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Mass transfer of hydrophobic organic chemicals between silicone sheets and through plant leaves and low-density polyethylene

Hamid Ahmadi [a, 1], Damien Johann Bolinius [a, *, 1], Annika Jahnke [b], Matthew MacLeod [a]

[a] Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, Svante Arrhenius väg 8, SE-114 18, Stockholm, Sweden
[b] Department of Cell Toxicology, Helmholtz Centre for Environmental Research (UFZ), Permoserstr. 15, DE-04318, Leipzig, Germany

HIGHLIGHTS

- We determined mass transfer kinetics for 3 PAHs and 6 PCBs between a spiked and an unspiked sheet of PDMS.
- We determined mass transfer kinetics for 2 PAHs through different leaves and LDPE.
- Our results for the transfer of fluoranthene between two disks of PDMS differ by a factor 12 from those published earlier.
- We demonstrate a passive dosing method to measure the mass transfer coefficients of organic chemicals through leaves.

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ABSTRACT

Plant leaves play an important role in the fate of hydrophobic organic contaminants (HOCs) in the environment. Yet much remains unknown about the permeability of leaves by HOCs. In this pilot study we measured (i) the kinetics of mass transfer of three polycyclic aromatic hydrocarbons (PAHs) and six polychlorinated biphenyls between a spiked and an unspiked sheet of polydimethylsiloxane (PDMS) in direct contact with each other for 24 h and (ii) kinetics of mass transfer of two PAHs through leaves and low-density polyethylene (LDPE) in a passive dosing experiment by inserting these matrices between the two sheets of PDMS for 48 h. The kinetics of mass transfer of fluoranthene between PDMS sheets in direct contact were a factor of 12 slower than those reported in the literature. The kinetics of mass transfer of fluorene and phenanthrene through leaves were within the range of those previously reported for 2,4-dichlorophenoxyacetic acid through isolated cuticles. Our results provide a proof-of-concept demonstration that the passive dosing method applied in this study can be used to measure the mass transfer coefficients of organic chemicals through leaves. Key recommendations for future experiments are to load the PDMS at the highest feasible concentrations to avoid working at analyte levels close to the limit of detection, to keep the leaves moist and to minimize potential pathways for contamination of the PDMS sheets by exposure to laboratory air.

1. Introduction

The environmental fate of hydrophobic organic contaminants (HOCs), including many persistent organic pollutants (POPs), is affected by partitioning to vegetation, especially into the waxy outer cuticle of leaves and needles (Simonich and Hites, 1995). Foliage of trees in forested areas can increase the deposition of semi-volatile organic compounds from the atmosphere to the soil in comparison with non-forested soils, through litter fall and wax shedding, a phenomenon known as the forest filter effect (Horstmann and McLachlan, 1998; Su and Wania, 2005). In addition to the potential of foliage to facilitate the transfer of POPs to soil, vegetation consumed by herbivores is a vector for transfer of POPs from the atmosphere to organisms higher up in the food chain (Welsch-Pausch et al., 1995).

The variability in chemical uptake behavior of leaves of different plant species remains largely unknown (Kömp and McLachlan, 1997; Riederer and Schönherr, 1985; Barber et al., 2004; Moeckel et al., 2008). An improved understanding of how organic pollutants are taken up by leaves would allow better predictions of the fate of these chemicals in the environment and the related risks

* Corresponding author.
E-mail address: damien.bolinius@aces.su.se (D.J. Bolinius).
[1] Dual first authorship.

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(Nizzetto et al., 2010). Key aspects are to increase the amount of data available on (i) partition ratios between leaves, air and water, (ii) the kinetics of transfer of HOCs into and through leaves and (iii) the variability of these partition ratios and transfer rates between plant species.

In this study we have conducted pilot experiments aimed at measuring the transfer kinetics of HOCs through leaves. The most important part of the leaf with respect to the uptake kinetics of POPs from air is believed to be the cuticle (Riederer, 1990), the outermost layer of the leaf which is in direct contact with the atmosphere and provides protection against dehydration and infections. Mass transfer coefficients of organic compounds through leaf cuticles have been measured by Riederer and Schönherr (Riederer and Schönherr, 1985; Schönherr and Riederer, 1989; Riederer, 1990; Kirsch et al., 1997) amongst others, for a wide variety of plant species and chemicals but to a lesser extent for POPs or similar chemicals, as discussed in the review by Barber and coworkers (Barber et al., 2004).

The cuticle is a complex heterogeneous structure, consisting of a combination of extractable lipids such as waxes that will dissolve in organic solvents and polymeric lipids such as cutin and cutan (Nip et al., 1986; Holloway, 1994; Gupta, 2014). Studies with isolated cuticles that had the cuticular waxes removed showed an increase in transfer rates of up to 4 orders of magnitude for the chemical (2,4-dichlorophenoxy)acetic acid, indicating that highly organized crystalline waxes in the outer layer of the cuticle can form an effective barrier for the uptake of chemicals into leaves (Riederer and Schönherr, 1985). The same authors also found a wide variability in the cuticle permeability between plant species, and that the sorption capacity of isolated cuticles is much lower than that of isolated cutin (Riederer and Schönherr, 1984), which was confirmed more recently for polycyclic aromatic hydrocarbons (PAHs) (Chen et al., 2008; Li et al., 2010).

Recently, the silicone polydimethylsiloxane (PDMS) has been employed in passive dosing studies designed to measure the kinetics of chemical transport across different media (Mayer et al., 2005; Trapp et al., 2007; Kim et al., 2014; Li et al., 2016). There is a wide range of literature on the use of PDMS for passive sampling (Reichenberg et al., 2008; Jahnke et al., 2009) and dosing (Smith et al., 2010). An approach to measure mass transfer coefficients using PDMS sheets was originally developed to quantify the effect of medium composition on the diffusive mass transfer rates of HOCs (Mayer et al., 2005) and was later applied to measure mass transfer coefficients of PAHs through slices of root vegetables such as potato and carrot (Trapp et al., 2007). The measurements are accomplished using two sheets of PDMS, one of which (the “donor”) is loaded with the chemicals of interest, while the other PDMS sheet is largely free of chemicals (the “acceptor”). Mass transfer through the medium of interest can be measured by placing it between the donor and acceptor sheets (Fig. 1) and measuring the concentration of chemicals in the acceptor sheet over time. An important advantage of this set-up is that it is not required to measure the concentration in the leaves, which can be difficult to analyze. A modified version of the method by Trapp et al. (2007) using two donor layers was recently used to measure the partition ratios of a wide range of PAHs between water and isolated cuticles from *Euonymus japonicas* (evergreen spindle), confirming the high uptake rate and sorption capacity of the leaf cuticle (Kim et al., 2014).

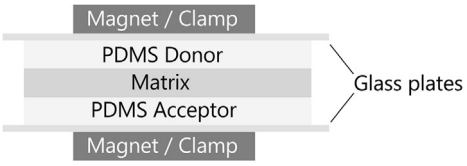

Fig. 1. Experimental setup with the glass plates and the assembly in between pressed together by magnets or metal clamps.

Here, we report our application of the method of Trapp et al. (2007) to measure the mass transfer coefficients of several PAHs and polychlorinated biphenyls (PCBs) between PDMS sheets in direct contact with each other and the transfer of the PAHs fluorene and phenanthrene through leaves of two plant species and through low-density polyethylene (LDPE). Our goal in this pilot experiment was to test the applicability of the method to intact leaves, and to make a first set of measurements to determine how fast HOCs penetrate leaves of different plant species. We discuss how our results for intact leaves compare with mass transfer rates measured through isolated cuticles that have been reported in the literature.

2. Material and methods

2.1. Chemicals, solvents and materials

Methanol (HiPerSolv) was purchased from VWR Chemicals (Fontenay-sous-Bois, France). Acetone and isooctane (Suprasolv) were obtained from Merck (Darmstadt, Germany). Water was purified by a Milli-Q water purification system (Merck, Darmstadt, Germany). All chemical standards were purchased from Larodan (Solna, Sweden). The analytes used in this study, presented in detail in Table s1, were a range of PAHs and PCBs with well characterized physicochemical properties. Each of the target compounds had a corresponding internal standard, either deuterated (PAHs) or carbon-13 labeled (PCBs), that was spiked to the extraction solvent. PCB 53 was used as a recovery reference standard, which was spiked to the final extracts before analysis.

PDMS sheets of the type SSP-M823 with a thickness of 610 μm and a density between 1.12 and 1.16 g/mL were obtained from Shielding solutions (Essex, U.K.), the European distributor of Specialty Silicone Products. PDMS sheets were first cut with a scalpel into rectangles measuring 18 × 28 mm and were then washed twice in methanol over a total period of at least 48 h.

Four different matrices were prepared to be placed between the two PDMS sheets. Leaves from romaine lettuce (*Lactuca sativa var. longifolia* Lam.) and a Hydrangea species were obtained from a local vendor and rhododendron leaves (*Rhododendron ponticum* L.) were collected from a bush on the Stockholm University campus. These plant species were chosen because of their availability and because they showed large differences in the morphology of their leaves. All the leaves were wiped gently with wet paper tissues to remove dirt and then blotted dry. Care was taken not to use any leaves that were damaged. Experiments were performed on sections cut with a scalpel from random areas of the leaves that excluded the central vein, and on pieces of LDPE cut with a scalpel from plastic zipper storage bags (Grippie, b.n.t Scandinavia ab., Arlöv, Sweden) and rinsed using methanol. All matrices were cut to the same size as the PDMS sheets. The mass of LDPE used in the experiment was on average 7.3% ± 3.1% (Stdev.) of the total mass of the PDMS donor and acceptor. The thickness of each of the matrices was measured using a caliper and is presented in Table s1.

2.2. Loading of the PDMS donor sheets

Loading of the PDMS sheets with PAHs and PCBs was achieved using a similar method to that used by Birch and colleagues for passive dosing vials (Birch et al., 2010). The sheets were transferred to a glass beaker containing 75 mL of methanol, to which 1 μg of each chemical dissolved in isooctane was added. The glass beaker