Environmental Pollution 284 (2021) 117532

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Characteristics and risk assessment of organophosphate esters and phthalates in soils and vegetation from Dalian, northeast China☆

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ARTICLE INFO

Keywords:
Organophosphate esters
Phthalates
Soil
Vegetation
Risk assessment

ABSTRACT

We investigated the concentration, composition, and potential risk of organophosphate esters (OPEs) and phthalates (PAEs) in soils and vegetation from rural areas of Dalian, Northeast China. The residues of total OPEs and PAEs in soils were in the range of 33.1–136 ng/g dw (dry weight) and 465–5450 ng/g dw, while the values in plants were 140–2360 ng/g dw and 2440–21800 ng/g dw, respectively. The concentrations of both chemicals in the plant rhizosphere soils were significantly lower than those in the bulk soils, suggesting an enhanced degradation or uptake by plant. The contaminations in soils also varied for different land use types with the concentrations generally higher in paddy soils than those in maize soils. The OPE and PAE concentrations in plant leaves were slightly higher than those in their corresponding roots. The bioconcentration factors of OPEs & PAEs were significantly negatively correlated with their octanol-water partition coefficients. A hazard assessment suggested potential medium to high risks from tricresyl phosphate (TMPP) and di-*n*-butyl phthalate (DNBP) for the agricultural soils in Dalian of China. Although the ecological risks of OPEs and PAEs in the rhizosphere soils were lower than those in the bulk soils, the relevant risk could still endanger human health via oral intake of these plants. The daily dietary intakes of OPEs and PAEs via vegetable and rice consuming were estimated, and the result suggests a higher exposure risk via ingestion of leafy vegetable than rice.

1. Introduction

Organophosphate esters (OPEs) and phthalates (PAEs) are two groups of semivolatile organic compounds and ubiquitous in various environmental components. OPEs are predominantly used as a flame retardant and plasticizer. For the restriction and phase-out of polybrominated diphenyl ethers, production and usage of OPEs have been increasing as flame retardants in commercial consumers and industrial products (Li et al., 2019). PAEs are handled as plasticizers and additives in large quantities for their superior performance in improving the flexibility and workability of polymeric materials (Wang and Fan, 2014). The global usage of PAEs is estimated to be ~6.0 million tons annually (Tan et al., 2018), and the world consumption of OPEs has already reached ~680,000 t in 2015 (Van der Veen and de Boer, 2012).

Since OPEs and PAEs are not chemically bonded to products, they can be easily emitted or released into ambient environment (Steinmetz et al., 2016; Van der Veen and de Boer, 2012). Some OPEs showed the toxicological evidence of endocrine, immune toxic effect, thyroid hormone disruption, and impaired sperm quality (Wang et al., 2020). Some PAEs are suspected endocrine disrupting chemicals (EDCs), and thus have adverse effects on reproductive health and development, even with very low concentrations (Net et al., 2015b). Six PAEs, including di-(2-ethylhexyl) phthalate (DEHP), dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DNBP), butyl-benzyl phthalate (BBzP), and di-*n*-octyl phthalate (DNOP) have been categorized as the priority environmental pollutants by the United States Environmental Protection Agency (US EPA), the European Union (EU), and on the list of priority pollutants in Chinese waters, while DEHP has also been classified as a probable human carcinogen by US EPA (Lv et al., 2018).

Soil is one of the major reservoirs of hydrophobic organic compounds (Cui et al., 2017), while agriculture soil is the main gathering area of OPEs and PAEs due to the widespread use of plastic films and

☆ This paper has been recommended for acceptance by Da Chen.

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https://doi.org/10.1016/j.envpol.2021.117532
Received 2 March 2021; Received in revised form 31 May 2021; Accepted 1 June 2021
Available online 5 June 2021

greenhouse coverings (Hu et al., 2003; Lv et al., 2018) and inputs through sewage irrigation, surface runoff (Cui et al., 2017), and sewage sludge used as soil amendment (Net et al., 2015b). Thus, researches on the bioaccumulation and ecological risks of OPEs and PAEs in the agricultural system have received special attention. Relatively high concentrations of OPEs (Cui et al., 2017; Wan et al., 2016) and PAEs (Cai et al., 2008; Net et al., 2015a) have been reported in farmland soils. Those chemicals accumulated in soils may be absorbed by crops and vegetables, and subsequently transferred to humans through food chain (Wang et al., 2010). Dietary ingestion has been considered to be a significant route for human exposure to PAEs (Tsai et al., 2016) and OPEs (He et al., 2018; Zhang et al., 2016), especially via plant-based food intake (Poma et al., 2017). Meanwhile, rice consuming has been recognized as the main pathway of human exposure to OPEs in China (Zhang et al., 2016). However, information on the occurrence and distributions of OPEs and PAEs in agriculture fields is still limited, especially in Japonica rice (*Oryza sativa* subsp. *geng*) fields from Northeast China.

Therefore, the aims of this study were to: (1) investigate the concentrations and distributions of OPEs and PAEs in soils and their corresponding plants from the rural areas of Dalian, Northeast China; (2) determine the uptakes and translocations of OPEs and PAEs within the soil-plant system; and (3) assess the ecological and human exposure risks of OPEs and PAEs in this area.

2. Materials and methods

2.1. Sampling information

A total of 22 top soil (0–10 cm depth) and 25 vegetation samples were collected from Qingduizi Town and Chengzitan Town in Dalian of Northeast China on September 8, 2019. All sampling sites were located at the rural farmland areas without any industrial activities, such as plastic processing. Each sample consisted of 5 sub-samples was collected from the surrounding area (50 × 50 m^2) of each site. All the samples can be divided into five different land use types: 4 paddy fields (Japonica rice, grain filling stage), 2 maize fields (heading stage), 2 vegetable fields (Chinese cabbage, rosette stage), 1 orchard (peach, fruiting stage), and 2 uncultivated lands (green bristlegrass). At each site, the rhizosphere (attached to plant root surface or at least <1 cm from root surface) and non-rhizosphere (at least >5 cm from most roots) soils of plants were collected separately. Their corresponding plants were also collected and divided into shoots and roots. All samples were put into polyethylene zip bags and transported to the laboratory immediately. Plants were divided into roots, leaves (including stem), and seeds (only for rice). All plant tissues were first washed carefully with tap water to remove soil particles, and then rinsed thoroughly with deionized water for 3 times. Soil and plant samples were both freeze-dried, grounded, sieved (through a 60-mesh), and stored at −20 °C until further analysis. The grounder and sieve were washed with deionized water and dried between uses. More details are shown in Table S1, Supporting Information (SI).

2.2. Sample extraction and purification

Soil samples (~0.5 g) were accurately weighted, put into 15 mL glass centrifuge tubes, spiked with 6 labeled surrogate standards (tri(2-chloroethyl) phosphate-d_{12} (TCEP-d_{12}), tris (1-chloro-2-propyl) phosphate-d_{18} (TCIPP-d_{18}), and triphenyl phosphate-d_{15} (TPHP-d_{15}) for OPEs; diethyl phthalate-d_4 (DEP-d_4), di-*n*-butyl phthalate-d_4 (DNBP-d_4), and di-2-ethylhexyl phthalate-d_4 (DEHP-d_4) for PAEs), dispersed in the 10 mL mixture of *n*-hexane, dichloromethane (DCM), and acetone (2:2:1 v/v/v), sonicated for 15 min, and then centrifuged for 5 min. The extraction and centrifugation were repeated 3 times. The extracts were combined, concentrated, and purified by a silica gel column (diameter: 1 cm; length: 15 cm) packed with 1 cm of anhydrous Na_2SO_4 and 4 cm 3% deactivated silica gel. Ethyl acetate (20 mL) was used to elute the OPEs and PAEs. Approximately 1 g of plant samples were accurately weighted, spiked with surrogate standards, and extracted 2 cycles with DCM: n-hexane (1:1, v/v) by an Accelerated Solvent Extractor (ASE350, Dionex Inc.) at 1500 psi and 100 °C each for 5 min. The extract was first purified by the silica gel column as described above, and then followed by a Supelclean ENV I-Carb (GCB) SPE cartridge (500 mg, 6 mL). The soil or plant eluate was solvent exchanged to isooctane, concentrated to ~0.5 mL and added with internal standard. OPEs, PAEs, and PAE isotope surrogate standards were acquired from Dr. Ehrenstorfer (Augsburg, Germany), while OPE isotope surrogate standards were purchased from Toronto Research Chemicals Inc. (Toronto, Canada). Silica gel (100–200 mesh size) was purchased from Merck Co. (Germany). All solvents were high performance liquid chromatography (HPLC) grade and provided from J&K Technology Co., Ltd. (Beijing, China).

2.3. Instrumental analysis

Samples were analyzed for 8 OPEs and 6 PAEs using an Agilent 7890 GC-5975MS in electron ionization (EI) mode applied with a DB5-MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm). The targeted OPEs included tri-*n*-butyl phosphate (TNBP), tri(2-chloroethyl) phosphate (TCEP), tris (1-chloro-2-propyl) phosphate (TCIPP), tris(2-butoxyethyl) phosphate (TBOEP), triphenyl phosphate (TPHP), 2-ethylhexyl diphenyl phosphate (EHDPP), triphenyl-phosphine oxide (TPPO), and tricresyl phosphate (TMPP), while the targeted PAEs included DMP, DEP, di-*iso*-butyl phthalate (DiBP), DNBP, dicyclohexyl phthalate (DCHP), and di-2-ethylhexyl phthalate (DEHP) (Table S2, SI). The carrier gas was helium (purity 99.999%) at 1.2 mL/min. The temperature program was 60 °C for 1 min, 12 °C/min to 312 °C, and then for 10 min. Temperatures for the transfer line, ionization source, and quadrupole were set at 290 °C, 230 °C, and 150 °C, respectively. Details are described in our previous study (Wang et al., 2021).

2.4. Quality assurance and quality control

All glassware was baked at 450 °C for at least 4 h and rinsed with *n*-hexane for 3 times before use. A blank was analyzed simultaneously with every 10 samples to assess potential contamination. Method detection limit (MDL) was estimated as the mean concentration of blanks plus 3x the standard deviation. The MDLs of 8 OPEs and 6 PAEs were 0.07–2.10 and 0.58–45.4 ng/g for soils and 0.17–10.0 and 1.44–104 ng/g for plants, respectively (see Table S3, SI). The surrogate recoveries in all samples for TCEP-d_{12}, TCIPP-d_{18}, TPHP-d_{15}, DEP-d_4, DNBP-d_4, and DEHP-d_4 were 78.3 ± 15.8%, 86.0 ± 10.0%, 86.2 ± 16.8%, 61.4 ± 6.0%, 93.1 ± 5.1%, 97.3 ± 4.8%, respectively. The results were blank but not surrogate recovery corrected.

2.5. Bioaccumulation and translocation assessments

Bioaccumulation and translocation of OPEs and PAEs were evaluated by bioconcentration factors (*BCFs*) and shoot-root transfer factors (*TFs*). The *BCF* was calculated as the ratio of chemical's concentration in the plant root (C_{roots}, ng/g dw) divided by its concentration in the corresponding rhizosphere soil (C_{soil}, ng/g dw), while the *TF* was defined as the ratio of chemical's concentration in the shoot or leaf (C_{shoot}, ng/g dw) divided by its concentration in the corresponding root, as follows:

$$BCF = \frac{C_{root}}{C_{soil}} \quad (1)$$

$$TF = \frac{C_{shoot}}{C_{root}} \quad (2)$$

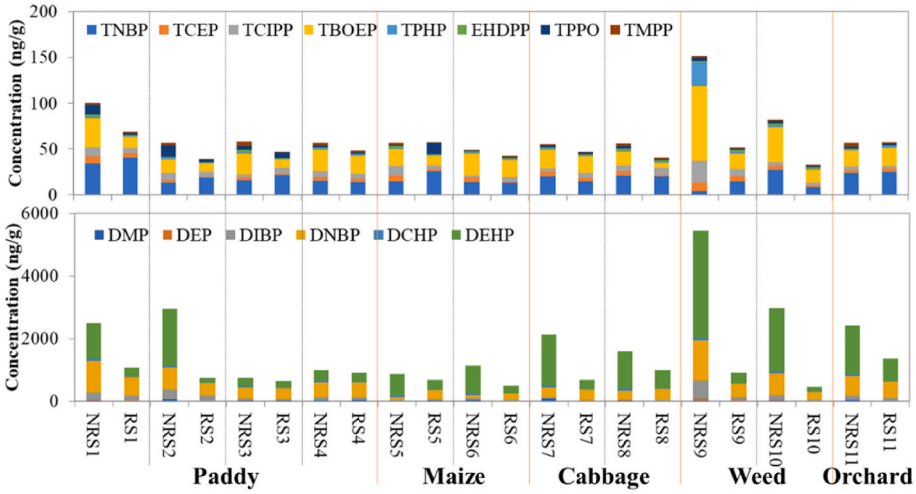

Fig. 1. Concentrations of OPEs and PAEs in the rhizosphere and non-rhizosphere soils.

2.6. Ecological risk assessment

Based on the concentrations of the detected OPEs and PAEs in soil, risk quotient (*RQ*) was used to conduct the ecological risk assessment as follows:

$$RQ = \frac{MEC}{PNEC_{soil}} \quad (3)$$

where *MEC* is the measured soil concentration (ng/g dw). $PNEC_{soil}$ is the predicted no effect concentration (ng/g dw) in soil. The level of risk can be classified into three levels according to the commonly recommended criteria: $RQ < 0.1$ indicates a low risk; $0.1 \leq RQ < 1$ indicates a medium risk or adverse effect; $RQ > 1$ indicates a high risk, which is worthy of serious attention (Niu et al., 2019). The $PNEC_{soil}$ values for OPEs and PAEs are shown in Table S4, SI.

2.7. Daily dietary intake assessment

The daily dietary intakes (*DDIs*, ng/kg-BW/day) of OPEs and PAEs via consuming of Chinese cabbage and rice were calculated as follows:

$$DDI = (C \times IRF \times EF \times ED) / (BW \times AT) \quad (4)$$

Where *C* is the OPE or PAE concentration in the fresh Chinese cabbage or rice (ng/g ww, assuming the moisture contents of Chinese cabbage and rice as 90%); *IRF* is the daily ingestion rate (g/day); *EF* is the exposure frequency (assuming 365 day/year); *ED* is the exposure duration (years); *AT* is the averaging time (day, 365*ED*); and *BW* is the body weight (kg). The values of all parameters used for *DDIs* are shown in Table S5, SI.

3. Results and discussion

3.1. Concentrations of OPEs and PAEs in soils

The concentrations of OPEs and PAEs in soils are shown in Fig. 1 and Table S6, SI. The total concentrations of OPEs in all soils ranged from 33.1 to 136 ng/g dry weight (dw) with a mean value of 58.5 ± 22.6 ng/g dw (median: 56.5 ng/g dw). The OPE concentrations varied widely for sampling sites and land use types. Generally, wasteland soils (mean ± standard deviation: 75.7 ± 44.9 ng/g dw) showed relatively high concentrations of OPEs, followed by paddy field (58.9 ± 19.1 ng/g dw), orchard (57.0 ± 0.37 ng/g dw), maize field (51.5 ± 7.04 ng/g dw), and vegetable garden (48.4 ± 8.58 ng/g dw). It is interesting that the less disturbed wasteland soil showed a higher concentration than these farmland soils. This may be related to the fact that the agricultural activities on the farmlands, such as fertilization and irrigation, promote the input of organic pollutants in soil. Paddy field had relatively higher concentrations than other farmlands, which may due to the frequent irrigation, indicating a potential health risk associated with rice consuming. Among all OPEs, TNBP (19.4 ng/g dw) and TBOEP (mean:19.5 ng/g dw) were the most abundant compounds in soils, followed by TCIPP, TCEP, and TPPO. Relatively high compositions of TBOEP were also discovered in soils from a plastic waste recycling area in northern China (Wan et al., 2016).

The soil concentrations of OPEs in this study were lower than those in the urban soils (0–5 cm depth, collected in December, mean: 110 ng/g dw) of Guangzhou, China (Cui et al., 2017), but comparable to those from a plastic waste recycling area in Hebei, China (0–15 cm depth, collected in June, mean: 80 ng/g dw) (Wan et al., 2016) and those collected nationwide in China (0–5 cm depth, collected from March to August, median: 36.6 ng/g dw) (Wang et al., 2019).

The total concentrations of PAEs in soils ranged from 465 to 5450 ng/g dw with a mean value of 1490 ± 1180 ng/g dw (median: 999 ng/g dw). With agricultural modernization, plastic mulching and plastic film greenhouses have become very popular throughout China. Agricultural plastic film has been considered as one of the most important sources of PAEs in soil (Sun et al., 2016; Wang et al., 2015). Meanwhile, the cultivation methods and field managements may also introduce PAE contamination into soil (Xu et al., 2008). The mean concentration of PAEs decreased in the order of wasteland soil > orchard soil > paddy soil > vegetable soil > maize soil, which was similar with the distribution of OPEs. However, a previous study (Kong et al., 2012) found that PAE concentrations decreased in the sequences of vegetable soil > wasteland soil > farmland soil > orchard soil in the suburban area of Tianjin, China, which may due to the more frequent human intervention in vegetable garden. DEHP was the most dominant phthalate, followed by DNBP and DiBP. This agreed with the fact that these PAEs were more abundantly applied as plastic additives than other PAEs (Guo et al., 2012). Since DEHP has been classified as a possible human carcinogen by USEPA (USEPA, 2007), the relatively high concentration of DEHP in soil may pose a potential health risk through food chain. The concentrations of OPEs and PAEs in soils also varied between the two sampling locations with the mean soil concentrations in the Qingduizi Town (OPEs: 66.3 ± 30.0 ng/g, PAEs: 1800 ± 1530 ng/g) slightly higher than those in the Chengzitan Town (OPEs: 52.1 ± 12.5 ng/g, PAEs: 1230 ± 768 ng/g).

Numerous studies have been conducted to investigate the PAE levels in soils of China and found that the levels of PAEs in soils of China are generally at the high end of the global range (Lv et al., 2018). The PAE concentrations in the soils of this study were comparable to those in the

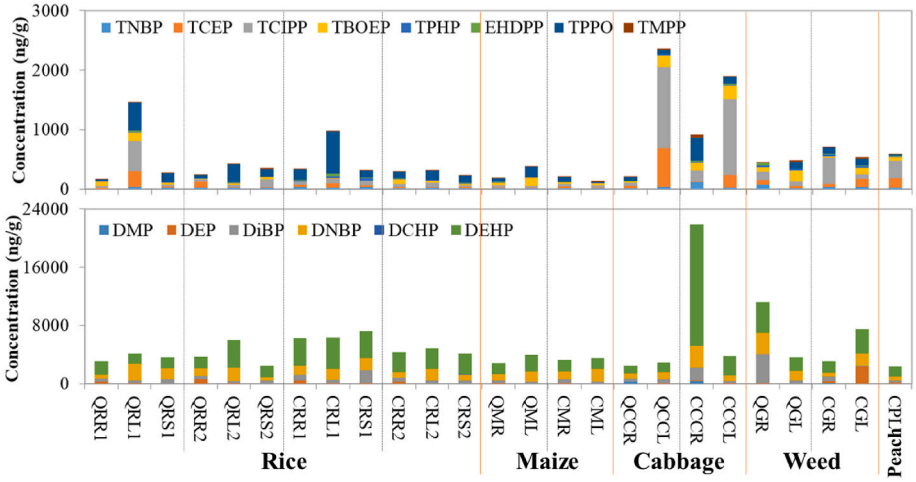

Fig. 2. Concentrations of OPEs and PAEs in the roots (R), leaves (L), and seeds (S) of different plants. (The initial Q stands for Qingduizi and C for Chengzitan; the second letter R is for rice, M for maize, CC for Chinses cabbage, G for weed, and P for peach).

suburban soils from Tianjin (0–20 cm depth, collected in November, mean values: vegetable garden 1580 ng/g; wasteland 582 ng/g; farmland 521 ng/g; orchard 333 ng/g) (Kong et al., 2012), farmlands in the Yangtze River Delta (0–15 cm depth, collected in June, mean: 782 ng/g) (Sun et al., 2016), and Sanjiang Plain (0–20 cm depth, collected in May, vegetable garden 308 ng/g; paddy field 532 ng/g) (Wang et al., 2017b), but slightly lower than those from Shandong Peninsula (0–40 cm depth, collected in May, mean: 6470 ng/g) (Li et al., 2016) and Yellow River Delta (0–20 cm depth, collected in September, mean: 2975 ng/g) of China (Yang et al., 2013).

Plants can enhance the disappearance of soil organic pollutants through either root uptake (Mueller et al., 2006) or biodegradation/rhizoremediation (Huang et al., 2010). Rhizosphere microorganisms can significantly influence the types and quantities of root exudates and the physiological and biochemical processes in plants by changing the hormone content and rhizosphere nutrient status (Tinker and Sanders, 1975). Rhizosphere microorganisms can either activate or immobilize organic pollutants in soil and can also degrade these pollutants (Shaw and Burns, 2003). Enzymatic activity and heterogeneity in rhizosphere soil was higher than those in non-rhizosphere soil owing to the higher microbial activity (Gao et al., 2020). For total concentrations, both OPEs and PAEs in the rhizosphere soils were generally lower than those in the corresponding non-rhizosphere (bulk) soils (OPEs: $p = 0.016$; PAEs: $p = 0.008$). For individual chemical, statistically significant differences ($p < 0.05$) were found for TCEP, TBOEP, EHDPP, TMPP, DMP, DCHP, and DEHP, but not for the others.

3.2. Concentrations of OPEs and PAEs in plants

The concentrations of OPEs and PAEs in plant roots, leaves, and seeds (only for rice) were analyzed and shown in Fig. 2 and Table S7, SI. The total OPEs in plants ranged from 140 to 2360 ng/g dw, with a mean of 582 ± 558 ng/g dw (median: 354 ng/g dw). TCIPP was the dominant OPEs in plants, with a mean concentration of 207 ng/g dw, followed by TPPO (mean: 154 ng/g dw), TCEP (mean: 83.7 ng/g dw), and TBOEP (mean: 69.7 ng/g dw). These results may be related to the fact that long-chain aryl-, chloro-, and alkyl OPEs are more bioaccumulative than those of short-chain moieties (Wang et al., 2017a). Meanwhile, the OPEs concentrations varied widely with different plant species. For plant leaves, the mean concentrations of ΣOPEs followed the order of Chinese cabbage > rice > weed > peach > maize; whereas for roots, the order was weed > Chinese cabbage > rice > maize.

The OPE concentrations in the rice seeds (including rice and husk, mean: 298 ng/g dw) in this study were much higher than those (0.38–287 ng/g dw, mean: 69.9 ng/g dw) measured in the rice samples collected from four representative areas: Hubei, Chongqing, Sichuan, and Guangxi of China (Zhang et al., 2016), cereal samples (mean: 2.3 ng/g wet weight, ww) from Brisbane, Australia (He et al., 2018), and grains (mean: 36.9 ng/g ww) from Belgium (Poma et al., 2018). The OPE concentrations in the Chinese cabbage leaves (2130 ng/g dw) in this study were much higher than those detected in the leafy vegetables (5.9–90.6 ng/g dw) from Tianjin of China (Zhang et al., 2016) and vegetables (mean: 2.6 ng/g ww) from Brisbane, Australia (He et al., 2018).

The total concentrations of PAEs in plants ranged from 2440 to 21800 ng/g dw, with a mean of 5160 ± 5060 ng/g dw (median: 3790 ng/g dw). DEHP showed the highest mean concentration (2840 ng/g dw), which was several times higher than the others, followed by DNBP (mean: 1330 ng/g dw) and DiBP (mean: 672 ng/g dw). For plant leaves, the ΣPAEs followed the order: weed ≈ rice > maize > Chinese cabbage, while for plant roots, the ΣPAEs followed the order: Chinese cabbage > weed > rice > maize. The relatively high concentrations of OPEs and PAEs in the roots of Chinese cabbages may be due to the active human intervention in vegetable garden, such as fertilization and irrigation (Kong et al., 2012).

The ΣPAEs in the rice seeds (both rice and husk, mean: 4390 ng/g dw) in this study were much higher than those in rice (mean: 199.8 ng/g dw) from local markets in Harbin and Shanghai, China (Guo et al., 2012) and those in rice (10.4 ng/g ww) from market of Tianjing, China (Ji et al., 2014). The ΣPAEs in the Chinese cabbage leaves (mean: 3360 ng/g dw) in this study were also much higher than those in vegetables (mean: 9.233 ng/g ww) from market of Tianjing (Ji et al., 2014), vegetables (mean: 330 ng/g dw) from an agricultural area of Chongqing (He et al., 2020), and vegetables (mean: 536 ng/g dw) from the Yangtze River Delta, China (Wei et al., 2020), but comparable with those detected in the vegetables (mean: 2560 ng/g dw) from suburban plastic film greenhouses in east China (Wang et al., 2015).

3.3. Bioaccumulation and translocation of OPEs and PAEs in plants

A significantly positive correlation (Spearman test, $r = 0.561$, $p < 0.001$) was discovered between chemical concentrations in the roots and their corresponding rhizosphere soils, suggesting that OPEs and PAEs in plant roots were mainly taken up from rhizosphere soils. To evaluate the uptake abilities of OPEs and PAEs by roots, *BCFs* were calculated (Table S8, SI). *BCFs* were in the range of 0.13–233 (median: 6.68) and 0.08–287 (median: 6.37) for OPEs and PAEs, respectively. The *BCF* values differed with chemical and plant species. The median *BCF* values

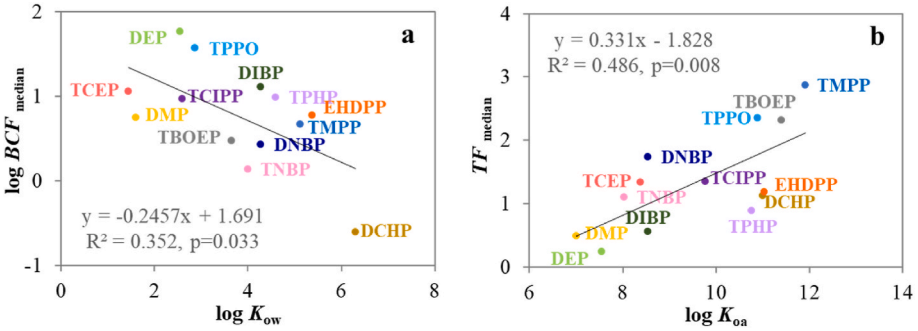

Fig. 3. Relationships between log*BCFs* (median) and logK_{ow} (a) and between log*TFs* (median) and logK_{oa} (b) of the OPEs and PAEs.

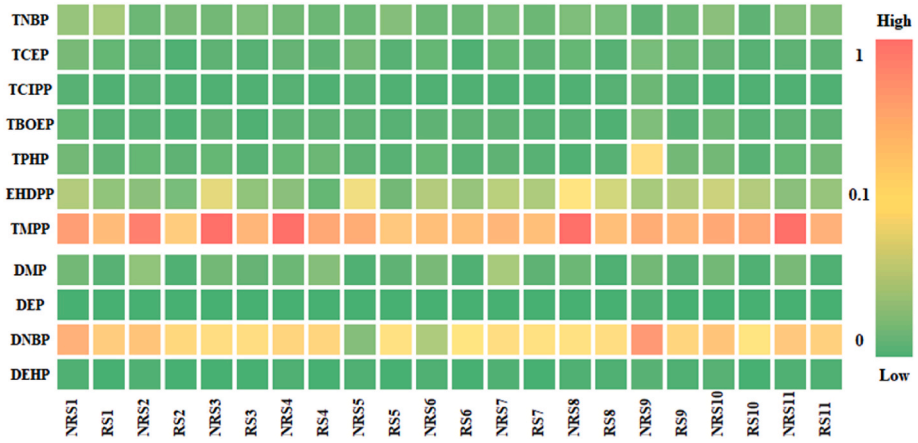

Fig. 4. Risk quotients (*RQs*) of major OPEs and PAEs in the rhizosphere and non-rhizosphere soils.

of individual compounds were in the order: TPPO > TCEP > TPHP > TCIPP > EHDPP > TMPP > TBOEP > TNBP for OPEs, and DEP > DiBP > DEHP > DMP > DNBP > DCHP for PAEs. The *BCF* values in this study were comparable with those calculated for vegetables (*BCFs*: 0–13.4) from greenhouses and open fields of Guangzhou, China (Zeng et al., 2020) and plants (*BCFs*: 5.8–17.9) grown near an electronic waste recycling site of East China (Ma et al., 2013), but higher than those reported in wheat (0.24–0.50) from Hebei Province, China (Wan et al., 2016).

TFs are the ratio of the chemical's concentration in the shoot or leaf to its concentration in the root. *TFs* were in the range of 0.064–32.8 (median: 1.59) for OPEs and 0.052–9.6 (median: 0.79) for PAEs, respectively (Table S9, SI). The transfer factors were higher for OPEs than PAEs, suggesting that the translocation of OPEs within plant may be easier. The median *TF* values of OPEs were in the order: TMPP > TPPO > TBOEP > TCIPP > TCEP > EHDPP > TNBP >1 > TPHP (0.89) with nearly all *TFs* >1, except for TPHP. Meanwhile, the median *TF* values of PAEs were in the order: DNBP > DCHP > DEHP >1 > DiBP > DMP > DEP.

The uptake, transport, and bioaccumulation of organic contaminants by plants can be significantly influenced by their physicochemical properties (Calderon-Preciado et al., 2012), such as the octanol-water

Table 1
Estimated daily dietary intakes (*DDIs*, ng/kg-BW/day) of OPEs and PAEs via consuming of Chinese cabbage and rice for local toddlers and adults.

DDI	Toddler							Adult						
	Chinses cabbage			Rice			Total	Chinses cabbage			Rice			Total
(ng/kg-BW/day)	Min	Max	Median	Min	Max	Median	Median	Min	Max	Median	Min	Max	Median	Median
TNBP	18.0	19.0	18.5	6.7	14.5	7.7	26.2	4.6	4.9	4.8	8.1	17.6	9.4	14.2
TCEP	131	402	267	6.2	12.2	7.4	274	33.7	104	68.6	7.5	14.8	9.0	77.7
TCIPP	775	834	805	12.6	48.6	20.7	825	200	215	207.2	15.3	59.0	25.1	232
TBOEP	120	136	128	0.9	18.1	13.1	141	30.8	35.1	33.0	1.1	22.0	15.9	48.9
TPHP	6.4	13.4	9.9	1.3	18.9	2.7	12.6	1.6	3.4	2.5	1.6	23.0	3.2	5.8
EHDPP	0.3	14.9	7.6	0.7	4.3	1.8	9.4	0.1	3.8	2.0	0.9	5.3	2.2	4.2
TPPO	42.0	72.2	57.1	46.5	56.2	48.3	105	10.8	18.6	14.7	56.5	68.3	58.7	73.4
TMPP	7.4	13.1	10.3	2.7	6.5	3.7	14.0	1.9	3.4	2.6	3.2	7.9	4.5	7.2
OPEs	1160	1440	1300	91	139	119	1420	299	372	335	111	169	144	480
DMP	34.7	38.7	36.7	6.5	18.4	7.2	43.9	8.9	10.0	9.5	8.0	22.3	8.7	18.2
DEP	15.6	27.1	21.3	5.4	9.3	6.7	28.1	4.0	7.0	5.5	6.5	11.3	8.2	13.7
DiBP	162	353	257	179	691	206	464	42	91	66	217	840	250	317
DNBP	483	566	524	157	674	449	973	124	146	135	191	819	546	681
DCHP	1.5	2.3	1.9	1.9	4.3	2.4	4.3	0.4	0.6	0.5	2.3	5.2	2.9	3.4
DEHP	818	1610	1220	604	1450	874	2090	211	416	313	733	1760	1060	1370
PAEs	1790	2320	2060	969	2850	1540	3600	462	598	530	1180	3460	1870	2400

partition coefficient (K_{ow}) and octanol-air partition coefficient (K_{oa}) (Collins et al., 2006; Gao and Collins, 2009). The lipophilicity of chemical determines how easily it can be released from soil organic matter and move across plant membranes, and to what extent it can partition onto plant lipid, limiting the long-distance transport. A significantly negative correlation was found between log *BCF* (median values) and logK_{ow} of both OPEs and PAEs (Fig. 3 a; $R^2 = 0.352$, $p = 0.033$), demonstrating that uptake of OPEs and PAEs by plant was mainly depend on their K_{ow} values. A high K_{ow} suggests that this chemical tends to be tightly bound to soil particles and difficultly released and taken up by plant (Collins et al., 2006). However, no significantly linear relationship ($p > 0.05$) was found between *TFs* of OPEs and PAEs and their logK_{ow} values, which may due to their fast degradation or metabolism within plants (Hu et al., 2016). Interestingly, a significantly linear relationship was found between *TF* (median values) and logK_{oa} values of OPEs and PAEs (Fig. 3 b; $R^2 = 0.486$, $p = 0.008$), suggesting that the accumulations of the OPEs and PAEs in shoots may be controlled by their K_{oa} values. Uptake from the atmosphere by leaves might also be an important pathway for chemicals with log$K_{oa} > 6$ (Cousins and Mackay, 2001).

3.4. Ecological and human risk assessments

The ecological risks of TPPO and DCHP were not assessed due to the lack of physicochemical parameters. The *RQs* for soils in this study were in the range of 0.001–1.66 for OPEs (median: 0.013) and 3.90×10^{-5}-0.717 for PAEs (median: 0.003), respectively (Fig. 4). The median values of *RQs* were in the order: TMPP (0.56) > 0.1 > EHDPP > TNBP > TPHP > TCEP > TBOEP > TCIPP for OPEs and DNBP (0.21) > 0.1 > DMP > DEHP > DEP for PAEs. TMPP and DNBP showed the highest *RQs*. The exhibit high risks (*RQs* >1) were discovered for TMPP in the NRS3 (paddy), NRS4 (paddy), NRS8 (Chinese cabbage), and NRS11 (peach), which were all non-rhizosphere soils. The relatively higher ecological risk in the non-rhizosphere soil than the rhizosphere soil suggested that the plant may degrade or absorb those chemicals from soil, by which the plant may transport the risk onto humans through food chain.

Vegetables is considered as the major dietary source of PAEs (Yang et al., 2018), while rice is considered as the major dietary source of OPEs for the Chinese population (Zhang et al., 2016). The *DDI* values of OPEs and PAEs for toddlers and adults are listed in Table 1. Relatively high *DDIs* were discovered for consuming the Chinese cabbage and rice (husk and rice) measured in this study. The median *DDI* values of ΣOPEs and ΣPAEs were 1420 and 3600 ng/kg-BW/day for toddlers and 480 and 2400 ng/kg-BW/day for adults, respectively. Toddlers exhibited higher *DDIs* than adults due to their lower body weights, and consequently higher exposure risks due to their susceptibility to toxicity. Overall, the results suggested relatively high risks via daily ingestion of vegetables. *DDIs* of OPEs and PAEs via vegetable consuming were both higher than those via rice consuming for toddlers, whereas *DDIs* of OPEs via vegetable consuming were higher than rice consuming for adults. In addition, *DDIs* of OPEs and PAEs via rice consuming for toddlers were both slightly lower than those for adults, which may due to more rice consuming for adults.

4. Conclusion

The concentrations, bioaccumulation, translocation, and potential ecological and exposure risks of OPEs and PAEs in soils and plants from the rural areas of Dalian, Northeast China were investigated. Relatively high concentrations of OPEs and PAEs were discovered in soils and plants from these areas, especially in the paddy fields and vegetable gardens. The OPE and PAE concentrations in the bulk soils were significantly higher than those in the rhizosphere soils, suggesting plant can either degrade or absorb those chemicals. The BCFs of OPEs and PAEs were significantly negatively correlated with their octanol-water partition coefficients, whereas their translocation factors were significantly positively correlated with the octanol-air partition coefficients. Medium to high risks from TMPP and DNBP were discovered in the agricultural soils of these rural areas. The relatively high contaminations of OPEs and PAEs in the vegetables and rice seeds may also pose potential risks to residents via daily dietary intakes. Further studies are required in the future in case of the safety of ecological systems and agricultural products.

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.

Acknowledgements

This study was supported by the National Natural Science Foundation of China (Nos. 21976023 and 41877401), the Fundamental Research Funds for the Central Universities, China (DUT19LK43), and the Petro China Innovation Foundation (2019D-5007-0502).

Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117532.

Credit author statement

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