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Measurement of partition coefficients for selected polycyclic aromatic hydrocarbons between isolated plant cuticles and water

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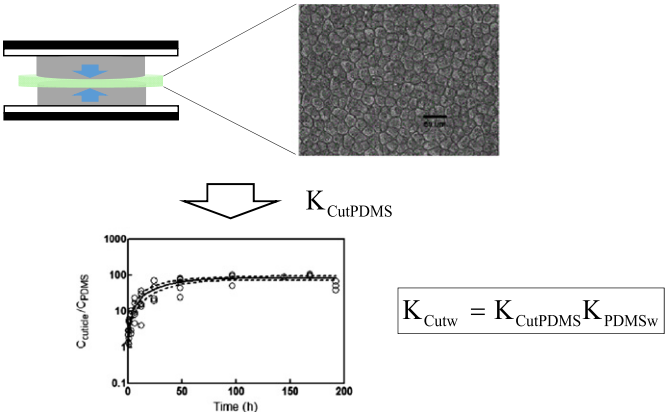
HIGHLIGHTS

- Partitioning of PAHs between plant cuticles and water was evaluated.
- Sorption capacity of cuticles for PAHs was close to that of 1-octanol.
- Physical breakdown of cuticular membranes lowers their sorption capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

Partition coefficients between plant cuticles and water (K_{cutw}) were measured for 10 selected polycyclic aromatic hydrocarbons (PAHs) to evaluate the sorption capacity of plant cuticular layers for hydrophobic organic chemicals. The partitioning properties of PAHs between cuticles and water were evaluated by using (1) isolated cuticular layers and (2) leaf homogenate. The abaxial and adaxial cuticular layers of *Euonymus japonicus* were isolated by enzymatic digestion. A third-phase partitioning method using poly(dimethylsiloxane) (PDMS) was used to obtain K_{cutw}. The K_{cutw} values for the selected PAHs showed no significant differences between the abaxial and adaxial cuticular layers and ranged between $10^{4.1}$ and $10^{7.6}$. These values are close to or slightly higher than their 1-octanol/water partition coefficient (log K_{ow}), indicating high sorption capacity of plant cuticles. On the contrary, partition coefficients between the lipid tissues of homogenized leaves and water were lower than those obtained using isolated cuticular layers by factors of 3.7–190, which is likely due to the breakdown of lipid layers. This indicates that the sorption of hydrophobic organic chemicals by plant leaves is better evaluated using isolated cuticles and that the sorption potential of plant leaves may be underestimated when leaf homogenates are used.

1. Introduction

Hydrophobic organic contaminants (HOCs) accumulate in living organisms via various transport processes. Unlike accumulation and

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other fate-related processes in aquatic environments, those in terrestrial environments have not yet been clearly understood (Kelly et al., 2007). Plants are especially important in the fate of hydrophobic organic contaminants in the terrestrial environment because of their high biomass, large surface area of lipophilic exterior and biological activity that results in the exchange of HOCs with other media (Gouin et al., 2002; Simonich and Hites, 1994; Terzaghi et al., 2013).

For evaluation of these transfer processes, the partition coefficients between a plant and the environment are commonly estimated using the 1-octanol/water partition coefficient (K_{ow}) or the 1-octanol/air partition coefficient (K_{oa}) (e.g., Riederer, 1990; Tao and Hornbuckle, 2001; Tian et al., 2013; Trapp and Matthies, 1995). Modeling studies on the dynamic transfer of HOCs among different environmental media also indicate that the model outcomes are highly sensitive to the partition coefficients used as surrogates for plant/water or plant/air partition coefficients (Steyaert et al., 2009; Tao and Hornbuckle, 2001). Thus, low uncertainties in the value of partition coefficients between the plant materials and the environment are desired for the evaluation of transport processes of HOCs.

Plant leaves contain cuticular layers composed of lipid polymers believed to have high affinity to HOCs; thus, these cuticular layers affect the dynamic transport processes of HOCs (Kerstiens, 2006). However, reported partition coefficients between plant compartments and air or water have been limited to certain volatile organic chemicals (Welke et al., 1998), agrochemicals (Li et al., 2012; Popp et al., 2005; Shechter and Chefetz, 2008; Shechter et al., 2006) and some HOCs such as lower molecular weight polycyclic aromatic hydrocarbons (Calderón-Preciado et al., 2013; Gao et al., 2008; Li and Chen, 2009; Li et al., 2010; Lin et al., 2007; Shechter and Chefetz, 2008). Most of the aforementioned sorption studies are limited to organic chemicals with log K_{ow} less than 5.0. Because sorption to plant leaves should be an important pathway for the global transport of highly hydrophobic organic chemicals, including those classified as persistent organic pollutants, experimental values of partition coefficients for those chemicals should be of high value.

Analytical difficulties with highly hydrophobic organic chemicals arise because of their low water solubility and vapor pressure, leading to high partition coefficients. However, difficulties associated with the determination of high partition coefficients for HOCs have been overcome using third-phase partitioning methods (Kim and Kwon, 2010; Kim et al., 2010; Lee et al., 2014; ter Laak et al., 2005). In these techniques, the partition coefficient between the dissolved/suspended organic matter and water is precisely quantified by measuring the partition coefficient between a polymeric phase and aqueous solution containing dissolved/suspended organic matter if the polymer/water partition coefficient is already known.

Consequently, we evaluated the partition coefficients of selected HOCs between isolated plant cuticles and water (K_{cutw}). Ten polycyclic aromatic hydrocarbons (PAHs) were chosen as model HOCs with their log K_{ow} ranging between 3.9 and 6.9 because dynamic exchange processes between plant leaves and the environment are important for them (Simonich and Hites, 1994; Terzaghi et al., 2013), and their log K_{ow} values cover wide range to extend the understanding of partitioning between plant cuticles and water toward more hydrophobic chemicals. *Euonymus japonicus* was chosen as the model plant species. The Abaxial and adaxial cuticular membranes were isolated by enzymatic digestion and the K_{cutw} values were measured using a three-phase system: poly(dimethylsiloxane) (PDMS)–isolated cuticular membrane–water. Relationships between log K_{cutw} and log K_{ow} were derived. In addition, partition coefficients between leaves and water (K_{lw}) were also measured using leaf homogenate solution after mechanically homogenizing the leaves in an aqueous buffer solution. The lipid-normalized values of K_{lw} were compared with those measured using isolated cuticular membranes.

2. Material and methods

2.1. Materials and chemicals

The leaves of *Euonymus japonicus* were collected from trees in spring 2010 in the campus of Ajou University. The leaves were freshly grown and fully developed. Their cuticles were isolated using the procedure described below, and the leaves were homogenized using a cell homogenizer to prepare a leaf homogenate solution for the evaluation of K_{lw}.

High-purity chemical standards were used for all PAHs. Acenaphthene (ACE, 99%), phenanthrene (PHE, 98%), anthracene (ANT, 99%), fluoranthene (FLU, 98%), pyrene (PYR, 99%), benzo[*a*]anthracene (BaA, 99%), chrysene (CHR, 99.9%), benzo[*a*]pyrene (BaP, 99.1%), dibenz[*a*,*h*]anthracene (DA, 99.9%), and benzo[*ghi*]perylene (BghiP, 99.6%) were selected as model PAHs and were purchased from Sigma-Aldrich (St. Louis, MO, USA), Supelco (Bellefonte, PA, USA), or Fluka (Buch, Switzerland). All partitioning experiments were conducted using a mixture of selected PAHs. Citric acid (≥99.5%), pectinase, and cellulose extracted from *Aspergillus niger* were purchased from Sigma-Aldrich.

Medical-grade poly(dimethylsiloxane) (PDMS) sheets with thicknesses of 0.5 and 1 mm and density of 1.17 g cm^{-3} were purchased from Specialty Silicone Products, Inc. (Ballston Spa, NY, USA). For the partitioning experiments, PDMS was cut into disks of various diameters, cleaned in a Soxhlet extractor using *n*-hexane and methanol for 2 h each, and stored in acetonitrile until use.

2.2. Isolation of cuticular layers from Euonymus japonicus

The cuticular layers of *Euonymus japonicus* were isolated by an enzymatic isolation method using pectinase and cellulase that digest plant cell walls (Orgell, 1955; Lendzian et al., 1986; Santier and Chamel, 1998; Schreiber & Schönherr, 2009). The sampled leaves were rinsed with deionized water. After the moisture was removed, the leaf was cut into a 6.5-mm-diameter disk. A citric acid buffer solution (0.01 mol L^{-1}, pH 3.0 adjusted by adding 0.1 N KOH) containing 20 mg mL^{-1} of pectinase and 20 mg mL^{-1} of cellulase was added to a clean Erlenmeyer flask containing leaf disks. The flask was wrapped with an aluminum foil to avoid exposure to light and placed on a hot plate at 32 °C for two weeks. The adaxial and abaxial cuticular layers were separated from the enzyme solution and were rinsed with deionized water to remove enzymes and cellular debris. They were submerged into 1 M hydrochloric acid solution and stored for one day to prevent the potential reactions of cuticles with cellular debris. After the cleaning processes, the isolated cuticles were rinsed with deionized water and dried at 105 °C for 18 h and stored in a clean glass vial at ambient temperature until further use (Orgell, 1955; Lendzian et al., 1986). The average mass of the abaxial layers (0.18 ± 0.01 mg) measured as a bundle of ten layers using a microbalance did not differ from that of the adaxial layers (0.18 ± 0.01 mg). Because the density of a cuticular layer is approximately 1,100 kg·m^{-3} (Onoda et al., 2012), the average volume of the isolated cuticular layer was estimated to be 0.16 μL. Microscopic images of isolated cuticular membranes are shown in Fig. S1, Supplementary Material.

2.3. Determination of partition coefficients between isolated cuticles and water (K_{cutw})

The K_{cutw} values were obtained using PDMS as the third phase. PDMS disks (6 mm diameter, 1 mm thickness) were loaded with 10 PAHs (ACE, PHE, ANT, FLR, PYR, BaA, CHR, BaP, DahA, and BghiP) using a method described earlier (Kim and Kwon, 2010; Lee et al., 2012). Briefly, the PDMS disks were placed in a glass vial containing the loading solution (methanol:water (6:4) solutions with PAHs at two different concentration levels; detailed values are shown in Table S1, Supplementary Material). Then, the vial was shaken in dark for three days at 25 °C and 150 rpm. After the loading process, the PDMS disks were rinsed