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Partitioning of hydrophobic organic contaminants between polymer and lipids for two silicones and low density polyethylene

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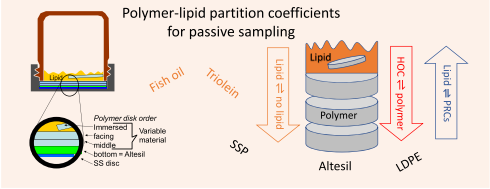
HIGHLIGHTS

- Relatively fast lipid diffusion in Silicone and LDPE.
- Partition coefficients provided for 78 hydrophobic substances.
- Lipid type and temperature does not affect partitioning.
- Partitioning not affected by polymer lipid sorption.
- Passive sampling results can be converted to lipid based equivalent.

GRAPHICAL ABSTRACT



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ABSTRACT

Polymers are increasingly used for passive sampling of neutral hydrophobic organic substances (HOC) in environmental media including water, air, soil, sediment and even biological tissue. The equilibrium concentration of HOC in the polymer can be measured and then converted into equilibrium concentrations in other (defined) media, which however requires appropriate polymer to media partition coefficients. We determined thus polymer-lipid partition coefficients (K_{PL}) of various PCB, PAH and organochlorine pesticides by equilibration of two silicones and low density polyethylene (LDPE) with fish oil and Triolein at 4 °C and 20 °C. We observed (i) that K_{PL} was largely independent of lipid type and temperature, (ii) that lipid diffusion rates in the polymers were higher compared to predictions based on their molecular volume, (iii) that silicones showed higher lipid diffusion and lower lipid sorption compared to LDPE and (iv) that absorbed lipid behaved like a co-solute and did not affect the partitioning of HOC at least for the smaller molecular size HOC. The obtained K_{PL} can convert measured equilibrium concentrations in passive sampling polymers into equilibrium concentrations in lipid, which then can be used (1) for environmental quality monitoring and assessment, (2) for thermodynamic exposure assessment and (3) for assessing the linkage between passive sampling and the traditionally measured lipid-normalized concentrations in biota. LDPE-lipid partition coefficients may also be of use for a thermodynamically sound risk assessment of HOC contained in microplastics.

1. Introduction

Equilibrium passive sampling (EPS) in environmental media involves enrichment of organic pollutants into a micrometer thin

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polymer while keeping matrix and interfering constituents outside the polymer (Mayer et al., 2003). Concentrations in polymers equilibrated with media ($C_P \rightleftharpoons$media) can then be converted to equilibrium partitioning concentrations in other defined media, given the appropriate polymer to media partition coefficient is available (Gilbert et al., 2016). Dividing $C_P \rightleftharpoons$media by polymer-water partition coefficients, for example, yields freely dissolved concentrations (Cfree) (Booij et al., 2016; Friedman et al., 2009; Kraaij et al., 2003); while dividing them with a polymer-lipid partition coefficient (K_{PL}) would yield equilibrium concentrations in lipids ($C_L \rightleftharpoons$media) (Jahnke et al., 2014a; Mäenpää et al., 2011). The $C_L \rightleftharpoons$media provides a basis for thermodynamic exposure assessment and bioaccumulation and toxicity evaluation.

Recently, EPS has been extended to biological tissue using solid phase microextraction (SPME) fibers (Ossiander et al., 2008) and polydimethylsiloxane (PDMS) sheets (Jahnke et al., 2011), including *in vivo* applications (Allan et al., 2013). Analyte concentrations measured in polymers equilibrated with biological tissue can then be converted to equilibrium concentrations in lipids ($C_{L \rightleftharpoons tissue}$) using K_{PL}. A $C_{L \rightleftharpoons tissue}$ derived from in-tissue EPS showed good agreement with lipid-normalized concentrations obtained using conventional solvent extraction of tissue (Jahnke et al., 2011). Furthermore, concentrations in passive samplers equilibrated with soil and sediment have been shown to be proportional to lipid-normalized concentrations in organisms (C_L) exposed to or originating from the same habitat (Friedman et al., 2009; Kraaij et al., 2003). Lipid-normalized PCB concentrations in chironomid larvae, for example, differed by less than a factor of two from $C_{L \rightleftharpoons media}$ obtained by EPS of the habitat sediment (Mäenpää et al., 2011). However, derived $C_{L \rightleftharpoons media}$ should not be interpreted as predictions of actual lipid-based HOC concentrations within the organism; rather, they serve as a well-defined thermodynamic reference that quantifies the partitioning driven exposure level within a given media or habitat (Jahnke et al., 2014a). Actual levels may differ from equilibrium due to biomagnification, metabolism, natural variability, and other confounding factors.

The K_{PL} required to convert measured polymer concentrations into lipid-based concentrations are scarce in the literature, having only been reported for PCB, hexachlorobenzene, and a few organochlorine pesticides in silicone (Dürig et al., 2016; Jahnke et al., 2008). Reported partition coefficients showed negligible variation over the different lipids applied. However, it remained unclear as to whether observed polymer weight enhancements were caused by lipid adhering to the polymer surface or through lipid absorption into the polymer. The formation of a lipid film on the polymer would require a partition coefficient correction; while absorption into the polymer could change the polymer's partitioning properties. For PDMS-coated SPME fibers, for example, contact with lipid (and other matrices) has been shown to have little effect ($\leq$10%) on their sorption partitioning properties (Jahnke and Mayer, 2010).

The study aims are (1) to analytically determine K_{PL} for a wide range of HOC for two silicone polymers and low density polyethylene (LDPE) (2) to quantify the influence of temperature and lipid nature on K_{PL}, and (3) to clarify whether polymer-lipid contact affects its partition coefficient. In addition, we provide a short discussion on future applications for K_{PL}.

2. Working principle

An experimental system was designed that not only determined partition coefficients but also allowed the influence of adsorbed and absorbed lipid to be assessed. The upper disk of a polymer disk stack was brought into contact with an analyte-spiked lipid and allowed to equilibrate through uptake. An additional disk was immersed in the lipid (Fig. 1). The bottom disk in the stack (not in contact with the lipid) was dosed with performance reference compounds (PRC) that equilibrate with the lipid in the opposite direction to the target compounds. This method was applied using triolein and fish oil at 4 °C and 20 °C for periods of between 8 and 42 days. After selected contact periods, all disks and the lipids were analyzed for spiked contaminants. Since HOC diffuse rapidly in polymers (Rusina et al., 2010; Rusina et al., 2007), we assumed that they would migrate faster than the lipid, and thus would attain equilibrium quicker. This setup would allow a comparison of partitioning by the lipid-dosed substances in the presence (immersed disk) and absence (bottom disk) of lipid in the polymer. Polymer diffusion of fish oil and triolein was also studied in a separate experiment, using two silicones (Altesil, SSP) and LDPE.

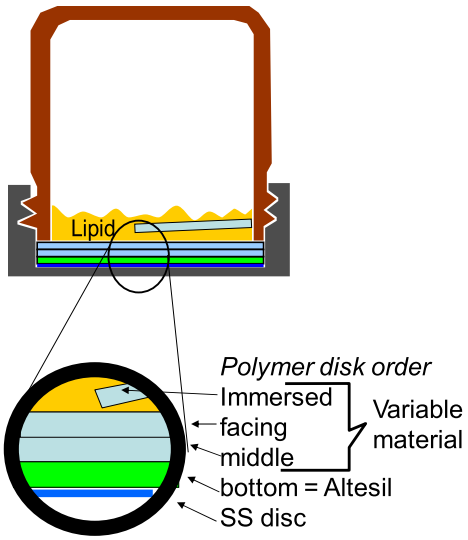

Fig. 1. Experimental setup for the polymer-lipid partition experiment. A stack of polymer disks was placed onto a stainless-steel disk (SS) in the lid of a glass jar and brought into contact with lipid dosed with target substances. One disk was directly immersed in the lipid. The bottom Altesil disk (isolated in the LDPE incubation) was dosed with performance reference compounds.

3. Method and materials

3.1. Materials

Translucent Altesil silicone rubber sheets (300 × 300 cm and 0.5 mm thick) were purchased from Altec Products Limited (UK), 0.25 mm thick SSP-M823 silicone rubber membranes were obtained from Specialty Silicone Products (Ballston Spa, NY, USA), and LDPE (0.07 mm thick) was obtained from Brentwood Plastics (Brentwood, MO, USA). The polymers were pre-extracted in a Soxhlet apparatus (Altesil, SSP) or by shaking in ethyl acetate for four days (LDPE). Partitioning experiments were undertaken using the 16 EPA PAH, 22 OCP, and 24 PCB, including dioxin-like PCB. Fourteen PCB not occurring in industrial mixtures were used as PRC. (a full substance list is provided in the Supplementary information, (S1). These substances, substance mixtures, along with recovery internal standards (PCB 209, mirex, ^{13}C-*gamma*-HCH, ^{13}C-2,4-DDT, ^{13}C-PCB 52, ^{13}C-PCB 180) and syringe internal standards (1,2,3,4-tetrachloronaphthalene (TCN), PCB 143), were obtained from various suppliers in The Netherlands. Olive oil (extra virgin) was purchased in a local supermarket (max. free fatty acids <1% as oleic acid); fish oil (Tobis omega-3 fish oil) was obtained from P.W. Health Supplies (Pharmacist Tracey Peake MRPharmS, UK). Triolein (glyceryl trioleate, ≥ 97.0% pure) and Tricosane (lipid analysis internal standard) were obtained from Sigma-Aldrich. All solvents