



Uptake and translocation of organophosphate esters by plants: Impacts of chemical structure, plant cultivar and copper

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ARTICLE INFO

Handling Editor: Frederic Coulon

Keywords:

Organophosphate esters
Chemical structure
Plant cultivar
Heavy metals
Hydrophobicity

ABSTRACT

Organophosphate esters (OPEs) are normally used as flame retardants, plasticizers and lubricants, but have become environmental pollutants. Because OPEs are normally present alongside heavy metals in soils, the effects of interactions between OPEs and heavy metals on plant uptake of OPEs need to be determined. In this study, we investigated the effects of OPEs chemical structure, plant cultivar and copper (Cu) on the uptake and translocation of OPEs by plants. The bioaccumulation of OPEs varied among plant cultivars. They were preferentially enriched in carrot, with the lowest concentrations observed in maize. OPEs with electron-ring substituents (ER-OPEs) exhibited a higher potential for root uptake than did OPEs with open-chain substituents (OC-OPEs), which could be attributed to the higher sorption of ER-OPEs onto root charged surfaces. This was explained by the stronger noncovalent interactions with the electron-rich structure of ER-OPEs. The presence of Cu slightly reduced the distinct difference in the ability of roots to take up OC-OPEs and ER-OPEs. This was explained by the interactions of Cu ions with the electron-rich structure of ER-OPEs, which suppressed the sorption of ER-OPEs on the root surface. A negative relationship between the logarithms of the translocation factor and octanol-water partition coefficient (K_{ow}) was observed in treatments with either OPEs only or OPEs + Cu, implying the significant role of hydrophobicity in the OPEs acropetal translocation. The results will improve our understanding of the uptake and translocation of OPEs by plant cultivars as well as how the process is affected by the chemical structure of OPEs and Cu, leading to improvements in the ecological risk assessment of OPEs in the food chain.

1. Introduction

Organophosphate esters (OPEs) have been observed in the atmosphere (Kurt-Karakus et al., 2018), water (Li et al., 2019), soil/sediment (Tan et al., 2016; Ren et al., 2019) and biota (Kucharska et al., 2015). Soil is the major environmental sink for OPEs, and high concentrations have been reported in farmland (Ji et al., 2019), multi-waste recycling areas (Wang et al., 2018) and e-waste-contaminated soils (Matsukami et al., 2015; Ge et al., 2020). The total OPEs in general soil samples was reported to be in the range of 10–320 ng/g (Chongqing, China) and 38–470 ng/g (Turkey) (He et al., 2017; Kurt-Karakus et al., 2018). At a

multi-waste recycling site in China, the concentration of 12 OPEs (Σ_{12} OPE) was significantly higher in an open recycling operation soil (120–2100 ng/g) than in a semi-closed recycling operation soil (59–320 ng/g) (Wang et al., 2018). An accumulation of OPEs was found in plants following a study of Σ_{18} OPE concentrations in intertidal plants in Laizhou Bay (China), with levels of 33–57 ng/g in roots, 3.9–7.5 ng/g in stems and 2.8–4.1 ng/g in leaves (Wang et al., 2020). OPEs are frequently detected in foods (Poma et al., 2017; Li et al., 2019), presenting a potential risk to public health through the food chain (Zhang et al., 2016). Therefore, plant uptake, translocation and accumulation of OPEs have been extensively studied.

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<https://doi.org/10.1016/j.envint.2021.106591>

Received 16 February 2021; Received in revised form 17 April 2021; Accepted 19 April 2021

Available online 29 April 2021

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The fate of OPEs within the soil-plant system is influenced by their chemical properties. The wide range of octanol-water coefficients (K_{ow}) of OPEs (logarithm of K_{ow} , -0.65 to 10.43) implies different environmental behaviours across OPE analogues. Positive relationships between the root concentration factor (RCF) and $\log K_{ow}$ of OPEs have been reported in wheat, whereas the opposite relationship was reported for the translocation factor (TF) and $\log K_{ow}$ (Wan et al., 2016). Highly hydrophobic OPEs, such as 2-ethylhexyl diphenyl phosphate (EHDPP) and tris (2-ethylhexyl) phosphate (TEHP), are prone to be taken up and fixed by roots, resulting in the restriction of acropetal translocation (Liu et al., 2019; Wang et al., 2019). However, most studies have focused on the impact of hydrophilia on OPE absorption by plants, whereas the chemical structure of OPEs has been ignored, even though it may play an important role. Additionally, plant cultivars and their physiological properties are also affected the behaviour of organic chemicals (Su and Zhu 2007; Wang et al., 2016; Liu et al., 2019). Plants with high lipid contents tend to accumulate hydrophobic chemicals, and the partitioning of organic compounds near the plant root epidermis is dominated by root lipid substances (Chiou et al., 2001). The uptake behaviour of polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), and perfluoroalkyl substances has been reported to be positively or negatively correlated with root lipid content (Zhu et al., 2007; Huang et al., 2010; Wen et al., 2016). The role of plant lipid content in OPE uptake and translocation is still unclear, but it might play a role in the fate of OPEs within the soil-plant system.

Co-contamination of heavy metals and organic chemicals has been reported in many areas (Mattina et al., 2003; Zhang et al., 2010; Liu et al., 2017; Chen et al., 2020a). Plant growth can be influenced by heavy metals because they may damage the root cell membrane (Strange and Macnair, 1991; Demidchik et al., 1997), increase root permeability (Wang et al., 2016), chelate with organic compounds (Luo et al., 2015) and change the hydrophobicity of organic chemicals (Deng et al., 2018). Furthermore, many studies have demonstrated the changing of uptake and translocation behaviour of organic chemicals by heavy metals (Lu et al., 2014; Wang et al., 2017). Hydrophobic PBDEs and polychlorinated biphenyls have been indiscriminately taken up and translocated to aerial parts after exposure to heavy metals (Wang et al., 2016; Wang et al., 2017). However, the uptake of PAHs is weakened in the presence of Cu, Pb and Cr (Deng et al., 2018).

OPEs existed in e-waste recycling site soils widely (Matsukami et al., 2015; Ge et al., 2020), where were always found to be contaminated by Cu and its concentration can reach up to 1870 mg/kg (Liu et al., 2021). In addition, Cu is an essential element for plant growth and owns higher mobilization than other heavy metals (Burzynski, 2001). It indicated that high level of Cu might be easily taken up by plant and toxic to the plants, which had been evidenced by some studies (Fargasova, 2004; Kumar et al., 2021). However, little information is available about the impacts of heavy metals on OPE uptake behaviour in plants, and it remains unknown whether different OPEs follow different rules under the influence of heavy metals.

In this study, six vegetable and crop cultivars, i.e., carrot (*Daucus carota* L.), zucchini (*Cucurbita moschata* Poir.), soybean (*Glycine max* L.), lettuce (*Lactuca sativa* L.), tomato (*Lycopersicon esculentum* Mill.) and maize (*Zea mays* L.), were selected as common and popular food species. Twelve OPE congeners from four categories were tested (alkyl-, aryl-, chlorinated- and hybrid-OPEs): triethyl phosphate (TEP), triisopropyl phosphate (TiPP), tripropyl phosphate (TnPP), tri-*n*-butyl phosphate (TnBP), TEHP, triphenyl phosphate (TPhP), trimethylphenyl phosphate (TMPP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl)phosphate (TDCPP), tris(2-butoxyethyl) phosphate (TBOEP) and EHDPP. According to the difference in substituents, they were further categorized into OPEs with open-chain substituents (OC-OPEs; including TEP, TiPP, TnPP, TnBP, TEHP, TCEP, TBOEP and EHDPP) or OPEs with electron-ring substituents (ER-OPEs; including TPhP, TMPP, TCPP and TDCPP). These OPEs have frequently been detected in the environment (Wan et al.,

2016; He et al., 2019). We investigated the critical factors affecting the uptake and translocation of OPEs, i.e., plant cultivar type, OPE properties and the presence of Cu. We also attempted to evaluate the impacts of K_{ow} and substituent type on the uptake and translocation of OPEs and explored the mechanisms.

2. Materials and methods

2.1. Chemicals and reagents

Twelve target OPEs and mass-labelled standards used as a surrogate standard (SS) and internal standard (IS) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA) or AccuStandard, Inc. (New Haven, CT, USA). All solvents and standards used in this study were of HPLC grade or higher. The details of the OPEs are provided in Table S1.

2.2. Study design

Carrot, zucchini, soybean, lettuce, tomato and maize seeds were obtained from the Guangdong Academy of Agricultural Sciences, Guangzhou. Seeds were sterilized in 5% (v/v) NaClO solution for 10 min, thoroughly washed with deionized water, and germinated at room temperature (20 – 25 °C) in darkness.

Krasnozem soil (clay, 40%; silt, 18%; sand, 42%) was collected from a farm located in Guangzhou, Guangdong (23.17° N, 113.37° W). Soil samples were air-dried, sieved through a 2-mm mesh, and homogenized at room temperature. No OPEs were detected in the test soil. Soil was spiked with a mixture of the twelve OPEs to reach a final concentration of 500 ng/g. The OPE-spiked soil was then amended with $\text{Cu}_2(\text{OH})_2\text{CO}_3$ to reach a final concentration of 800 $\mu\text{g/g}$. Soils were blended every day and kept at 20 – 25 °C for 1 month. The soils were exposed to 10 dry-wet cycles to guarantee the homogeneity of the OPEs and Cu in the soil. Two treatments (OPEs only and OPEs + Cu) were set. Five healthy seedlings of a uniform size for each plant cultivar were transplanted into a ceramic pot together with 0.5 kg of soil.

All treatments were applied with three replicates. The soil moisture was maintained at 60% of its water holding capacity by applying deionized water. All pots were placed in a greenhouse where the temperature was 25 – 30 °C during the day and 15 – 20 °C at night. After 2 months of cultivation, the plants were harvested and separated into roots and shoots, which were then washed with tap water and deionized water, wrapped in aluminium foil and stored at -20 °C. Plant biomass was measured (Fig. 1). Soil samples were immediately stored in a freezer at -20 °C. Plant and soil samples were subsequently freeze-dried for 72 h, ground into powder, and stored at -20 °C prior to chemical analysis. Soils without OPEs were used as controls to monitor the potential atmospheric deposition of OPEs during the experiment.

2.3. Chemical analysis

Analysis of OPEs. The analysis of OPEs in soils and plants followed a previously published method, with a minor modification (Poma et al., 2018). Briefly, 0.2 g of plant tissues or soil samples were placed in a 15-mL Teflon tube, spiked with IS mixtures containing d_{27} -TnBP, d_{15} -TPhP and d_{12} -TCEP, and extracted with 5 mL of acetonitrile overnight after vortexing for 1 min. The mixture was then ultrasonicated for 10 min and centrifuged at 4000 rpm for 10 min, and the supernatants were transferred to a clean amber vial. The extraction step was repeated twice more. All extracts were combined, blown down using nitrogen gas (N_2) to near dryness, and dissolved with 0.5 mL of hexane. The extracts were further purified using a Florisil cartridge (500 mg, 3 mL, Supelco) pre-conditioned with 6 mL of ethyl acetate (ETAC) and 6 mL of hexane. The Florisil cartridges were eluted with 12 mL of dichloromethane (DCM): hexane (1:4, v:v) (E1, discarded) and 10 mL of ETAC (E2, collected). Then, E2 was evaporated to dryness under N_2 and resolubilized in 0.5

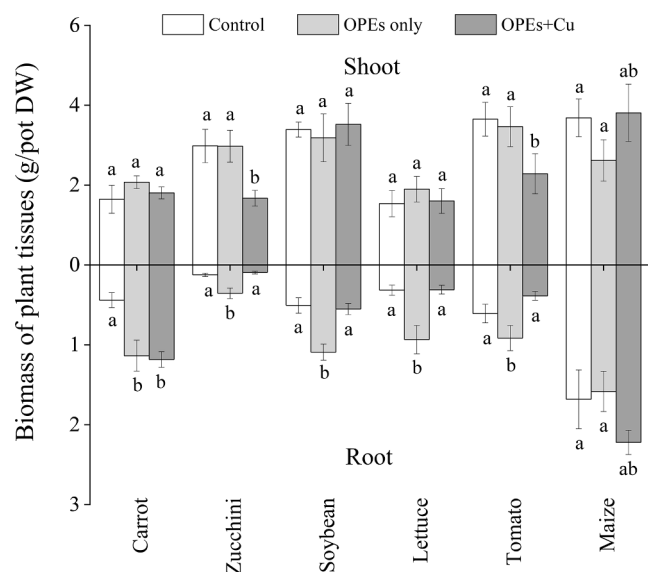


Fig. 1. Biomass of plant cultivars postexposure to OPEs only or OPEs + Cu. OPEs concentration was 0 ng/g DW in control treatment and 500 ng/g DW in OPEs only and OPEs + Cu treatments. Cu concentration was 800 μ g/g DW in OPEs + Cu treatment. The columns and bars represent mean \pm standard deviation ($n = 3$). Different letters indicate significant difference at the level of 0.05 based on LSD test.

mL of hexane. The extracts were then loaded onto an aminopropyl silica cartridge (500 mg, 3 mL, Agela) preconditioned with 6 mL of DCM: hexane (1:1, v:v) and 6 mL of hexane. The aminopropyl silica cartridge was eluted with 10 mL of hexane (E3, discarded) and 12 mL of DCM: hexane (1:1, v:v) (E4, collected). Subsequently, E4 was blown down to dryness with N_2 , dissolved in 200 μ L of SS mixture (with d_{21} -TnPP and d_{15} -TDCPP), and transferred to vials for instrumental analysis.

Analysis of Cu. The analytical method used to measure Cu in soil and plant samples followed our previous study with some modifications (Jiang et al., 2016). In brief, soils and plant tissues were acidified with a mixture of $HNO_3:HClO_4:HF$ (1:1:1, v:v:v) or $HNO_3:HClO_4$ (9:1, v:v), respectively. The analysis of total Cu was performed using inductively coupled plasma-mass spectrometry (ICP-MS; Agilent, Santa Clara, CA, USA). To measure the available Cu, soil samples were homogenized with 0.01 M $CaCl_2$ (1:5, m:v) and then centrifuged for 15 min after extraction by shaking for 2 h. The extracts were filtered, acidified with HNO_3 , and analysed using ICP-MS. Certified reference materials were GBW07453 and GBW10020 (Citrus Leaf) for soil and plant, respectively.

2.4. Instrumental analysis

A gas chromatography (GC) instrument (7890A Agilent) coupled to a 7000A triple quadrupole mass spectrometer (Agilent) operating in electron-impact mode was used for the analysis of OPEs. A pulsed splitless injection of 2 μ L at 250 $^{\circ}C$ was used to introduce the sample to the GC column, and high-purity helium was used as the carrier gas at 2.25 mL/min. GC separation was performed using a DB-5MS column (30 m \times 250 μ m \times 0.25 μ m, Agilent). The GC oven program was as follows: hold at 90 $^{\circ}C$ for 1 min, increase the temperature to 220 $^{\circ}C$ at 10 $^{\circ}C$ /min, then to 240 $^{\circ}C$ at 20 $^{\circ}C$ /min, then to 280 $^{\circ}C$ at 5 $^{\circ}C$ /min and hold for 1 min, then to 320 $^{\circ}C$ at 50 $^{\circ}C$ /min and hold for 3 min, and finally increase the temperature to 325 $^{\circ}C$ in 0.5 min. Details on the quantitation and qualification ions for OPEs can be found in Table S2.

2.5. Quality control and assurance

The average recoveries were $96 \pm 5\%$ and $93 \pm 3\%$ for Cu in soils and plants, respectively. Five deuterated standards, including d_{27} -TnBP, d_{12} -

TCEP, d_{15} -TPhP, d_{21} -TnPP and d_{15} -TDCPP, were added to correct for the possible loss of analytes during sample preparation. Surrogate recoveries for plant and soil samples ranged from 78% to 120% and 91% to 130%, respectively. Quality control was performed by analysing the procedural blanks, with the random injection of solvent blanks, standards and duplicated samples installed in parallel every 12 samples to avoid any potential contamination. All samples were covered with aluminium foil or stored in glass tubes. The limits of quantification (LOQ) for individual OPEs (Table S3) were based on a signal-to-noise ratio of 10. All results were determined based on the dry weight of the plants or soil.

2.6. Statistical analysis

All data analyses were performed using Origin 9.0 and Microsoft Excel 2013. The statistical significance of differences (p -value < 0.05) in chemical concentrations in the plants and soils was tested using analysis of variance. Correlations, least significant differences (LSDs) and other statistical outcomes were calculated using SPSS 25.0. For each OPE, the root concentration factor was calculated as the ratio of the OPE concentration in roots (C_{root}) to that in the soil (C_{soil}), and the TF was calculated as the OPE concentration in shoots divided by that in roots.

3. Results and Discussion

3.1. Plant growth in the presence of OPEs and OPEs + Cu

In treatments with OPEs only, the root biomass increased slightly compared to the control (Fig. 1). Although some studies have reported the uptake and translocation of OPEs by plants, there is no published data regarding changes in plant growth upon exposure to OPEs, and our study is firstly report negligible phytotoxicity or ecotoxicity of OPEs in terms of plant growth at the level of 500 ng/g. In the OPEs + Cu treatments, the presence of Cu resulted in different effects on plant growth, with the biomass of zucchini, soybean, lettuce, and tomato remarkably reduced, and with zucchini growth being most strongly inhibited.

3.2. Differences in OPE accumulation among plant cultivars

In treatments with OPEs only, the $\Sigma_{12}OPE$ concentrations in plant tissues were significantly different across plant cultivars (Fig. 2, $p < 0.05$). In general, the $\Sigma_{12}OPE$ concentrations in carrot were significantly higher than those in the tissues of other plants, with average values of 7500 ng/g in roots and 9200 ng/g in shoots (Table S4). The $\Sigma_{12}OPE$ concentrations in carrot was followed in order by those in zucchini, soybean, lettuce, tomato and maize. The OPEs in shoots were predominantly from acropetal translocation. The contribution of OPEs from atmospheric deposition was negligible, with OPEs not detected in plants grown in clean soils (i.e., not spiked with OPEs), although one previous study found that some organic contaminants in shoots could have originated from the air (Chen et al., 2019).

The highest levels of OC-OPEs and ER-OPEs were observed in carrot, with values of 1100 and 6500 ng/g in roots, 4900 and 4300 ng/g in shoots, respectively (Table S5). It is worth noting that ER-OPEs were preferentially taken up by plants compared to OC-OPEs (Fig. 3). The ER-OPEs concentrations ranged from 620 to 6500 ng/g in roots, accounting for 75–89% of the $\Sigma_{12}OPE$ s. Oppositely, ER-OPEs (250–4300 ng/g) and OC-OPEs (240–4900 ng/g) in shoots were at similar levels.

To explain the different behaviours of ER-OPEs and OC-OPEs in roots and shoots, we calculated the RCF and TF values of each OPE. The RCF values of the $\Sigma_{12}OPE$ s ranged from 0.14 (tomato) to 1.30 (carrot) (Table S6). This agreed well with the results of some previous studies found that carrot had a higher uptake capacity for hydrophobic chemicals (Sun et al., 2015; Liu et al., 2019). The RCF values of ER-OPEs were significantly higher than those of OC-OPEs (Fig. 4). This could be

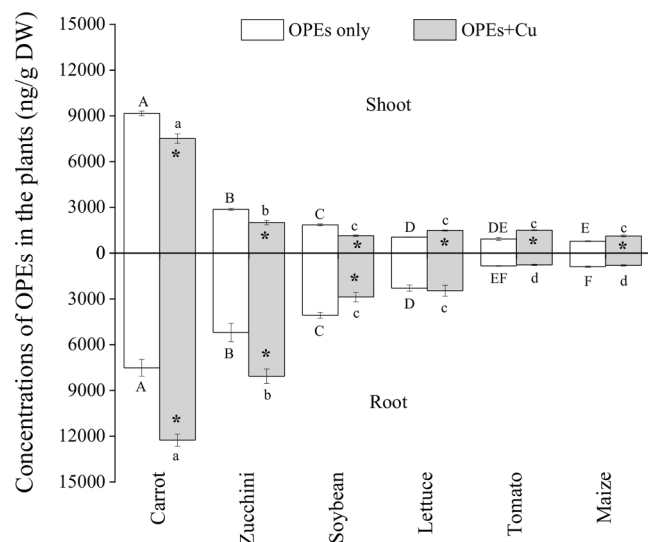


Fig. 2. Concentrations of Σ_{12} OPEs (ng/g DW) in plant tissues. Carrot (*Daucus carota* L.), zucchini (*Cucurbita moschata* Poir.), soybean (*Glycine max* L.), lettuce (*Lactuca sativa* L.), tomato (*Lycopersicon esculentum* Mill.), and maize (*Zea mays* L.) were target plants. OPEs concentration in soils was 500 ng/g DW, and Cu concentration was 0 and 800 $\mu\text{g/g}$ DW in OPEs only and OPEs + Cu treatment, respectively. The columns and bars represent mean \pm standard deviation ($n = 3$). Different letters indicate significant difference at the level of 0.05 based on LSD test. The asterisks represent significant different OPEs concentration in roots or shoots ($p < 0.05$) between OPEs only and OPEs + Cu treatments.

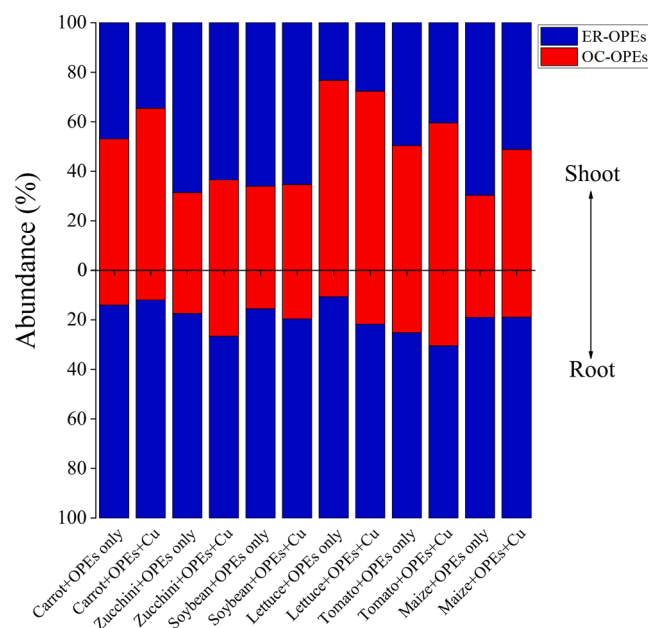


Fig. 3. Composition of OC-OPEs and ER-OPEs in plant tissues. OPEs concentration in soils from treatments with OPEs only and OPEs + Cu was 500 ng/g DW. Cu concentration in treatments with OPEs only and OPEs + Cu was 0 and 800 $\mu\text{g/g}$ DW, respectively.

attributed to the noncovalent interactions between root charged surfaces and ER-OPEs, which have electron-rich structures. Organic compounds are reported to interact with root exudates through covalent bonds, hydrogen bonds or Van der Waals forces (Zhang et al., 2010; Miller et al., 2016; Chen et al., 2020a). The interactions of electron-rich π systems or structures play an important role in the sorption of organic compounds and their availability or mobility in soil (Chen et al., 2020a). In this study, the benzene- or alkyl-ring substituent groups of ER-OPEs

around the phosphate radical served as an electron donor and formed an electron-rich structure that interacted with root surfaces, thereby enhancing their adsorption onto root surfaces and facilitating uptake by roots. In addition, an acidic environment has been reported to benefit the dipole interaction between electron acceptors and electron-rich π systems or structures (Zhang et al., 2010). The acidic soil conditions ($\text{pH} = 5.01$) in this study might enhance the dipole interaction between root charged surfaces and the electron-rich structures of ER-OPEs. These results suggest that the electron-ring structure of ER-OPEs has a significant impact on the uptake of OPEs by plants.

The TF values of the Σ_{12} OPEs ranged from 0.46 in soybean to 1.2 in carrot (Table S7). Unlike the RCF values, there were no significant differences between the TF values of OC-OPEs and ER-OPEs (Fig. 4). In addition, there was a negative correlation between $\log \text{TF}$ and $\log K_{ow}$ (Fig. 5, $p < 0.001$). These findings suggest that K_{ow} is the key parameter determining the translocation of OPEs in plants, regardless of the chemical structure and substituent type. Similar results were observed in some previous studies, in which the translocation of OPEs with high hydrophobicity was weaker than that of OPEs with low hydrophobicity (Wan et al., 2016; Wan et al., 2017). Organic compounds with a high K_{ow} have been reported to be preferentially absorbed by the root epidermis rather than the inner root (Schreiber, 2010), with few compounds translocated along the evapotranspiration stream (Collins et al., 2006). Moreover, the negative relationship between $\log \text{TF}$ and $\log K_{ow}$ for ER-OPEs was similar to that for OC-OPEs, which was consistent with the insignificant TF values for these two groups of OPEs.

3.3. Effects of Cu on root uptake and shoot translocation of OPEs.

The Cu concentrations were 92–460 $\mu\text{g/g}$ and 9.6–45 $\mu\text{g/g}$ in roots and shoots, respectively (Figure S1), with the highest levels in soybean roots and lettuce shoots.

Cu amendment significantly increased the Σ_{12} OPE concentrations in plant (Fig. 2). The Σ_{12} OPEs increased by 63% and 55% in the roots of carrot and zucchini, respectively, and by 41%, 62% and 43% in the shoots of lettuce, tomato and maize, respectively. Accordingly, both RCF and TF values of the Σ_{12} OPEs did not change significantly with Cu amendment (Figure S2, $p = 0.634$ and 0.771, respectively). Heavy metals have been reported to affect the root lipid biosynthetic pathway and induce a peroxidative reaction in membrane lipids, which could alter the hydrophobicity of plant roots, thereby affecting the adsorption behaviour and uptake of organic contaminants by plants (Deng et al., 2018). For example, it was previously demonstrated that highly hydrophobic PBDEs indiscriminately penetrated into defective root systems and revealed that Cu can increase root cell membrane permeability and break down the root exclusion mechanism (Wang et al., 2016). Moreover, Cu^{2+} can promote the sorption of metal-chelating compounds onto roots via electrostatic attraction from negatively charged root cell membranes (Qu et al., 2007), resulting in an increase in the amount of metal-organic complexes adsorbed onto roots, which facilitates the phytoavailable concentrations of organic compounds and improves their uptake in roots (Chen et al., 2020a). In addition, Cu may inhibit the biodegradation of organic pollutants, changing their uptake by roots (Chen et al., 2020b).

It is worth noting that the increase of ER-OPEs in roots (67% for carrot and 38% for zucchini) was less than that of OC-OPEs (140% for zucchini and 120% for lettuce). Taking all plant cultivars together, the RCF values of OC-OPEs and ER-OPEs still exhibited significant differences (Fig. 6). The ratio of RCF values in the OPEs + Cu treatments ($\text{RCF}_{\text{OPEs+Cu}}$) to that in the OPE-only treatments ($\text{RCF}_{\text{OPEs only}}$) was 1.26 for ER-OPEs, much lower than the value of 1.60 for OC-OPEs ($p < 0.05$). This could be attributed to the strong interactions between Cu^{2+} and ER-OPEs, which have an electron-rich structure enabling them to form the cation- π bridge with Cu ions. Such interactions then decreased the hydrophobicity of ER-OPEs (Deng et al., 2018), decreased root lipid content and suppressed their sorption onto roots (Qu et al., 2007; Chen

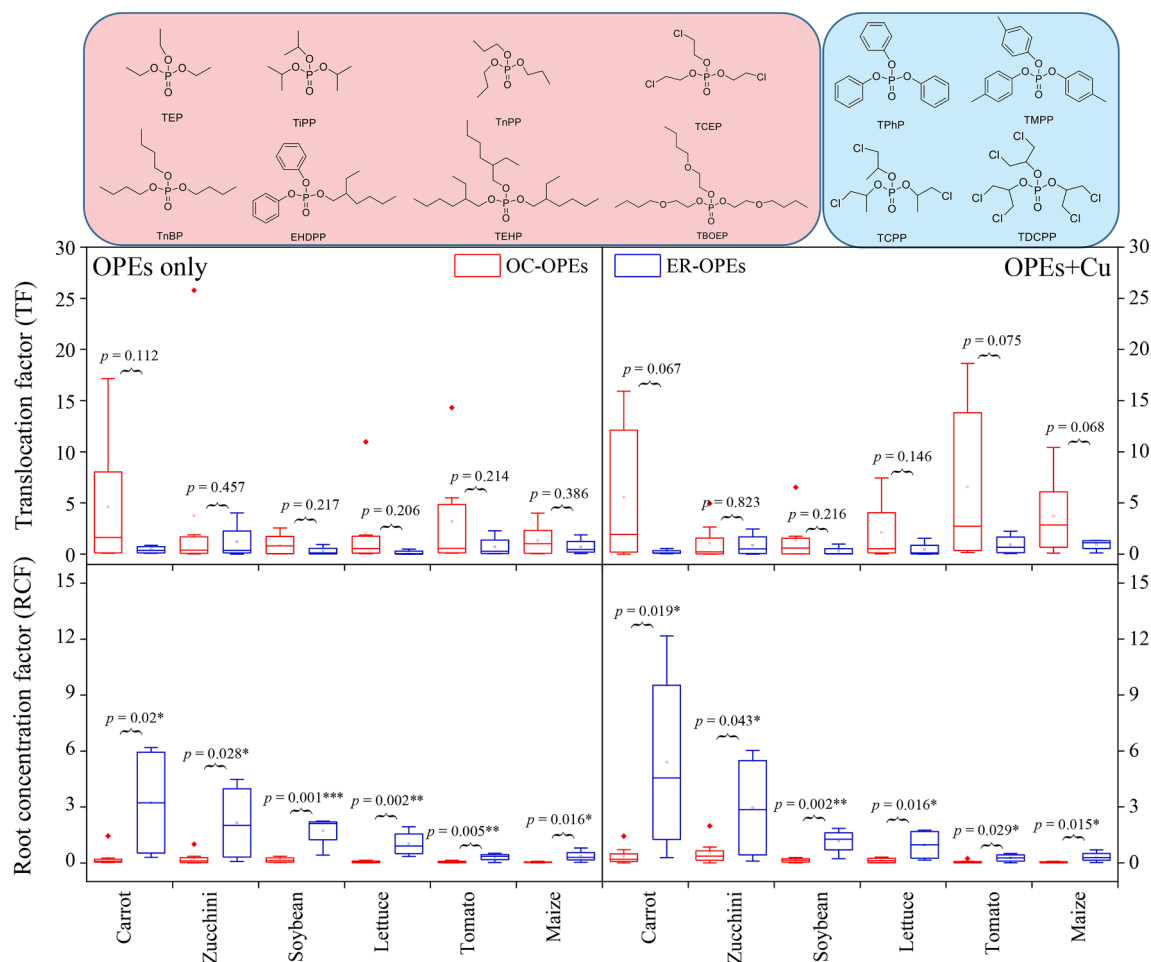


Fig. 4. Root concentration factor (RCF) and translocation factor (TF) between OC-OPEs and ER-OPEs. OC-OPEs include TEP, TiPP, TnPP, TnBP, TEHP, TCEP, TBOEP, and EHDPP; ER-OPEs include TMPP, TPhP, TCPP, and TDCPP. OPEs concentration was 500 ng/g DW in OPEs only and OPEs + Cu treatments. Cu concentration in OPEs only and OPEs + Cu treatments was 0 and 800 $\mu\text{g/g}$ DW, respectively.

et al., 2020a).

The TF values of the OC-OPEs only increased in tomato and maize, whereas ER-OPEs had higher TF values in lettuce and tomato. The relationship between \log TF and $\log K_{ow}$ also exhibited a significant negative correlation ($p < 0.001$, Fig. 5), confirming the key role of hydrophobicity in the accumulative characteristics of OPEs in shoots (Wan et al., 2017; Liu et al., 2019). It is worth noting that there was no significant difference between the regression lines of treatments with OC-OPEs only and OC-OPEs + Cu in the variation analysis ($p > 0.05$). The same result was observed for treatments with ER-OPEs only and ER-OPEs + Cu, indicating that the translocation behaviour from roots to shoots was not influenced by Cu.

3.4. Potential contributors to the uptake and translocation of OPEs

Molecular geometry. The distinct differences in uptake behaviour between OC-OPEs and ER-OPEs across plant cultivars in the present study indicate that molecular geometry is key in the behaviour of OPEs in the soil-plant system. As for OC-OPEs and ER-OPEs, they own different substituents. The electron-rich substituents of ER-OPEs slightly shape the molecular geometry and can change their interactions with root charged surfaces; thus, substituent type plays an important role on uptake behaviour. Our study revealed for the first time that for organic chemicals with different substituents, their molecular geometry determines their uptake behaviour by plants.

Hydrophobicity (K_{ow}). Organic compounds with high hydrophilicity can easily pass through the Casparian strip and translocate acropetally

into stems and leaves, where those hydrophobic compounds are trapped in the undeveloped root apex or bound with certain proteins in the xylem sap (Dettenmaier et al., 2009; Liu et al., 2019). The negative correlation between the \log TF and $\log K_{ow}$ of OPEs was consistent with the results of previous studies, indicating that OPEs with high hydrophobicity are extremely difficult to transport to the aerial parts of plants via the xylem (Wan et al., 2016; Liu et al., 2019). By contrast, TiPP, TnPP, TCEP and TCPP, which have a low K_{ow} , should be more readily acropetally transferred as their TF values were generally >1.0 in all plant cultivars (Table S7). This pattern agreed well with a greenhouse study that revealed the favoured uptake of low-volatile, water-soluble TCEP and TCPP by lettuce and strawberry (*Fragaria ananassa*. L) in shoots rather than roots (Hyland et al., 2015).

Exposure to Cu. The different concentrations of OPEs in roots or shoots between treatments with OPEs only and OPEs + Cu confirmed that Cu altered the uptake and acropetal translocation of OPEs (Table S4 and S8). The root architecture, i.e., root diameter, volume, surface area, tips, root cell membrane and root crossings, can be destroyed by heavy metals (Patsikka et al., 2002; Deng et al., 2018). This damage significantly changes the root exclusion mechanism, increasing the permeability of root cell membranes and breaking the root Casparian strip, thus benefiting the non-selective entrance of hydrophobic compounds into the defective root via the apoplastic pathway (Luo et al., 2015; Wang et al., 2016; Chen et al., 2020a). The lipid biosynthetic pathway is also affected by Cu, which induces peroxidation in the membrane lipids and ultimately causes the obstruction of chemical adsorption onto cell membranes (Deng et al., 2018). In addition, the electron-poor surface of

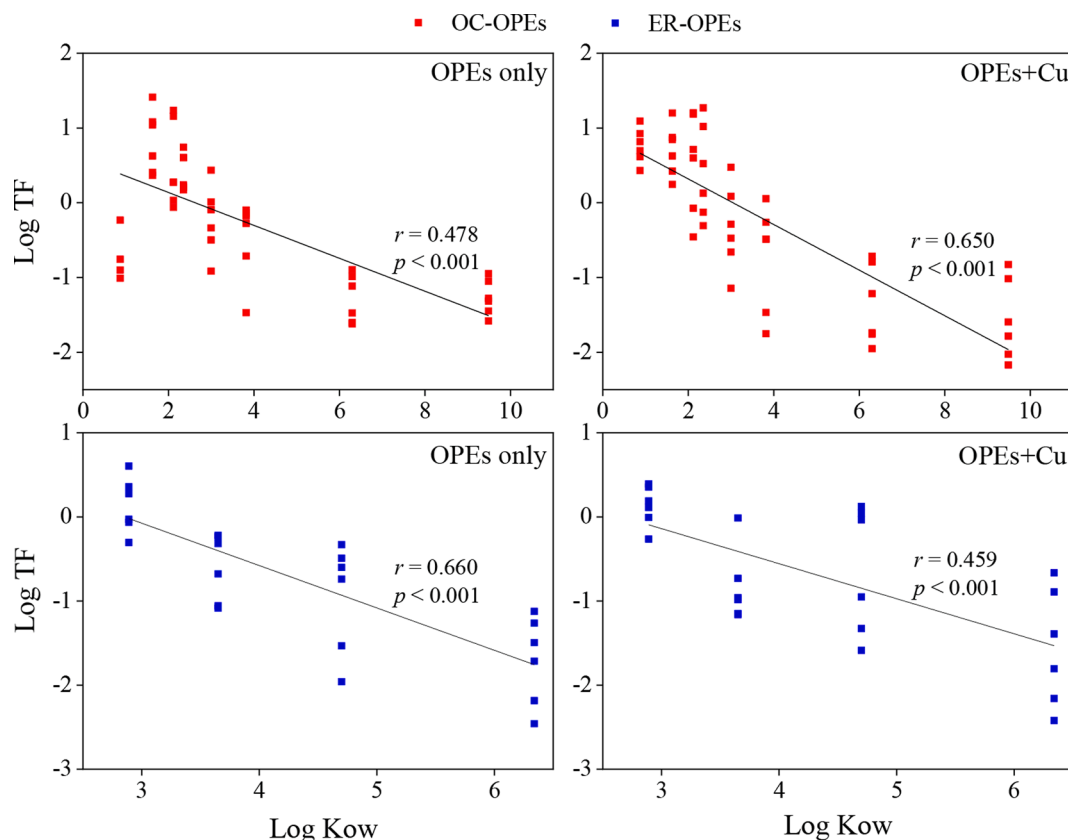


Fig. 5. Log TF and log K_{ow} of OC-OPEs and ER-OPEs in six plant cultivars. OPEs concentration was 500 ng/g DW in OPEs only and OPEs + Cu treatments. Cu concentration in OPEs only and OPEs + Cu treatments was 0 and 800 $\mu\text{g/g}$ DW, respectively.

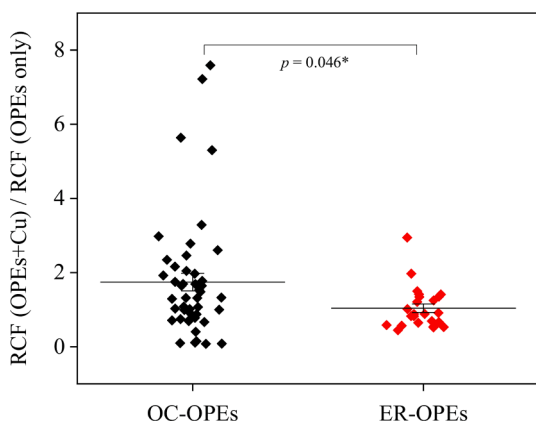


Fig. 6. Different ratio of RCF in OPEs + Cu treatments ($\text{RCF}_{\text{OPEs+Cu}}$) to OPEs only treatments (RCF_{OPEs}) between OC-OPEs and ER-OPEs. OPEs concentration was 500 ng/g DW in OPEs only and OPEs + Cu treatments. Cu concentration in OPEs only and OPEs + Cu treatments was 0 and 800 $\mu\text{g/g}$ DW, respectively.

Cu cations interacts more strongly with the electron-rich structure of ER-OPEs rather than OC-OPEs, facilitating the formation of metal-chelating ER-OPEs and their uptake in roots. In this study, the interactions between the electron-rich structure of ER-OPEs and Cu ions led to more significant changes in root uptake of ER-OPEs compared to OC-OPEs (Figs. 4 and 6).

Plant cultivars. In the present study, both OC-OPEs and ER-OPEs were preferentially enriched in the roots and shoots of carrot (Table S5), whereas the lowest concentrations were found in maize tissues. This indicates that the uptake and acropetal translocation of OPEs differed among plant categories, which is consistent with previous findings that

OPE uptake rates varied across carrot, lettuce, wheat (*Triticum aestivum* L.) and mung bean (*Vigna radiata* L. Wilczek) (Liu et al., 2019). These results are possibly explained by the distinct uptake kinetics and accumulation abilities of OPEs in the roots of different plants, which have different transpiration capacities and protein content in roots and apoplastic sap (Wan et al., 2017). Although the root lipid content has been reported to be one of the controlling factors in the accumulation of organic chemicals in roots (Huang et al., 2010, Wen et al., 2016), the RCF values of most OPEs were not significantly correlated with root lipid content in this study (Figure S3 and Table S6). The mechanism remains unclear and requires further study.

By investigating the uptake and acropetal translocation of OPEs in six plant cultivars, this study investigated the influence of the molecular geometry and K_{ow} of OPEs, Cu and plant cultivar type on OPE behaviour in the soil-plant system. Molecular geometry rather than K_{ow} was the key factor of OPE uptake, which was explained by the strong interactions between the electron-rich substituents of ER-OPEs, root surfaces, and Cu^{2+} , whereas K_{ow} was more critical in acropetal translocation. The presence of Cu significantly altered OPEs uptake and translocation, and the role of plant cultivar type was limited. Our findings will lead to a better understanding of the underlying mechanisms of OPEs uptake and translocation, benefiting the ecological risk assessment of OPEs accumulation in the food chain, particularly co-contaminated with heavy metals.

CRediT authorship contribution statement

Beibei Hu: Investigation, Validation, Methodology, Formal analysis, Writing - original draft, Writing - review & editing. **Longfei Jiang:** Conceptualization, Methodology, Supervision, Writing - original draft, Writing - review & editing, Funding acquisition. **Qian Zheng:** Formal analysis, Writing - review & editing. **Chunling Luo:** Conceptualization,

Writing - original draft, Writing - review & editing, Supervision, Funding acquisition. **Dayi Zhang:** Formal analysis, Writing - original draft. **Shaorui Wang:** Writing - original draft. **Yucheng Xie:** Visualization. **Gan Zhang:** Resources.

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. 32061133003, 41603086 & 42077334), the Local Innovative and Research Teams Project of Guangdong Pearl River Talents Program (2017BT01Z134), the Guangdong Foundation Program for Science and Technology Research (2019B121205006) and the Doctoral Scientific Research Foundation of Guangdong Province (2018A030310663).

Appendix A. Supplementary data

Plant lipid content analysis; physicochemical properties of selected OPEs in this study; GC-MS/MS quantitation/qualification parameters of OPEs; limit of quantitation (LOQ) of OPEs; concentrations of OPEs in plant cultivars from OPEs only treatments; concentration, RCF, and TF of OC-OPEs and ER-OPEs; RCF of OPEs in the six plant cultivars; TF of OPEs in the six plant cultivars; concentrations of Cu in the different plants; average RCF and TF of Σ_{12} OPEs in OPEs only and OPEs + Cu treatments; concentrations of OPEs in plant cultivars from OPEs + Cu treatments; root lipid content (%) of different plants. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envint.2021.106591>.

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