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Identifying the contributions of root and foliage gaseous/particle uptakes to indoor plants for phthalates, OPFRs and PAHs

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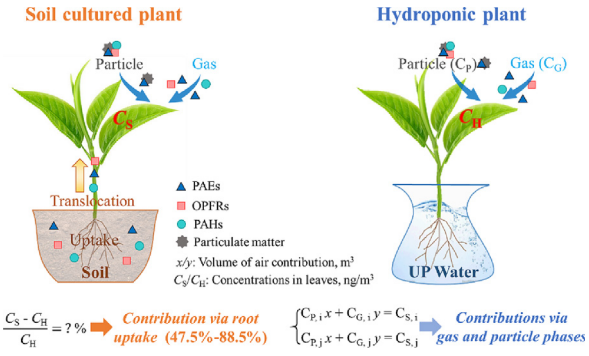
HIGHLIGHTS

- Root and foliage uptake ratios were calculated based on soil and hydroponic plants.
- Root uptake of SVOCs is the main source for leaves of soil-cultured plants.
- Gas and particle contributions to the SVOCs in hydroponic plants were estimated.
- Hydroponic plants are more suitable as biosamplers for indoor organic pollutants.

GRAPHICAL ABSTRACT



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ABSTRACT

Understanding the uptake pathways of organic chemicals in plants can help us use plants as biosentinels for human exposure, and as remediation tools for contaminated sites. Herein, we investigated the relative contributions of root and foliar (gas and particle) uptake pathways to indoor ornamental plants for phthalates (PAEs), organophosphorus flame retardants (OPFRs), and polycyclic aromatic hydrocarbons (PAHs). We looked at different kinds of indoor ornamental plants via pot and hydroponic control experiments, comparing the levels between their leaves and indoor air gaseous and particle phases, floor dust, and window film. Contributions of soil and foliage uptakes were calculated based on chemical concentrations in leaves of hydroponic and soil cultured plants and their mass uptake rates. Across all compounds, the contributions of root uptake to the chemicals in soil cultured plants ranged from 47.5 % to 88.5 %. We used binary first-order mass conservation equations to calculate the contributions of foliage uptake via gaseous and particle phases to the chemicals with similar K_{ow} in plant leaves. Foliar uptake of PAEs occurred mainly via particle adsorption, for light PAHs via gaseous absorption, and for OPFRs via both particle and gaseous uptakes. Negative correlations between chemicals' foliage uptake ratios and their K_{ow} and K_{oa} values suggest that foliage uptake may be influenced by both chemical hydrophilicity and lipophilicity.

1. Introduction

Organophosphorus flame retardants (OPFRs), phthalates (PAEs), and polycyclic aromatic hydrocarbons (PAHs) are semivolatile organic compounds (SVOCs) of concern due to their ubiquity, persistence, and toxicity to humans and the environment (Greaves and Letcher, 2017; Serrano et al.,

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2014; Sun et al., 2021). OPFRs and PAEs are widely used in textiles, furniture, electronics, coating, polyvinyl chloride (PVC) plastic, and polyurethane foam (Katsikantami et al., 2016; Sun et al., 2018; Wei et al., 2015; Zhang et al., 2022). PAHs are produced as a by-product of combustion and can be found in tobacco smoke, smoke from open fires for heating or cooking, and elsewhere (Nguyen-Duy and Chang, 2017; Oliveira et al., 2019). PAEs and OPFRs have been frequently detected in the indoor environment due to their extensive applications in products, while PAHs are often produced from anthropogenic sources indoors (Orecchio et al., 2013; Pantelaki and Voutsa, 2019; Sedlackova et al., 2021; Tri Manh and Kannan, 2015). Some PAEs, OPFRs, and PAHs have been found to be carcinogenic, neurotoxic, endocrine disrupting, mutagenic, and bioaccumulative, and have been identified as "priority pollutants" by environmental regulators around the world (Christia et al., 2019; Kim et al., 2013; Soltani et al., 2014).

Plants can take up and accumulate organic chemicals mainly through root uptake or foliar absorption (Collins et al., 2006). The uptake pathways of chemicals by plants are complex and can be difficult to disentangle. Root uptake may be the main pathway for both water and soil cultured plants to accumulate brominated flame retardants (BFRs) and OPFRs, especially in the early life stage.(Fan et al., 2020; Wu et al., 2018; Zhang et al., 2021) Atmospheric SVOCs can also enter into the aerial plant parts via either gaseous or particle depositions (Collins et al., 2006; Liu et al., 2019; Zhu et al., 2020). In general, Cousins and Mackay (Cousins and Mackay, 2001) proposed that for chemicals with log K_{ow} (octanol-water partition coefficient) <2.5 and log K_{aw} (dimensionless Henry's law constant) < -1, root uptake via transpiration should be the important pathway, while for chemicals with log $K_{oa} > 6$ (octanol-air partition coefficient) and log $K_{aw} > -6$, foliar uptake should be the most important pathway. However, this may vary by location, plant species, and by the specific SVOCs involved, and overall, there is still a lack of knowledge on the contributions of root uptake and foliar absorption to the individual SVOC levels within plants.

Plants and their tissues (e.g., pine needle, tree bark, or moss) have been widely used as passive biosamplers for investigating numerous organic chemicals in the environment. (Cabrerizo et al., 2012; McLachlan, 1999) Different plants and tissues have been used for particular purposes due to their special characteristics, such as the wax coating of pine needle, and the high surface to volume ratio of tree bark and moss. In the indoor environment, plants have rarely been used as biosamplers for pollutants (Wang et al., 2021), in part because most indoor ornamental plants have multiple sources or uptake pathways with uncertain contribution ratios. Therefore, determining the relative contributions of root and foliar uptakes are essential for using the ornamental plant as the biomonitor of indoor SVOCs or sentinel of human exposure to SVOCs (Wang et al., 2021), as well as understanding the plant uptake mechanisms of these chemicals. Here, we conducted a 40-day pot and hydroponic experiment with 4 different ornamental plant species in order to identify the main sources or uptake pathways of PAEs, OPFRs, and PAHs in plant leaves, and to evaluate their contributions to these compounds in leaves.

2. Material and method

2.1. Sample information

We selected four species of indoor ornamental plants, *Spathiphyllum kochii* Engl. et Krause (Abbr. SK, also known as Spathe flower), *Chlorophytum comosum* (Thunb.) Baker (CC, Bracketplant), *Epipremnum aureum* (EA, Scindapsus), and *Hedera nepalensis* var. *sinensis* (Tobl.) Rehd (HN, Ivy) for this experiment based on their high adsorption capacity of formaldehyde (He and Peng, 2019; Xu et al., 2011; Yuwei et al., 2011). We conducted a 40-day controlled experiment using both soil and hydroponic cultures in a laboratory room (area: 42 m^2) at a height of 1.5 m from May 2021 to June 2021. For each of the plants, we covered the surface of either the soil or the water with aluminum foil to prevent volatilization and air deposition. All plants were placed in the same room for 30 days before this experiment. We watered the plants with ultrapure water and changed the hydroponic water every 5 days during the first 30-day cultivation and the 40-day experiment. All treatments were performed in triplicate. Every 10 days we collected samples of the plant leaves (3 pieces each), floor dust, and window film (area: 400 cm^2, wiped using a precleaned tissue paper with dichloromethane). Dust and plant samples were freeze-dried, ground, homogenized, and sieved into 60 mesh.

We collected both active and passive air samples. Active air particle and gaseous samples were collected using a glass fiber filter (GF, 46 mm diameter, baked at 450 °C for 4 h) followed by polyurethane foam (PUF, 2 cm diameter, 9 cm length, precleaned using Soxhlet extraction with ethyl acetate for over 72 h) at a height of 1.5 m using a low volume active air sampler (LV-AAS) with a flow rate of ~4 L/min (details are shown in Table S1, SI). Passive air samplers using low density polyethylene (LDPE, 10 cm × 5 cm, 0.01 cm thickness), polydimethylsiloxane sheet (PS, 10 cm × 5 cm, 0.1 cm thickness), and silicone wristband (WB, 19 cm perimeter, 1.1 cm width, 0.1 cm thickness) were also deployed and collected simultaneously with plant leaves (every 10 days) to provide a time-integrated assessment of contaminant levels. Floor dust and window film, LDPE, PS, and WB were collected to help to identify the potential sources of SVOCs in plant leaves. All samples were stored at −20 °C until further analysis.

2.2. Sample extraction

Dust (~0.5 g), leaf (~0.2 g), GF, PUF, or glass wipe samples were spiked with deuterated surrogate standards (diethyl phthalate-d_4 (DEP-d_4), DNBP-d_4, and DEHP-d_4 for PAEs; tris(2-chloroethyl) phosphate-d_{12} (TCEP-d_{12}) and triphenyl phosphate-d_{15} (TPHP-d_{15}) for OPFRs; acenaphthylene (ACY)-d_8, phenanthrene (PHE)-d_{10}, chrysene (CHR)-d_{12}, and perylene (PYR)-d_{12} for PAHs), ultrasonicated with a mixture of DCM: *n*-hexane: acetone (2:2:1, v/v/v) for 20 min and repeated three times. LDPE, PS sheet, or wristband samples were spiked with surrogate standards, extracted by shaking with ethyl acetate for 30 min and then soaking for 12 h, and repeated three times. The extract was concentrated, cleaned up on a silica gel column containing 4 cm silica gel (63–200 μm, baked at 450 °C for 8 h, 3 % deactivated) topped with 1 cm of anhydrous sodium sulfate (baked at 450 °C for 4 h), and eluted with ethyl acetate. For plant samples, the extract was further cleaned up using a PSA cartridge (200 mg, 3 mL) and eluted with ethyl acetate.

2.3. Instrumental analysis

The target compounds included 8 PAEs (dimethyl phthalate (DMP), DEP, di-isobutyl phthalate (DIBP), DNBP, BBzP, dicyclohexyl phthalate (DCHP), DEHP, and di-(2-ethylhexyl) terephthalate (DEHT)), 9 OPFRs (tri-isobutyl phosphate (TIBP), TNBP, TCEP, tris(2-chloro-isopropyl) phosphate (TCIPP), tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), TPHP, 2-ethylhexyl diphenyl phosphate (EHDPP), triphenyl phosphine oxide (TPPO), and tricresyl phosphate (TMPP)), and 12 PAHs (ACY, acenaphthene (ACE), fluorene (FLU), PHE, anthracene (ANT), fluoranthene (FLA), PYR, benzo[*a*]anthracene (BaA), CHR, benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), and Benzo[*a*]pyrene (BaP)) (Table S2, SI). All samples were analyzed using a Shimadzu GCMS-QP2020 in the SIM mode with an electron ionization impact source. Separation was conducted on a DB-5MS 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.

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

All glassware was baked at 450 °C for >4 h and rinsed with hexane before use. We collected field blanks for the window film, LV-AAS, LDPE, PS, and WB samples by exposing the sampler material in the same room for 1 min. A procedural blank was run alongside each batch of 5 samples to assess potential contamination. We calculated the method detection limit

(MDL) as the mean value of blanks plus three times the standard deviation (Table S3, SI). The surrogate recoveries of plant leaf samples were 81.7 ± 9.7 %, 86.1 ± 8.7 %, 83.7 ± 9.1 %, 89.6 ± 10.4 %, 84.9 ± 12.4 %, 87.6 ± 10.1 %, 88.1 ± 9.6 %, 82.5 ± 10.6 %, 90.2 ± 11.8 % for DEP-d_4, DNBP-d_4, DEHP-d_4, TCEP-d_{12}, TPHP-d_{15}, ACY-d_8, PHE-d_{10}, CHR-d_{12}, and PYR-d_{12}, respectively (details of all samples in Table S4, SI). All samples were blank- and recovery-corrected.

2.5. Data analysis and statistics

Levels of target compounds were reported as ng/g dw in plant and dust, ng/m^3 in active air samples, ng/m^2 in window film, and ng/sampler in LDPE, PS, and WB samples. Statistical analyses were conducted using the Microsoft Excel 2019 and SPSS 22 software packages. Normality of data was tested using the Shapiro-Wilk's test. Spearman's correlation analysis was used to determine the relationships between individual OPFR, PAE, and PAH congeners in different matrices, with statistical significance reported as $p < 0.05$. Data for the Principal Component Analysis (PCA) were normalized using the z-score.

2.6. Estimation of the contributions of foliage and root uptakes to the SVOC burdens in plant

SVOCs in plant leaves may originate from both root uptake (including root-to-shoot translocation) and foliar uptake, and undergo translocation and biodegradation within plant (Collins et al., 2006). However, for the hydroponic plants, since the ultrapure water is free of organic contaminants, SVOCs in their leaves may only come from foliar uptake.

Here, we hypothesize that the growth states of hydroponic and soil cultured plants were comparable. Therefore, their air-foliage exchange and biodegradation amounts of SVOCs were similar. The mass balance (ng) for SVOCs in the leaves of the soil and hydroponic cultured plants (C_L) can be expressed as follows:

$$V\frac{dC_L}{dt} = mtc_{A/L}A_LC_A + mtc_{M/R}A_RC_M \times TF_{R/L} - mtc_{L/A}A_LC_L - mtc_{R/M}A_RC_L \times TF_{L/R} - kC_LV \quad (1)$$

$$V\frac{dC_L}{dt} = mtc_{A/L}A_LC_A + mtc_{M/R}A_RC_M \times TF_{R/L} - \left(mtc_{L/A}A_L - mtc_{R/M}A_R \times TF_{L/R} - kV\right)C_L \quad (2)$$

where V (m^3) is the volume of the leaves, $mtc_{j/k}$ (m/h) the mass transfer coefficients between environmental media j and k (denoted by the subscripts A for air, L for leaf, M for growing media, i.e., water and soil, and R for root), A_L the contact area of the leaf, A_R the contact area of the root, $TF_{R/L}$ (−) the translocation factor from roots to leaves, $TF_{L/R}$ (−) the translocation factor from leaves to roots, and k (h^{-1}) the first order transformation rate constant for the leaves. By grouping all the terms associated with each concentration into an overall process flow rate "k_i" (m^3/h, analogously to the technique employed in multimedia fugacity modeling (Mackay, 2001)), we get the following:

$$V\frac{dC_L}{dt} = k_AC_A + k_MC_M - k_LC_L \quad (3)$$

where k_AC_A is the mass flow rate (mol/h) from the air to the leaf, k_MC_M the mass flow rate from the growing media to the leaf, and k_LC_L the mass flow rate out of the leaf. For hydroponic plants, C_M is considered as 0, since the ultra-pure water was free of SVOCs. At steady state, this gives the following equations for the concentrations in the hydroponic (C_H, ng/g) and soil-cultured (C_S, ng/g) plants in Eqs. (4) and (5), respectively.

$$0 = k_AC_A - k_LC_H; \text{i.e.,}\ C_H = \frac{k_AC_A}{k_L} \quad (4)$$

$$0 = k_AC_A + k_MC_M - k_LC_S; \text{i.e.,}\ C_S = \frac{k_AC_A + k_MC_M}{k_L} \quad (5)$$

Further, we can also assume that k_L was the same for the hydroponic and the soil cultured plants, based on previous results showing little transfer from leaves to clean growing media (< 10 %), and since the plants were grown under the same conditions and had similar dimensions, the mass transfer coefficients for biodegradation and volatilization from the leaves to the air were likely equal between the different growing media. Thus, the relative contribution of the air to leaf pathway to plant mass uptake (R_f) is shown in Eq. (6), and the contribution from the soil to the leaf (R_S) in Eq. (7):

$$R_f = \frac{k_AC_A}{k_AC_A + k_MC_M} = \frac{C_H}{C_S} \quad (6)$$

$$R_S = 1 - \frac{C_H}{C_S} = \frac{C_S - C_H}{C_S} \quad (7)$$

Lipids serve as important compartments in the partitioning of organic compounds into organisms (Geisler et al., 2012). To investigate whether interactions other than nonpolar partitioning (membrane lipid-water and storage lipid-water) to SVOCs can more accurately explain the partition between plants and water logK_{ow} based model, logK_{mw} and logK_{sw} were estimated using Eqs. (8) and (9) (this kind of estimation for partitioning between plants and air was not conducted due to the lack of related data) (UFZ, n.d.):

$$\log K_{mw} = vV + sS + aA + bB + eE + c \quad (8)$$

$$\log K_{sw} = v'V + s'S + a'A + b'B + e'E + c' \quad (9)$$

where K_{mw} and K_{sw} are the membrane lipid-water and storage lipid-water partition coefficients estimated based on poly-parameter linear free energy relationships (pp-LFERs) model; Capital letters V, S, A, B, and E, representing the intermolecular interactions that govern the partition process, are cavity formation, polar interactions, H-bond interactions, van der Waals interactions, respectively (Geisler et al., 2012).

2.7. Estimation of the contributions of gaseous and particle absorptions to the foliage uptake of SVOCs

The foliage uptake of SVOCs includes both particle and gaseous absorption. An experimental evidence suggested that most SVOCs are persistent in plants, and metabolism is not a significant factor for the accumulation of these compounds (McLachlan, 1999), thus, we assume that the degradation rate of a certain SVOC in plant leaves is consistent whether it comes from the foliage absorption via gaseous or particle phases. Therefore, after deducting the degraded part, the residual SVOC is contributed from both the gaseous and particulate phases. Previous studies have suggested that the permeability of plant cuticles to organic chemicals was linearly related with its K_{ow} (Collins et al., 2006; Riederer et al., 2002). Thus, we assume that two congeners in the same chemical group sharing similar K_{ow} values have the same absorption pathways, patterns, and contributions of gaseous and particulate absorptions. Since the hydroponic plants in this study only absorb SVOCs from gaseous and particle phases by foliar uptake, the contributions of gaseous and particle absorption can be calculated by the following binary first-order mass conservation formulas:

$$\begin{cases} C_{P1}V_P + C_{G1}V_G = m_1 \\ C_{P2}V_P + C_{G2}V_G = m_2 \end{cases} \quad (10)$$

$$R_P = \frac{C_PV_P}{M} \quad (11)$$

$$R_G = \frac{C_GV_G}{M} \quad (12)$$

Fig. 1. Concentrations of PAEs, OPFRs, and PAHs in plant leaves (H: hydroponic, S: soil-cultured), dust (D), window film (WF), and active gaseous (APUF) and particle (GF) samples.

where C_{P1} and C_{P2} are the concentrations (ng/m^3) of two SVOC congeners with similar K_{ow} value in the air particle phase; C_{G1} and C_{G2} are their concentrations (ng/m^3) in the air gaseous phase; m_1 and m_2 are their masses (ng) per unit mass (1 g) leaf; V_P and V_G are the effectively adsorbed air volumes (m^3) for particle and gaseous SVOCs, respectively, assuming that V_P and V_G for congeners with similar K_{ow} are the same; R_P and R_G are the contribution ratios of particulate and gaseous uptakes to the SVOC burden in leaf (M). We note that this estimation could only be used for those compounds within the same chemical group which have similar K_{ow} values.

3. Results and discussion

3.1. Concentrations of PAEs, OPFRs, and PAHs in different matrices

The concentrations of PAEs, OPFRs and PAHs in different ornamental plant leaves, window film, dust, and active air samples are shown in Fig. 1. The concentrations of PAEs, OPFRs, and PAHs in the particle phase (GF) ranged from 95.5 to 301, 1.62 to 3.44, and 1.83 to 4.08 ng/m^3, respectively, while those in the gaseous phase (APUF) were 1600–3980, 7.59–12.7, and 85.6–247 ng/m^3, respectively. The SVOC concentrations in the particle phase were significantly lower than these in the gaseous phase. The PAE, OPFR, and PAH concentrations in the dust samples were 10,500–368,000, 2840–8930, and 2900–8440 ng/g, while those in the window films were in the range of 74,900–406,000, 2240–6140, and 946–9100 ng/m^2, respectively. The PAE, OPFR, and PAH concentrations in the air, dust, and window film samples varied widely during the exposure period.

The concentrations of PAEs, OPFRs, and PAHs in the leaves of hydroponic plant were in the range of 1750–13,000 (mean: 5250 ± 3420), 41.7–1749 (mean: 94.2 ± 42.6), and 66.2–547 (mean: 222 ± 143) ng/g, while those in the leaves of soil cultured plants were 2700–28,100 (mean: 13,800 ± 7270), 132–525 (mean: 305 ± 126), and 156–787 (mean: 414 ± 171) ng/g, respectively. All target compounds were 100 % detected. Generally, the concentrations of PAEs, OPFRs, and PAHs in the soil-cultured plants were significantly higher than those in the time-matched hydroponic plants with the mean values in the soil cultured plants 2–5 times of those in the hydroponic ones. This result suggested that soil was an important source of PAEs, OPFRs and PAHs for the soil cultured indoor plants. Surprisingly, the concentrations of PAEs, OPFRs, and PAHs in plant leaves did not increase with time but fluctuated, suggesting the partitioning between chemicals in the plants and the environment may reach equilibrium and vary with the environmental contamination. The mean concentrations of PAEs, OPFRs, and PAHs in the hydroponic CC leaves were the highest followed by the hydroponic EA and SK, whereas the SVOC levels in the soil cultured SK leaves were the highest, followed by the soil cultured CC, HN, and EA. This implies that CC may have more effective absorption capacity of airborne SVOCs from the ambient air than other indoor plants. This is consistent with the fact that people use *Chlorophytum comosum* to absorb indoor formaldehyde gas (Zhao et al., 2014).

3.2. Compositions of PAEs, OPFRs, and PAHs in different matrices

The compositions of PAEs, OPFRs, and PAHs in the plant leaves, window film, dust, and active air samples are shown in Fig. 2. For PAEs, DNBP (38.7 %) was the dominant congener in the plant leaves followed by DEHP (29.9 %), DEHP was the dominant PAE in the dust, window film, and air particle phase followed by DNBP, whereas DMP dominated in the gaseous phase followed by DIBP. For OPFRs, TCEP was the most abundant congener in the plant leaves, dust, and air particle phase, while TCIPP and TNBP were the dominant congeners in window film and gaseous phase, respectively. It is noteworthy that compositions of TCEP in the soil plant leaves were significantly higher than those in the hydroponic plant leaves, suggesting that TCEP, a relatively hydrophilic compound (logK_{ow}: 1.44), mainly enters plant leaves through root uptake followed by upward translocation. For PAHs, PHE was the dominant congener in all samples, followed by FLU in the leaves and gaseous phase, but by FLA in the dust and particle phase. Although, the compositions of three chemical groups varied with sampling matrices, they were similar in the hydroponic and soil cultured plant leaves, dust, and particle phase. Meanwhile, PAH compositions in the leaves were also comparable with those in the gaseous phase. This indicated that the sources of target compounds in the hydroponic and soil cultured plants may be similar, especially for PAEs and PAHs. Furthermore, similar compositions of PAEs, OPFRs, and PAHs were found in the 4 different soil cultured plants, indicating similar uptake and accumulation processes of SVOCs by herbaceous and vine plants.

3.3. Source apportionment

Correlations of PAE, OPFR, and PAH concentrations among plant leaves, dust, window film, particle phase, gaseous phase, LDPE, PS, and WB are tested using Spearman's correlation analysis and are shown in Figs. S1–S3 of SI. PAEs in all leaves were almost significantly positively correlated with those in the GF, dust window film, and LDPE samples ($p < 0.05$), but not the APUF, PS, or WB samples, while PAHs in the leaves showed significant positive correlations with those in the APUF, PS, and WB samples, but not in the GF, dust, window film, or LDPE samples. However, for OPFRs, the situation was complex. OPFRs in the leaves were only significant positive correlated with some APUF (or GF, depending on plant species), dust, and WB samples. This suggested that PAEs and PAHs in plants may be mainly associated with particle and gaseous phases, respectively, whereas the OPFRs in plants may originate from multiple sources or complex biological processes, such as biodegradation or biotransformation. Correlations between leaves and matrices were generally similar for the hydroponic and soil cultured plants, indicating that although the absorption pathways of SVOCs by plants differ with different cultivation methods, the absorption amounts and composition characteristics of these chemicals may mainly depend on their properties. Meanwhile, the SVOC compositions in the hydroponic and soil cultured plant leaves were also similar, indicating that SVOCs absorbed by root and then translocated to leaf were similar to those absorbed by leaf. In other words, the factors controlling the root uptake and root-to-shoot translocation of chemicals resembles those of foliage uptake. Thus, the three indoor plants in this study, whether soil or hydroponic cultured, can be effective biomonitors in the indoor environment.

Principle component analysis (PCA) was performed in order to identify the main sources of these chemicals (Fig. 3). Two principal components were extracted accounting for 70.2 % of the cumulative variances. PC1, accounting for 54.4 % of the total variance, exhibited high loadings on most chemicals with relatively high K_{oa}. This indicated that PC1 may be related to air particle or soil particle sources. PC2, accounting for 15.8 % of the total variance, exhibited high positive loadings on chemicals with low K_{oa}, e.g., PHE, TCIPP, DEP, DMP, and DIBP. DEP has been detected in household and personal care products, such as dry-cleaning fluids, body lotion, and perfumes. DMP is applied in insect repellent. DIBP is used as crosslinker and plasticizer (USEPA, 2020). TCIPP has been widely detected in insulation and sealant foams (Hartmann et al., 2004). Thus, PC2 indicated emissions from household or personal care products. In the score plot, plant leaf (both hydroponic and soil cultured), LDPE, dust, and window film samples were grouped together with GF samples (Fig. 3b), indicating that particulate phase was their main source.

3.4. Contributions of root and foliage uptakes to SVOCs in plant leaves

The contribution ratios of root and foliage uptakes to the chemical levels in different plants are shown in Fig. 4. DEHP, DEHT, BaA, CHR, and BaP were not employed in the calculation due to their high deviations of concentrations in plant leaves. HN was not used since it is a vine plant. The root uptake ratios of SVOCs were 55.4 %–88.5 % (mean: 73.2 %), 47.5 %–81.4 % (70.4 %), and 54.5 %–88.3 % (69.4 %) for SK, CC, and EA, respectively. The contribution of root uptake to a certain SVOC congener in the plants is species-dependent (Liu et al., 2019). Air–foliage exchange has been suggested to be the primary uptake pathway of rice for

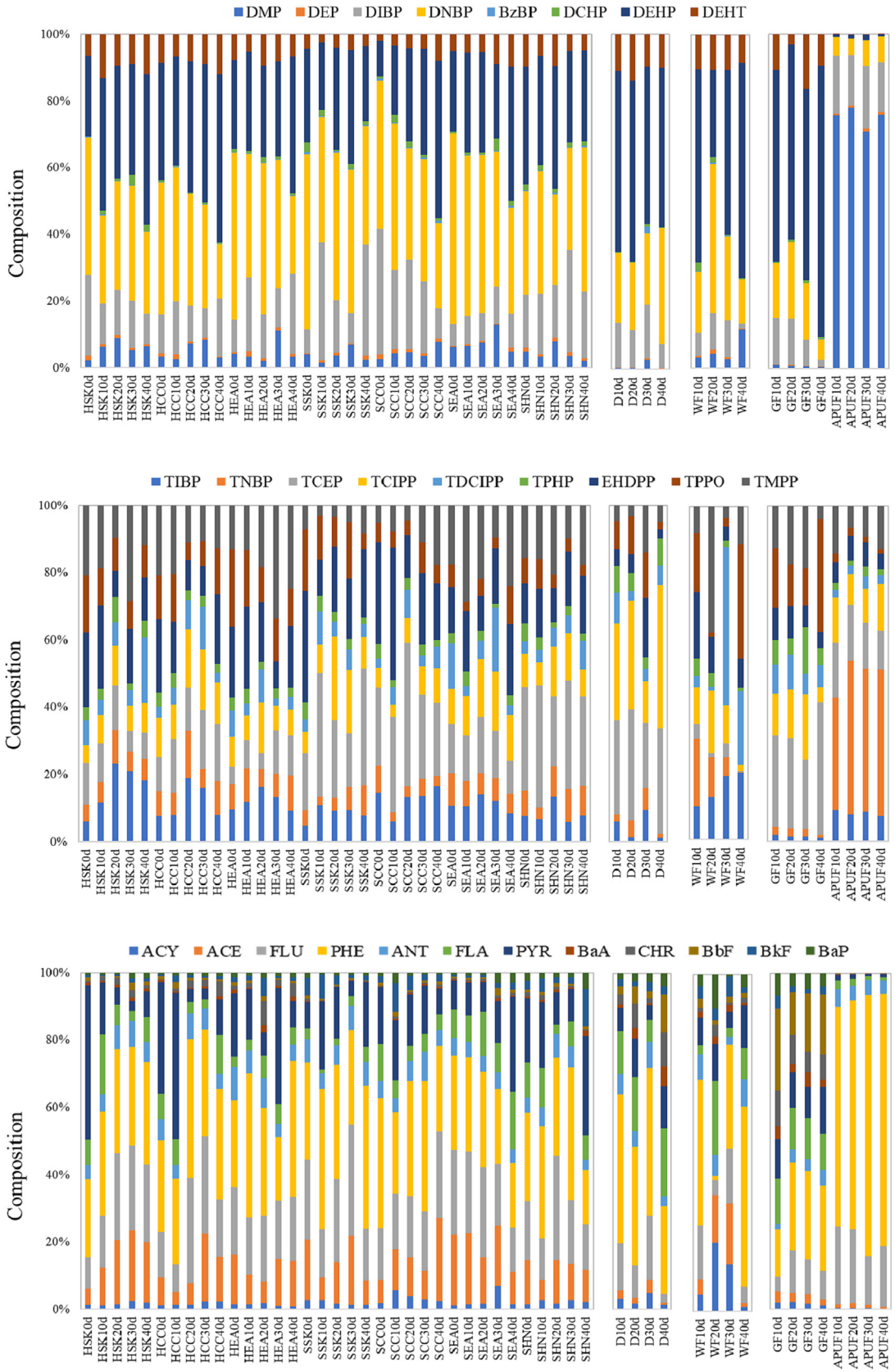

Fig. 2. Compositions of PAEs, OPFRs and PAHs in indoor plant leaves (H: hydroponic, S: soil-cultured), dust (D), window film (WF), and active gaseous (APUF) and particle (GF) samples.

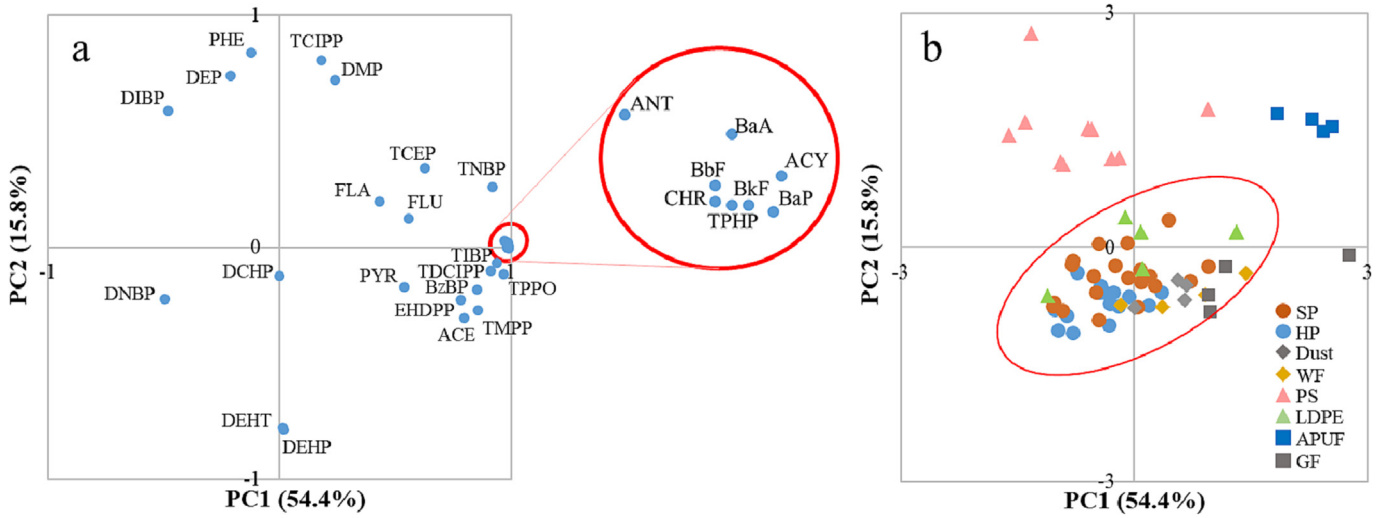

Fig. 3. Principal component loading plot (a) and score plot (b).

PBDEs (Wang et al., 2015). Another study using chambers to expose wheat to polybrominated diphenyl ethers (PBDEs) via various routes, suggested that most of the PBDE burdens (>80 %) in wheat leaves originated from foliage uptake rather than root uptake (0.34–18.7 %) (Zhu et al., 2020). However, root uptake from soil was still important (47.5–88.5 %, mean: 71.0 %) for soil cultured plants in the real indoor environment of this study, which was in a line with previous studies (Wang et al., 2020; Zhang et al., 2021). The different result may be due to the different environment, contamination, plant species or chemical's properties.

As shown in Fig. 5, significant negative correlations were found between R_f and logK_{oa} and R_f and logK_{ow} of compounds in different plants. Relatively low foliage uptake ratios but high root uptake ratios were found for SVOCs with high K_{ow} values, suggesting that hydrophobic compounds are more likely to be absorbed by plant roots than leaves. This

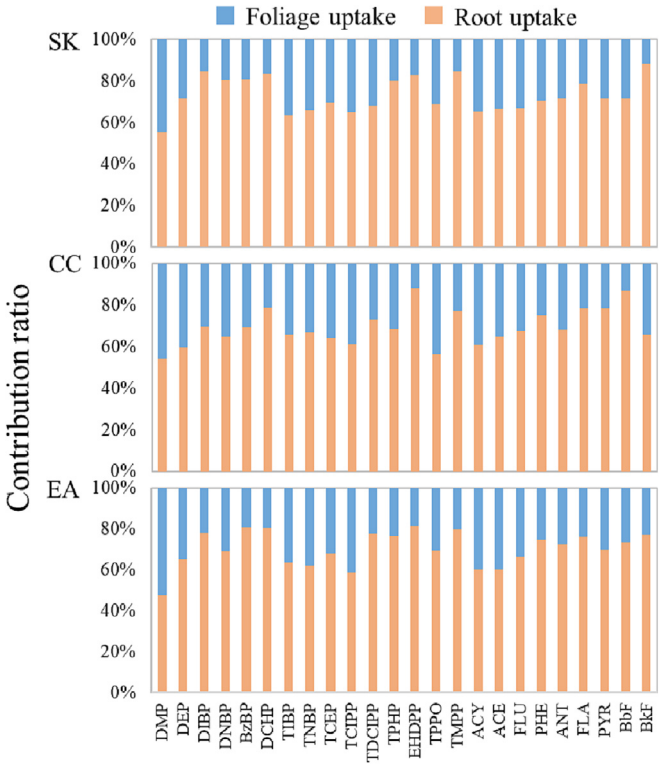

Fig. 4. Foliage and root uptake ratios for PAEs, OPFRs, and PAHs in different plants.

may be attributed to the transpiration pull. A previous study found that the chemicals with high hydrophobicity could be taken up by binding with the proteins in plant roots, carried to root lipid constituents, but be harder to be translocated to shoots (Liu et al., 2019). Another study also suggested that it is the combination of the solubility of chemicals in water and the solubility in cell membrane that determines the root uptake and translocation of chemicals in plant, considering that these chemicals absorbed by plant root must penetrate the epidermis, cortex, endodermis, and pericycle to reach the xylem (McFarlane and Berry, 1974; Sheppard, 1996; Trapp et al., 1994; Trapp and McFarlane, 1994). Since hydrophobic compounds may be adsorbed or stored in lipid, cell wall, or cell membrane, storage lipid-water partition coefficient (K_{sw}) or membrane lipid-water partition coefficient (K_{mw}) may be a more appropriate control factor for the acropetal translocation of SVOCs than K_{ow}. This hypothesis could be confirmed by better correlations of R_f vs K_{sw} and R_f vs K_{mw} than R_f vs K_{ow} (Fig. 5). Moreover, based on the *R*-value (Fig. 5 c and d), the storage lipid content (i.e., K_{sw}) may better explain the translocation characteristics of SVOCs than membrane lipid content (K_{mw}).

Foliage uptake ratios were higher for the SVOCs with lower K_{oa} values (Fig. 5b), suggesting the relatively volatile compounds were absorbed by leaves. However, foliage uptake ratio was not directly negatively correlated with logK_{oa}, but was segmented linear with logK_{oa} with three segments (Fig. 5b): For SVOCs with logK_{oa} of 6.34–8.81, their foliage uptake ratios were significantly negatively correlated with the logK_{oa}. For SVOCs with logK_{oa} of 9.77–11.91, their foliage uptake ratios were negatively correlated with the logK_{oa} again, but with different linear relationships and slope factors. Whereas, for SVOCs with logK_{oa} of 8.81–9.77, their foliage uptake ratios seemed independent of logK_{oa}. This was in consistent with a mathematical analysis by McLachlan M S (McLachlan, 1999), who elucidated that foliage uptake of SVOCs occurs primarily via one of three processes: equilibrium partitioning between the vegetation and the gaseous phase, kinetically limited gaseous deposition, and particle-bound deposition. He developed a framework using the relative differences in accumulation behavior as a function of chemical's K_{oa} for identifying the major foliage uptake process. The framework suggests that for compounds with low logK_{oa} (< ~ 8.5), their foliage uptake may be significantly correlated with logK_{oa}, and depend on the equilibrium partitioning between the plant and the gaseous phase. For compounds with intermediate logK_{oa} (~ 8.5–11), their foliage uptake may be independent of K_{oa}, but still dominated by the kinetically limited gaseous deposition. In this case, the storage capacity of plant for chemical with logK_{oa} of 8.5–11 is too high to reach an equilibrium. For compounds with high logK_{oa} (> ~ 11), their foliage accumulation may be in line with K_{oa} again, and primarily by particle-bound deposition.

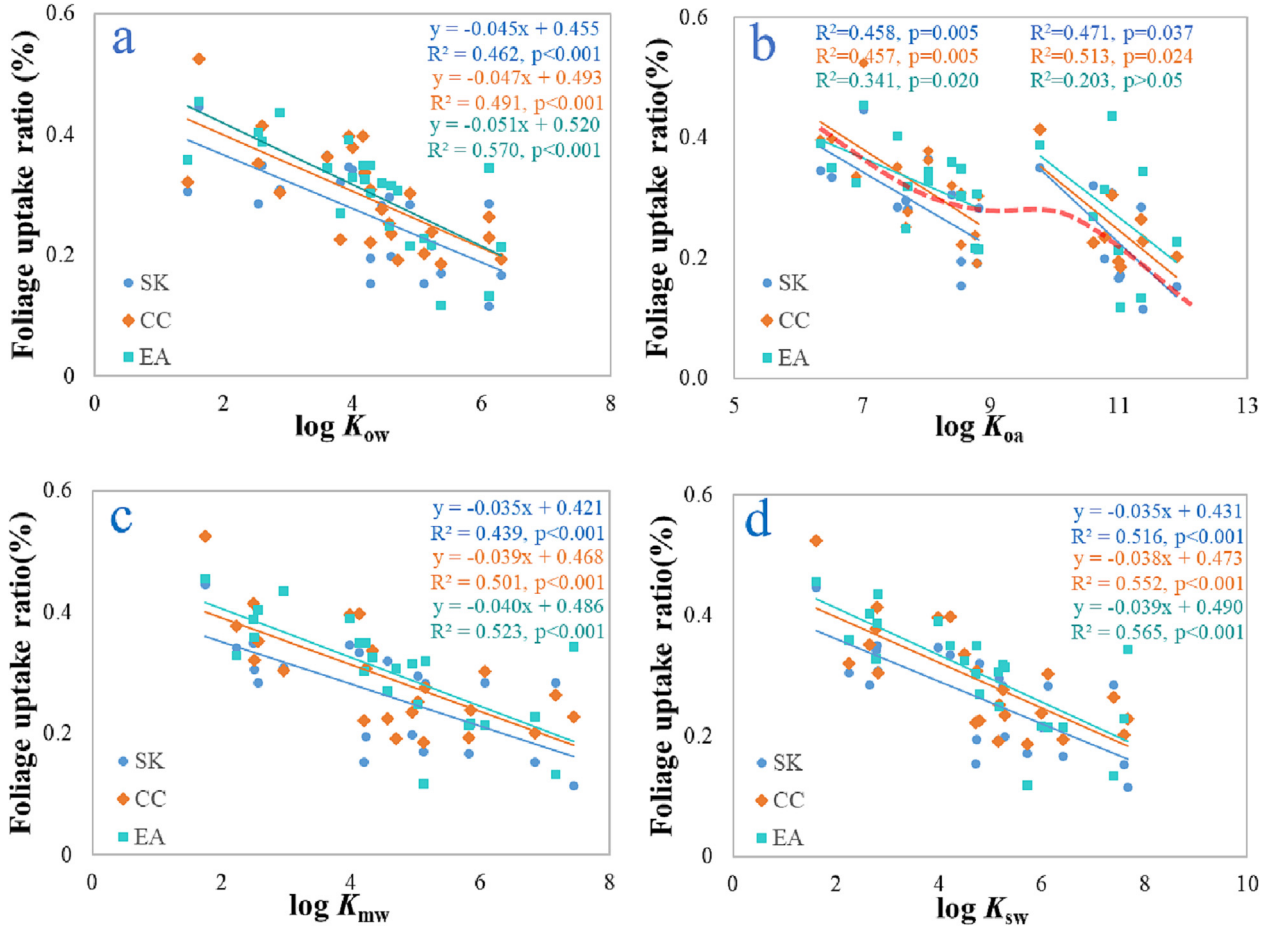

Fig. 5. Linear regression of R_f and K_{ow} (a), K_{oa} (b), K_{mw} (c), and K_{sw} (d).

3.5. Contributions of gaseous and particle absorptions to the foliage uptake of SVOCs

Previous studies focused on the behaviors of SVOC congeners in the plants (Sun et al., 2019; Wang et al., 2011; Zhang et al., 2021) were not based on actual experiments in indoor environment. It is reported that PBDE levels in the wax of leaf were significantly higher than those in the inner leaf, stem, and root (Zhu et al., 2020). Thus, plant leaves have the best potential to be the biomonitor of SVOCs in indoor environment. Nevertheless, research on foliar uptake of SVOCs is still limited, as well as the computational model for the contribution of gaseous and particulate SVOC uptakes. The model we used here helps us easily calculate the contribution ratios of gaseous and particle SVOCs in plant leaves, which makes it possible to reflect the contaminants of gaseous and particle SVOCs in indoor environment by testing SVOC levels in plant leaves.

Three pairs of chemicals, TIBP vs TDCIPP, TNBP vs TPHP, and BkF vs BaP from the same chemical group used in this estimation obtained the meaningful contribution values (>0). The contribution ratios of gaseous

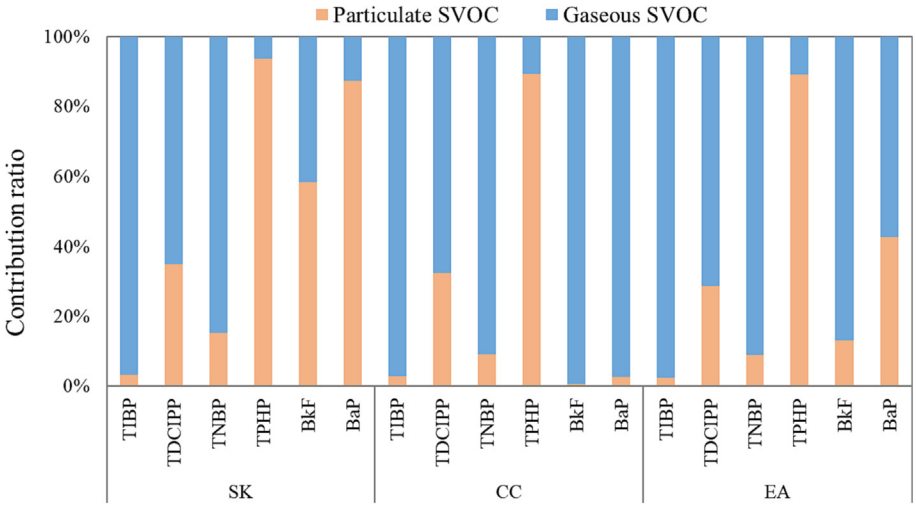

Fig. 6. Contribution ratios of foliage uptakes via gaseous and particle phases on the typical SVOCs in different plant leaves.

and particle absorptions to these pairs of chemicals in the hydroponic SK, CC, and EA are shown in Fig. 6. The contribution ratios of particle uptake were 2.3 %–3.1 % for TIBP, 28.8 %–34.9 % for TDCIPP, 9.0 %–15.1 % for TNBP, 89.2 %–93.7 % for TPHP, 0.5 %–58.3 % for BkF, and 2.6 %–87.4 % for BaP, respectively. Similar contributions of gaseous and particle uptakes were found for TIBP vs TDCIPP and TNBP vs TPHP in the three kinds of plants. Generally, congener with the lower K_{oa} value in the paired chemicals has a higher gaseous uptake ratio, since it is inclined to exist as gaseous form. A chemical's volatility and K_{oa} value can significantly influence the air-particle partitioning and subsequently affect its foliage uptake. Collins et al. (Collins et al., 2006) suggested that SVOCs with $\log K_{oa} > 11$ are more inclined to be particle-bound and can desorb from the particle into the leaf. However, another exposure environment showed that particle-bound PBDEs were the main source of PBDEs with $\log K_{oa}$ range of 6.55–9.66 in wheat leaves (Zhu et al., 2020). Thus, K_{oa} may be not the only determining factor for the foliage uptake of a certain compound. Some SVOCs with $\log K_{oa} < 11$, such as TPHP (10.8), in leaves in this study may still derive from particle phase. Moreover, the composition of plant (e.g., content of lipid, fiber, and carbohydrate) can also significantly affect the uptake of organic chemicals (Bohme et al., 1999; Simonich and Hites, 1994). Thus, the different compositions of the plants and their specific absorption mechanism of PAHs may be the reason of the different contributions of gas and particle uptakes for BkF and BaP in SK leaves compared with those in the other two plants.

Significant correlations were found between SVOC concentrations in plant leaves (both hydroponic and soil cultured) and these in air particle or gaseous phases, indicating that indoor ornamental plants have the capacity to act as the biosamplers of SVOCs in indoor air. Meanwhile, hydroponic plant can be regarded as a better biomonitor due to its simple sources (less root uptake). SVOC concentrations in the hydroponic CC were relatively higher than those in the hydroponic SK and EA, and even more significantly correlated to SVOC levels in ambient air. Thus, the hydroponic CC leaf acted as a more effective biosampler than the other two types of plants.

3.6. Limitations

This study is subject to several limitations. First, this experiment was conducted in a real indoor environment with fluctuating SVOC concentrations, which may cause an inconsistent foliar uptake speed and large deviation of SVOC concentrations in the tested plants during different sampling periods. Second, the concentrations of SVOCs in soil were not analyzed and discussed in this study, although as shown since the cultivated soils used for these plants were the same, we could still disentangle relative contributions. Third, the degradation of SVOCs in plants was assumed to be negligible. Fourth, the growth states of plants were considered similar in the hydroponic and soil matrices.

Despite the limitations, both hydroponic and soil cultured houseplants with the advantages of easy access, low cost, and more acceptable to participants, are qualified passive biosamplers in the indoor environment, where possible, we recommend using hydroponically grown plants as biosamplers.

4. Conclusion

Here, we investigated the relative contributions of root and foliar uptakes via gas and particle phases to the indoor ornamental plants for phthalates, OPFRs, and PAHs. Root uptake pathway is the main contribution way to most of the target chemicals in soil cultured plants, whereas foliar uptake via gaseous absorption and particle adsorption both contribute to the chemicals in hydroponic plants, and their contribution ratios depended on chemical hydrophilicity and lipophilicity. Overall, the model introduced in this study provided a novel method for calculating the ratios of different uptake pathways for plants, which contributes to a better understanding of the uptake mechanisms of SVOCs in plants.

CRediT authorship contribution statement

Yan Wang: Conceptualization, Writing – original draft, Writing – review & editing, Supervision, Project administration, Resources, Funding acquisition. **Zihao Zhang:** Methodology, Investigation, Formal analysis, Data curation, Writing – original draft. **Yue Xu:** Resources, Writing – review & editing, Funding acquisition. **Timothy F.M. Rodgers:** Methodology, Writing – review & editing. **Mukaddas Ablimit:** Investigation, Formal analysis. **Junze Li:** Investigation, Formal analysis. **Feng Tan:** Resources, Writing – review & editing.

Data availability

Data will be made available on request.

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.scitotenv.2023.163644.

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