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Using a Novel Petroselinic Acid Embedded Cellulose Acetate Membrane to Mimic Plant Partitioning and In Vivo Uptake of Polycyclic Aromatic Hydrocarbons

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A new type of composite membrane is introduced to mimic plant uptake of hydrophobic organic contaminants (HOCs). Petroselinic acid (cis-6-octadecenoic acid), the major component of plant lipids, was embedded in the matrix of cellulose acetate polymer to form the petroselinic acid embedded cellulose acetate membrane (PECAM). Accumulation of the polycyclic aromatic hydrocarbons (PAHs) naphthalene (Nap), phenanthrene (Phe), pyrene (Pyr), and benz(a)pyrene (Bap) by PECAM was compared with their uptake by plants. The accumulation of Nap, Phe, Pyr, and Bap by PECAM reached equilibrium in 24, 48, 144, and 192 h, respectively. The petroselinic acid−water partition coefficients (log K_{pw}, 3.37, 4.90, 5.24, and 6.28 for Nap, Phe, Pyr, and Bap, respectively) were positively correlated with the hydrophobicity of the compounds (R^2 = 0.995) and were almost the same as the lipid-normalized root partition coefficients (log K_{lip}) for the corresponding compounds. Their relationship can be expressed as log K_{pw} = 0.98 log K_{lip}. The normalized plant uptake coefficients (log K_u) obtained by in vivo experiments with a range of plant species (2.92, 4.43, 5.06, and 6.13 on average for Nap, Phe, Pyr, and Bap, respectively) were slightly lower than those of the log K_{pw} values for the corresponding compounds, presumably due to their acropetal translocation and biodegradation inside plants. This work suggests that PECAMs can well mimic plant partitioning and in vivo uptake of PAHs and may have good potential as a nonliving accumulator to mimic plant uptake of PAHs and perhaps other HOCs.

Introduction

There has been much interest recently in the use of nonliving accumulators such as passive samplers to biomimetically accumulate hydrophobic organic contaminants (HOCs) in environmental matrices. By far the most commonly used passive samplers for this purpose are the lipid-containing passive samplers such as semipermeable membrane devices (SPMDs). Nonpolar organic solvents such as hexane and octanol or neutral lipids such as triolein are incorporated or embedded in the membranes (*1*−*5*). Lipid-containing SPMDs are composed of lipophilic materials and have been shown to have some potential to mimic the uptake of HOCs by living organisms (*4*). They have been used to predict the bioavailability of HOCs in aquatic environments (*4*−*8*). However, so far the employment of lipid-containing passive samplers to predict the bioavailability of HOCs to plants has been very limited (*9*−*11*).

The major components of plant roots can be categorized as plant lipids, carbohydrates, and water. Of these, root lipids play a key role in plant uptake of HOCs due to the strong tendency of HOCs to partition into root lipids (*12*−*14*), although recent studies by Zhang and Zhu (*15*) have suggested that plant carbohydrates also contribute to plant uptake of HOCs. Furthermore, the uptake of HOCs by plant roots has been shown to be a passive and diffusive process with the exception of a few hormone-like compounds (*16*). Therefore, the uptake of HOCs by plant roots is mainly characterized by lipid dominating partition processes and might be expected to be similar to their accumulation by lipid-containing passive samplers. However, in all previous studies, lipophilic materials such as triolein, a prominent constituent of fish lipids, were selected for incorporation into SPMDs with the particular purpose to mimic the bioaccumulation of organic contaminants in the tissues of aquatic organisms. No attention has been paid to plant specific composition with the aim of exploring SPMD to mimic plant accumulation of organic contaminants.

Plant membrane lipids are primarily composed of 16-carbon and 18-carbon fatty acids containing up to three double bonds (*17*). Plant carbohydrates are similar in composition to cellulose (*18*). Therefore, we speculated that petroselinic acid (cis-6-octadecenoic acid)-containing cellulose acetate membrane could be as surrogate to mimic the uptake of HOCs by plant roots. On the basis of this hypothesis, we proposed a new type of composite membrane, petroselinic acid embedded cellulose acetate membrane (PECAM). The configuration of PECAM is similar to the TECAM developed by Xu et al. (*5*). Petroselinic acid drops were embedded in a matrix of cellulose acetate polymers. This design provides advantages for the membrane, such as a larger contact area between petroselinic acid and polymers, which permits rapid and high partitioning of HOCs from the surrounding media across the membrane.

The first step in estimating PECAMs is to simulate plant accumulation of HOCs. The objective of this work was therefore to compare partitioning and uptake of HOCs by PECAMs with plants. The polycyclic aromatic hydrocarbons (PAHs) naphthalene (Nap), phenanthrene (Phe), pyrene (Pyr), and benz(a)pyrene (Bap) were selected as the model compounds. The kinetics and isotherms for sorption of the PAHs by PECAMs were first studied. Membrane-water partition coefficients for these compounds were explored and compared with their plant root-water partition coefficients. In vivo plant uptake of PAHs was further investigated for a range of plant species and compared with PAH accumulation in PECAMs.

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Materials and Methods

Chemicals. Naphthalene (Nap), phenanthrene (Phe), pyrene (Pyr), and benz(a)pyrene (Bap) were purchased from Acros Organics (New Jersey) with a labeled purity of >99% and used as received. The logarithmic octanol−water distribution coefficients (log K_{ow}) of the four PAHs are 3.33, 4.57, 5.13, and 6.13, respectively (*19*).

Membrane and Plant Preparation. PECAMs and simple cellulose acetate membranes (CAMs) without addition of petroselinic acid were prepared in the same way as triolein embedded cellulose acetate membranes (TECAMs) (*5*). Detailed procedures are provided in the Supporting Information.

Corn (*Zea mays* L.), ryegrass (*Lolium multiflorum* L.), wheat (*Triticum aestivum* L.), sorghum (*Sorghum bicolor* L. Moench.), barley (*Hordeum vulgare* L.), and rice (*Oryza sativa* L.) were used as the test plants. Seeds were purchased from the Chinese Academy of Agricultural Sciences, Beijing, China. Plant cultivation was as described in a previous study (*20*). The growth periods of the different plant species varied from 5 to 10 weeks until they had developed mature roots. The roots used in sorption studies were cut from the plants, blotted dry with tissue paper, and freeze-dried for 48 h in a lyophilizer (FD-1, Beijing Boyikang Instruments Ltd.). To obtain a well-mixed sample, the dried roots were ground, passed through a 0.5 mm sieve, and blended. Root lipid contents were determined following the same procedures that we previously employed (*20*).

Sorption Experiments. Equilibrium uptake of Nap, Phe, Pyr, and Bap by PECAM (petroselinic acid, 5% dry weight) was measured in triplicate using a batch adsorption technique. A series of PAH solutions with a range of initial concentrations (Nap 250−20000, Phe 25−1000, Pyr 2.5−120, Bap 0.1−4 μg/L, respectively) were prepared using half-strength Hoagland solution as the matrix and with 200 mg/L NaN_3 as a biocide. The solid-to-liquid ratios (PECAM mass in mg/solution in mL) were 50:10, 50:100, 6:100, and 6:200 for Nap, Phe, Pyr, and Bap, respectively, with the aim to give 30−80% sorption of each compound at equilibrium. The ratio for sorption of Phe by PECAM with different petroselinic acid contents was 20:100. No fouling by microbial growth was visible on PECAMs within the exposure time employed.

For sorption of PAHs by plant root materials, the initial concentrations of solute and conditions were the same as for sorption by PECAMs. The solid-to-liquid ratios (sorbent mass in mg/solution in mL) for Nap, Phe, Pyr, and Bap sorption by plant roots were 180:30, 2:20, 5:100, and 5:200, respectively. The tubes were closed with Teflon-lined caps and shaken for 6, 48, 72, and 120 h for the equilibrium sorption of Nap, Phe, Pyr, and Bap, respectively. Following the equilibration and subsequent 30 min sedimentation of plant materials, the vials were centrifuged at 1000 $\times g$ for 30 min and the supernatant from each tube was analyzed for solute. The PAH 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 less than 2% which is negligible.

Plant Uptake Experiments. Seedlings with mature roots were transferred to amber glass culture containers through a hole drilled in the cap. The open area between the cap and the group of plants in each container was sealed with acrylic adhesive. Roots were immersed below the surface of the culture solution with the same initial concentrations of PAHs as the ones in the sorption experiments, and cultured hydroponically for 48 h for Nap and Phe and 240 h for Pyr and Bap. Three replicates were prepared for each treatment. The growing conditions were the same as described above for plant preparation.

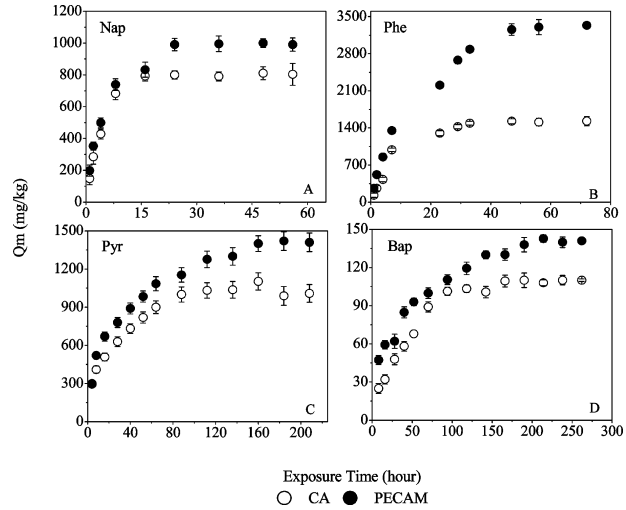

FIGURE 1. Sorption kinetics of Nap, Phe, Pyr, and Bap by CAMs (without embedded petroselinic acid) and PECAMs (5% petroselinic acid embedded). Q_m = mass of the solute accumulated per unit mass of the membranes. Error bars represent SD values (standard deviation).

Sample Extraction and Analysis. Membrane samples were rinsed with distilled water, wiped with clean filter paper, and dialyzed in 10 mL of hexane for 24 h. Dialysis solutions were evaporated under a gentle stream of nitrogen, solvent-exchanged into methanol and stored prior to analysis. PECAMs were stable in hexane with negligible weight loss of petroselinic acid and cellulose acetate during dialysis, and therefore no cleanup of the samples was required. Clean up may be required in soil application because particles smaller than the membrane pores may transfer into the membranes.

Plant samples were rinsed thoroughly with distilled water, blotted with tissue paper, and separated into roots and shoots. Freeze-dried chopped plant roots (0.1 g dry weight) were thoroughly mixed with 1−2 g of anhydrous sodium sulfate, loaded into a Soxhlet thimble, and extracted with 100 mL of dichloromethane/acetone (1:1, v/v) at 60 °C for 24 h. The extract was reduced to 5 mL with a rotary evaporator, purged to about 1−2 mL under a gentle nitrogen stream, and then cleaned with Florisil SPE (1 g/6 mL) and the eluates were evaporated, solvent-exchanged into methanol, and stored prior to analysis.

PAHs in samples were analyzed by HPLC (Agilent 1200 series) equipped with an ultraviolet detector for Nap and Phe and a fluorescence detector for Pyr and Bap using a reverse-phase C_{18} column (4.6 × 150 mm, 5 μm particle size). Details of the instrumental conditions were the same as those used in our previous work (*21*). The recoveries of Nap, Phe, Pyr, and Bap in the controls were 85−93% for PECAMs and 87−94% for plants. Data were analyzed using the Origin 7.5 software package.

Results and Discussion

Partitioning of PAHs to PECAMs and Ryegrass Roots. To obtain the partition coefficients of PAHs for PECAM and to compare with their partition coefficients for plants, sorption kinetics and isotherms were first investigated for PECAMs and ryegrass roots. Figure 1 displays the kinetic sorption of Nap, Phe, Pyr and Bap by CAMs and PECAMs. Sorption of Nap, Phe, Pyr, and Bap reached apparent equilibrium in 12, 24, 72, and 96 h for CAMs, and 24, 48, 144, and 192 h for PECAMs. The time for PAHs to reach equilibrium between PECAM and water was correlated with their hydrophobicity. The equilibrium time for PAH partitioning between water and PECAM is comparable to that of TECAM reported by Xu et al. (*5*) and shorter than those reported elsewhere

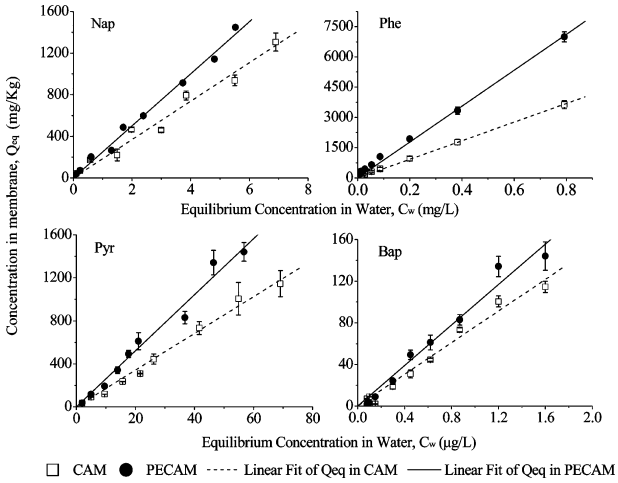

FIGURE 2. Sorption of Nap, Phe, Pyr, and Bap by PECAMs and CAMs. Error bars represent SD values.

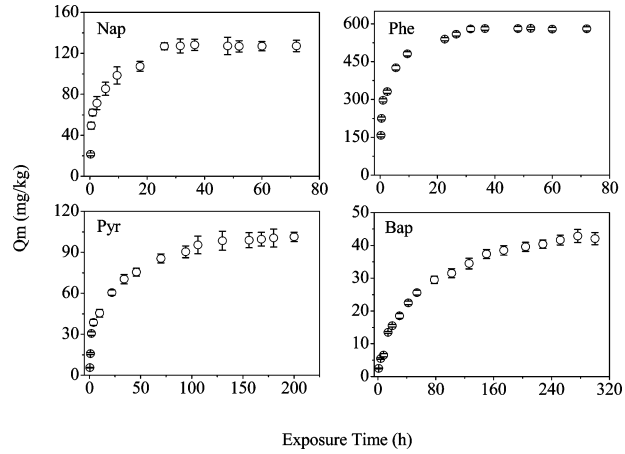

FIGURE 3. Uptake kinetics of PAHs by ryegrass roots. Q_m = concentration of PAHs in ryegrass roots on dry weight basis. Error bars represent SD values.

(*22*−*25*). PECAM is an integrated membrane in which the petroselinic acid is uniformly mixed with the cellulose acetate membrane material (see the SEM results in Figure S1 in the Supporting Information). Thus, the resistance to mass transfer from the outer membrane to the lipid was minimized. Furthermore, 0.1 g petroselinic acid can be distributed on a surface area of cellulose acetate of approximately 10 000 cm^2, resulting in a larger contact area between the petroselinic acid and the PAHs in solution, thereby permitting rapid exchange kinetics. Moreover, the membrane material of PECAMs is cellulose acetate which is hydrophilic and can decrease the surface tension between PECAMs and the culture solution.

For both PECAMs and CAMs, all of the PAHs followed linear equilibrium uptake isotherms between membranes and solution phases with regression R^2 values ranging from 0.956 to 0.994 (Figure 2 and Table 1). The slopes of the equilibrium sorption isotherm represent the equilibrium membrane-water partition coefficients K_{PECAM} and K_{CAM}, respectively. The accumulation of PAHs in PECAMs contributed to both sorption to cellulose acetate and uptake to petroselinic acid. Therefore, K_{PECAM} is the sum of the equilibrium partition coefficients for petroselinic acid−water (K_{pw}) and cellulose acetate-water (i.e., K_{CAM}). K_{pw} can be obtained by subtracting K_{CAM} from K_{PECAM} and the values of log K_{pw} are listed in Table 1. A good linear association was observed between log K_{pw} values of the PAHs and their respective logK_{ow} values with the following relationship:

$$\log K_{pw} = 1.026 \log K_{ow} + 0.032 \qquad R^2 = 0.995, P < 0.01, n = 4 \tag{1}$$

In comparison this equation is very similar to the relationship between logK_{ow} and logK_{tw} of triolein-water partition coefficients obtained by Xu et al. (*5*).

Sorption of Nap, Phe, Pyr, and Bap by ryegrass roots is provided in Figure S2 in the Supporting Information. Similar to the results for PECAMs, the sorption isotherms for PAHs by ryegrass roots are highly linear (R^2 values from 0.989 to 0.998), characteristic of a partition-dominated process. Due to the relatively polar characteristics of carbohydrates in plants, the partition contribution by carbohydrates becomes unimportant relative to that by the lipids for compounds with high hydrophobicity (*14*). Values of the plant-water partition coefficients (K_{pl}) for ryegrass roots can be normalized by lipid contents. The corresponding lipid-normalized parti-

TABLE 1. Partition Parameters of PAHs for PECAMs and Ryegrass Roots[a]

compound	K_{pw} (L/kg)[b]	R^2	K_{pl} (L/kg)[b]	R^2	log K_{pw}	log K_{lip}
Nap	116.7 ± 5.1	0.994	79.2 ± 2.9	0.991	3.37	3.42
Phe	2979.2 ± 49.3	0.992	2101.4 ± 31.2	0.993	4.90	4.84
Byr	8770.0 ± 184.6	0.956	7223.0 ± 262.9	0.989	5.24	5.38
Bap	95273.0 ± 1318.2	0.991	76755.7 ± 1430.9	0.998	6.28	6.41

[a] K_{pw}: petroselinic acid-water partition coefficient for PECAMs. K_{pl}: plant root-water partition coefficient for ryegrass. log K_{pw} and log K_{lip}: log values for K_{pw} and lipid normalized K_{pl}. [b] Data are expressed as mean ± SD, $n = 3$.

TABLE 2. Partition Parameters of Phe for PECAMs and Plant Roots[a]

		PECAM			plant		
test plant	lipid content	K_{pw} (L/kg)[b]	log K_{pw}	R^2	K_{pl} (L/kg)[b]	logK_{lip}	R^2
corn	2.01	1570.3 ± 98.5	4.89	0.996	1555.3 ± 100.6	4.89	0.956
ryegrass	2.86	2205.7 ± 141.6	4.89	0.991	2153.5 ± 127.5	4.88	0.991
wheat	3.45	2756.4 ± 178.2	4.90	0.995	2699.7 ± 211.8	4.89	0.973
sorghum	4.98	3943.7 ± 287.4	4.90	0.997	3348.2 ± 273.6	4.83	0.974
barley	6.17	4843.1 ± 381.9	4.89	0.997	4347.8 ± 372.4	4.85	0.971
rice	7.21	5760.5 ± 396.4	4.90	0.998	4900.9 ± 390.2	4.83	0.997

[a] K_{pw}: petroselinic acid-water partition coefficient for PECAMs. K_{pl}: plant root-water partition coefficient. log K_{pw} and log K_{lip}: log values for K_{pw} and lipid normalized K_{pl}. [b] Data are expressed as mean ± SD, $n = 3$.

TABLE 3. Uptake Coefficients (K_u) of PAHs by Plants[a]

	Nap		Phe		Pyr		Bap	
test plant	K_u (L/kg)[b]	log K_u	K_u (L/kg)[b]	log K_u	K_u (L/kg)[b]	log K_u	K_u (L/kg)[b]	log K_u
corn	15.2 ± 3.6	2.88	554.4 ± 34.9	4.44	2122.6 ± 124.6	5.02	22486.7 ± 1075.3	6.05
ryegrass	20.8 ± 5.5	2.86	760.2 ± 38.6	4.42	2361.8 ± 113.5	4.92	38863.8 ± 1583.2	6.13
wheat	27.4 ± 8.4	2.90	1042.3 ± 85.3	4.48	4140.3 ± 274.9	5.08	53066.4 ± 2746.1	6.19
sorghum	38.8 ± 7.6	2.89	1311.4 ± 79.8	4.42	5114.0 ± 319.2	5.17	70138.6 ± 3274.4	6.15
barley	64.6 ± 4.9	3.02	1595.9 ± 120.4	4.41	6721.6 ± 306.1	5.13	86089.5 ± 3729.2	6.14
rice	69.4 ± 3.2	2.98	1801.8 ± 135.3	4.39	7537.3 ± 426.5	5.02	100932.1 ± 5827.7	6.15

[a] K_u: slope of the uptake isotherms. logK_u: log values for lipid normalized K_u. [b] Data are expressed as mean ± SD, $n = 3$.

tion coefficients (logK_{lip}) are summarized in Table 1. A good linear relationship was observed between logK_{pw} and logK_{lip} which can be expressed by the following equation:

$$\log K_{pw} = 0.98 \log K_{lip} \qquad R^2 = 0.999,\ P < 0.01, n = 4 \tag{2}$$

The log values of K_{pw} and K_{lip} were almost the same for each compound tested and the log K_{pw} and log K_{lip} exhibit an excellent 1:1 relationship, which provides evidence for the feasibility of petroselinic acid in PECAMs in simulating root lipids to mimic the partitioning of PAHs to ryegrass roots.

Comparison of Phenanthrene Partitioning by PECAMs and by Plants with Different Root Lipid Contents. Partitioning of Phe was further compared between a series of plant roots with different lipid contents and the PECAMs in which petroselinic acid was embedded with the same contents as the root lipids. Sorption isotherms of Phe by PECAMs and plant roots are given in Figure S3 of the Supporting Information and the partition coefficients obtained are summarized in Table 2. Values of petroselinic acid−water partition coefficients K_{pw} and the plant-water partition coefficients (K_{pl}) varied from 1570.3 L/kg to 5760.5 L/kg and 1555.3 L/kg to 4900.9 L/kg, respectively. The log values for petroselinic acid−water partition coefficients (logK_{pw}) were 4.89−4.90. The corresponding root lipid−water partition coefficients (logK_{lip}) were 4.83−4.89. Consistence between logK_{pw} and logK_{lip} suggests that lipid−water partitioning is the key process for the uptake of Phe to either plant roots or the PECAMs, and indicates that the petroselinic acid in PECAMs plays a similar role in Phe uptake to that of root lipids, and Phe has approximately the same partition behavior in PECAMs and plant roots.

Comparison of Plant Uptake and PECAM Accumulation of PAHs. In vivo uptake of PAHs by plants was compared with its accumulation in PECAMs. Kinetic uptake of PAHs by plants is provided in Figure 3 by taking ryegrass as an example. Plant uptake approached apparent equilibrium in 24, 48, 144, and 240 h for Nap, Phe, Pry, and Bap, respectively. Therefore, the exposure times for plant uptake were chosen as 2 d for Nap and Phe and 10 d for Pry and Bap, respectively. Uptake isotherms of Nap, Phe, Pry, and Bap by the roots of different plant species are close to linear over the range of concentrations investigated (Figure S4 of the Supporting Information) with regression (R^2) values ranging from 0.937 to 0.999. The uptake coefficients (K_u, slope of the uptake isotherms) of Nap, Phe, Pry, and Bap for different plant species are listed in Table 3. The value of K_u increased with increasing hydrophobicity of the compounds and root lipid content of plants. Normalizing to the lipid content results in a fairly consistent log K_u with average values of 2.92, 4.43, 5.06, and 6.13 for Nap, Phe, Pry, and Bap. The values of petroselinic acid−water partition coefficients log K_{pw} were 3.37, 4.90, 5.24, and 6.28 for Nap, Phe, Pyr, and Bap, respectively. In comparison, the log K_u values obtained by the in vivo study were slightly lower than the values of log K_{pw} as well as the log K_{lip} values obtained by sorption experiment. However, the similarity between values of log K_u and log K_{pw} increased with increasing hydrophobicity of the compounds. Plant uptake of HOCs is rather complicated. In addition to the major process of root accumulation, translocation and metabolism of HOCs can occur inside plants (*21, 26*). More highly hydrophobic PAHs had a greater tendency to partition and accumulate in organic constituents of the plant roots and this resulted in a lower acropetal translocation as well as likely less biodegradation. As a result, the similarity between values of logK_u and logK_{pw} increased. This suggests that PECAM is likely to be more applicable to biomimetic plant accumulation of highly hydrophobic organic contaminants.

Method Overview. The results of the present work indicate that petroselinic acid−water partition coefficients (log K_{pw}) are almost the same as the lipid-normalized root partition coefficients (log K_{lip}) for the PAHs, and PECAM can mimic plant partitioning and uptake of PAHs in hydroponic solution. This work was limited to biomimetic and plant uptake of PAHs in solution. It is well-known that processes of organic contaminants in soil such as sorption and desorption are crucial in the determination of their bioavailability. Further research is required to expose PECAMs to soils as passive samplers to mimic plant uptake of PAHs and perhaps other HOCs.

Acknowledgments

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Supporting Information Available

Preparation of PECAMs and scanning electron micrographs of the membranes, as well as the figures for sorption of Nap, Phe, Pyr, and Bap by ryegrass roots, sorption of Phe by PECAMs and plants, and in vivo uptake of PAHs by different plants are provided. This information is available free of charge via the Internet at http://pubs.acs.org.

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