghua Qi: Methodology. Helong Ren: Methodology. Yingxin Yu: Writing – review & editing, Supervision, Conceptualization. Taicheng An: Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2024.124597.

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