



Occurrence and air-soil exchange of organophosphate flame retardants in the air and soil of Dalian, China[☆]

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ABSTRACT

We investigated the concentrations, distributions, potential sources, and air-soil exchange of 10 OPFRs in the air and soil of Dalian. The concentrations of Σ_{10} OPFRs in the soil were in the range of 1.07–288 ng/g (mean: 14.0 ng/g), while the concentrations of Σ_{10} OPFRs in the passive air samples were in the range of 313–4760 pg/m³ (mean: 1630 pg/m³). Generally, the concentrations of OPFRs are relatively high in urban areas compared with those in suburban and rural areas, indicating the influence of intensive anthropogenic activities on local OPFR concentrations. Tris(2-chloroisopropyl) phosphate (TCIPP) was the most abundant congener, followed by tris(2-chloroethyl) phosphate (TCEP) and tri-*n*-butyl phosphate (TNBP). Spearman correlation analysis illustrated that OPFRs in the air shared common sources, while the sources of OPFRs in the soil were diverse. Net volatilization of TNBP from the soil to the air was observed at all sampling sites, whereas opposite trends were observed for TCIPP, TDCIPP, TBOEP, TPHP, EHDPP, TEHP, TPPO, and TMPP. The exchange trends of TCEP were characterized as volatilization in urban areas, but equilibrium in rural ones. TCEP showed the highest volatilization flux (1100 ng/m³/d), whereas TCIPP showed the highest deposition flux (–171 ng/m³/d). The significant diffusive fluxes of certain OPFRs, especially of those with suspected toxicities, suggested potential high exposure levels to these chemicals.

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1. Introduction

Organophosphate esters (OPEs) is an important class of chemicals that have been widely used as flame retardants, plasticizers, and anti-foaming agents in various industrial and household products, such as textiles, plastics, electronics, decoration materials, and furniture (Abdallah and Covaci, 2014; Marklund et al., 2005; Reemtsma et al., 2008; van der Veen and de Boer, 2012). Since the ban of commercial polybrominated diphenyl ethers (PBDEs) by the Stockholm Convention, production and application of organophosphate flame retardants (OPFRs) have increased rapidly over the last decade (Li et al., 2019). Halogenated-OPEs such as tris(2-chloroisopropyl) phosphate (TCIPP) and tris(2-chloroethyl) phosphate (TCEP) are mainly used as flame retardants, whereas non-halogenated OPEs such as triphenyl phosphate (TPHP) and tris(methylphenyl) phosphate (TMPP, also known as TCrP) are

mainly used as plasticizers (Marklund et al., 2003). OPFRs are dispersed rather than chemically bounded to materials, thus they can be easily leached out of these materials by dissolution, volatilization, and abrasion (van der Veen and de Boer, 2012). OPFRs have been discovered in various environmental matrices including water (Cristale et al., 2013; Xing et al., 2018), sediment (Cao et al., 2017), air (Salamova et al., 2014), and soil (Kurt-Karakus et al., 2018; Wang et al., 2019).

The physicochemical properties of OPFR congeners, such as their solubility and vapor pressure, are in a wide range. Therefore, some OPFRs, e.g. tri-*n*-butyl phosphate (TNBP) and TCEP, tend to be mainly resided in the gas phase, while others, e.g. TMPP mainly in the particle phase (Okeme et al., 2018). OPFRs have been detected in remote areas, such as Arctic (Moeller et al., 2012) and East Antarctic (Cheng et al., 2013), indicating that they can undergo long-range transport through air or water (Moeller et al., 2011). Previous research showed that concentrations of OPEs were up to 170 pg/m³ in the remote air of North American (Castro-Jimenez et al., 2016) and up to 1300 pg/m³ in airborne particles over the Arctic ocean (Yu et al., 2015), potentially due to the atmospheric transport.

Soil is considered as a major reservoir or sink for semivolatile

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organic compounds (SVOCs) in terrestrial environment (Meijer et al., 2003). Meanwhile, SVOCs in soil can also volatilize into the atmosphere due to the changes of sources or climate causing a secondary pollution (Ren et al., 2019). Therefore, exchange process displays a key role in the transport and environmental fate of SVOCs on regional and global scales (Degrendele et al., 2016; Meijer et al., 2003). The diffusion exchange of SVOCs can be influenced by various factors, such as temperature, soil properties (e.g., soil organic matter, aromaticity, and moisture), land covers, and emission sources (Cabrerizo et al., 2011; Degrendele et al., 2016; Nizzetto et al., 2010), leading to significant regional differences. As a reservoir of essential pollutants, soil can affect human health through the quantity, quality, and safety of food and water (Keesstra et al., 2016). Moreover, organic pollutants, such as SVOCs, can cause chemical degradation of soil, and further influence the biotic and abiotic soil functions, the quality of crops, and the health of animals and humans (Keesstra et al., 2018). Our study may contribute to control the land degradation and to improve the knowledge of soil pollution in China.

Previous studies mostly focused on routinely detection of OPFRs in one environmental medium, such as water or air (Li et al., 2017; Shi et al., 2016; Wang et al., 2015). To our knowledge, only one study illustrated the air-soil exchange trends of OPFRs (Yadav et al., 2018). Therefore, the objectives of this study were to: (1) determine the concentrations, compositions, and regional distributions of OPFRs in the air and soil of Dalian, a typical coastal city in the Northeast China; (2) assess their potential sources; and (3) estimate their air-soil exchange trends and fluxes in this area.

2. Materials and methods

2.1. Sampling collection

We collected 49 surface soil samples (0–5 cm, July 30–August 1, 2017) and 20 polyurethane foam (PUF) passive air samples (deployed for 40 days, July 30–September 8, 2017) in Dalian (Fig. 1). Each soil sample consisted of five subsamples. Passive air samplers equipped with polyurethane foam disk (PUF-PAS, 14 cm diameter, 1.35 cm thick, and 0.017 g/cm³ density; pre-cleaned by dichloromethane (DCM) and ethyl acetate) were deployed within 50 m to the corresponding soil sites. Before the deployment, ¹³C labeled PCBs, including ¹³C-PCB28, 52, 101, 138, 153, and 180, were added as performance reference compounds (PRCs) to correct air sampling rates at different sites. All samples were wrapped with aluminum foils, placed into polyethylene zip-bags, and stored at –20 °C until further analysis. More details are shown in Table S1 of Supporting Information (SI). Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) of soils were extracted by Milli-Q water (1 g soil: 10 mL water) and analyzed using a multi N/C 2100 total organic carbon analyzer (Tables S1 and SI). The passive air sampling rate (2.63–8.16 m³/d) and sampling volume (105–327 m³) at different sites are listed in Tables S2 and SI.

2.2. Sampling preparation and extraction

Approximately 5 g freeze-dried soil or a PAS PUF disk was spiked with surrogate standards (*d*₁₂-TCEP, *d*₁₈-TCIPP, and *d*₁₅-TPHP) and extracted with DCM: n-hexane (1:1, v/v) using an accelerated solvent extraction system (ASE350, Dionex Inc.) at 100 °C and 1500 psi for 5 min static time and 2 cycles. The extract was then concentrated and purified by a column containing 4 cm silica gel (3% deactivated) topped with 1 cm of anhydrous Na₂SO₄. This column was first eluted with 15 mL DCM: hexane (1:1 v/v, F1), and then 15 mL ethyl acetate (F2). The F2 eluate was solvent exchanged to isooctane, concentrated to ~0.5 mL, and added with hexamethyl

benzene as the internal standard.

2.3. Instrumental analysis

Ten OPFRs were analyzed, including TNBP, TCEP, TCIPP (mix of isomers), tris (2-chloro-1-(chloromethyl) ethyl) phosphate (TDCIPP), tris(2-butoxyethyl) phosphate (TBOEP), TPHP, 2-ethylhexyl diphenyl phosphate (EHDPP), tris(2-ethylhexyl) phosphate (TEHP), triphenylphosphine oxide (TPPO), and TMPP (mix of isomers). Samples were analyzed using an Agilent 7890 GC-5975MS applied with a DB5-MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm). The GC oven temperature started at 70 °C for 2 min, increased to 300 °C at 15 °C/min, and held for 10 min. The carrier gas is helium with a flow rate of 1.5 mL/min. Ion source and transfer line temperature were maintained at 230 °C and 280 °C, respectively.

2.4. QA/QC

One procedural blank and one field blank (PUF) were run with each batch of 10 samples. TCIPP and TCEP were the main contaminants in the blanks with concentrations <10% of the actual samples. Method detection limits (MDLs) were calculated as the mean of blanks plus 3 times the standard deviation of the target compounds. The MDLs of OPFRs for the air and soil samples were 0.40–69.8 pg/m³ and 0.66–167 pg/g, respectively (Tables S3 and SI). The surrogate recoveries in the air and soil samples were 80.9 ± 18.7% and 88.3 ± 11.5% for *d*₁₂-TCEP, 88.3 ± 15.2% and 92.8 ± 10.7% for *d*₁₈-TCIPP, and 91.0 ± 18.3% and 98.1 ± 11.2% for *d*₁₅-TPHP, respectively. Results in this study were only corrected by the blanks.

2.5. Calculation of fugacity fraction

We used the following equations to estimate the fugacity fractions of OPFRs in air and soil, as well as their air-soil exchange directions (Harner et al., 2001).

$$f_s = C_s RT / 0.41 \phi_{OM} K_{oa} \quad (1)$$

$$f_a = C_a RT \quad (2)$$

where C_s and C_a are the concentrations (mol/m³) of OPFRs in the soil and air gas phase, respectively. C_s was calculated by using a soil density of 1430 kg/m³ (Yadav et al., 2018). Since passive air sampler can collect both gas and fine particles, C_a (gas phase) was calculated as the passive air concentration multiplied by the percentage of individual OPFR congener in the gas phase ($C_{gas} / (C_{gas} + C_{fine-particle})$), calculated using the measured concentrations by active air sampling at S46, see Tables S3 and SI). R is the gas constant (8.314 J/mol/K); T is the daily average temperature (K); ϕ_{OM} is the fraction of soil organic matter, which is 1.5 times of total organic carbon (TOC); and K_{oa} is the octanol-air partition coefficient. The fugacity fractions of OPFRs were calculated as follows:

$$ff = f_s / (f_s + f_a) \quad (3)$$

Theoretically, a ff value of 0.5 indicates an air-soil equilibrium state. However, considering the uncertainties, a fugacity fractions between 0.25 and 0.75 presents a relatively equilibrium state, $ff > 0.75$ indicates a net volatilization from soil into air, while $ff < 0.25$ represents a deposition from air into soil (Wang et al., 2012).

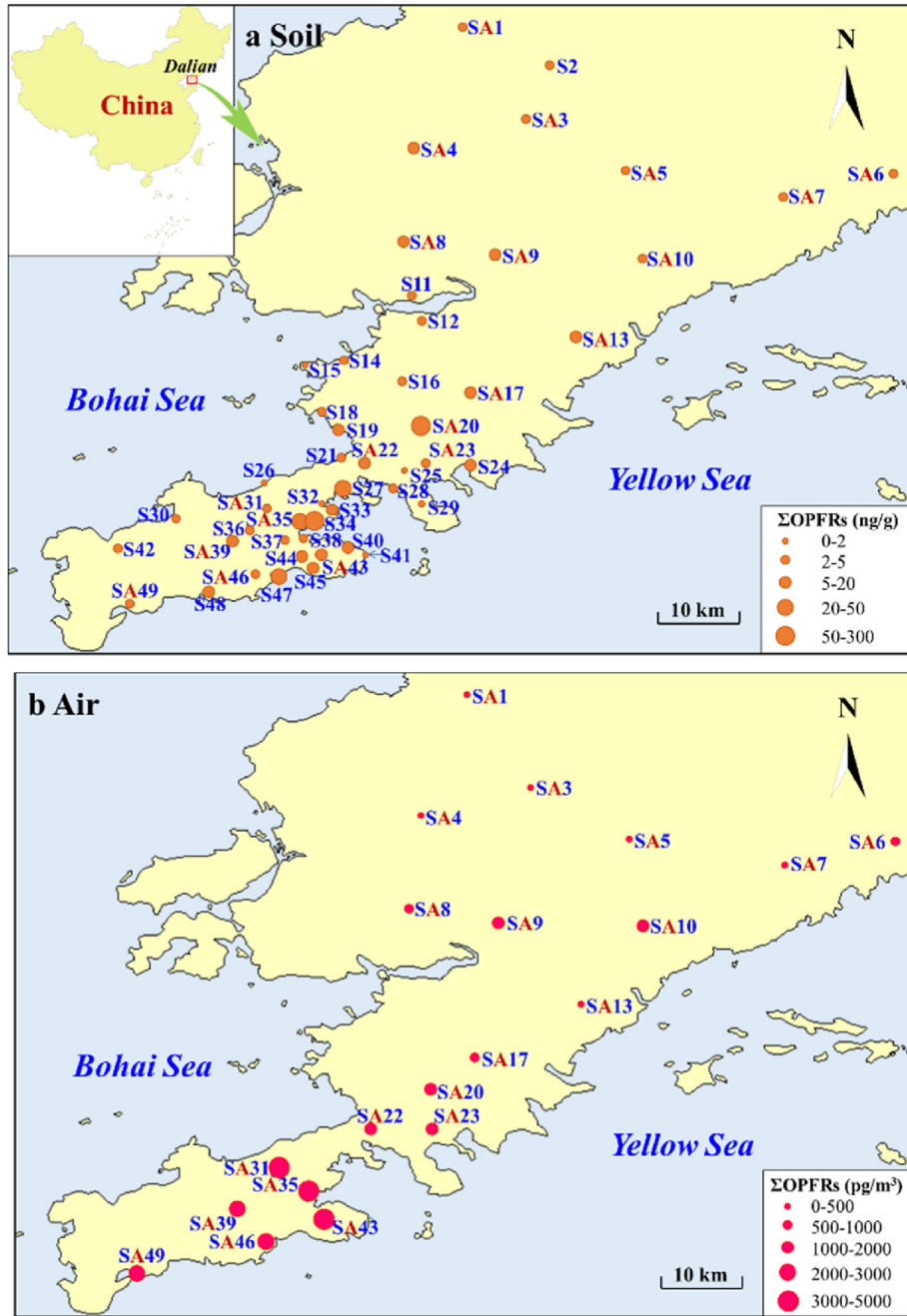


Fig. 1. Concentrations and distributions of OPFRs in the soil (a) and air (b) of Dalian.

2.6. Calculation of air-soil diffusive exchange flux

The air-soil diffusive flux N_v (mol/h) of OPFRs can be calculated as follows (Backe et al., 2004):

$$N_v = D_v(f_s - f_a) \tag{4}$$

$$1/D_v = 1/D_e + 1/(D_a + D_w + D_{bio}) \tag{5}$$

where D_v is the sum of air-soil diffusion values (mol/Pa/h), D_e is the diffusion value of atmospheric boundary above the soil (mol/Pa/h), D_a is the effective diffusion value of air in soil (mol/Pa/h), D_w is the effective diffusion value of water in soil (mol/Pa/h), and D_{bio} is the diffusion value of soil bioturbation (mol/Pa/h). D values can be

calculated as follows:

$$D_e = k_v AZ_a \tag{6}$$

$$D_a = Z_a AB_{sa}/Y \tag{7}$$

$$D_w = Z_w AB_{sw}/Y \tag{8}$$

$$D_{bio} = k_{bio} AZ_s \tag{9}$$

where A is the study area (m^2), assuming as $1 m^2$, B_{sa} and B_{sw} are the effective diffusion coefficients of molecule, k_{bio} is the bioturbation mass transfer rate, assuming as 2.2×10^{-6} m/h

(Sweetman et al., 2002), k_v is the mass transfer rate of air boundary layer assuming to be 4 m/h, Y is the distance of diffusion path, assuming as 0.05 m.

$$B_{sa} = B_a v_a^{10/3} / (v_a + v_w)^2 = 0.43 \times 0.2^{10/3} / [24 \times (0.2 + 0.3)^2] = 3.35 \times 10^{-4} \text{ m}^2/\text{h}$$

$$B_{sw} = B_w v_w^{10/3} / (v_a + v_w)^2 = 4.3 \times 10^{-5} \times 0.3^{10/3} / [24 \times (0.2 + 0.3)^2] = 1.30 \times 10^{-7} \text{ m}^2/\text{h}$$

where B_a and B_w are the molecular diffusion coefficient (m^2/d) in air and water, and assumed to be 0.43 and 4.3×10^{-5} , respectively. v_a and v_w are the air and water volume fractions in soil, and assumed to be 0.2 and 0.3, respectively (Sweetman et al., 2002).

3. Results and discussion

3.1. Concentrations of OPFRs in the soil and air

The concentrations of OPFRs in soil samples are shown in Fig. 1a and Tables S4 and SI. The concentrations of Σ_{10} OPFRs in the soil ranged from 1.07 to 288 ng/g with a median value of 4.23 ng/g. The highest concentration of Σ_{10} OPFRs was found at S34 (288 ng/g), a park near a large residential area, whereas the lowest concentration was found at S29 (1.07 ng/g), a remote seaside. TCIPP (0.32–280 ng/g) was the most abundant compound in the soil, followed by TDCIPP, TNBP, and TCEP. The concentrations of OPFRs varied largely with sampling site, and relatively high concentrations were mainly distributed in samples collected from densely populated areas such as S27, S34, S35, S44, and S47. Generally, the concentrations of OPFRs in urban areas (28.3 ± 67.8 ng/g) were higher than those in suburban (9.62 ± 21.4 ng/g) and rural areas (3.77 ± 1.14 ng/g). The significantly high emission in urban areas may be related to the intensive human activities, such as heavy traffic, dense industries, and large consumption of commercial and building materials (Li et al., 2018). Meanwhile, the relatively high OPFR concentrations in farmland soils from several rural areas (S9 and S17) may due to the agricultural activities, such as wastewater irrigation (Trujillo-Gonzalez et al., 2017) or organic fertilizer application (Kumar et al., 2019). Besides sources strength, organic matter is also an essential factor affecting the concentration of SVOCs in soils. Significant positive correlations were discovered between soil DOC and Σ OPFRs ($r = 0.399$, $p = 0.005$), and also for several OPFR congeners such as TNBP ($r = 0.497$, $p < 0.001$), TDCIPP ($r = 0.318$, $p = 0.026$), TPHP ($r = 0.41934$, $p = 0.002$), EHDPP ($r = 0.382$, $p = 0.007$), and TMPP ($r = 0.351$, $p = 0.013$). However, no significant correlations were found between any OPFR congeners and TON ($p > 0.169$).

Data on the concentration and distribution of OPFRs in the soil are limited. The mean concentrations (14.0 ± 42.6 ng/g) of OPFRs in the soil of this study are comparable with those in the surface soil of Chongqing (mean: 77.4 ng/g) (He et al., 2017), farmland soil (80 ng/g) in Hebei Province, China (Wan et al., 2016), surface soil from 89 cities across China (17.5 ± 27.3 ng/g) (He et al., 2019), and soil near an airport of US (median: 14.3 ng/g) (Li et al., 2019), but much lower than those in the soil from an e-waste recycling workshop in Vietnam (725 ng/g) (Matsukami et al., 2015), urban sites in Guangzhou (250 ng/g), China (Cui et al., 2017), and a plastic waste treatment site in northern China (398 ng/g) (Wan et al., 2016).

The concentrations of Σ_{10} OPFRs in passive air samples ranged from 313 to 4760 pg/m^3 with the mean and median value of 1630 pg/m^3 and 1320 pg/m^3 , respectively (Fig. 1b and Tables S4 and SI). The OPFR concentrations in the air also varied significantly with sampling site. The highest air concentration was measured at Site A31 (3050 pg/m^3), a park, while the lowest concentration was found at Site A5 (0.79 pg/m^3), a rural site. Spatially, relatively high

concentrations were mainly distributed at sites from the populated or heavy traffic areas, such as A31 (4763 pg/m^3), A35 (3812 pg/m^3), A39 (2683 pg/m^3), A43 (3551 pg/m^3), and A46 (2760 pg/m^3), whereas relatively low concentrations were mostly discovered at sites from rural areas such as A1 (360 pg/m^3), A3 (341 pg/m^3), A4 (418 pg/m^3), A5 (313 pg/m^3), and A7 (363 pg/m^3). The most abundant OPFR congener in the air samples was TCIPP, followed by TCEP and TDCIPP. The spatial distribution showed that the total OPFR concentration in the urban area (mean: 3210 ± 1030 pg/m^3) was much higher than those in the suburban (1270 ± 953 pg/m^3) and rural areas (720 ± 435 pg/m^3).

The air concentrations of OPFRs (mean 1632 ± 1330 pg/m^3) in our study were much higher than those from the remote areas, such as the European (430 ± 57 pg/m^3) (Salamova et al., 2014) and Canadian Arctic sites (363 ± 409 pg/m^3) (Suhling et al., 2016) and the northeast Atlantic and Arctic Oceans (gas: 17 pg/m^3 ; particulate: 58 pg/m^3) (Li et al., 2017), but comparable with those in the Black Sea (1700–6160 pg/m^3) (Castro-Jimenez et al., 2014), Toronto of Canada (2650 pg/m^3) (Abdollahi et al., 2017), and an airport in New York state, US (median: 3880 pg/m^3) (Li et al., 2019).

3.2. Composition of OPFRs

The compositions of OPFRs in the air and soil are showed in Fig. 2. TCIPP was the dominant congener in the air followed by TCEP, TDCIPP, and TNBP with the average proportions of $55.0 \pm 9.31\%$, $18.5 \pm 7.36\%$, $9.43 \pm 8.79\%$, and $5.74 \pm 3.62\%$, respectively. This result is similar to those measured in air samples from the Mediterranean and Black Seas (TCIPP $42 \pm 10\%$ and TCEP $15 \pm 8\%$) (Castro-Jimenez et al., 2014) and an airport in New York state, US (Li et al., 2019), but differ with those measured in the indoor air of Nepal (TCEP 6% and TCIPP 12%) (Yadav et al., 2017).

The dominant congener detected in the soil was also TCIPP (mean: $37.7 \pm 20.4\%$), followed by TNBP ($28.5 \pm 15.6\%$), TCEP ($9.34 \pm 10.0\%$), and TMPP ($6.88 \pm 8.23\%$). This was different from the OPFR compositions in soil samples from Guangzhou, China (TBOEP 42.8%, TMPP 17.2%, TNBP 10.9%, and TCEP 9.70%) (Cui et al., 2017) and Nepalese (TMPP 35–49% and TCIPP 8–25%) (Yadav et al., 2018). Previous studies suggest that TMPP is used as additive in hydraulic fluids, jet oils (Li et al., 2019), cables, and electrical appliances, and also as plasticizer in various plastic products (van der Veen and de Boer, 2012). The relatively high proportion of TMPP may be due to the emission from plastic-derived consumer materials (Yadav et al., 2017).

TCIPP and TCEP were the dominant congeners both in soil and air samples, which may be related to their wide applications as flame retardants in consumer products. TCEP has been widely applied in flexible and rigid PUF, textile coatings, and rubbers (Wu et al., 2016; Xu et al., 2016). It is persistent in the environment due to its poor degradation potential (Wei et al., 2015). TCEP has been gradually phased out in Europe since the 1990s, whereas no regulation has been made on the application of TCEP in China (He et al., 2015; Wu et al., 2016). Thus, TCEP levels in China are generally higher than those in most other countries. Moreover, the relative abundances of TPHP and TMPP in the soil were significantly higher than those in the air, which may be due to their relatively low vapor pressure and high octanol-air partitioning coefficient leading to their high depositions in soil.

3.3. Source apportionment

The Spearman correlation coefficients among 10 OPFRs in the air and soil are shown in Fig. 3a. All OPFR compounds in the air showed significant positive correlations ($p \leq 0.025$) with each other (except for TBOEP vs TPPO, $p = 0.088$). Despite the fact that these

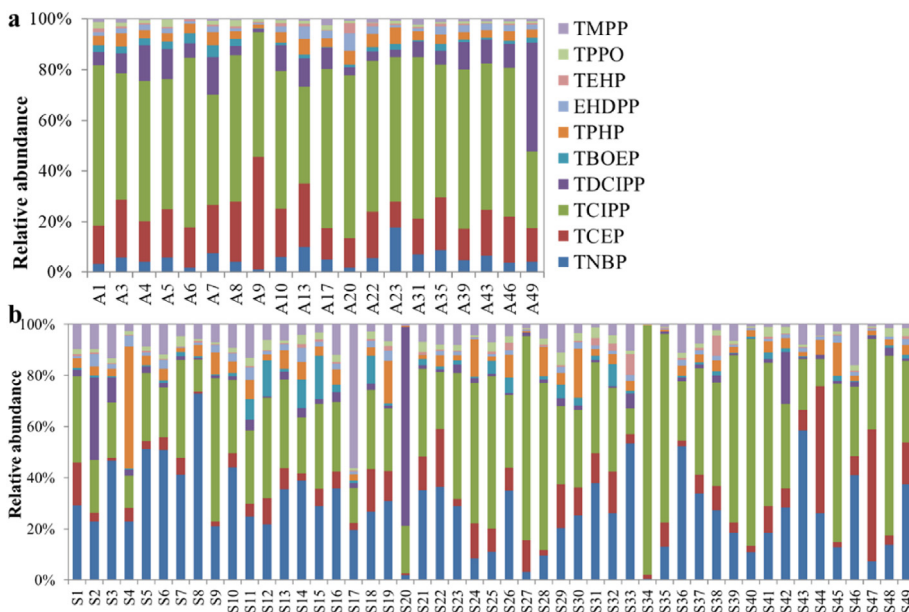


Fig. 2. Compositions of OPFRs in the air and soil.

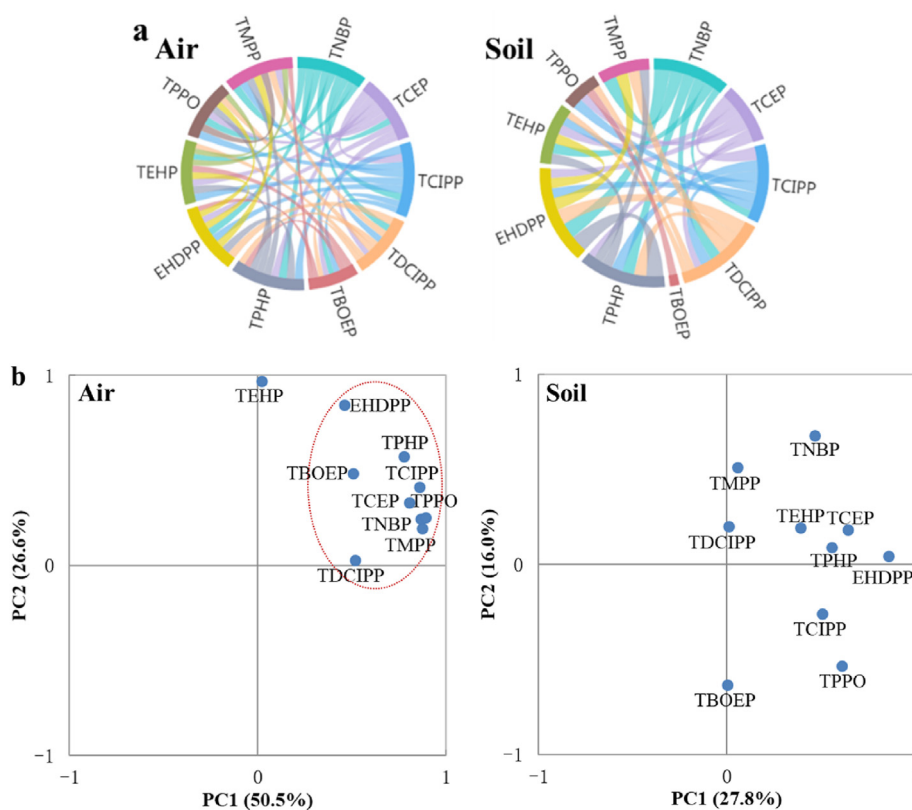


Fig. 3. Correlations (a) and PCA loading plot (b) for OPFRs in the air and soil. (In the chord diagram, the intensity of the band corresponds to the significance of the correlation between particular OPFR pair as assessed using Spearman's rank correlation; only significant correlations ($p < 0.05$) are visualized.).

OPFRs have a variety of applications, the correlations suggest that they may share common sources (Salamova et al., 2016), such as volatilization during the production and application of OPFRs. However, the sources of OPFRs in the soil may be more complex. Significant positive correlations ($p < 0.05$) were also found among most OPFR congeners in soil except for TBOEP, TPPO, and TMPP.

This indicated that these three OPFRs may originate from different sources. These can also be proved by the principal component analysis (PCA, Fig. 3b). Almost all the OPFRs gathered together in the loading plot of air, whereas the OPFRs dispersed in the loading plot of soil, especially for TBOEP, TMPP, TPPO, and TDCIPP. This also suggested that the sources of OPFRs in the soil were diverse.

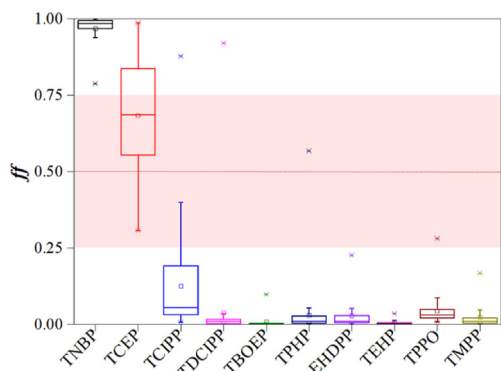


Fig. 4. Air-soil fugacity fractions (ff) of individual OPFRs. (Central line: the median value, Square: the mean value, Box: the inter-quartile range (25th–75th percentiles), Whiskers: the range of data excluding the outliers (shown as stars)).

Significant correlation between TCIPP and TCEP was found in both air ($r = 0.887$, $p < 0.001$) and soil ($r = 0.554$, $p < 0.001$), which may be due to their co-application as flame retardant or the replacement of TCEP by TCIPP (van der Veen and de Boer, 2012). EDHPP was significantly positively correlated with TPHP in both air ($r = 0.842$, $p < 0.001$) and soil ($r = 0.721$, $p < 0.001$). TPHP is often detected in EHDPP mixtures, considered to be one of the impurities (Ballesteros-Gomez et al., 2015).

No obvious correlations were found between concentration of individual OPFR congener ($p > 0.05$), indicating that dispersion of gaseous OPFRs in the air was not the major source of these chemicals in soils. Therefore, the relatively high concentrations of OPFRs

in soil may be due to other sources, such as wastewater discharge or atmospheric deposition.

3.4. Air-soil diffusive exchange trend and flux

The OPFRs in soil can re-volatilize from contaminated soil into the atmosphere causing a secondary pollution. Therefore, the air-soil diffusion plays an important role in controlling the levels of OPFRs in the air, as well as in the soil. The fugacity fractions of 10 OPFRs are shown in Fig. 4. TNBP showed the highest ff value with a median of 0.996, followed by TCEP (median: 0.685). TNBP ($\log K_{oa}$: 7.55) tended to volatilize from the soil into the air at all sampling sites (ff : 0.788–0.999), whereas the status of TCEP ($\log K_{oa}$: 7.98) varied from equilibrium in the suburban and rural areas to volatilization in the urban area (ff : 0.307–0.986). For the other OPFRs with $\log K_{oa} > 9$, including TCIPP, TDCIPP, TBOEP, TPHP, EHDPP, TEHP, TPPO, and TMPP, they were mostly deposited from the air into the soil except for several sites located near the residential area or industrial area, e.g., Sites 20, 27, and 34. The exchange trends of OPFRs in this study were similar to those found near an international airport in New York, US (Li et al., 2019), which also indicated a net deposition of TBOEP, TEHP, TDCIPP, and TMPP from air to soil, with the soil acting as a “sink” for these compounds. However, our results were significantly different from those in an industrial area of Nepal, where the ff values of all OPFRs were close to 1 (Yadav et al., 2018).

To our knowledge, no study has assessed the diffusive exchange of OPFRs between air and soil so far. The air-soil diffusive exchange fluxes of 10 OPFRs in urban, suburban, and rural areas of Dalian are shown in Fig. 5. The highest volatilization flux was found for TCEP

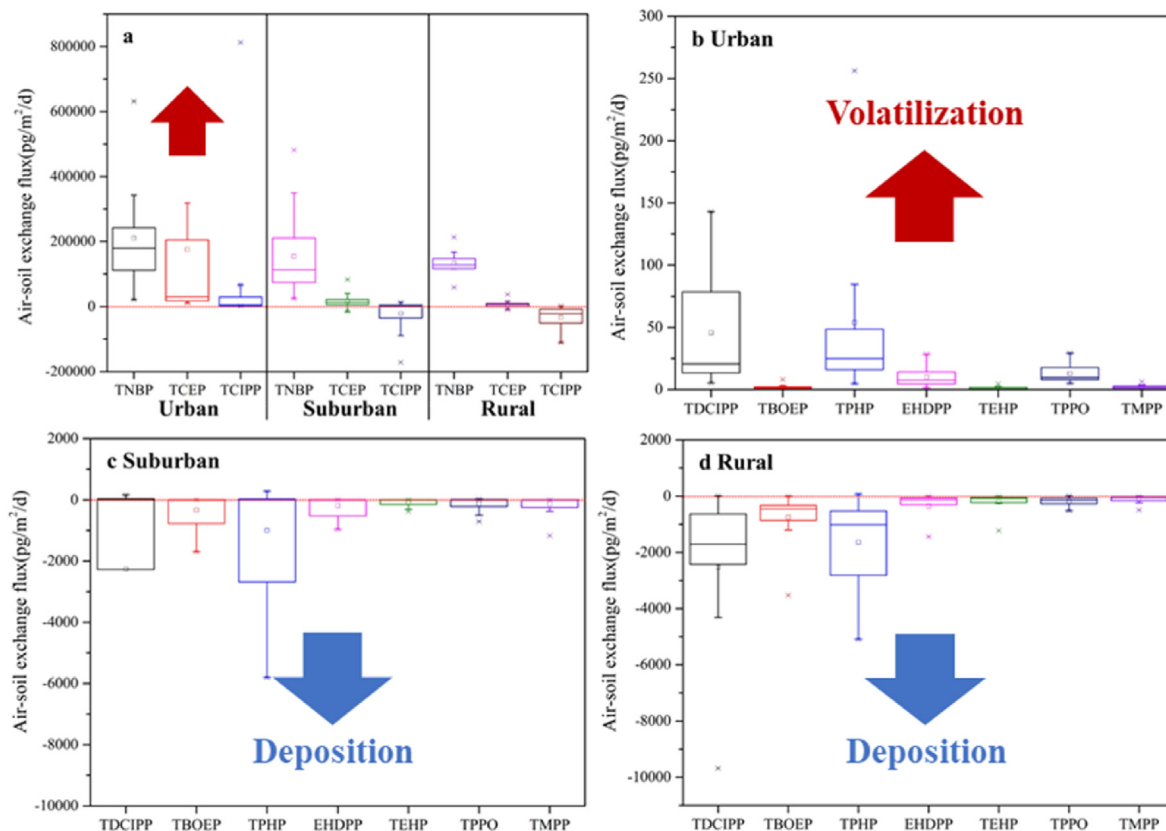


Fig. 5. (The central line represents the median value, the square the mean value, the box the inter-quartile range (25th–75th percentiles), and the whiskers the range of data excluding the outliers, shown as stars).

at Site 47 (1100 ng/m²/d) near a bus terminal, whereas the highest deposition flux was found for TCIPP at Site 15 (−171 ng/m²/d), a seaside park. TNBP had the highest median volatilization flux (21.9–632 ng/m²/d, median: 130 ng/m²/d), followed by TCEP (−15.2–1100 ng/m²/d, median: 14.1 ng/m²/d) and TCIPP (−171–813 ng/m²/d, median: 1.75 ng/m²/d), whereas the diffusive fluxes of other OPFRs were relatively low (<10.9 ng/m²/d). The significant diffusive exchange fluxes of certain OPFRs suggested an exposure potential to high levels of these chemicals.

4. Conclusion

We investigated the concentrations, compositions, and sources of 10 OPFRs in the air and soil of Dalian, China, as well as their air-soil exchange trends and fluxes. Our findings indicated that the OPFRs are widespread in Dalian. The concentrations of OPFRs were generally higher in the urban areas than those in the suburban and rural areas due to the high emissions. TNBP was volatilization at all sites, TCEP varied from equilibrium to volatilization, whereas the rest OPFRs were mostly deposited from the air into the soil. Significant exchange fluxes of TNBP, TCEP, and TCIPP were discovered in this area, indicating an exposure potential. Considering the toxic properties of these chemicals, health concern and further investigation are needed in the future.

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.

CRediT authorship contribution statement

Yan Wang: Conceptualization, Data curation, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Zhiyuan Li:** Data curation, Formal analysis, Visualization, Writing - original draft. **Feng Tan:** Resources, Writing - review & editing. **Yue Xu:** Writing - review & editing. **Hongxia Zhao:** Writing - review & editing. **Jingwen Chen:** Resources, Writing - review & editing.

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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.2020.114850>.

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