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The influence of copper and soil type on the uptake, translocation of organophosphate esters by corn☆

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ABSTRACT

Recent studies have highlighted the potential risks of organophosphate esters (OPEs) accumulating in the food chain; however, the key factors governing their uptake and translocation in plants remain unclear. In this study, we investigated the primary drivers influencing the fate of OPEs in corn (Zea mays L.). Our results show that log *Kow*, DOC content, and Cu concentration play critical roles in regulating OPEs uptake. Specifically, log *Kow* were negatively correlated with both the shoot concentration factor (SCF, $R^2 > 0.70$) and translocation factor (TF, $R^2 > 0.42$), indicating that less hydrophobic OPEs are more readily translocated to plant tissues. Corn grown in magalitic soil accumulated OPEs at levels averaging 24% higher than those grown in krasnozem, corresponding to 2.2 times greater DOC content in magalitic soil. Cu addition (1600 mg/kg) led to a 181% and 47% increase in OPEs accumulation in roots grown in krasnozem and magalitic soils, respectively, likely due to Cu-induced disruption of root cell membrane permselectivity. Plants in krasnozem soil experienced more severe Cu-induced toxicity, attributed to its lower pH (4.47), resulting in greater OPEs accumulation than in magalitic soil. Moreover, enhanced correlations between SCF ($R^2 > 0.70$), TF ($R^2 > 0.58$), and log *Kow* following Cu exposure suggest that Cu may inhibit active transport while promoting passive diffusion. These findings offer a comprehensive understanding of OPEs behavior in the plant-soil system and provide important insights for evaluating the environmental risk of OPEs contamination in crops.

1. Introduction

Organophosphate esters (OPEs) are widely used as nonreactive additives in various industrial appliances and electronic products, particularly following the global ban on the production and use of halogenated flame retardants, such as polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) (van der Veen and de Boer, 2012; Vorkamp et al., 2018). Recently, OPEs have been detected across various environmental matrices, including the atmosphere (Zhang et al., 2024), aquatic systems (Ke et al., 2024), soils (Wang et al., 2025a), and even within organisms (Yin et al., 2024), due to their widespread use. These compounds pose potential ecological and human health risks because of their inherent toxicity (Huang et al., 2025).

Plant play a pivotal role in the entry of OPEs into the food chain, making the behavior of OPEs within soil–plant systems an area of growing research interest (Wan et al., 2017; Wang et al., 2025b; Wang et al., 2024b). The uptake of OPEs by plant is influenced by both the physicochemical properties of the compounds (Gong et al., 2020; Wan et al., 2016a) and soil characteristics such as soil organic carbon (SOC) (Li et al., 2023) and heavy metal content (Qin et al., 2024).

Among the physicochemical attributes of OPEs, hydrophobicity is the most influential factor. The octanol-water partition coefficient (log *K*ow), which reflects hydrophobicity, is a key determinant of OPEs uptake, translocation, and accumulation in plants (Wang et al., 2024a).

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Compounds with log *K*ow > 4 tend to accumulate primarily in plant roots. These highly hydrophobic OPEs are readily absorbed and retained by root-associated organic matter (Liu et al., 2019a; Wan et al., 2016a). Moreover, the translocation factor of OPEs decreases sharply as log *K*ow increases (Liu et al., 2019b). Because plant lipids are also hydrophobic, higher root lipid content has been associated with greater OPEs accumulation in roots (Liu et al., 2019b).

Soil properties, particularly soil organic carbon (SOC), are also reported as a key factor influencing OPEs bioaccumulation. Elevated SOC levels have been associated with decreased OPEs concentrations in plants, highlighting the role of SOC in partitioning OPEs at the soil-root interface (Hyland et al., 2015). SOC serves as a critical sorbent for nonpolar and moderately polar organic compounds, controlling the partitioning of contaminants between soil particles and pore water, as well as their mobility, transformation, biodegradation, and bioavailability for uptake by biota (Borgman and Chefetz, 2013; Mattina et al., 2006; Yang et al., 2017). Strong sorption to SOC has been shown to limit the availability of OPEs to microorganisms and plant roots (Jachero et al., 2017; Li et al., 2015; Miller et al., 2016), aligning with greenhouse experiments that suggest a positive correlation between SOC content and plant uptake of OPEs (Hyland et al., 2015). The mobility of contaminants in soil is also influenced by dissolved organic carbon (DOC), which can facilitate their movement through competitive adsorption onto soil particles or by forming soluble complexes with DOC (Cristale et al., 2017; Haham et al., 2012; Miller et al., 2016). Affinities between chemicals and soil particles vary across soil types, potentially altering OPEs behavior in the plant-soil system. However, the specific effects of soil type on OPEs uptake by plants remain unclear.

The integrity of the plant root cell wall, which is essential for maintaining selective permeability, can be compromised by heavy metals (Mostofa et al., 2015), thereby influencing the uptake behavior of environmental contaminants (Su and Zhu, 2006; Xu et al., 2006). In addition, heavy metals can disrupt root lipid biosynthesis and alter root hydrophobicity by inducing peroxidative reactions in membrane lipids, subsequently affecting the plant uptake of organic contaminants (Deng et al., 2018). However, studies specifically examining the influence of heavy metals on OPEs uptake remain limited. Only Hu et al. reported that copper increased OPEs concentrations in six plant species (Hu et al., 2021b), and Qin et al. found that Cu enhanced the accumulation of hydrophilic OPEs in rice tissues (Qin et al., 2024). Further research is needed to elucidate the role of heavy metals in influencing the uptake of OPEs by plants well. The mobility and bioavailability of heavy metals are strongly influenced by soil pH, with acidic soils typically promoting higher metal availability. Therefore, soil type, through pH variation, may regulate metal toxicity and, in turn, impact the uptake and translocation of OPEs in plants. Nonetheless, direct evidence supporting this relationship is still lacking.

To address these gaps, this study investigates the uptake and translocation of OPEs in corn (*Zea mays* L.) under different contamination levels in two soil types: krasnozem and margalitic soil. Four OPEs with varying chemical structures were selected: TCEP (chlorinated), tri-n-butyl phosphate (TnBP; alkyl-), TPhP (aryl-), and EHDPP (hybrid alkyl-aryl-). Additionally, treatments with three levels of Cu were implemented to examine the combined effects of OPEs and Cu on plant uptake and translocation in co-contaminated soils. This study provides a comprehensive understanding of the fate of OPEs in the plant-soil system and contributes valuable insights for assessing potential risks associated with OPEs contamination in crops.

2. Materials and methods

2.1. Soil collection

The krasnozem soil was collected from Guangzhou City, Guangdong Province (23.17°N, 113.37°E), and the magalitic soil was obtained from Shenyang City, Liaoning Province (41.97°N, 123.05°E). The total OPEs concentration in krasnozem soil was 37 ng/g, while that in magalitic soil was less than 23 ng/g. The Cu concentrations in krasnozem and magalitic soils were 47 mg/kg and 19 mg/kg, respectively. Upon collection, the soils were air-dried at room temperature in the laboratory. Plant debris and large stones were removed, after which the soil was homogenized and passed through a 2 mm sieve.

2.2. Chemicals and reagents

Standards for organophosphate esters (OPEs), including tri(2-chloroethyl) phosphate (TCEP), tri-n-butyl phosphate (TnBP), and triphenyl phosphate (TPhP), as well as surrogate standards such as tris(2-chloroethyl) phosphate-d12 (d12-TCEP), tri-n-butyl phosphate-d27 (d27-TnBP), triphenyl phosphate-d15 (d15-TPhP), tris(1,3-dichloroisopropyl) phosphate-d15 (d15-TDCP), and tripropyl phosphate-d21 (d21-TnPP), were procured from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). The standard for 2-ethylhexyl diphenyl phosphate (EHDPP) was purchased from AccuStandard, Inc. (New Haven, CT). All standards had a purity of over 98%. Chemical names, abbreviations, formulas, and other key properties of the OPEs are detailed in Table S1 (Zeng et al., 2021). All chemicals were stored in amber glass vials at −20 °C to ensure stability. Additional organic reagents, including acetonitrile, acetone, ethyl acetate, dichloromethane, chloroform, n-hexane, methanol, isooctane, and toluene, were of gas chromatography (GC) or high-performance liquid chromatography (HPLC) grade.

2.3. Plant culture and exposure to OPEs and Cu

Corn (Zea mays L.) was selected as the test plant. Seeds were sterilized in a 5% (v/v) NaClO solution for 10 min, thoroughly rinsed with deionized water, and germinated in OPEs-free moist sand at room temperature in the dark. In several OPEs-contaminated soils, the total OPEs concentration approaches 1 mg/kg. For example, Tang et al. reported a maximum concentration of 986.0 ng/g in surface soils from a polluted area in the Yangtze River Delta (Tang et al., 2021), while Wan et al. detected concentrations as high as 1250 ng/g in soils surrounding a plastic waste treatment site (Wan et al., 2016b). Besides, extremely high levels of Cu can be found in agricultural soils located near mining areas. For instance, Luo et al. reported Cu concentrations of up to 1062 mg/kg in contaminated agricultural soils surrounding a copper mine in eastern Nanjing (Luo et al., 2006). Similarly, Giri and Singh et al. detected Cu levels as high as 1986.4 mg/kg in agricultural soils from copper mining regions in India (Giri et al., 2017). Wang et al. also recorded a maximum Cu concentration of 1614 mg/kg in farmland near the Tongguan mining area (Wang et al., 2022). Therefore, the highest concentrations of OPEs and Cu used in this study were 1000 ng/g and 1600 mg/kg, respectively. Soil spiked with OPEs at concentrations of 0, 100, 200, 500, and 1000 ng/g (concentrations of each individual compound were 0, 25, 50, 125, 250 ng/g). For treatments involving co-contamination, $Cu_2(OH)_2CO_3$ was added at Cu concentrations of 0, 400, 800, and 1600 mg/kg to soil spiked with 200 ng/g OPEs. The soils were homogenized daily and subjected to four wet-dry cycles. Five germinated seeds were planted in each ceramic pot, and soil moisture was maintained using deionized water throughout the one-month cultivation period. Each experiment set was conducted in triplicate. All pots were kept in a greenhouse with natural sunlight under controlled temperature conditions: 25 – 30 °C during the day and 15 – 20 °C at night.

After harvest, the biomass of the corn plants was measured and separated into roots and above-ground tissues. Plant biomass and stem length data are presented in Fig. 1 and S1. Soil samples were immediately stored at −20 °C for subsequent analysis.

2.4. Determination of lipid content

The determination of lipid content in plant tissues was conducted

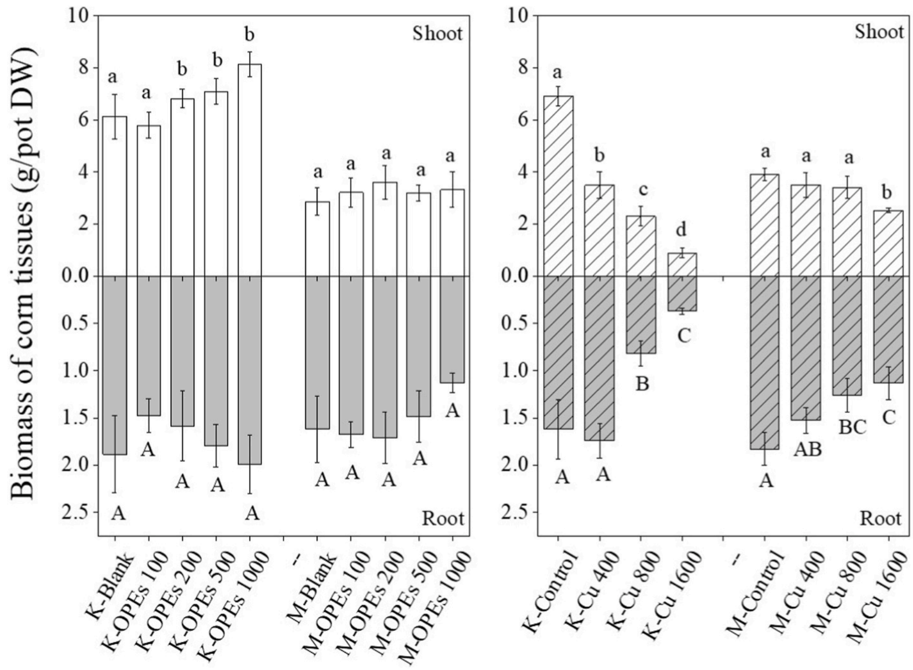

Fig. 1. Biomass of corn roots and shoots under different treatments (K: krasnozem; M: margalitic soil). OPEs concentrations in the treatments Blank, OPEs 100, OPEs 200, OPEs 500, and OPEs 1000 were 0, 100, 200, 500, and 1000 ng/g DW, respectively. In the OPEs + Cu treatment, OPEs levels were 200 ng/g DW. Copper concentrations in Control, Cu 400, Cu 800, and Cu 1600 treatments were 0, 400, 800, and 1600 mg/kg DW, respectively. Values represent means ± SD (n = 3).

following the method described by Wen et al. (2016). Briefly, 1.0 g of dried plant material was subjected to Soxhlet extraction for 12 h using 100 mL of a chloroform–methanol mixture (2:1, v/v). The resulting extract was concentrated to approximately 5 mL using a rotary evaporator, then loaded onto an unpaired aminopropyl column (500 mg/3 mL, Agela Technologies Inc.). Lipids were eluted with 5 mL of a chloroform/acetone solution (4:1, v/v). The eluate was dried under a nitrogen stream, and the lipid content was determined by gravimetric analysis.

2.5. Determination of OPEs

Five plants from each pot were combined. Subsequently, soil and plant samples were dried and homogenized. The extraction, analysis, and cleanup of OPEs in soil and plant samples were conducted based on previously described methods with minor modifications (Poma et al., 2018; Zhang et al., 2016). Briefly, 200 mg (dry weight) of corn tissue or soil samples were placed into a 15 mL Teflon tube. Samples were spiked with 200 μL of an surrogate standard (SS) mixture prior to extraction, followed by the addition of 5 mL acetonitrile (ACN). The mixture was vortexed for 1 min and left in a fume hood overnight. The following day, ultrasonic extraction was performed on the samples. Cleanup was conducted using solid-phase extraction (SPE) with Florisil and aminopropyl silica (APS, 500 mg, 3 mL, Agela) cartridges. After evaporation, the target compounds were reconstituted in 200 μL of an isooctane and internal standard (IS) mixture. The final extracts were transferred to injection vials for analysis using gas chromatography-tandem mass spectrometry (GC-MS/MS).

2.6. Instrumental analysis of OPEs

OPEs were analyzed using an Agilent 7890A gas chromatograph equipped with an electron-impact (EI) source operating in electron impact mode. GC separation was performed using a DB-5MS column (30 m × 250 μm inner diameter × 0.25 μm film thickness; Agilent J&K GC Columns, USA) under selected ion monitoring (SIM) mode. A 1 μL aliquot of the sample extract was injected in pulsed splitless mode at an injection temperature of 250 °C. The pulse pressure was set to 9.954 psi, with a septum purge flow rate of 3 mL/min and a split purge flow rate of 54 mL/min. A full list of the targeted OPEs and their corresponding MS/MS quantitation parameters is provided in Table S2.

2.7. Determination of Cu

Soil and plant samples were digested using mixed acid solutions. For soil samples, a 1:1:5 vol ratio of $HNO_3/HClO_4/HF$ was used, while plant samples were digested with a 9:1 vol ratio of $HNO_3/HClO_4$. Elemental concentrations were measured using inductively coupled plasma-mass spectrometry (ICP-MS). Certified reference materials (GBW07453, GSS-24, GBW10020, and GSB-11) were utilized for quality control. Recovery rates for Cu were 93 ± 5% in plant samples and 96 ± 3% in soil samples.

2.8. Determination of soil properties

To measure pH, 5 g of soil was weighed into a plastic centrifuge tube containing 25 mL of water. The mixture was shaken for 30 min and allowed to settle for 10 min before pH was measured using a pH meter. For dissolved organic carbon (DOC) analysis, 5 g of soil was added to a plastic centrifuge tube containing 25 mL of 0.01 mol/L $CaCl_2$ solution. The mixture was shaken on a shaker at 200 rpm for 30 min, followed by centrifugation at 4500 rpm for 15 min. The supernatant was filtered through filter paper to remove large soil particles and then through a 0.45 μm aqueous filter. DOC was measured using a total organic carbon (TOC) analyzer. Soil organic carbon (SOC) was directly measured using a TOC analyzer with 0.2 g of soil sample. The data for soil properties are provided in Table S3.

2.9. Quality control/quality assurance

The recoveries of OPEs surrogate standards in plant samples ranged from 90.9% to 130.3%. The average recovery rates for Cu were 93 ± 5% in plant tissues and 96 ± 3% in soils. Quality control was maintained by analyzing procedural blanks, randomly injecting solvent blanks, standards, and duplicate samples, which were included in parallel with every twelve samples to monitor potential contamination. Limits of detection (LOD) for OPEs were determined based on a signal-to-noise ratio (S/N) of 3. OPEs concentrations in the control samples were below the LOD for all compounds. All data are reported on a dry weight basis. Means and standard deviations were calculated from triplicate measurements. In this study, foliar uptake of OPEs from the air was negligible, as OPEs concentrations in plant tissues from control samples (without OPEs) were below the LOD. Therefore, the distribution of OPEs in corn tissues clearly demonstrates that plants can uptake OPEs from the soil and translocate them to the shoot tissues.

2.10. Statistical analysis

All data analysis was performed using Microsoft Excel 2013. Statistical significance of variations in chemical concentrations across different treatments ($p < 0.05$) was evaluated using analysis of variance (ANOVA). Root concentration factors (RCFs) were calculated as the ratio of chemical concentrations in roots to those in soil (Croot/Csoil), while translocation factors (TFs) were calculated as the ratio of chemical concentrations in shoots to those in roots (Cshoot/Croot).

3. Results and discussion

3.1. Plant growth

The biomass of corn shoots and roots under different treatments is presented in Fig. 1. In both krasnozem and margalitic soils, root growth generally showed no significant difference between the blank (non-spiked with OPEs) and OPE-spiked treatments ($p > 0.05$). However, a slight increase in shoot biomass was observed in krasnozem soil ($p < 0.05$), while no significant change was detected in margalitic soil. Overall, plants grown in krasnozem soil exhibited significantly higher shoot biomass ($p < 0.05$) compared to those grown in margalitic soil.

When exposed to Cu, the biomass of corn showed a clear inhibitory effect ($p < 0.05$) across almost all treatments, indicating Cu toxicity effects on corn physiology. Compared to the control, significant reductions ($p < 0.05$) were observed in krasnozem soil, with shoot biomass decreasing by 49.4 – 87.2% and root biomass by 49.4 – 77.0%. In contrast, in margalitic soil, reductions in biomass were only observed at the highest Cu treatment (Cu1600), where shoot and root biomass decreased to 65% and 62%, respectively, of the control levels. Notably, Cu-induced biomass inhibition was significantly more pronounced in krasnozem soil than in margalitic soil ($p < 0.05$, Fig. 1 and S1), suggesting that plants in krasnozem soil experienced greater Cu toxicity.

Root lipid contents under different treatments were also assessed (Table S4). In the OPEs-only treatments, the lipid content of corn roots was generally higher in margalitic soil compared to krasnozem soil ($p < 0.05$).

3.2. Cu content in corn

As expected, Cu concentrations in both shoots and roots increased with higher levels of spiked Cu (Fig. 2). In krasnozem soil treatments, Cu concentrations ranged from 20.2 ± 3.21 to 80.9 ± 12.2 ng/g in shoots and from 40.1 ± 4.23 to 2450 ± 386 ng/g in roots, with the highest concentrations observed in the Cu1600 treatment. Similarly, Cu concentrations in plants grown in margalitic soil increased with spiked Cu levels, with shoot and root Cu concentrations rising from 13.9 ± 2.12, 35.2 ± 5.22 μg/g in the control treatment to 34.4 ± 3.20, 797 ± 35.6 μg/g in the Cu1600 treatment. Comparatively, Cu accumulation in shoots and roots was significantly higher in krasnozem soil than in margalitic soil. In krasnozem soil, Cu concentrations in shoots and roots were up to 123 and 300 times greater, respectively, than in margalitic soil. This pronounced Cu accumulation in krasnozem soil likely explains the more severe inhibitory effects observed on plant growth in this soil compared to margalitic soil.

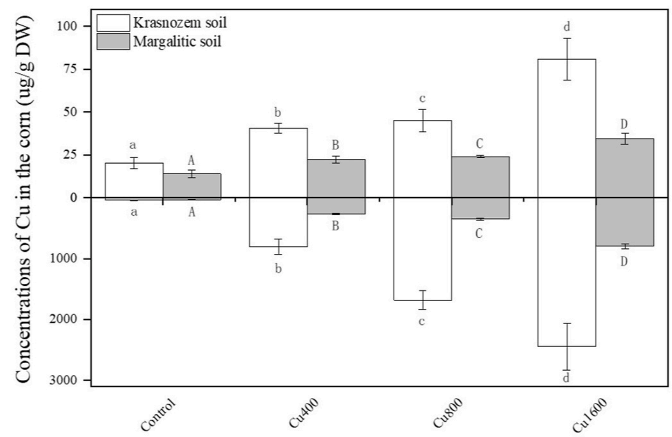

Fig. 2. Distribution of Cu in corn exposed to OPEs with Cu. Copper concentrations in Control, Cu 400, Cu 800, and Cu 1600 treatments were 0, 400, 800, and 1600 mg/kg DW, respectively. OPEs concentrations in the soil were maintained at 200 ng/g DW. Values represent means ± SD (n = 3).

3.3. The uptake and translocation of OPEs in corn tissues

In this study, no OPEs were detected in the polyurethane foam (PUF) samplers placed in the greenhouse, suggesting that OPEs evaporation from the soil and atmospheric deposition had minimal contributions to the OPEs presence in corn tissues. Since all four OPEs were detectable in corn grown in both krasnozem and margalitic soils, root uptake from the soil was identified as the primary pathway for OPEs permeation and translocation in corn (Wang et al., 2016).

OPEs-Only Treatments. The distribution of OPEs in corn tissues under different treatments is shown in Fig. 3. In general, concentrations of Σ_4OPEs in roots and shoots increased significantly with higher OPEs levels in both krasnozem and margalitic soils ($p < 0.05$, Table S5). In krasnozem soil, Σ_4OPEs concentrations ranged from 46 ± 1.6 to 220 ± 28 ng/g in roots and from 34 ± 2.1 to 200 ± 30 ng/g in shoots. In margalitic soil, OPEs concentrations in shoots were comparable to those in krasnozem soil; however, root OPEs concentrations were generally higher in margalitic soil. Among the congeners, TCEP and TnBP showed significant increases in both roots and shoots, with TCEP being the predominant congener in plant tissues from both soil types. TCEP accounted for approximately 31 – 57% of total OPEs in roots and 41 – 90% in shoots (Fig. 3).

The root concentration factor (RCF) of TCEP was the highest among the four OPEs in both krasnozem and margalitic soils, while the RCF values for the other three OPEs generally followed the order EHDPP > TPhP > TnBP (Table S6). Slightly higher RCF values for individual OPEs congeners were observed in margalitic soil compared to krasnozem soil. For example, RCF values of TnBP in margalitic soil were approximately 230%, 220%, and 180% higher than those in krasnozem soil under OPEs200, OPEs500, and OPEs1000 treatments, respectively ($p < 0.05$). Similarly, shoot concentration factors (SCF) of OPEs were higher in margalitic soil compared to krasnozem soil (Table S7). Conversely, translocation factors (TF) of OPEs were significantly lower in margalitic soil than in krasnozem soil (Table S8). Negative correlations were observed between SCF, TF, and log *Kow* in both soil types (Fig. 4), while no significant correlation was found between RCF and log *Kow*.

Treatments of OPEs with Cu. Following Cu exposure, concentrations of Σ_4OPEs in both roots and shoots increased in krasnozem and margalitic soils (Fig. 5), with the highest concentrations observed in the Cu1600 treatment. In krasnozem soil, shoot and root OPEs concentrations increased by an average of 39% and 181%, respectively. Similarly, in margalitic soil, shoot and root OPEs concentrations increased by

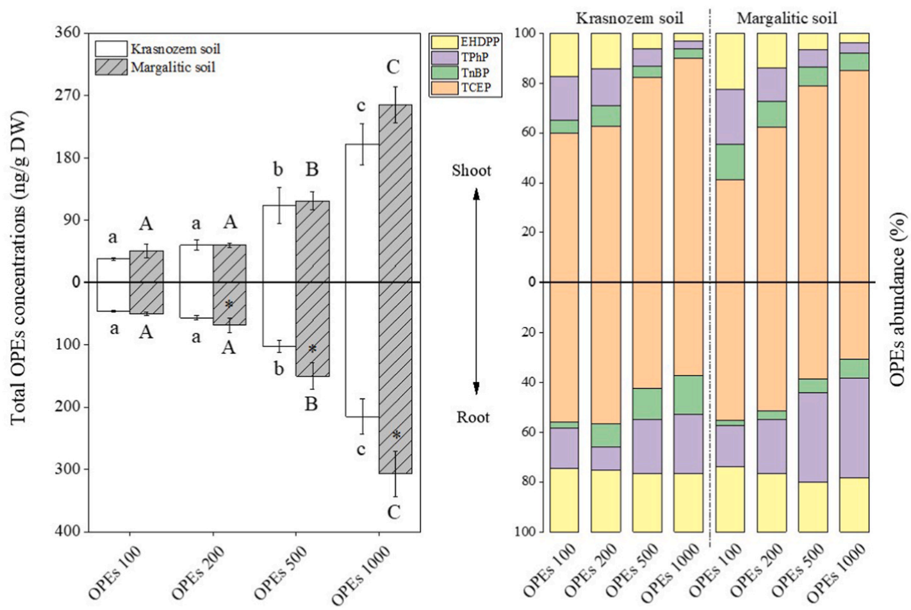

Fig. 3. Concentrations and compositions of OPEs in corn shoots and roots grown in krasnozem and margalitic soils. OPEs concentrations in OPEs100, OPEs200, OPEs500, and OPEs1000 treatments were 100, 200, 500, and 1000 ng/g soil DW, respectively. Values represent means ± SD (n = 3). Asterisks indicate significant differences in OPEs concentrations between krasnozem and margalitic soils in roots or shoots (p < 0.05).

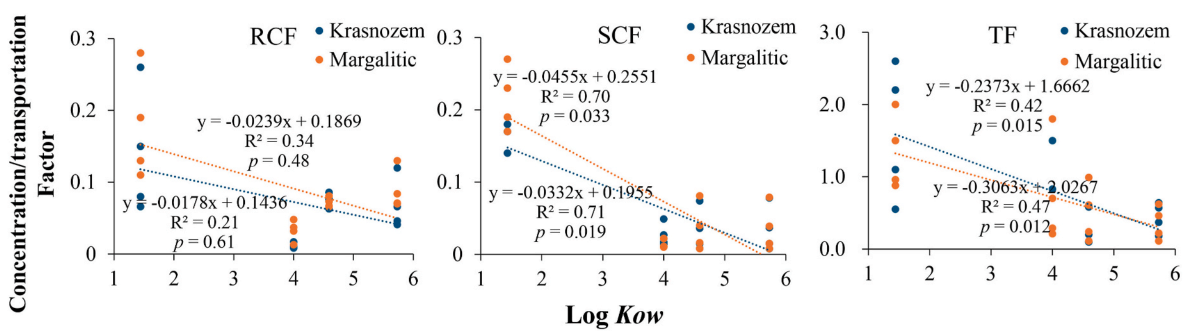

Fig. 4. Relationships between bioconcentration factors (RCF, SCF, TF) and log *Kow* for all OPEs-only treatments in krasnozem and margalitic soils.

approximately 60% and 47%, respectively. OPEs congeners distributions in roots were notably altered by Cu exposure in both soil types, while shoot OPEs concentrations merely increased or remained unchanged across Cu exposure levels. TCEP remained the dominant OPEs congener in corn tissues, particularly in shoots, where it accounted for 62.4 – 71.5% of total OPEs in both krasnozem and margalitic soils (Fig. S2). In shoots, the proportion of TCEP significantly increased with Cu exposure, rising from 24% to 51% in krasnozem soil and from 42% to 52% in margalitic soil.

Root OPEs concentrations and their increases were significantly higher in krasnozem soil compared to margalitic soil across all Cu treatments ($p < 0.05$, Fig. 5). For example, the RCFs of TnBP, TPhP, and EHDPP in krasnozem soil were approximately 140%, 102%, and 93% higher than in margalitic soil. Furthermore, RCFs in krasnozem soil showed dramatic increases under Cu stress, with TnBP, TPhP, and EHDPP increasing by 15.4-, 2.81-, and 2.19-fold, respectively. In contrast, in margalitic soil, the corresponding increases were only 1.1-, 2.7-, and 0.29-fold.

The relationships between RCF, SCF, TF, and the log *Kow* of OPEs are illustrated in Fig. 6. After Cu exposure, RCF in margalitic soil, as well as SCF and TF in both soils, showed negative correlations with log *Kow*, highlighting the influence of OPEs hydrophobicity on plant uptake. Cu addition generally altered the relationships between RCF, SCF, TF, and log *Kow* (Fig. S3). Under Cu stress, linear relationships between log *Kow* and these factors became more pronounced, suggesting that Cu exposure enhanced the impact of hydrophobicity on OPEs uptake and translocation.

4. Discussion

4.1. Uptake and translocation of OPEs

Typically, less hydrophobic compounds with log *Kow* < 1.8, such as methyl tert-butyl ether and caffeine, are readily absorbed by plant roots and transported into the xylem via the transpiration stream (Burken and Schnoor, 1998; Dettenmaier et al., 2009). The notably high RCF, SCF, and TF values for TCEP observed in this study indicate that TCEP is easily taken up and translocated by plants. This aligns with previous research showing that TCEP, a low-volatility and water-soluble compound, favors high uptake and upward translocation into edible plant sections, such as leaves and stems, in significant proportions (Eggen et al., 2013; Hyland et al., 2015; Wan et al., 2016a). In contrast, the RCF values for the other three OPEs (EHDPP, TPhP, and TnBP) with log *Kow* ≥ 4 followed the order EHDPP > TPhP > TnBP. These OPEs exhibited much lower acropetal transportation compared to TCEP, supporting the notion that non-ionized organic chemicals with log *Kow* > 4 are more likely to partition into root lipid membranes. These compounds demonstrate a higher tendency to accumulate in roots due to their

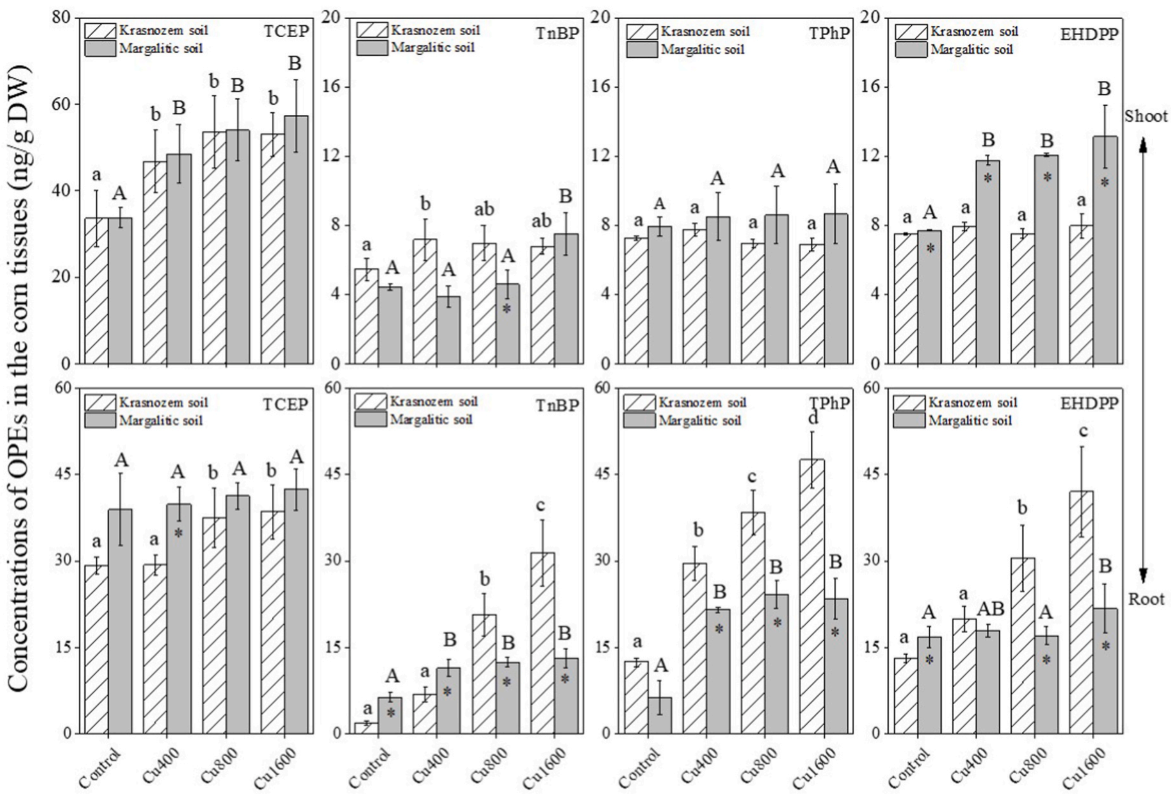

Fig. 5. OPEs concentrations in corn exposed to OPEs and Cu co-contamination. Copper concentrations in Control, Cu400, Cu800, and Cu1600 treatments were 0, 400, 800, and 1600 mg/kg DW, respectively. OPEs concentrations in the soil were maintained at 200 ng/g DW. Values represent means ± SD (n = 3). Asterisks indicate significant differences in OPEs concentrations between krasnozem and margalitic soils in roots or shoots ($p < 0.05$).

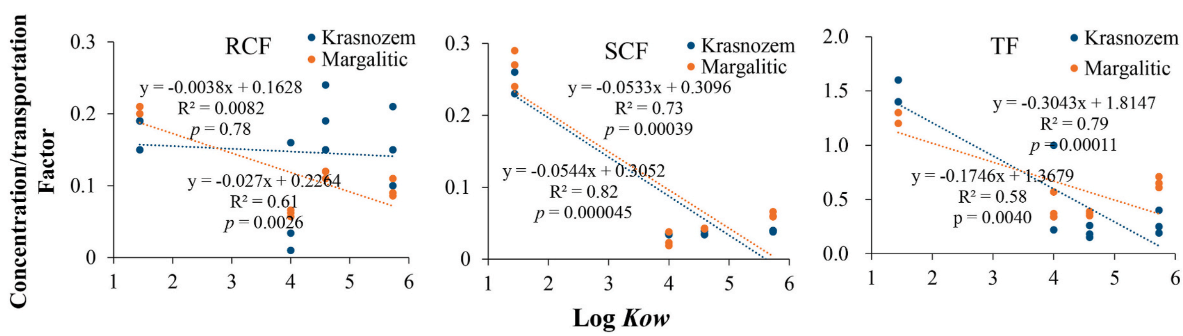

Fig. 6. Relationships between bioconcentration factors (RCF, SCF, TF) and log *Kow* for all OPEs and Cu co-treatments in krasnozem and margalitic soils.

hydrophobicity, they are less capable of entering the xylem stream for upward transportation (Burken and Schnoor, 1998; Collins et al., 2006). Interestingly, the TF values for TCEP were consistently greater than 1, indicating that TCEP tends to accumulate in shoots rather than roots. The TF values showed a negative correlation with the log *Kow* of OPEs in both soil types, emphasizing the critical role of hydrophobicity in determining the translocation behavior of OPEs in plants.

4.2. Factors influencing the uptake and translocation of OPEs in plants

Plant. In this study, plant grown in krasnozem and margalitic soils exhibited differing abilities to accumulate OPEs. In the soil-plant system, factors such as plant cultivars (Eggen et al., 2013; Liu et al., 2019a), root exudates (Miller et al., 2016), and soil particles (Hyland et al., 2015) are generally recognized as key determinants influencing the uptake of organic chemicals. Among these, plant characteristics, particularly root lipid content, play a critical role in governing the uptake process. Previous studies have highlighted the tight relationship between root lipid content and the uptake of hydrophobic persistent organic pollutants (POPs), such as polybrominated diphenyl ethers (PBDEs) and polycyclic aromatic hydrocarbons (PAHs) (Dobslaw et al., 2021; Kang et al., 2010). Additionally, the accumulation and translocation of perfluorooctane sulfonate (PFOS) were shown to correlate with plant protein and lipid content (Wen et al., 2016). Our results indicated that OPEs were preferentially enriched in corn roots with higher root lipid content in margalitic soil, underscoring the importance of root lipids in OPEs uptake. Previous findings have also shown that lipid content significantly impacts the occurrence of OPEs in plant tissues (Liu et al., 2019a). However, the uptake of TCEP, a hydrophilic compound, may not be mediated by root lipids. Instead, its uptake could be linked to protein content, as lipid content primarily governs the uptake of hydrophobic compounds.

OPEs Structures: The functional groups of organophosphate esters (OPEs) are critical factors influencing their uptake and translocation in plants. For example, Cao et al. found that the root accumulation capacity of *Myriophyllum aquaticum* was closely related to the substituents on OPEs (Cao et al., 2023). Specifically, OPEs accumulation in roots increased with longer alkyl chains, a greater number of halogen substituents, and longer branched alkyl chains. Similarly, Wang et al., in a study on lettuce, demonstrated that OPEs substituents significantly affect both uptake and metabolism (Wang et al., 2024c). They observed that as the alkyl chain length of OPEs increased, their upward translocation in lettuce decreased, while their metabolic activity increased. In the present study, we also observed significant differences in OPEs uptake and translocation depending on the type of substituent. Chlorinated OPEs exhibited the highest uptake and translocation ability, followed by alkyl-substituted OPEs, while aromatic-substituted OPEs showed the lowest uptake. This can be explained by two key factors: First, the nature of the substituent directly influences the hydrophobicity of OPEs. In our study, the log *Kow* values followed the order: chlorinated OPEs < alkyl-substituted OPEs < aromatic-substituted OPEs. This suggests that hydrophobicity is a primary determinant of plant uptake and translocation. Second, the electronic cloud distribution of substituents may also play a role. For instance, in this study, the chlorinated groups in TCEP may interact with the root surface via dipole interactions, enhancing adsorption and promoting uptake. These findings are consistent with our previous research (Hu et al., 2021b).

Cu Exposure. Under Cu treatments, the uptake and translocation of the four OPEs were altered in both krasnozem and margalitic soils, consistent with previous findings (Hu et al., 2021a; Wang et al., 2017; Wang et al., 2016). Cu exposure was strongly correlated with reduced root and shoot biomass, reflecting its toxic effects on plant growth. This observation aligns with prior reports on corn and other plants (Wang et al., 2017; Wang et al., 2016). The significantly higher uptake and accumulation of OPEs in krasnozem soil compared to margalitic soil may be attributed to differences in Cu toxicity, as the inhibited plant growth in krasnozem soil suggested greater damage under Cu exposure.

Excessive Cu can disrupt plant root cell membranes (Alva et al., 1999; Ardestani et al., 2013; Xu et al., 2006) and impair root perm-selectivity (Wang et al., 2016) by affecting lipid biosynthesis pathways or inducing peroxidative reactions in membrane lipids. This damage likely enhances OPEs entry into roots in both soil types. While noncovalent interactions between Cu^{2+} and the electron-rich structures of OPEs have been reported to suppress the sorption of electron-rich OPEs (ER-OPEs) and reduce their accumulation (Hu et al., 2021a), this phenomenon was not observed in the current study.

Across both control and Cu treatments, SCF and TF values exhibited negative correlations with log *Kow*, emphasizing the role of hydrophobicity in acropetal translocation of OPEs in plants. Similar results were reported for twelve OPEs in various crops in previous research (Hu et al., 2021a). Interestingly, the relationship between log *Kow* and OPEs acropetal translocation was stronger after Cu exposure. This suggests that both active transport and passive diffusion contribute to OPEs translocation, with Cu inhibiting transport protein activity and increasing the relative contribution of passive diffusion. Consequently, log *Kow* became a better predictor of OPEs acropetal translocation under Cu stress.

***Soil Property*.** It is well established that plant uptake of pollutants is largely governed by their bioavailability in the soil, as only the fraction dissolved in pore water constitutes the available portion in the soil-plant system. Soil dissolved organic matter (DOC) plays a critical role in the sorption–desorption processes of organic pollutants in soil. DOC can compete with pollutants for adsorption sites on soil particles or preferentially bind with them, forming bioavailable pollutants or pollutant-chelates (Miller et al., 2016). Higher root OPEs concentrations were observed in margalitic soil compared to krasnozem soil, likely due to the higher DOC content in margalitic soil. The elevated DOC could increase the mobility of OPEs by enhancing their availability in pore water, thereby facilitating plant uptake.

Due to the influence of soil physicochemical properties on plant growth, corn roots grown in margalitic soil exhibited higher lipid content, which in turn enhanced the uptake of OPEs. The elevated OPEs concentrations in corn roots from margalitic soil compared to krasnozem soil are likely the result of the combined effects of DOC and root lipid content. However, DOC modulates the plant uptake of OPEs through several pathways, and its overall influence is only weakly correlated with the log *Kow* of OPEs. In contrast, root lipid content governs the uptake of OPEs by plants exclusively through its relationship with the hydrophobicity of OPEs. Therefore, by comparing the uptake of individual OPEs across different soils, it is possible to infer which factor plays a more dominant role. Our results showed that the differences in plant uptake of individual OPEs between margalitic and krasnozem soils did not exhibit a linear relationship with log *K*ow, suggesting that hydrophobic interactions were not the primary driver. Hence, lipid content is not the key factor—DOC is likely the dominant contributor.

Empirical studies have shown that the behavior of metals in soil depends on various factors, including soil pH, soil organic matter (SOM), and plant species (Clarholm and Skyllberg, 2013; Zeng et al., 2011). Among these, soil pH plays a pivotal role in regulating the mobility and sorption of metals. Acidic soils exhibit stronger complexation of metallic ions, resulting in higher levels of extractable metals, which are more toxic to plants than in neutral soils (Sauve et al., 2000; Temminghoff et al., 1997). In this study, the bioavailable Cu^{2+} ions in the acidic krasnozem soil were up to 8.5 times higher than in margalitic soil. This elevated bioavailability of Cu in krasnozem soil likely contributed to stronger interference with plant physiological processes, leading to greater increases in OPEs content in plant tissues compared to margalitic soil.

4.3. Comparison with field studies

This study was conducted as a short-term pot experiment, which has inherent limitations in fully replicating the long-term dynamics of OPEs and Cu accumulation in actual agricultural soils. Factors such as climate variability and plant growth cycles are difficult to simulate under controlled conditions. Besides, although repeated wet-dry cycles were applied after the addition of OPEs and Cu, discrepancies remain between the behavior of freshly introduced pollutants in pot experiments and those aged under long-term field contamination. As a result, our findings may differ to some extent from field observations. Fortunately, current field studies show considerable consistency with our results. For example, Fan et al. confirmed in field experiments with corn and peanut that more hydrophilic OPEs tend to accumulate in plant roots (Fan et al., 2022). Similarly, Wang et al. investigated OPEs uptake in plants from the intertidal wetlands of Laizhou Bay and found that the bioavailability of all OPEs in field conditions was primarily determined by hydrophobicity, with higher hydrophobicity associated with lower uptake (Wang et al., 2021). However, some contrasting findings have also been reported. Wan et al. suggested that highly hydrophobic compounds may accumulate more readily in roots than their hydrophilic counterparts (Wan et al., 2016b). Notably, they also pointed out that hydrophilic OPEs are more likely to be translocated to above-ground tissues. We speculate that certain hydrophilic OPEs may be taken up efficiently but are rapidly translocated upward, occasionally resulting in lower concentrations in roots compared to more hydrophobic OPEs. Regrettably, few field studies have explored the effects of dissolved organic carbon or heavy metals on the plant uptake and translocation of OPEs, limiting our ability to conduct direct comparative analyses. Furthermore, our study compared only two soil types, krasnozem and magalitic soils, which does not capture the full range of soil variability. Future research is needed to address these knowledge gaps and expand the understanding of OPEs behavior in diverse field conditions.

4.4. Implications and limitation

This study focused on the effects of soil type and copper (Cu) on the uptake and translocation of OPEs in corn, providing important theoretical support for the risk management of co-contaminated agricultural soils. The findings demonstrate that the hydrophobicity of OPEs is a key factor determining their plant uptake and translocation. Differences in soil types lead to variations in dissolved organic carbon (DOC) content, which in turn significantly influence the bioavailability of OPEs. Additionally, pH differences among soils can alter Cu activity, thereby affecting the plant uptake of OPEs in Cu-OPEs co-contaminated soils. These insights offer direct guidance for optimizing soil remediation strategies, such as organic matter regulation or pH adjustment. Notably, the preferential accumulation of TCEP (a low log *Kow* compound) in corn shoots (TF $>$ 1) highlights its potential risk for transfer through the food chain. This underscores the need to include hydrophilic OPEs in agricultural product safety monitoring programs. However, as this study was conducted under short-term pot conditions that may not fully replicate field environments, and given the current lack of relevant field data for comparison, the conclusions drawn here require further validation through long-term field investigations.

CRediT authorship contribution statement

Yujie Wang: Writing – original draft, Methodology, Investigation. **Aoyu Wang:** Visualization, Investigation. **Longfei Jiang:** Writing – review & editing, Supervision, Resources, Conceptualization. **Beibei Hu:** Supervision, Resources, Conceptualization. **Chunling Luo:** 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.

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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.2025.126681.

Data availability

Data will be made available on request.

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