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Improved Approaches for Modeling the Sorption of Phenanthrene by a Range of Plant Species

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Equilibrium sorption of phenanthrene and its relationship with plant lipid contents were investigated using roots and shoots of alfalfa, ryegrass, tomato, potato, carrot, cucumber, zucchini, and pumpkin. Lipid extractions using chloroform and hexane were compared, and the influence of dechlorophyllization on lipid determinations was evaluated. The sorption isotherms were close to linear ($R^2 > 0.923$, $P < 0.05$) and the plant–water partition coefficients (K_{pw}) of phenanthrene obtained from the isotherms exhibited significant and positive correlations with plant lipid contents ($R^2 > 0.664$, $P < 0.05$). The correlations were more significant ($R^2 > 0.906$, $P < 0.001$) when dechlorophyllization was included in the lipid extraction. The measured sorption was higher than that estimated using the octanol–water partition coefficient (K_{ow}) but was very close to the estimate using the triolein–water partition coefficient (K_{tw}). This study leads us to conclude that dechlorophyllization is necessary for plant lipid determination and that K_{tw} is more accurate as a substitute for the lipid–water partition coefficient (K_{lp}) than K_{ow} . These novel approaches may provide substantial improvements in the application of partition-limited models for the estimation of plant uptake of organic contaminants.

Introduction

Plant uptake from soils is an important pathway for hydrophobic organic contaminants (HOCs) into the food chain (1, 2). An improved understanding of the uptake and accumulation of HOCs by plants will have considerable benefits for risk assessment associated with soil contamination and control of food contamination (3).

The uptake of an organic contaminant by plants from soil is considered to depend on the properties of the contaminant, the plant species, and the soil. A number of studies have observed unusual uptake of HOCs from soil via the roots by some plant species such as zucchini, squash, and carrot (4–6). In addition, plant composition can be expected to influence plant uptake and accumulation of organic contaminants. Lipids are an essential constituent of all plant

cells and include fatty acids, free sterols, acylglycerols, and polar lipids (7, 8). A number of studies (9–14) have reported the significant influence of lipid contents on the sorption or uptake of organic contaminants based on correlation analysis. For example, Simonich and Hites (9) observed higher concentrations of polynuclear aromatic hydrocarbons (PAHs) in plants with higher lipid contents. Thus, a number of models use plant lipid content as a key input parameter to predict plant uptake of HOCs (15–18), and Müller et al. (15) were the first investigators to use multicompartment modeling to describe leaf (lipid)/atmosphere partitioning of HOCs. However, a thorough understanding of the role of plant lipids in uptake of organic contaminants by a range of plant species is still lacking, and there is very little information readily available on the lipid contents of different plant species.

The uptake of organic contaminants by plants has been shown to be a passive, diffusive process, with the exception of a few hormone-like chemicals such as the phenoxy acid herbicides for which there is some evidence of active uptake (19). Chiou et al. (18) suggested that the passive transport of HOCs to plants may be treated as a series of partitions between plant water and plant components and proposed a partition-limited model for plant passive uptake of organic contaminants from soil or water. This has been tested in some plant species with satisfactory results (13, 14, 20). The model analysis indicated that plant lipid content was predominant for the sorption or uptake of HOCs, and therefore Chiou and co-workers (13) further simplified the partition-limited model into a lipid model. However, they observed that sorption as estimated by the lipid model was notably lower than the measured sorption of lindane and hexachlorobenzene by roots and shoots of wheat seedlings. They ascribed the discrepancy to the likely underestimation of the plant lipid contents and less effectiveness of octanol as a partition medium than plant lipids. Barbour et al. (14) also observed underestimation of sorption of benzene, 1,2-dichlorobenzene, and phenanthrene by shoots of annual rye, tall fescue, red fescue, and spinach and by roots of annual rye, and they speculated that plant lipids were a more effective partition solvent than octanol. To address these speculations it is necessary to investigate the accuracy of plant lipid determination and to evaluate the appropriateness of using the octanol–water partition coefficient (K_{ow}) to substitute for the lipid–water partition coefficient (K_{lp}) in modeling plant uptake of HOCs.

In the present study we sought to elucidate the role of lipids in plant sorption of phenanthrene and to test and validate the partition-limited model for plant uptake of phenanthrene by using the roots and shoots of eight plant species. Specific attention was given to progressive improvement of the application of the partition-limited model by considering (1) the effectiveness of different polarities of lipid extraction solvents (hexane and chloroform) on sorption estimates, (2) improvement resulting from dechlorophyllization of plant shoots for lipid extraction, and (3) the adequacy of using K_{ow} to substitute for K_{lp} in modeling plant uptake of phenanthrene.

Materials and Methods

Chemical. Phenanthrene was purchased from Acros Organics (New Jersey) with a labeled purity of >99% and used as received. The logarithmic octanol–water distribution coefficient is 4.46 (21), and the logarithmic triolein–water distribution coefficient is 4.84 (14). Stock phenanthrene solution was prepared at a concentration of 1000 mg L⁻¹ in MeOH. The working solution (1 mg L⁻¹) was prepared by

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diluting the stock solution with the background solution (half-strength Hoagland solution as the matrix and 200 mg L⁻¹ NaN₃ as the biocide).

Plants and Plant Composition. Italian ryegrass (*Lolium multiflorum* L.), alfalfa (*Medicago sativa* L.), pumpkin (*Cucurbita pepo* L.), zucchini (*Cucurbita moschata* Poir.), cucumber (*Cucumis sativus* L.), tomato (*Lycopersicon esculentum* Mill.), potato (*Solanum tuberosum* L.), and carrot (*Daucus carota* L. var. *sativa* DC) were used as the test plants. Growth conditions are given in the Supporting Information. At harvest, plants were carefully removed from the growth medium, separated into roots and shoots, blotted dry with tissue paper, and immediately weighed to determine their fresh weights. The root and shoot samples were then frozen at -80 °C overnight, freeze-dried for 48 h in a lyophilizer (FD-1, Beijing Boyikang Instruments Ltd.), and weighed to determine their dry weights. The water content was calculated from the difference between the fresh and dry weight divided by the fresh weight. The dried roots and shoots were then ground separately and sieved (<0.25 mm) prior to determination of lipid content and the sorption experiments.

Lipid Quantification. Lipid determination followed the same principles as employed previously (22–24). Subsamples of the dried plant materials (0.4–0.6 g) were subjected to Soxhlet extraction with 100 mL of mixed chloroform and methanol (2:1, v/v) for 12 h. The extract was then condensed in a rotary evaporator to approximately 5 mL and subsequently dried under a stream of nitrogen. The lipid material was removed by two sequential extractions with 20 mL of solvent (either chloroform or hexane), filtered through No. 5 Whatman filter paper into a preweighed glass tube to remove precipitates, and completely dried to a constant weight. The weight of the residue was recorded as the plant lipid content. The remainder of the plant excluding the water and lipids was defined as the plant carbohydrates.

Lipid contents in shoots with dechlorophyllization were determined by adding a step following the Soxhlet extraction to remove chlorophyll and other pigments in shoots using an unpaired aminopropyl column following the procedure described by Rizov and Doulis (25). Briefly, the whole lipid extract was condensed to approximately 5 mL, then loaded as a continuous plug into the unpaired aminopropyl column (500 mg/3 mL, from Agela Technology, detailed description in Supporting Information), and then washed with 5 mL of chloroform/acetone (4:1). The flow velocity was maintained at approximately 1 mL min⁻¹, and pressure was applied with a 20 mL glass syringe. The eluate was then dried under a stream of nitrogen. Other steps were the same as described above. All lipid analyses were performed in triplicate.

Sorption Studies. Sorption of phenanthrene by freeze-dried and pulverized plant materials was studied using a batch equilibration technique in triplicate. A series of phenanthrene solutions with a range of initial concentrations (0.05–1.00 mg L⁻¹) were prepared using half-strength Hoagland solution as the matrix and with 200 mg L⁻¹ NaN₃ as a biocide. A subsample of 0.005 g of dry plant material and 20 mL of phenanthrene solution were combined in 40 mL glass centrifuge tubes with Teflon-lined caps. The solid-to-liquid ratios were chosen to allow 30% to 80% of the added solute to be sorbed at equilibrium. For each isotherm experiment, controls were prepared for quality assurance. Blank control contained solute and water but no plant material, and it was used to measure any phenanthrene losses. Recoveries suggested that the losses of phenanthrene by evaporation, degradation, and sorption to the glass vials during the experiment were negligible. Background control contained plant material and water but no solute, and it was used to detect any contamination. The tubes were shaken for 48 h on a tumble shaker at 100 rpm at 20 ± 1 °C. Kinetic measurements showed that 24 h was sufficient time for the

sorption of phenanthrene by plant material to attain equilibrium. Following the equilibration and subsequent 30 min sedimentation of plant materials, the vials were centrifuged at 1000g for 30 min and the supernatant from each tube was analyzed for solute. The phenanthrene concentration in the plant phase was calculated from the difference between the initial and final concentrations in the water phase because the loss of solute by processes other than sorption was found to be negligible. The standard deviation of six replicate determinations of phenanthrene standard solution at a concentration of 1.00 mg L⁻¹ was 1.6% after 72 h of shaking. Phenanthrene concentrations were measured using an Agilent Technologies 1200 series HPLC equipped with a photodiode array detector. Phenanthrene was determined using an Eclipse XDB-C18 column (5 μm, 4.6 × 150 mm), a mobile phase of methanol/water (90/10), and absorbance at a wavelength of 254 nm. Data were analyzed using the Origin 7.0 software.

The Partition-Limited Model. The partition-limited model for the plant sorption of HOCs from water can be described by the following three models (13): the sorption model,

$$Q_{eq} = C_w K_{pl} \quad (1)$$

the composition model,

$$Q_{eq} = C_w (f_{lip} K_{lip} + f_{ch} K_{ch} + f_{pw}) \quad (2)$$

and the lipid model

$$Q_{eq} = C_w f_{lip} K_{lip} \approx C_w f_{lip} K_{ow} \quad (3)$$

where Q_{eq} is the concentration of solute in the plant (mg of contaminant/kg of plant material) at equilibrium. C_w is the concentration of solute in water (mg of contaminant/kg of water) at equilibrium. In eq 1 the ratio Q_{eq}/C_w (K_{pl}) is equivalent to the slope of the corresponding sorption isotherm.

Solute sorbed to plant materials is distributed between water and various plant organic constituents, which can be divided into two major categories: lipids and carbohydrates. Therefore, sorption can be described as the composition model, where K_{lip} and K_{ch} are the lipid–water partition coefficient and the carbohydrate–water partition coefficient of the solute, respectively. f_{lip} , f_{ch} , and f_{pw} are the respective weight fractions of lipids, carbohydrates, and water in the plant. The K_{ch} value used in eq 2 was assumed to be 3 for compounds with $\log K_{ow} \geq 4.0$ (18). Even though lipids make up a small fraction of the plant mass, they are the predominant storage site of phenanthrene ($\log K_{ow} = 4.46$). As such, the partition contribution by carbohydrates becomes unimportant relative to that by lipids, and the sorption of phenanthrene into plant materials can be estimated simply by the lipid model (13). Moreover, K_{lip} of a solute can be replaced by the corresponding K_{ow} as an approximation (26).

Results

Plant Composition. Table 1 shows the growth periods, water contents, and lipid contents of the plant materials on a dry weight basis. The water contents varied from 86.82% to 96.20% and were slightly higher than the values in the USDA Nutrient Database (27), possibly because the plants were grown hydroponically. Two sets of lipid contents, determined by dissolving in chloroform and in hexane, are given. The plants were found containing a wide range of lipid contents. The lowest (3.01%) root lipid content dissolved in chloroform was found in ryegrass and the highest (7.97%) in carrot, and the corresponding values in shoots were 4.07% in tomato and 11.75% in ryegrass. Root lipid contents dissolved in

TABLE 1. Determined Weight Percent Composition of the Plant Species Studied

plant species	growth period (wk)	plant part	water (%)	lipid—chloroform, dry basis (%) ^a	lipid—hexane, dry basis (%) ^b
alfalfa	6	roots	87.86	3.40 ± 0.41	1.74 ± 0.07
		shoots	86.82	4.19 ± 0.50	2.43 ± 0.43
ryegrass	6	roots	88.97	3.01 ± 0.22	2.43 ± 0.21
		shoots	90.08	11.75 ± 0.76	8.69 ± 0.03
tomato	7	roots	93.75	3.78 ± 0.23	2.98 ± 0.15
		shoots	96.20	4.07 ± 0.34	3.70 ± 0.05
potato	7	roots	94.25	6.04 ± 0.15	3.77 ± 0.23
		shoots	93.62	5.88 ± 0.37	4.06 ± 0.31
carrot	11	roots	90.75	7.97 ± 0.39	4.41 ± 0.78
		shoots	90.27	6.23 ± 0.34	4.85 ± 0.01
cucumber	5	roots	95.32	4.75 ± 0.67	3.93 ± 0.57
		shoots	96.13	6.44 ± 0.13	3.38 ± 0.57
zucchini	5	roots	93.07	6.60 ± 0.05	4.45 ± 0.02
		shoots	94.84	5.61 ± 0.36	3.86 ± 0.31
pumpkin	5	roots	93.53	6.24 ± 0.17	4.39 ± 0.21
		shoots	92.69	5.86 ± 0.24	3.35 ± 0.34

^a Lipid contents dissolved in chloroform. Data are expressed as mean ± SE, *n* = 3. ^b Lipid contents dissolved in hexane. Data are expressed as mean ± SE, *n* = 3.

FIGURE 1. Sorption of phenanthrene by ryegrass roots on dry weight basis: experimentally determined values vs those estimated from two sets of lipid contents (dissolved in chloroform and hexane) and $\log(K_{ow})$ and also those estimated from the two sets of lipid contents and $\log(K_{tw})$. Error bars represent the standard deviations of triplicate samples.

hexane ranged from the lowest (1.74%) in alfalfa to the highest (4.45%) in pumpkin, and values in shoots ranged from 2.43% in alfalfa to 8.69% in ryegrass. The lipid contents dissolved in chloroform were higher than those dissolved in hexane across all the plant materials. However, there were no clearly discernible trends among the plant species when the results from the two sets of lipid contents were combined. Alfalfa, tomato, and especially ryegrass had higher lipid contents in shoots than in roots when both lipid extraction solvents were employed.

Sorption Results. Kinetic plant sorption for phenanthrene reached equilibrium in 24 h (shown in Supporting Information, S1), which is consistent with the results of previous studies (9, 13, 14). Figure 1 displays the sorption of phenanthrene by ryegrass roots as an example, and the sorption data for all the root samples are given in Supporting Information (S2). Sorption isotherms of the plant roots are

TABLE 2. Experimental Values and Goodness of Fit (R^2) of the Plant–Water Partition Coefficient (K_{pl}) for Plant Roots and the Corresponding Lipid–Water Partition Coefficients $\log(K_{lip})$

plant species	plant–water partition coefficient, K_{pl} (L/kg), dry basis ^a	R^2	$\log(K_{lip})$, chloroform	$\log(K_{lip})$, hexane
alfalfa	2367 ± 22	0.988	4.84	5.13
ryegrass	2101 ± 31	0.993	4.84	4.94
tomato	2560 ± 14	0.991	4.83	4.93
potato	4223 ± 26	0.998	4.84	5.05
carrot	5109 ± 78	0.997	4.81	5.06
cucumber	3323 ± 39	0.994	4.84	4.93
zucchini	4579 ± 36	0.992	4.84	5.01
pumpkin	4193 ± 48	0.998	4.83	4.98
average			4.83	5.00

^a Data are expressed as mean ± SE, *n* = 3.

close to linear over the range of concentrations studied, with regression R^2 values from 0.988 to 0.998 (Table 2).

Values of the plant–water partition coefficients (K_{pl}), the slope of the sorption isotherm, varied from 2101 L kg⁻¹ to 5109 L kg⁻¹ for the roots of all eight plant species (Table 2), but when normalized to the chloroform-dissolved lipid contents, the corresponding lipid-normalized partition coefficients ($\log(K_{lip})$), obtained by dividing K_{pl} by the lipid content, were fairly consistent (4.81–4.84) (Table 2). However, the values of $\log(K_{lip})$ were less consistent when normalized to the hexane-dissolved lipid contents (4.93–5.13). When K_{pl} was plotted against the lipid contents (Figure 3 A), positive correlations were found between the K_{pl} values and the lipid contents obtained using both extraction solvents. The correlation between K_{pl} and the chloroform-dissolved lipid contents ($R^2 = 0.989$, $P < 0.0001$) was more highly significant than that between K_{pl} and hexane-dissolved lipid contents ($R^2 = 0.800$, $P < 0.01$).

Sorption of phenanthrene by ryegrass shoots and the shoots of all eight plant species are displayed in Figure 2 and in the Supporting Information (S3), respectively. The shoot sorption isotherms were similar to those of the roots in that they were close to linear over the concentration range studied with regression R^2 values ranging from 0.923 to 0.998 (Table 3).

Values of the plant–water partition coefficients ($\log(K_{pl})$) for plant shoots and the corresponding lipid-normalized

- measured sorption
- estimated with K_{ow} and lipid content from chloroform
- ▲ estimated with K_{ow} and lipid content from hexane
- estimated with K_{ow} and lipid content from chloroform & dechlorophyllization
- △ estimated with K_{ow} and lipid content from hexane & dechlorophyllization
- × estimated with K_{tw} and lipid content from chloroform & dechlorophyllization
- * estimated with K_{tw} and lipid content from hexane & dechlorophyllization

FIGURE 2. Sorption of phenanthrene by ryegrass shoots on dry weight basis: experimentally determined values vs those estimated from two sets of lipid contents without dechlorophyllization and $\log(K_{ow})$, those estimated from two sets of lipid contents with dechlorophyllization and $\log(K_{ow})$, and those estimated from two sets of lipid contents with dechlorophyllization and $\log(K_{tw})$. Error bars represent the standard deviations of triplicate samples.

FIGURE 3. Correlation between plant–water partition coefficients K_{pl} of plant roots (A) and shoots (B) for phenanthrene and two sets of lipid contents (dry weight basis). Error bars for K_{pl} and lipid content represent the standard deviations of triplicate samples.

partition coefficients ($\log K_{lip}$) are listed in Table 3. When K_{pl} was plotted against the lipid contents, positive correlations were found between the K_{pl} values and the lipid contents obtained by both extraction solvents as shown in Figure 3B. The K_{pl} for plant shoots was more closely correlated to the

TABLE 3. Experimental Values and Goodness of Fit (R^2) of the Plant–Water Partition Coefficient (K_{pl}) for Plant Shoots and Corresponding Lipid–Water Partition Coefficients $\log(K_{lip})$

plant species	plant–water partition coefficient, K_{pl} (L/kg), dry basis ^a	R^2	$\log(K_{lip})$, chloroform	$\log(K_{lip})$, hexane
alfalfa	1846 ± 18	0.988	4.64	4.88
ryegrass	4899 ± 134	0.923	4.62	4.75
tomato	1835 ± 73	0.991	4.65	4.70
potato	2737 ± 88	0.998	4.67	4.83
carrot	3771 ± 21	0.997	4.78	4.89
cucumber	1745 ± 49	0.994	4.43	4.71
zucchini	1935 ± 10	0.989	4.54	4.70
pumpkin	1466 ± 8	0.996	4.40	4.64
average			4.59	4.76

^a Data are expressed as mean ± se, $n = 3$

TABLE 4. Lipid Contents and Lipid–Water Partition Coefficients $\log(K_{lip})$ of Plant Shoots after Dechlorophyllization

plant species	lipid–chloroform		lipid–hexane	
	dry basis (%) ^a	$\log(K_{lip})$	dry basis (%) ^a	$\log(K_{lip})$
alfalfa	3.10 ± 0.04	4.77	2.25 ± 0.48	4.91
ryegrass	6.95 ± 0.05	4.85	6.94 ± 0.25	4.85
tomato	3.20 ± 0.10	4.76	3.20 ± 0.11	4.76
potato	4.09 ± 0.01	4.83	3.62 ± 0.36	4.88
carrot	4.93 ± 0.30	4.88	4.75 ± 0.53	4.90
cucumber	3.97 ± 0.21	4.64	2.47 ± 0.36	4.85
zucchini	2.90 ± 0.62	4.82	2.77 ± 0.92	4.84
pumpkin	2.94 ± 0.10	4.70	2.02 ± 0.26	4.86
average		4.78		4.86

^a Data are expressed as mean ± SE, $n = 3$.

lipid contents dissolved in hexane ($R^2 = 0.832$, $P < 0.01$) than to those dissolved in chloroform ($R^2 = 0.664$, $P < 0.05$).

Lipid Contents of Plant Shoot after Dechlorophyllization. Lipid contents in plant shoots dissolved in chloroform and hexane after dechlorophyllization are shown in Table 4. Comparing the results for all the plant species in Tables 1 and 4 we can deduce that the shoot lipid contents obtained without dechlorophyllization were 27.2 to 99.3% and 2 to 66% higher than those with dechlorophyllization in the lipid extraction procedure of the chloroform and hexane methods, respectively. Chloroform extracted more chlorophyll than did hexane. The differences in lipid contents between the two extraction solvents were reduced following the dechlorophyllization procedure. In addition, irrespective of the extraction method used, dechlorophyllization improved the correlation between the plant–water partition coefficients (K_{pl}) and the lipid contents (regression R^2 values changes from 0.832 to 0.959 for hexane and 0.664 to 0.906 for chloroform, shown in Figure 3B). The lines of K_{pl} plotted against lipid contents obtained by the two lipid extraction solvents were very similar to one another following dechlorophyllization (Figure 3B). Furthermore, dechlorophyllization increased the consistency between shoots and roots in lipid–water partition coefficients ($\log K_{lip}$) as can be observed in the data in Tables 2–4.

Sorption Estimation. Sorption estimated by the lipid model with plant lipid contents and K_{ow} and K_{tw} values are plotted in Figures 1 and 2 for ryegrass and in the Supporting Information (S2 and S3) for all plant species. Except for cucumber and pumpkin shoots estimated by lipid contents dissolved in chloroform, the estimated sorption with K_{ow} for all the plant materials was lower than the measured sorption,

irrespective of which lipid extraction solvent was used. We observed that the values of the lipid–water partition coefficient $\log K_{lip}$ for plant roots (Table 2) and for plant shoots after dechlorophyllization (Table 4) were much closer to the value of the triolein–water partition coefficient $\log K_{tw}$ (4.84). We therefore proceeded to estimate the sorption using K_{tw} as a substitute for K_{lip} and a conspicuous improvement in sorption estimation was obtained. The estimation lines using the lipid contents from chloroform and the measured sorption isotherms almost overlap each other for all the plant roots (shown in Supporting Information, S2). In the case of the plant shoots, very good estimation was obtained using K_{tw} and the lipid contents by hexane extraction with dechlorophyllization for all species and by chloroform extraction with dechlorophyllization with the exceptions of cucumber and pumpkin (shown in Supporting Information, S3). Chloroform appeared to be a good extraction solvent for both roots and shoots of all the plant materials tested except cucumber and pumpkin shoots.

Discussion

Significant positive correlations existed between the plant–water partition coefficients (K_{pl}) and the plant lipid contents. The variability of the coefficients among plant materials was minimized after normalization of the plant–water partition coefficients (K_{pl}) to the lipid contents. When included in the lipid purification procedure, dechlorophyllization increased the strength of the relationship between the plant–water partition coefficients (K_{pl}) and the lipid contents of plant shoots. This suggests that the lipid–water partitioning may be one of the key processes involved in plant uptake and translocation of HOCs by plants or plant components. Plant lipids are primarily composed of long chain fatty acids. Their highly lipophilic properties determine their hydrophobic quality and their important role in plant uptake of HOCs.

There are various extraction and purification methods for plant lipids (8, 22–25, 28, 29) including liquid–liquid extraction, Soxhlet extraction, and accelerated solvent extraction. A mixture of chloroform and methanol at a ratio of 2:1 (v/v) is accepted as a superior extractant for the thorough extraction of lipids from plant materials. However, this mixture tends to co-extract appreciable amounts of natural non-lipid materials. The simplest method for eliminating the non-lipid compounds consists of evaporating the solvents, followed by dissolving the residual lipids in a small volume of a relatively nonpolar solvent such as chloroform or hexane. Our results demonstrate that even following such procedure a significant amount of chlorophyll remains in plant lipids as evidenced by the observation that the lipid contents in shoots obtained with dechlorophyllization included in the lipid extraction procedures were lower than those without dechlorophyllization. In addition, it was observed that the peak for chlorophylls at m/z 872 was reduced by 92% with dechlorophyllization when we analyzed the lipid composition using TOF MS (Waters, U.S.A.) (shown in Supporting Information, S4). A dechlorophyllization procedure is therefore necessary for lipid determination. The results also indicate that dechlorophyllization can decrease the differences in lipid contents between polar (chloroform) and nonpolar (hexane) extraction solvents. Furthermore, very consistent lipid–water partition coefficients ($\log K_{lip}$) were achieved between plant shoots and roots by adding dechlorophyllization to the lipid extraction procedure. Barbour et al. (14) speculated that root lipids might be more hydrophobic than shoot lipids on the basis of the data for 1,2-dichlorobenzene and phenanthrene sorption by roots and shoots of annual rye. Our results illustrate that if the influence of chlorophyll on lipid determination is eliminated, the partition capacities of shoot lipids (represented by the $\log K_{lip}$ values) are analogous to those of root lipids.

Previous investigations and the present study have obtained good linear relationships between lipid contents and sorption of HOCs by plants. However, using the lipid model has provided a lower predicted sorption of phenanthrene than the measured values. Considering the imperative to substantiate the accuracy of plant lipid determinations we compared two lipid extraction solvents, chloroform (a polar type) and hexane (a nonpolar type), with or without dechlorophyllization of plant shoots. Estimation of sorption was not improved either by choice of lipid extraction solvent or by addition of dechlorophyllization in lipid extraction. This suggests that inaccuracy caused by the substitution of K_{ow} for K_{lip} might make an important contribution to the underestimation of sorption. The K_{ow} value is generally viewed as an indicator of a tendency of a compound to partition into an organic phase, and most models of organic contaminant accumulation in plants assume that the lipophilic storage compartment behaves like octanol. However, the present study showed a lower estimated sorption than the experimental data by using K_{ow} to substitute lipid–water partition coefficient K_{lip} . Kömp and McLachlan (30) observed that the plant/air partition coefficients (K_{pa}) for polychlorinated biphenyls in five grass and herb species were different from their K_{ow} values. Triolein ($C_{57}H_{104}O_6$), a common triglyceride, is a slightly better solvent than octanol. A very good estimation was achieved by using the triolein–water partition coefficients (K_{tw}) in place of K_{ow} to model contaminant partitioning and bioaccumulation (26, 31, 32). The present study has confirmed the possible usefulness of K_{tw} in modeling the plant/water partition for phenanthrene. Although we tested only K_{tw} to substitute for the plant/water partition (K_{pl}) in modeling, it is likely that it would also form a reasonable approximation to the partition between plant and atmosphere (K_{pa}).

The major contribution of the present study is our suggestion that a dechlorophyllization step should be added to the extraction procedure for the determination of lipids, especially in plant shoots or leaves containing large amounts of chlorophylls. In the estimation of plant equilibrium uptake of HOCs, use of the partition-limited model K_{tw} may be preferable to K_{ow} to substitute for the lipid–water partition coefficient K_{lip} . Although the improved model can accurately predict the sorption of phenanthrene by plants, studies on the nature of the plant contaminant storage properties are necessary in order to provide a general mechanism for support of this approach.

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Supporting Information Available

Plant growth conditions, the performance of the unpaired aminopropyl column from Agela Technology, kinetic sorption results for phenanthrene, sorption of phenanthrene by the roots and shoots of eight plant species, and TOF mass results.

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**Improved approaches for modeling the sorption of phenanthrene by
a range of plant species**

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Supporting Information: 7 pages, 4 figures.

Plant growth conditions:

Seeds were purchased from the Chinese Academy of Agricultural Sciences, Beijing, China. With the sole exception of potato, they were disinfected in 10% H₂O₂ (wt : wt) solution for 10 min, followed by thorough washing with de-ionized water and subsequently germinated on moist filter paper in the dark. After germination the pre-germinated seedlings with seminal leaves were transplanted to a container with perlite as the growth medium, and a modified Hoagland hydroponic solution was used at dilution ratios of 1/16, 1/8 and 1/4 for each of three weeks in succession and of 1/2 for the remaining growth period. The Hoagland solution contained the following nutrients: 4 mM Ca(NO₃)₂, 1 mM KH₂PO₄, 5 mM KNO₃, 2 mM MgSO₄, 1 mM NH₄NO₃, 50 µM EDTA-Fe, 25 µM KI, 50 µM H₃BO₃, 9 µM MnSO₄, 0.77 µM ZnSO₄, 0.3 µM CuSO₄ and 0.1 µM Na₂MoO₄. Seedlings were grown under growth chamber conditions with a day: night cycle of 16 h: 8 h and a temperature regime of 25°C: 20°C. Relative humidity was maintained between 50% and 60% and a light intensity of 300 µmol photons m⁻² s⁻¹ during the whole experimental period. The growth period of different plant species varied from 5 to 10 weeks until they had developed mature roots.

The performance of the unpaired aminopropyl column from Agela Technology:

(1) framework:

(2) Primary indices of silica gel matrix

Mean particle size (μm)	Mean pore size ($\text{\AA}$)	Pore volume (cm^3/g)	Surface area (m^2/g)
45	60	0.8	480

Figure S1. Kinetics of phenanthrene sorption onto potato roots for the initial concentration of 1 mg/L. Error bars represent the standard deviation of three triplicate samples.

Figure S2. Sorption of phenanthrene by the roots of eight plant species on dry weight basis: experimentally determined vs estimated from two sets of lipid contents (dissolved in chloroform and hexane) and $\log(K_{ow})$ and estimated from two sets of lipid contents and $\log(K_{tw})$. Error bars represent the standard deviation of triplicate samples.

Figure S3. Sorption of phenanthrene by the shoots of eight plant species on dry weight basis: experimentally determined vs estimated from two sets of lipid contents without dechlorophyllization and $\log(K_{ow})$, estimated from two sets of lipid contents with dechlorophyllization and $\log(K_{ow})$ and estimated from two sets of lipid contents with dechlorophyllization and $\log(K_{tw})$. Error bars represent the standard deviation of triplicate samples.

Figure S4. TOF mass spectrum of ryegrass shoot lipid extract (a) with dechlorophyllization and (b) without dechlorophyllization. TOF MS was operated in positive electrospray ionization (ESI⁺) mode. ESI⁺ conditions were as follows: capillary and cone voltage of 3.5 kV and 30 V, extraction cone voltage of 2.0 V; source and desolvation temperatures of 80 °C and 150 °C; cone and desolvation gas (N₂) flow rates of 100 and 400 L per hour, respectively; Pump flow rate of 10.0 µL per minute. The full-scan spectrum ranging from m/z 50 to 1000 was recorded by TOF MS.