Chemosphere 368 (2024) 143743

Contents lists available at ScienceDirect

Chemosphere

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

Characteristics, prediction, and risk assessment of phthalates, organophosphate esters, and polycyclic aromatic hydrocarbons in vegetables from plastic greenhouses of Northeast China

Xinhao Xu [a], Yan Wang [a,*], Yue Xu [b], Feng Tan [a]

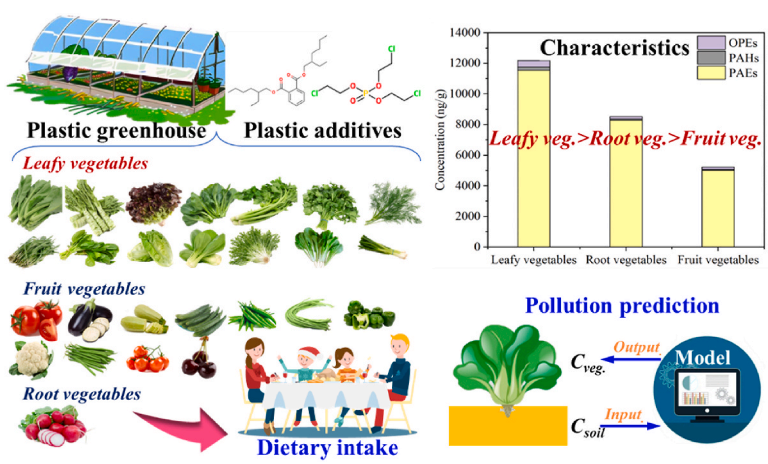
[a] Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian, 116024, China

[b] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550081, China

HIGHLIGHTS

- PAEs, OPEs and PAHs in greenhouse vegetables of northeastern China were studied.
- Leafy vegetables have higher contamination level than root and fruit vegetables.
- Chemicals' *BAFs* in vegetables were negatively related with their K_{ow}, K_{oa} and K_{oc}.
- Proposed a method for evaluating chemical's level in vegetable via soil monitoring.
- DEHP had the highest dietary exposure risk via vegetable, but still acceptable.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling editor: Milena Horvat

Keywords:
Plastic greenhouse
Vegetable
Phthalates
OPEs
Risk assessment
Contamination prediction

ABSTRACT

We investigated the contaminations of phthalates (PAEs), organophosphate esters (OPEs), and polycyclic aromatic hydrocarbons (PAHs) in the vegetables and their corresponding soils from 26 plastic greenhouses of Northeast China. PAEs, OPEs, and PAHs in the edible portion of vegetables were in the range of 2620–21800, 115–852, and 32.4–602 ng/g, while the levels of these chemicals in the greenhouse soils were 5770–18800, 196–935, and 109–1600 ng/g, respectively. PAEs are the main organic pollutants in greenhouses, which were 1-2 orders of magnitude higher than that of OPEs and PAHs. Leafy vegetables showed the highest contamination level, which is ~1–3 times that of root and fruit vegetables. Bioaccumulation factors (*BAFs*) of chemicals are significantly negatively correlated with their physicochemical properties, e.g., octanol-water partition coefficient and organic carbon partition coefficient. The partition-limited model can accurately predict the contamination level of greenhouse vegetables to a certain extent based on the chemical's concentration in the corresponding

* Corresponding author.
E-mail address: wangyandut@dlut.edu.cn (Y. Wang).

https://doi.org/10.1016/j.chemosphere.2024.143743
Received 26 August 2024; Received in revised form 17 October 2024; Accepted 11 November 2024
Available online 20 November 2024

soil. We assessed the hazard quotients of target compounds through daily intake of greenhouse vegetables, and found a low risk for di(2-ethylhexyl) phthalate. This research emphasized the potential dietary exposure risks caused by greenhouse leafy vegetables, and proposed a method for evaluating the risk of greenhouse vegetables through soil monitoring.

1. Introduction

Phthalates (PAEs) and organophosphate esters (OPEs) are two ubiquitous environmental contaminants, which have been widely used in many consumer and industrial products, including polyvinyl chloride (PVC) materials, food packaging, toys, cosmetics, etc. (Bu et al., 2019; Yesildagli et al., 2024)PAEs are mainly used as plasticizers to provide flexibility and durability, especially in plastic films and PVC, which contain up to 60% PAEs by weight (Zhang et al., 2018). OPEs are widely used as both flame retardants and plasticizers (Greaves and Letcher, 2017; Van der Veen and de Boer, 2012). PAEs and OPEs are only physically bound to products, and readily released into the environment. Polycyclic aromatic hydrocarbons (PAHs) consisting of two or more fused aromatic rings are principally derived from the incomplete combustion (Mojiri et al., 2019). PAHs have poor water solubility and excellent stability, and can accumulate and persist in soil or atmospheric particle over long periods of time (Argiriadis et al., 2014; Tong et al., 2018). PAEs, OPEs, and PAHs can pose potential threats to ecological risks and human health (Wang et al., 2015b) due to their endocrine disrupting (Arbuckle et al., 2018; Jurewicz and Hanke, 2011), carcinogenic, teratogenic, and mutagenic effects (Liang et al., 2022; Yu et al., 2018). These chemicals can enter human body through dietary intake, inhalation, or dermal absorption, of which the proportion through diet is up to 50% or more (Ma and Harrad, 2015).

Greenhouse agriculture has flourished in China since the 1960s, and the cumulative area of greenhouses nationwide has reached 1835.87 million hectares by 2023 (Guo et al., 2024). Greenhouse cultivation in China is mainly used for vegetable production, and more than 99% of them are plastic greenhouse (Chai et al., 2014). The annual use of plastic films in China exceeded 2 million tons in 2017 (NBSC, 2018). Additives in plastic films can release into the environment. Previous studies suggested that the PAE concentration in the plastic film mulch soil is five times higher than that without film (Kong et al., 2012), and 1 kg of PVC and polyethylene (PE) greenhouse films can emit 104 g and 122 g of DEHP into the environment, respectively (Wang et al., 2021a). Warm and humid conditions in greenhouses can also favor the release of organic contaminants from plastic films and the uptake of these contaminants by vegetables (Ma et al., 2015). Moreover, plastic film needs to be regularly replaced due to the reduced transparency by photoaging (Huo et al., 2016). Therefore, plastic films have become the important sources of PAEs and OPEs in the vegetable fields of China (Gong et al., 2021; Wang et al., 2013; Zhang et al., 2024).

Plants can absorb organic contaminants either from soil through root uptake or from air gas diffusion or particle deposition through leaves (Collins et al., 2006). However, there are many different varieties of vegetables consumed on a daily basis, and their uptake pathways and capacity for the chemicals also varies (Sun et al., 2015). Bioaccumulation factor (*BAF*), i.e., ratio of the chemical concentration in plant tissues to these in soil, is an effective parameter for characterizing the ability of contaminants to accumulate in plants. Physicochemical properties of chemicals, e.g., octanol-water partition coefficient (K_{ow}), octanol-air partition coefficient (K_{oa}), and soil adsorption coefficients (K_{oc}), can also affect their plant uptake activity. Therefore, it is possible to predict chemical's concentration in plants or vegetables according to their physicochemical properties and their concentrations in soil or soil water using models, such as the partition-limited model (Yesildagli et al., 2024). However, there is relatively little research on such prediction.

The objectives of this study were (1) to characteristics of PAEs, OPEs, and PAHs in the soils and the eatable parts of their corresponding vegetables in the plastic greenhouses of Northeast China; (2) to elucidate the influence factors on the uptake and bioaccumulation of PAEs, OPEs, and PAHs in the plastic greenhouse vegetables; (3) to predict the pollutant concentration in the edible parts of vegetables using soil and their properties, and (4) to assess the dietary exposure risks of PAEs, OPEs, and PAHs via vegetable consumption. The results of this study will be instructive for ensuring food safety and public health.

2. Material and methods

2.1. Sampling information

A total of 26 surface soil samples (0–10 cm) and 43 vegetable samples (including 26 plant species, e.g., cucumber, lettuce, radish, eggplant, etc.) were collected from 26 agricultural plastic greenhouses (see Fig. S1, Supplementary Information (SI)) in Dalian of Northeast China on March 7–8, 2023 (average temperature: 7 °C). All sampled greenhouses have a service life of over three years. Considering the transparency and impact on crop growth, farmers usually replace greenhouse films every 1–2 years. Large-scale plastic greenhouses only produce one or two vegetable varieties, while small-scale greenhouses grow several varieties. The detailed information on sampling sites and samples is given in Fig. S1 and Table S1, SI. All samples were wrapped with aluminum foil, put into polyethylene zipper bags, and immediately shipped to the laboratory. Stones and plant residues in the soil samples were removed. The fresh edible parts of the plants were collected, carefully washed with tap water followed with deionized water for three times. Soil and plant samples were freeze-dried, ground, homogenized, sieved (through 60 mesh), and stored at −20 °C until further analysis.

2.2. Sample extraction and purification

Soil or plant samples (~0.3 g) were accurately weighed, placed in a glass centrifuge tubes, and spiked with surrogate standards: dimethyl phthalate-d_4 (DMP-d_4), diethyl phthalate-d_4 (DEP-d_4), dibutyl phthalate-d_4 (DNBP-d_4), and di(2-ethylhexyl) phthalate-d_4 (DEHP-d_4) for PAEs; tri(2-chloroethyl) phosphate-d_{12} (TCEP-d_{12}), tri(1-chloro-2-propyl) phosphate-d_{18} (TCIPP-d_{18}), and triphenyl phosphate-d15 (TPHP-d_{15}) for OPEs; and naphthalene-d_8 (NAP-d_8), acenaphthene-d_{10} (ACE-d_{10}), phenanthrene-d_{10} (PHE-d_{10}), and chrysene-d_{12} (CHR-d_{12}) for PAHs. All samples were dispersed in dichloromethane (DCM), vortexed for 30 s, ultrasonicated for 20 min, centrifuged for 5 min, and then the supernatant was collected. The extraction procedure was then repeated 2 times using acetonitrile as the extractant. The extracts were combined, concentrated, and cleaned up by a silica gel column filled with anhydrous Na_2SO_4, primary secondary amine, 3% deactivated silica gel from top to bottom, and eluted with ethyl acetate.

2.3. Instrumental analysis

The target compounds included 10 PAEs, 11 OPEs, 16 PAHs (Tables S2 and SI). All samples were analyzed using a Shimadzu GCMS-QP2020 in the SIM mode with an electron ionization impact source. Separation was conducted on an SH-RXI-5sil MS column (30 m × 0.25 mm × 0.25 μm). Injector and transfer line temperatures were both 290 °C with helium as carrier gas at 1.5 mL/min. The oven temperature program was 60 °C for 1 min, and then 12 °C/min to 312 °C for 10 min. Temperatures for the ionization source and quadrupole were set at

230 °C and 150 °C, respectively.

2.4. Quality assurance and quality control (QA/QC)

To avoid potential contamination, plastic materials are not allowed to be used during the experiment. All glassware is ultrasonic cleaned with detergent, washed with tap water, rinsed with MilliQ water 3 times, and baked at 400 °C for 6 h. A procedure blank specimen was tested for each batch of 10 samples. Method detection limit (MDL) was estimated as the mean value of blanks plus three times the standard deviation. The MDLs of 16 PAHs、10 PAEs and 11 OPEs were 0.005–0.326、0.139–12.6 and 0.02952–2.39 ng/g for soils and 0.005–0.371、0.161–37.8 and 0.033–2.72 ng/g for vegetables, respectively (Table S3). The recoveries of TCEP-d_{12}, TCIPP-d_{18}, TPHP-d_{15}, DMP-d_4, DEP-d_4, DNBP-d_4, DEHP-d_4, NAP-d_8, ACE-d_{10}, PHE-d_{10}, and CHR-d_{12} in all samples were 81.4 ± 16.0%, 82.7 ± 19.8%, 86.7 ± 7.19%, 79.3 ± 17.8%, 80.4 ± 17.4%, 94.9 ± 18.6%, 88.5 ± 6.98%, 64.0 ± 16.6%, 84.4 ± 15.3%, 90.5 ± 9.41%, and 96.6 ± 11.5%, respectively. All samples were blank and recovery corrected. The concentration is expressed per dry weight (dw) of the sample.

2.5. Bioaccumulation metrics and contamination estimation of vegetables

Bioaccumulation factors (*BAFs*) are calculated to evaluate the potential transfer of PAHs, OPEs, and PAEs from soil to edible parts of vegetables according to Eq. (1) as follows:

$$BAF = \frac{C_e}{C_s} \tag{1}$$

where C_e (ng/g) is the concentration of chemical in the edible part of the vegetable, and C_s (ng/g) is the concentration of chemical in the corresponding soil.

We used the partition-limited model (Chiou et al., 2001) to further assess the impact of greenhouse soil contamination on the grown vegetables. The concentrations of pollutants in the vegetables grown on the contaminated agricultural soil can be estimated by the partition-limited model as follows (Wu and Zhu, 2019; Yesildagli et al., 2024):

$$C_{pt} = \alpha_{pt} C_{sw} \left(f_w + f_{ch} K_{ch} + f_{lip} K_{lip} \right) \tag{2}$$

where, C_{pt} is the concentration of organic compounds in the plants (mg/kg wet weight), α_{pt} is the quasi-equilibrium factor (dimensionless), assuming nonequilibrium conditions and α_{pt} as 0.39 (Wu and Zhu, 2019), C_{sw} is the concentration in the soil water (mg/L), f_w is the mass fraction of water in the plants (dimensionless), f_{ch} is the sum of the mass fraction of carbohydrates, cellulose, and proteins in the plants (dimensionless), f_{lip} is the mass fraction of the lipids in the plants (dimensionless), K_{ch} is the carbohydrate-water partition coefficient (L/kg), and K_{lip} is the lipid-water partition coefficient (L/kg). The details of parameterization and implementation of the partition-limited model for estimating the contaminant concentrations in the vegetables are given in the (Text S1), Supporting Information.

2.6. Daily intake estimation

Estimated daily intake (*EDI*, ng/kg body weight (bw)/d) of PAHs, PAEs, OPEs by eating vegetables was calculated by Eq. (3) as follows (USEPA, 2011):

$$EDI = \frac{C_v \times I \times EF \times ED}{BW \times AT} \times 10^{-6} \tag{3}$$

where C_v is the concentration of chemical in vegetable (ng/g), I is the daily intake rate of vegetable (mg/d), EF is the exposure frequency (d/y), ED is the exposure duration (y); BW is the body weight (kg), and AT is the average lifetime exposure (d). For C_v, the mean and 95th percentile concentrations were used for the average and high exposure scenarios, respectively.

The hazard quotient (*HQ*), which represents the risk of a certain PAH, PAE, or OPE congener in vegetable to human health through dietary intake was calculated as follows:

$$HQ = \frac{EDI}{RfD_0} \tag{4}$$

where RfD_0 (mg/kg/d) is the reference dose of chemical for oral intake of the contaminated vegetable. If the HQ value of chemical is > 1, there is an appreciable risk that non-cancer health effects will occur (Li et al., 2016). The values of all parameters used for assessing the *EDIs* and RfD_0 are shown in (Tables S4 and S5).

3. Results and discussion

3.1. PAEs, OPEs, and PAHs in the greenhouse soils

As shown in Fig. 1 (a, b, c), the total concentration of 10 PAEs in soil samples ranged from 5770 to 18800 ng/g (mean: 10800 ng/g), while the total concentration of 11 OPEs ranged from 196 to 935 ng/g (mean: 387 ng/g). PAHs were also analyzed for comparison, since they may originate from different sources and undergo different uptake pathways in plants compared to PAEs and OPEs. The total concentration of 16 PAHs ranged from 109 to 1600 ng/g (mean 345 ng/g). Sites 7 and 25 showed the highest total PAH concentration, reaching four and six times the average PAH concentration in soils, respectively, whereas Sites 12 and 22 had the highest OPE concentration (~2x of the mean concentration). The relatively high PAHs and OPE concentrations may be attributed to the use of farmyard manure or plant ash. However, there was no significant difference in the concentration of PAEs among different sampling sites, which may due to the significant release of PAEs from plastic greenhouse films (Wang et al., 2021a). Notably, the frequent replacement of plastic agricultural film will allow the additives in the film to continue to be released into the soil, leading to increased risks in the soil and vegetables.

The concentrations of PAEs, OPEs, or PAHs in greenhouse soils of this study were generally comparable with those in the greenhouse soils from other regions of China, but higher than those in the agriculture soils (Table S6). The total PAE concentrations in the soils of this study was slightly higher than that of greenhouse soil in Beijing (Σ_{15}PAEs: 140–2130 ng/g) (Li et al., 2016), and Guangdong province (Σ_{16}PAEs: 124–5760 ng/g) (Zeng et al., 2020), but lower than that in Shandong Peninsula, China. (Σ_{16}PAEs: 1.94–35.4 mg/kg) (Chai et al., 2014). The total OPE concentrations in the soils of this study were higher than those in the four Chinese provinces (Σ_{13}OPEs: 62.3–394 ng/g, mean: 230 ng/g) (Zhang et al., 2021), and was comparable to those collected from the waste recycling area in China (380 ng/g dw) (Cui et al., 2017). The total PAHs in greenhouse soils of this study were lower than those in the greenhouse soil of Beijing (mean 3510 mg/kg) (Ma et al., 2003) and Shandong Province (mean 407 ng/g) (Chai et al., 2017), urban soils in Dalian (mean 6440 ng/g) (Wang et al., 2009), agricultural soils in Shanghai (mean 1552 ng/g) (Tong et al., 2018), and rural soils in Nanjing, China (mean 1060 ng/g) (Wang et al., 2015a), and but were higher than those in agricultural soils of Huang-Huai plain, China (mean 129.5 μg/kg) (Yang et al., 2012).

DEHP is the dominant PAE congener in all soil samples, followed by DnBP, which is consistent with the fact that DEHP is the most widely used PAE in plastic films (Ma et al., 2015; Wang et al., 2015b; Zhang et al., 2019). The dominant congeners of OPEs were TEHP (52% of total OPEs), TCIPP (20%), and TCEP (18.6%). TEHP ($\log K_{ow} = 9.43$, $\log K_{oc} = 4.10$) has relatively strong hydrophobicity, leading to its superior adsorption and accumulation ability in soil (Han et al., 2022; Van der Veen and de Boer, 2012). TCIPP and TCEP are generally detected at high levels in the effluent of sewage treatment plant, rainwater, road runoff,

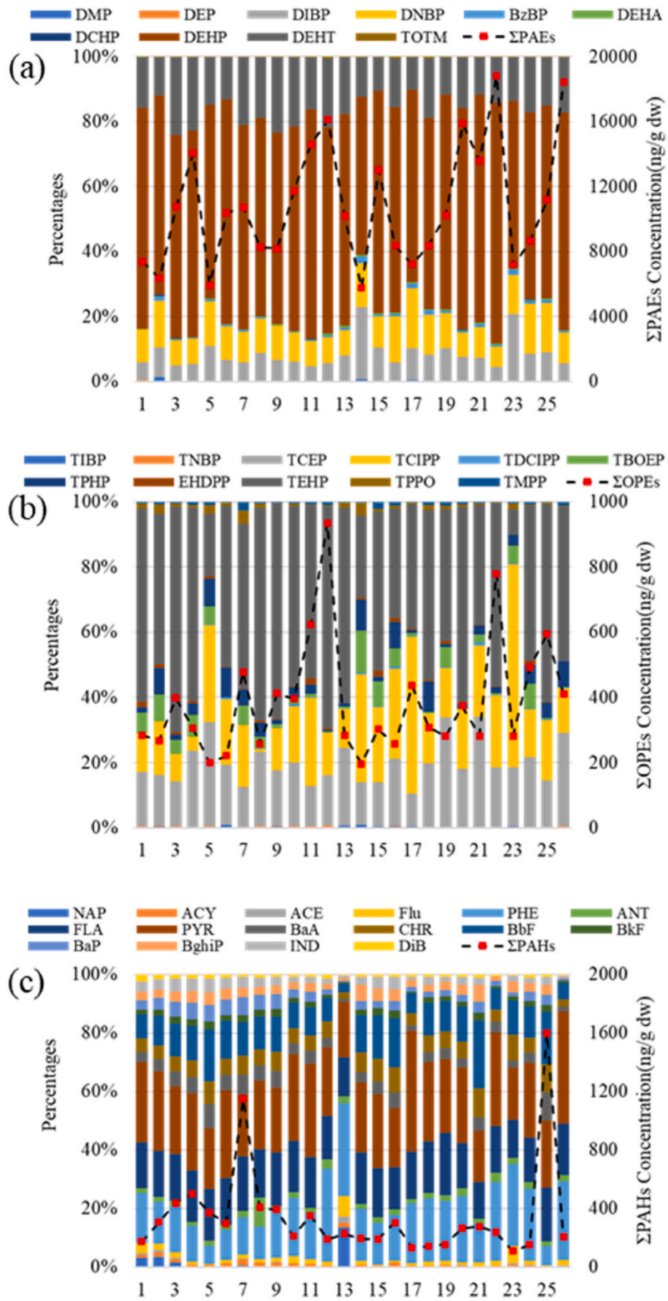


Fig. 1. Concentrations and compositions of PAEs (a), OPEs (b), and PAHs (c) in soils from different plastic greenhouses.

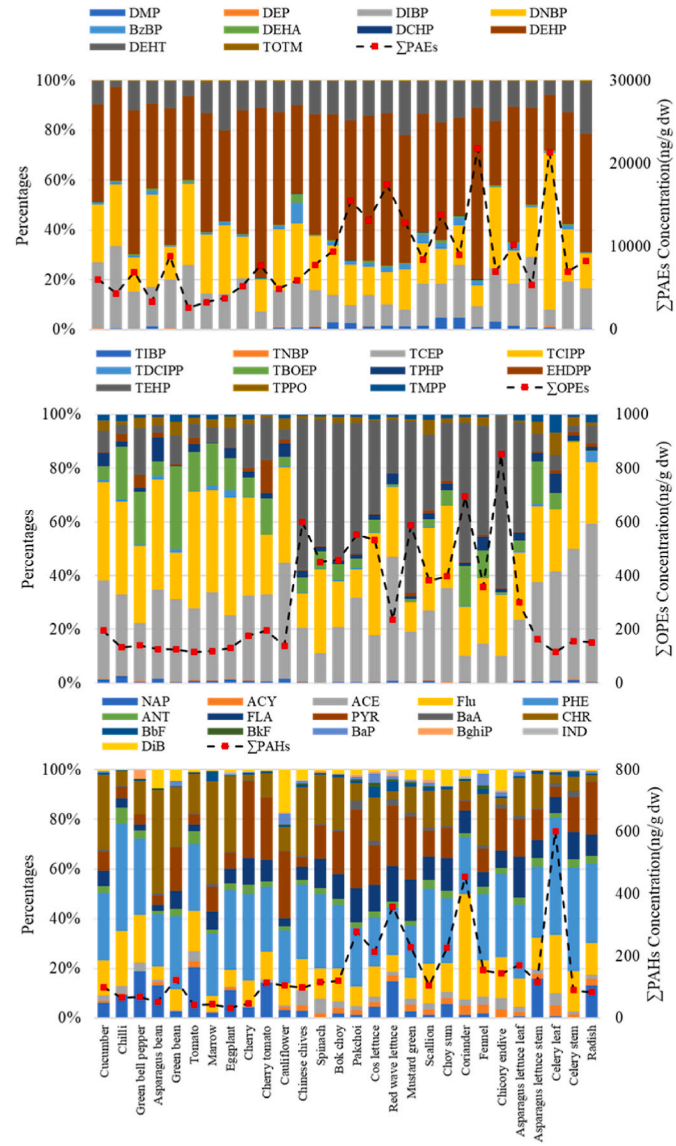


Fig. 2. Concentrations of PAEs, OPEs, and PAHs in different varieties of vegetables.

and surface water, which often used as the irrigation water (Kim and Kannan, 2018; Van der Veen and de Boer, 2012; Zeng et al., 2014).

3.2. PAHs, PAEs, and OPEs in the edible parts of vegetables

As shown in Fig. 2 , the concentrations of ΣPAEs in the edible parts of vegetables (including some cherries) ranged from 2620 to 21800 ng/g with a mean value of 8990 ng/g. DEHP was the dominant PAE congener with an average contribution of 48.7% to ΣPAEs, followed by DNBP and DEHT. Meanwhile, DCHP and DEP were found at relatively low concentrations. ΣOPEs in the vegetables ranged from 115 to 852 ng/g (mean: 307 ng/g). TEHP (37.4%) and TCIPP (24.6%) were the most frequently detected OPEs. ΣPAHs in the vegetables ranged from 32.4 to 602 ng/g (mean: 156 ng/g). PHE (29.0%) was the dominant congener followed by PYR, Flu, and CHR.

The concentrations of PAEs, OPEs, and PAHs varied widely with vegetable variety and sampling site. Although the contamination of the same vegetable species varied with greenhouses, the difference is not statistically significant. This suggested that greenhouse environment can affect the vegetable contamination to some extent, but not the influence is insignificant, which may be due to the similar contamination levels among greenhouses. Among all vegetables, fennel (*Foeniculum vulgare* Mill.), chicory endive (*Cichorium endivia* L.), and celery (*Apium graveolens* L.) had the highest concentration of PAEs, OPEs, and PAHs, respectively. A previous study (Bahrami et al., 2021; Li et al., 2018) also found that celery had the highest PAH concentrations among the vegetables.

The collected vegetables in this study can be categorized into 3 types: leafy vegetables, root vegetables, and fruit vegetables (Table S1). The mean values of ΣPAEs, ΣOPEs, and ΣPAHs, in leafy vegetables (11600 ng/g, 428 ng/g, and 217 ng/g) were significantly higher than those in the root vegetables (8280 ng/g, 151 ng/g dw, and 83.0 ng/g dw) and the fruit vegetables (5200 ng/g, 145 ng/g, and 72.2 ng/g). It is worth noting that even from the same greenhouse, leafy vegetables, such as celery, had significantly higher concentrations than those of the fruit vegetables, e.g., asparagus beans (*vigna unguiculata* (L.) Walp.) and tomatoes (*solanum lycopersicum* L.). This suggested that the vegetable specie (or type) is still a crucial factor in controlling the uptake of pollutants (Hu et al., 2021). Moreover, the growth period and the height of plants may also affect their contaminations. A shorter growth period and a higher plant height may lead to a less pollution in the vegetables from soil. The significantly high concentrations in leaf vegetables probably due to the particle deposition and gaseous diffusion of airborne pollutants via foliar uptake (Zhang et al., 2024). This can also be proved by the relatively high concentrations of these pollutants in vegetable leaves than these in stems, such as celery or romaine lettuce. Most leafy vegetables have relatively large leaf areas and stretched leaf blades, which makes them can easily capture more organic pollutants through airborne gaseous, particle, or dust fall forms. However, those organic pollutants absorbed by leaves are mainly stored in the cuticle wax, and difficult to enter the inner part of the leaf or further translocate to other tissues (Wang et al., 2024; Zeng et al., 2022). Generally, the contaminations in the root vegetables were slightly higher than those in the fruit vegetables, which may be attribute to the difficult translocation of the hydrophobic compounds from root to shoot (Paris et al., 2018; Zhang et al., 2020). Moreover, organic chemicals with higher hydrophobicity are more likely to accumulate in root and difficult to translocate to the above-ground organs (Wan et al., 2017). Hydrophobic chemicals can directly bind to lipid contents in plant roots (Sun et al., 2015) or bind to proteins, who carry them to the lipid components (Liu et al., 2019). The abilities of plants to absorb and translocate organic pollutants are affected by a number of factors (Gao and Zhu, 2004; Liang et al., 2024). First, the storage and metabolic capacities of cellular organelles for organic pollutants, as well as the lipid content or transporter proteins, differ with plant species and tissues (Cheng et al., 2020, 2021; Gong et al., 2020). Second, the physicochemical properties of organic pollutants can also affect their uptake and translocation in plants, such as K_{ow}, K_{oc}, and molecular structure (Fan et al., 2022).

3.3. Bioaccumulation efficiency

To assess the absorption and bioaccumulation capacity of vegetables (eatable parts) for PAEs, OPEs, and PAHs, their *BAF* value (Table S6) were calculated. As shown in Fig. 3 (a, b, c), log*BAFs* of leafy vegetables (PAEs: −0.996~2.58, OPEs: −1.86~1.49, and PAHs: −2.62~2.31) were generally higher than log*BAFs* of root vegetables (PAEs: −1.04~0.698, OPEs: −1.52~0.801, and PAHs: −2.47~2.12) and fruit vegetables (PAEs: −1.52~1.87, OPEs: −1.98~1.49, and PAHs: −2.53~2.10). This results further confirmed that pollutants in leafy vegetables may originate from both foliar and root absorptions, especially foliar absorption. The log*BAFs* of PAEs, OPEs, or PAHs for different vegetables were shown in Fig. S2, SI. The relatively low *BAFs* also suggested that root absorption and acropetal translocation of PAEs, OPEs, and PAHs in vegetables are limited.

Considering that plant uptake, translocation, and bioaccumulation of organic pollutants have been demonstrated to be significantly affected by their physicochemical properties (Calderón-Preciado et al., 2012), we further investigated the relationship between log*BAFs* and K_{ow}, K_{oa} or K_{oc} (Fig. 4 a, b, c), where the lipophilicity of chemicals determines the difficulty of their release from soil organic matter and transported across plant cell membranes, as well as their distribution in plant lipids, thus limiting their long-range transport (Wang et al., 2021b). As derived from Fig. 4a, the log*BAFs* (median) of PAEs ($P = 0.002$), OPEs ($P = 0.012$), and PAHs ($P < 0.001$) were all significantly negatively correlated with their logK_{ow} values. High K_{ow} values indicates that these chemicals tend to be tightly bound to soil particles, and are difficult to desorb and be taken up by plant (Collins et al., 2006; Wang et al., 2021b). Because K_{oc} is correlated with K_{ow}, the adsorption capacity of soil for pollutants increases with the increase of K_{ow}, which thereby reduce their uptake by plant (Chiou et al., 1998). The log*BAFs* (median) of PAEs ($R^2 = 0.803$, $P < 0.001$) and PAHs ($R^2 = 0.524$, $P = 0.02$) were also significantly negatively correlated with their logK_{oc} values (Fig. 4b), but not for OPEs ($P = 0.368$). Moreover, the log*BAFs* (median) of PAEs ($R^2 = 0.761$, $P <$

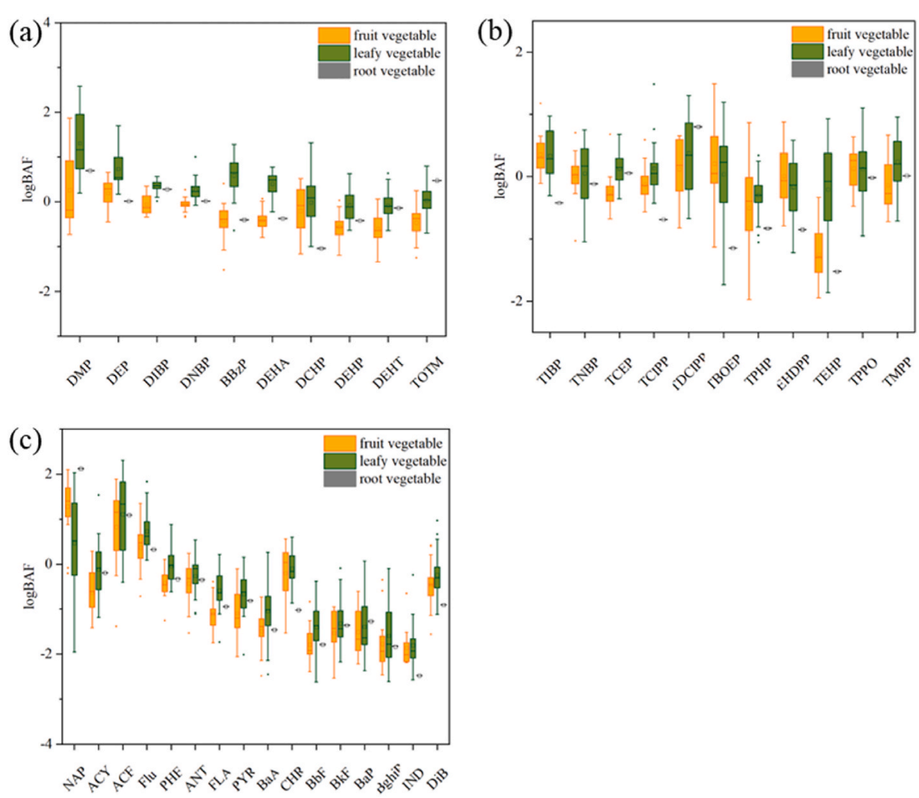


Fig. 3. Bioaccumulation factors of PAEs (a), OPEs (b), and PAHs (c) in the vegetables.

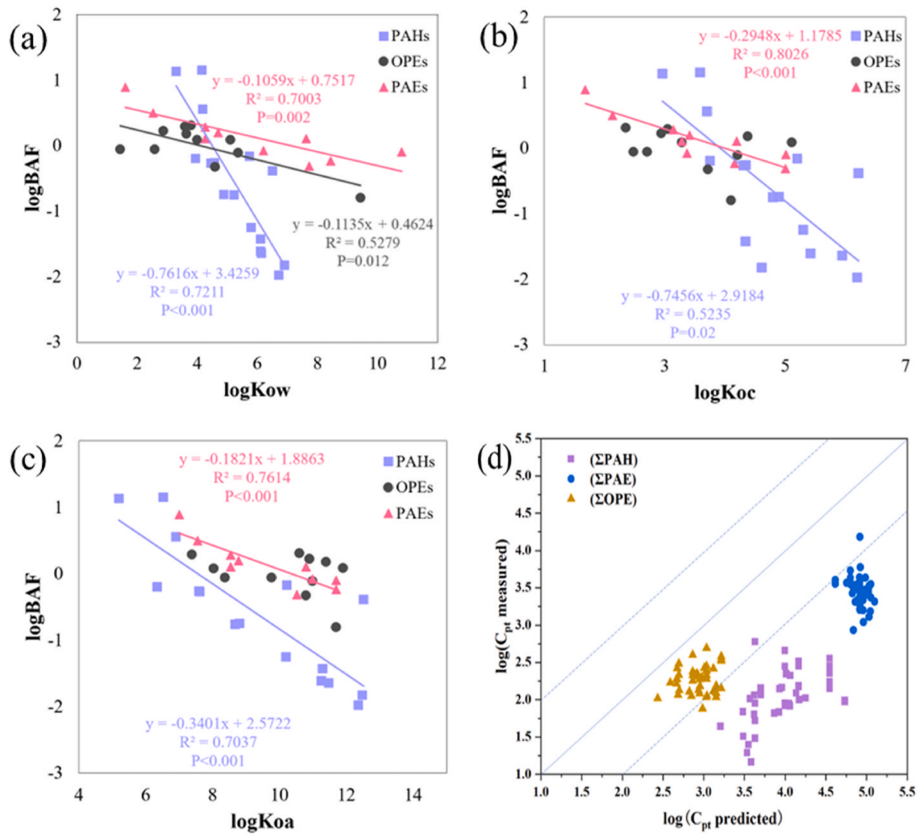


Fig. 4. Relationships between log*BAFs* of PAEs, OPEs, and PAHs and their logK_{ow} (a) logK_{oc} (b), or logK_{oa} (c), and relationship between the model-predicted concentrations and the measured concentrations in vegetables (d).

0.001) and PAHs ($R^2 = 0.704$, $P < 0.001$) were also significantly negatively correlated with their logK_{oa} values (Fig. 4c), but also not for OPEs ($P = 0.303$). This suggested that the plant uptake of PAEs and PAHs was highly negatively correlated with their K_{oa} values. High K_{oa} values indicate that these chemicals tend to be deposited on the particle and be absorbed by plant leaves (Collins et al., 2006). Although contaminants on particles can spread into the plant cuticle or infiltrate into the plant interior by being deposited onto plant leaves (Wang et al., 2024), level of airborne particles within the plastic greenhouses is relatively low, which leads to a low contribution of foliar uptake via particle phase. Moreover, chemicals with high K_{oa} may also have relatively strong hydrophobicity.

Since the absorption and accumulation processes of chemicals by vegetables significantly depends on their physicochemical properties, assuming that pollutants in vegetables mainly originate from root uptake, we can predict the concentration of pollutants in vegetables based on their concentrations in the corresponding soil and their properties. We conducted a linear stepwise regression analysis between chemicals' log*BAFs* and their logK_{ow}, logK_{oa}, and logK_{oc} values, and found that log*BAFs* was significantly correlated with logK_{oc} (log*BAFs* $= -0.47$log$K_{oc}$$+1.668$, $P < 0.001$), suggesting that soil adsorption coefficient is a crucial factor affecting the absorption of chemical by plants. Therefore, we used the partition-limited model (Chiou et al., 2001) to further assess the impact of greenhouse soil contamination on the grown vegetables. In the model calculations, we excluded TEHP, DEHT, DEHP, DEHA, and TOTM, because their logK_{ow} >7. The comparison between the partition-limited model predicted concentrations (total concentration) and the actual measured concentrations is shown in Fig. 4d. We found that this model is more accurate and suitable for the prediction of OPEs, whereas the predicted results for PAEs and PAHs are 1-2 orders of magnitude higher than the measured ones. This is due to the fact that PAHs and PAEs have higher K_{ow} values compared to OPEs (most OPE congeners with high concentrations have low K_{ow}), resulting in significant differences in predictions using the model. The α_{pt} value is close to 1 at near equilibrium between plant tissues and soil water, and <1 for the non-equilibrium condition. The α_{pt} value mainly depends on the water transport rate of plant and the amount of soil water required for the plant to reach absorption equilibrium. For the highly hydrophobic compound, α_{pt} value is predicted to be much less than 1. Previous studies (Wu and Zhu, 2019; Yesildagli et al., 2024) usually used an α_{pt} value of 0.39 for this prediction. However, according to our results, using an α_{pt} of 0.39 had significantly overestimated the PAE and PAH levels in the vegetables (mostly leaf vegetables) by 1-2 orders of magnitude. This may be attribute to that the PAEs and PAHs in the leafy vegetables were far from reaching absorption equilibrium with soil water. Thus, a more accurate prediction can be achieved by assuming the α_{pt} value as 0.03 for PAEs and PAHs. This partition-limited model is not applicable for assessing the contaminations in vegetables according to their soil levels for chemicals with logK_{ow} >7, since those chemicals are difficult for the acropetal translocation. Moreover, this model only considered the contribution through root uptake and ignored the contribution of leaf absorption, which may also cause some prediction errors.

3.4. Risk assessments

PAHs, PAEs and OPEs absorbed by vegetables can enter human body through diet intake. Vegetables have been considered as the major dietary source of PAEs (Yang et al., 2018). Here, we calculated the *EDIs* (mg/kg/day) of PAEs, OPEs, and PAHs in Dalian for both children and adults according to their mean (M) or 95% percentile (95th) concentration concentrations in the vegetables to estimate the risks posed by vegetable consuming (Fig. 5a, b, and c). We assumed that the average water content of all vegetables is 90%, and obtained the concentration

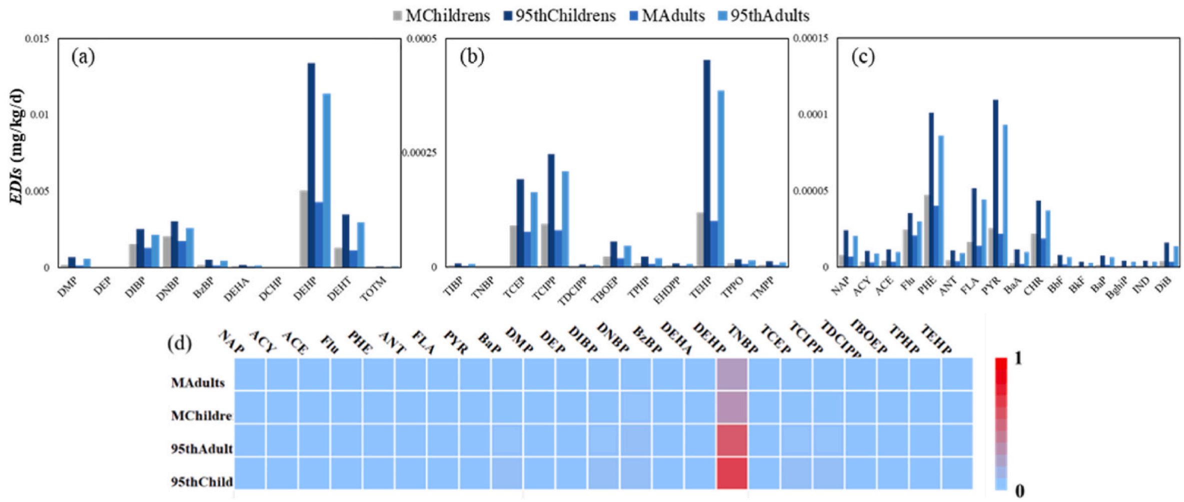


Fig. 5. Estimated daily intakes (*EDIs*) of PAEs (a), OPEs (b), and PAHs (c) via vegetable intake for children and adults and their potential *Hazard Quotient* values (d).

based on wet weight. The mean *EDI* values of PAEs, OPEs, and PAHs were 8.77×10^{-3}, 3.05×10^{-4}, and 1.43×10^{-4} mg/kg/d for adults, and 10.31×10^{-3}, 3.59×10^{-4}, and 1.68×10^{-4} mg/kg/d for children, respectively. Children had even higher *EDI* values and exposure risks than adults, which may due to their lower body weights, but higher susceptibility to toxicity. DEHP, TEHP, TCIPP, and TCEP had relatively high *EDI* values, which was consistent with previous studies (Yu et al., 2021; Zhang et al., 2021).

We also calculated the Hazard Quotient (*HQ*) for *EDI* to assess the risk according to the vegetable consumption on an average daily basis. As shown in Fig. 5d, the *HQs* of pollutants in all scenes were less than 1, suggesting an acceptable range of risk to human health. The *HQ* values (up to 0.670 for children at 95th percentile level) of DEHP were significantly higher than those of the other pollutants, indicating low levels of risks from DEHP. Considering other dietary intakes, exposure pathways, and combined toxicities of pollutants, such low health risks cannot be ignored. Therefore, the issues of organic pollution in greenhouse vegetables and human exposure through vegetable consumption deserve further attention.

4. Conclusion

We investigated the characteristics, accumulation, translocation, and potential dietary exposure risks of PAEs, OPEs, and PAHs in the vegetables grown in plastic agricultural greenhouses in Northeast China. Notably, PAEs, OPEs, and PAHs in the edible portion of leafy vegetables were significantly higher than those in the fruit vegetables and root vegetables, suggesting a higher dietary exposure risk from consuming leafy vegetables. *BAFs* of PAEs, OPEs, and PAHs in leafy vegetables were also significantly higher than those of other two kinds of vegetables, which may due to the considerable foliar uptake for the large proportion of leaf areas. The partition-limited model was used to predict the concentrations of pollutants in the vegetables according to their concentrations in the corresponding soil. This model can accurately predict the pollutant levels in the vegetables, when the quasi-equilibrium factor setting is reasonable. The estimated daily intakes and *HQs* of PAEs, OPEs, and PAHs via vegetable consuming indicated that these pollutants pose health risks at a low level. However, the risk of DEHP is still needed to be taken seriously considering other dietary intakes and exposure pathways. Therefore, stricter and more effective management strategies are required for the cultivation of leafy vegetable in plastic greenhouses to reduce the potential dietary intake risks of organic pollutants.

CRediT authorship contribution statement

Xinhao Xu: Writing – original draft, Methodology, Investigation, Formal analysis. **Yan Wang:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **Yue Xu:** Writing – review & editing, Methodology. **Feng Tan:** Writing – review & editing, 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.

Acknowledgments

This study was supported by the National Natural Science Foundation of China (No. 22376019), the Natural Science Foundation of Liaoning Province of China (2022-MS-143), and the Guizhou Provincial Science and Technology Projects (Qian Ke He Basic ZK [2024] General 672).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2024.143743.

Data availability

Data will be made available on request.

References

Arbuckle, T.E., Agarwal, A., MacPherson, S.H., Fraser, W.D., Sathyanarayana, S., Ramsay, T., Dodds, L., Muckle, G., Fisher, M., Foster, W., Walker, M., Monnier, P., 2018. Prenatal exposure to phthalates and phenols and infant endocrine-sensitive outcomes: the MIREC study. Environ. Int. 120, 572–583.

Argiriadis, E., Rada, E.C., Vecchiato, M., Zambon, S., Ionescu, G., Schiavon, M., Ragazzi, M., Gambaro, A., 2014. Assessing the influence of local sources on POPs in atmospheric depositions and sediments near Trento (Italy). Atmos. Environ. 98, 32–40.

Bahrami, S., Moore, F., Keshavarzi, B., 2021. Evaluation, source apportionment and health risk assessment of heavy metal and polycyclic aromatic hydrocarbons in soil and vegetable of Ahvaz metropolis. Hum. Ecol. Risk Assess. 27 (1), 71–100.

Bu, Z.M., Mmereki, D., Wang, J.H., Dong, C., 2019. Exposure to commonly-used phthalates and the associated health risks in indoor environment of urban China. Sci. Total Environ. 658, 843–853.

Calderón-Preciado, D., Renault, Q., Matamoros, V., Cañameras, N., Bayona, J.M., 2012. Uptake of organic emergent contaminants in spath and lettuce: an in vitro experiment. J. Agric. Food Chem. 60 (8), 2000–2007.

Chai, C., Cheng, H.Z., Ge, W., Ma, D., Shi, Y.X., 2014. Phthalic acid esters in soils from vegetable greenhouses in Shandong peninsula, east China. PLoS One 9 (4), e95701.

Chai, C., Cheng, Q.Q., Wu, J., Zeng, L.S., Chen, Q.H., Zhu, X.W., Ma, D., Ge, W., 2017. Contamination, source identification, and risk assessment of polycyclic aromatic hydrocarbons in the soils of vegetable greenhouses in Shandong, China. Ecotoxicol. Environ. Saf. 142, 181–188.

Cheng, Z.P., Wang, Y., Qiao, B.T., Zhang, Q.Y., Sun, H.W., 2021. Insights into mechanisms involved in the uptake, translocation, and metabolism of phthalate esters in Chinese cabbage (*Brassica rapa var. chinensis*). Sci. Total Environ. 768, 144945.

Cheng, Z.P., Yao, Y.M., Sun, H.W., 2020. Comparative uptake, translocation and subcellular distribution of phthalate esters and their primary monoester metabolites in Chinese cabbage (*Brassica rapa var. chinensis*). Sci. Total Environ. 742, 140550.

Chiou, C.T., McGroddy, S.E., Kile, D.E., 1998. Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments. Environ. Sci. Technol. 32 (2), 264–269.

Chiou, C.T., Sheng, G.Y., Manes, M., 2001. A partition-limited model for the plant uptake of organic contaminants from soil and water. Environ. Sci. Technol. 35 (7), 1437–1444.

Collins, C., Fryer, M., Grosso, A., 2006. Plant uptake of non-ionic organic chemicals. Environ. Sci. Technol. 40 (1), 45–52.

Cui, K.Y., Wen, J.X., Zeng, F., Li, S.C., Zhou, X., Zeng, Z.X., 2017. Occurrence and distribution of organophosphate esters in urban soils of the subtropical city, Guangzhou, China. Chemosphere 175, 514–520.

Fan, Y., Zeng, Y., Huang, Y.Q., Guan, Y.F., Sun, Y.X., Chen, S.J., Mai, B.X., 2022. Accumulation and translocation of traditional and novel organophosphate esters and phthalic acid esters in plants during the whole life cycle. Chemosphere 307, 135670.

Gao, Y.Z., Zhu, L.Z., 2004. Plant uptake, accumulation and translocation of phenanthrene and pyrene in soils. Chemosphere 55 (9), 1169–1178.

Gong, X.Y., Wang, Y., Pu, J., Zhang, J.J., Sun, H.W., Wang, L., 2020. The environment behavior of organophosphate esters (OPEs) and di-esters in wheat (*Triticum aestivum* L.): uptake mechanism, in vivo hydrolysis and subcellular distribution. Environ. Int. 135, 105405.

Gong, X.Y., Zhang, W.J., Zhang, S.Y., Wang, Y., Zhang, X.Y., Lu, Y., Sun, H.W., Wang, L., 2021. Organophosphite antioxidants in mulch films are important sources of organophosphate pollutants in farmlands. Environ. Sci. Technol. 55 (11), 7398–7406.

Greaves, A.K., Letcher, R.J., 2017. A Review of organophosphate esters in the environment from biological effects to distribution and fate. Bull. Environ. Contam. Toxicol. 98 (1), 2–7.

Guo, B., Zhou, B., Zhang, Z.M., Li, K.D., Wang, J.Y., Chen, J.F., Papadakis, G., 2024. A critical review of the status of current greenhouse technology in China and development prospects. Applied Sciences-Basel 14 (13), 5952.

Han, B.J., Chen, L.Y., Li, Y.J., Yu, L., Zhang, J.D., Tao, S., Liu, W.X., 2022. Spatial distribution and risk assessment of 11 organophosphate flame retardants in soils from different regions of agricultural farmlands in mainland China. Sci. Total Environ. 842, 156806.

Hu, B.B., Jiang, L.F., Zheng, Q., Luo, C.L., Zhang, D.Y., Wang, S.R., Xie, Y.C., Zhang, G., 2021. Uptake and translocation of organophosphate esters by plants: impacts of chemical structure, plant cultivar and copper. Environ. Int. 155, 106591.

Huo, C.Y., Liu, L.Y., Zhang, Z.F., Ma, W.L., Song, W.W., Li, H.L., Li, W.L., Kannan, K., Wu, Y.K., Han, Y.M., Peng, Z.X., Li, Y.F., 2016. Phthalate esters in indoor window films in a northeastern Chinese urban center: film growth and implications for human exposure. Environ. Sci. Technol. 50 (14), 7743–7751.

Jurewicz, J., Hanke, W., 2011. Exposure to phthalates: reproductive outcome and children health. A review of epidemiological studies. Int. J. Occup. Med. Environ. Health 24 (2), 115–141.

Kim, U.J., Kannan, K., 2018. Occurrence and distribution of organophosphate flame retardants/plasticizers in surface waters, tap water, and rainwater: implications for human exposure. Environ. Sci. Technol. 52 (10), 5625–5633.

Kong, S.F., Ji, Y.Q., Liu, L.L., Chen, L., Zhao, X.Y., Wang, J.J., Bai, Z.P., Sun, Z.R., 2012. Diversities of phthalate esters in suburban agricultural soils and wasteland soil appeared with urbanization in China. Environ. Pollut. 170, 161–168.

Li, C., Chen, J.Y., Wang, J.H., Han, P., Luan, Y.X., Ma, X.P., Lu, A.X., 2016. Phthalate esters in soil, plastic film, and vegetable from greenhouse vegetable production bases in Beijing, China: concentrations, sources, and risk assessment. Sci. Total Environ. 568, 1037–1043.

Li, H.D., Zhu, D.W., Lu, X., Du, H.X., Guan, S., Chen, Z.L., 2018. Determination and risk assessment of sixteen polycyclic aromatic hydrocarbons in vegetables. Toxic/Hazard. Subst. Environ. Eng. 53 (2), 116–123.

Liang, C., Mo, X.J., Xie, J.F., Wei, G.L., Liu, L.Y., 2022. Organophosphate tri-esters and di-esters in drinking water and surface water from the Pearl River Delta, South China: implications for human exposure. Environ. Pollut. 313, 120150.

Liang, J.F., Ji, X.M., Feng, X.X., Su, P.J., Xu, W.Z., Zhang, Q.Z., Ren, Z.H., Li, Y.L., Zhu, Q. Q., Qu, G.B., Liu, R.Z., 2024. Phthalate acid esters: a review of aquatic environmental occurrence and their interactions with plants. J. Hazard Mater. 470 (15), 134187.

Liu, Q., Wang, X.L., Yang, R.Y., Yang, L.P., Sun, B.B., Zhu, L.Y., 2019. Uptake kinetics, accumulation, and long-distance transport of organophosphate esters in plants: impacts of chemical and plant properties. Environ. Sci. Technol. 53 (9), 4940–4947.

Ma, L.L., Chu, S.G., Xu, X.B., 2003. Organic contamination in the greenhouse soils from Beijing suburbs, China. J. Environ. Monit. 5 (5), 786–790.

Ma, T.T., Wu, L.H., Chen, L., Zhang, H.B., Teng, Y., Luo, Y.M., 2015. Phthalate esters contamination in soils and vegetables of plastic film greenhouses of suburb Nanjing, China and the potential human health risk. Environ. Sci. Pollut. 22 (16), 12018–12028.

Ma, Y.N., Harrad, S., 2015. Spatiotemporal analysis and human exposure assessment on polycyclic aromatic hydrocarbons in indoor air, settled house dust, and diet: a review. Environ. Int. 84, 7–16.

Mojiri, A., Zhou, J.L., Ohashi, A., Ozaki, N., Kindaichi, T., 2019. Comprehensive review of polycyclic aromatic hydrocarbons in water sources, their effects and treatments. Sci. Total Environ. 696, 133971.

NBSC, 2018. China Rural Statistical Yearbook. National Bureau of Statistics of China. In China, 2018.

Paris, A., Ledauphin, J., Poinot, P., Gaillard, J.L., 2018. Polycyclic aromatic hydrocarbons in fruits and vegetables: origin, analysis, and occurrence. Environ. Pollut. 234, 96–106.

Sun, J.Q., Wu, X.Q., Gan, J., 2015. Uptake and metabolism of phthalate esters by edible plants. Environ. Sci. Technol. 49 (14), 8471–8478.

Tong, R.P., Yang, X.Y., Su, H.R., Pan, Y., Zhang, Q.Z., Wang, J., Long, M.C., 2018. Levels, sources and probabilistic health risks of polycyclic aromatic hydrocarbons in the agricultural soils from sites neighboring suburban industries in Shanghai. Sci. Total Environ. 616, 1365–1373.

USEPA, 2011. Exposure Factors Handbook, 2011 Edition. Final Report, Washington, DC. 2011.

Van der Veen, I., de Boer, J., 2012. Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. Chemosphere 88 (10), 1119–1153.

Wan, W.N., Huang, H.L., Lv, J.T., Han, R.X., Zhang, S.Z., 2017. Uptake, translocation, and biotransformation of organophosphorus esters in wheat (*Triticum aestivum* L.). Environ. Sci. Technol. 51 (23), 13649–13658.

Wang, C.H., Wu, S.H., Zhou, S.L., Wang, H., Li, B.J., Chen, H., Yu, Y.N., Shi, Y.X., 2015a. Polycyclic aromatic hydrocarbons in soils from urban to rural areas in Nanjing: concentration, source, spatial distribution, and potential human health risk. Sci. Total Environ. 527, 375–383.

Wang, D.G., Yang, M., Jia, H.L., Zhou, L., Li, Y.F., 2009. Polycyclic aromatic hydrocarbons in urban street dust and surface soil: comparisons of concentration, profile, and source. Arch. Environ. Contam. Toxicol. 56 (2), 173–180.

Wang, J., Chen, G.C., Christie, P., Zhang, M.Y., Luo, Y.M., Teng, Y., 2015b. Occurrence and risk assessment of phthalate esters (PAEs) in vegetables and soils of suburban plastic film greenhouses. Sci. Total Environ. 523, 129–137.

Wang, J., Luo, Y.M., Teng, Y., Ma, W.T., Christie, P., Li, Z.G., 2013. Soil contamination by phthalate esters in Chinese intensive vegetable production systems with different modes of use of plastic film. Environ. Pollut. 180, 265–273.

Wang, Y., Jiang, Y.Y., Xu, Y., Tan, F., 2024. Effects of uptake pathways on the accumulation, translocation, and metabolism of OPEs in rice: an emphasis on foliar uptake. Sci. Total Environ. 918, 170562.

Wang, Y., Wang, F., Xiang, L.L., Gu, C.G., Redmile-Gordon, M., Sheng, H.J., Wang, Z.Q., Fu, Y.H., Bian, Y.R., Jiang, X., 2021a. Risk assessment of agricultural plastic films based on release kinetics of phthalate acid esters. Environ. Sci. Technol. 55 (6), 3676–3685.

Wang, Y., Zhang, Z.H., Bao, M.J., Xu, Y., Zhang, L.J., Tan, F., Zhao, H.X., 2021b. Characteristics and risk assessment of organophosphate esters and phthalates in soils and vegetation from Dalian, northeast China. Environ. Pollut. 284, 117532.

Wu, X., Zhu, L.Z., 2019. Prediction of organic contaminant uptake by plants: modified partition-limited model based on a sequential ultrasonic extraction procedure. Environ. Pollut. 246, 124–130.

Yang, B., Xue, N.D., Zhou, L.L., Li, F.S., Cong, X., Han, B.L., Li, H.Y., Yan, Y.Z., Liu, B., 2012. Risk assessment and sources of polycyclic aromatic hydrocarbons in agricultural soils of Huanghuai plain, China. Ecotoxicol. Environ. Saf. 84, 304–310.

Yang, X., Chen, D.W., Lv, B., Miao, H., Wu, Y.N., Zhao, Y.F., 2018. Dietary exposure of the Chinese population to phthalate esters by a Total Diet Study. Food Control 89, 314–321.

Yesildagli, B., Goktas, R.K., Ayaz, T., Olgun, B., Dokumaci, E.N., Ozkaleli, M., Erdem, A., Yurtsever, M., Dogan, G., Yurdakul, S., Civan, M.Y., 2024. Phthalate ester levels in agricultural soils of greenhouses, their potential sources, the role of plastic cover material, and dietary exposure calculated from modeled concentrations in tomato. J. Hazard Mater. 468 (15), 133710.

Yu, Y.X., Peng, M.M., Liu, Y.L., Ma, J.J., Wang, N., Ma, S.T., Feng, N.N., Lu, S.Y., 2021. Co-exposure to polycyclic aromatic hydrocarbons and phthalates and their associations with oxidative stress damage in school children from South China. J. Hazard Mater. 401 (5), 123390.

Yu, Z., Han, Y., Shen, R., Huang, K., Xu, Y.Y., Wang, Q.N., Zhou, S.S., Xu, D.X., Tao, F.B., 2018. Gestational di-(2-ethylhexyl) phthalate exposure causes fetal intrauterine growth restriction through disturbing placental thyroid hormone receptor signaling. Toxicol. Lett. 294, 1–10.

Zeng, L.J., Huang, Y.H., Chen, X.T., Chen, X.H., Mo, C.H., Feng, Y.X., Lü, H.X., Xiang, L., Li, Y.W., Li, H., Cai, Q.Y., Wong, M.H., 2020. Prevalent phthalates in air-soil-vegetable systems of plastic greenhouses in a subtropical city and health risk assessments. Sci. Total Environ. 743, 140755.

Zeng, L.J., Huang, Y.H., Lu, H.X., Geng, J., Zhao, H.M., Xiang, L., Li, H., Li, Y.W., Mo, C. H., Cai, Q.Y., Li, Q.X., 2022. Uptake pathways of phthalates (PAEs) into Chinese flowering cabbage grown in plastic greenhouses and lowering PAE accumulation by spraying PAE-degrading bacterial strain. Sci. Total Environ. 815, 152854.

Zeng, X.Y., He, L.X., Cao, S.X., Ma, S.T., Yu, Z.Q., Gui, H.Y., Sheng, G.Y., Fu, J.M., 2014. Occurrence and distribution of organophosphate flame retardants/plasticizers in wastewater treatment plant sludges from the pearl river delta, China. Environ. Toxicol. Chem. 33 (8), 1720–1725.

Zhang, M., Wang, P., Lu, Y.L., Lu, X.T., Zhang, A.Q., Liu, Z.Y., Zhang, Y.Q., Khan, K., Sarvajayakesavalu, S., 2020. Bioaccumulation and human exposure of perfluoroalkyl acids (PFAAs) in vegetables from the largest vegetable production base of China. Environ. Int. 135, 105347.

Zhang, Q., Wang, Y.X., Jiang, X.X., Xu, H.Z., Luo, Y.Q., Long, T.T., Li, J., Xing, L.Q., 2021. Spatial occurrence and composition profile of organophosphate esters (OPEs) in farmland soils from different regions of China: implications for human exposure. Environ. Pollut. 276, 116729.

Zhang, Q.Y., Liu, Y.R., Li, S.Y., Li, H., Gao, M., Yao, Y.M., Wang, L., Wang, Y., 2024. Traditional and novel organophosphate esters in plastic greenhouse: occurrence, multimedia migration, and exposure risk via vegetable consumption. Environ. Sci. Technol. 58 (31), 13929–13939.

Zhang, Y.X., Huang, B., Sabel, C.E., Thomsen, M., Gao, X.Y., Zhong, M., Chen, Z.K., Feng, P.Y., 2019. Oral intake exposure to phthalates in vegetables produced in plastic greenhouses and its health burden in Shaanxi province, China. Sci. Total Environ. 696, 133921.

Zhang, Y.X., Huang, B., Thomsen, M., Sabel, C.E., Hess, F., Hu, W.Y., Tian, K., 2018. One overlooked source of phthalate exposure - oral intake from vegetables produced in plastic greenhouses in China. Sci. Total Environ. 642, 1127–1135.