Field estimates of polyurethane foam − air partition coefficients for hexachlorobenzene, alpha-hexachlorocyclohexane and bromoanisoles
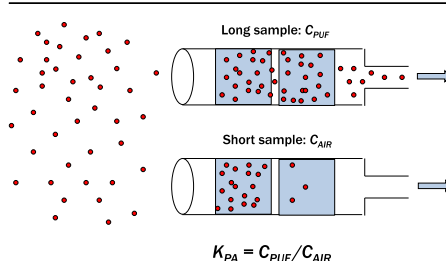
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HIGHLIGHTS

- Polyurethane foam-air partition coefficients (K_{PA}) are needed to estimate passive air sampling rates.
- K_{PA} were determined for two anthropogenic and two natural SVOCs in air sampling experiments over the Baltic Sea.
- K_{PA} predicted from octanol-air partitioning or polyparameter free energy models varied by factors of 3 to over 30.
- Such variability provides an incentive for further measurements and modeling with other SVOCs.

GRAPHICAL ABSTRACT

ABSTRACT

Partition coefficients of gaseous semivolatile organic compounds (SVOCs) between polyurethane foam (PUF) and air (K_{PA}) are needed in the estimation of sampling rates for PUF disk passive air samplers. We determined K_{PA} in field experiments by conducting long-term (24−48 h) air sampling to saturate PUF traps and shorter runs (2−4 h) to measure air concentrations. Sampling events were done at daily mean temperatures ranging from 1.9 to 17.5 °C. Target compounds were hexachlorobenzene (HCB), alpha-hexachlorocyclohexane (α-HCH), 2,4-dibromoanisole (2,4-DiBA) and 2,4,6-tribromoanisole (2,4,6-TriBA). K_{PA} (mL g^{-1}) was calculated from quantities on the PUF traps at saturation (ng g^{-1}) divided by air concentrations (ng mL^{-1}). Enthalpies of PUF-to-air transfer (ΔH_{PA}, kJ mol^{-1}) were determined from the slopes of log K_{PA}/mL g^{-1} versus $1/T$(K) for HCB and the bromoanisoles, K_{PA} of α-HCH was measured only at 14.3 to 17.5 °C and ΔH_{PA} was not determined. Experimental log K_{PA}/mL g^{-1} at 15 °C were HCB = 7.37; α-HCH = 8.08; 2,4-DiBA = 7.26 and 2,4,6-TriBA = 7.26. Experimental log K_{PA}/mL g^{-1} were compared with predictions based on an octanol-air partition coefficient (log K_{OA}) model (Shoeib and Harner, 2002a) and a polyparameter linear free relationship (pp-LFER) model (Kamprad and Goss, 2007) using different sets of solute parameters. Predicted K_P values varied by factors of 3 to over 30, depending on the compound and the model. Such discrepancies provide incentive for experimental measurements of K_{PA} for other SVOCs.

1. Introduction

Passive air samplers using polyurethane foam (PUF) disks have revolutionized air sampling for semivolatile organic compounds

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(SVOCs). Passive samplers are inexpensive and do not require a power source, features which allow them to be deployed over broad regions and in remote areas. The Global Atmospheric Passive Sampling (GAPS) Network using PUF disks has made it possible to acquire seasonally resolved air concentration data worldwide for organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) (Pozo et al., 2006, 2009).

A drawback of PUF disk samplers is that the more volatile members of SVOC classes reach saturation on the PUF during long deployment or at warmer temperatures, resulting in a curvilinear or plateau relationship between quantity of SVOC collected and deployment time (Harner et al., 2004, 2013; Melymuk et al., 2014; Shoeib and Harner, 2002a). Similarly, breakthrough of SVOCs past the PUF cartridge trap can occur during active (pumped) air sampling (Melymuk et al., 2014). One approach to these difficulties is to use sorbent resins or PUF-sorbent combinations which have a higher capacity for SVOCs (Li et al., 2011; Koblizkova et al., 2012; Melymuk et al., 2014; Shoeib et al., 2008; Shunthirasingham et al., 2010; Schuster et al., 2012). Another is to understand the collection limitations of PUF and adjust sampling conditions accordingly.

Air sampling rates ($m^3 d^{-1}$) in the GAPS program and other passive sampling campaigns are often determined by following the loss of depuration compounds (DCs), which are spiked onto the PUF disk before deployment. DCs are typically isotopically labeled SVOCs or unlabeled PCB congeners which are not commonly found in air. Correction for the curvilinear behavior of PUF collection can be made by calculating the effective sampling rates and total air volumes over the deployment period. Equations can be found in several papers (Harner et al., 2004, 2013; He and Balasubramanian, 2010; Gouin et al., 2005; Persoon and Hornbuckle, 2009; Petrich et al., 2013; Pozo et al., 2004, 2006). A template for these calculations is available from the GAPS network (Harner et al., 2013; Parnis et al., 2016a). A key property in these calculations is the partition coefficient of gas-phase DCs and target compounds between PUF and air. Experimental measurements of this partitioning have been made for PCB congeners by exposing PUF disks to laboratory air over 450 days (Shoeib and Harner, 2002a) at 22–23 °C. Seven congeners having 2–4 chlorines followed the relationship:

$$Log\ K_{PA}\big/\left(m^3 g^{-1}\right) = 0.6366 \log K_{OA} - 3.1774 \quad (1)$$

where K_{PA} is the partition coefficient, calculated from (mass SVOC g^{-1} PUF/(mass SVOC m^{-3} air) = $m^3 g^{-1}$. In this paper we express K_{PA} in units of $mL\ g^{-1}$ and use an adjusted form of this equation which accounts for $10^6\ mL\ m^{-3}$:

$$Log\ K_{PA}\big/\left(mL\ g^{-1}\right) = 0.6366 \log K_{OA} + 2.8226 \quad (2)$$

Kamprad and Goss (2007) determined K_{PA} ($mL\ g^{-1}$) for 103 organic compounds with diverse functionalities by measuring the chromatographic retention volume of analytes on a PUF column. Most of their compounds had lower molecular weights than the SVOCs commonly sought in ambient air, but some were within the SVOC range, *viz.* chlorobenzenes, 2–3 ring polycyclic aromatic hydrocarbons and PCBs with 2–3 chlorines. Other classes included carboxylic acids, ethers, esters, ketones, nitriles, amides, nitro-compounds and heterocyclic *N*- and *O*-compounds. Experimental data were fitted by multiple linear regression to a polyparameter linear free energy relationship (pp-LFER) of the form:

$$Log\ K_{PA}/mL\ g^{-1} = l_{16,p}L_{16,i} + s_P S_i + a_P A_i + b_P B_i + v_P V_i - c \quad (3)$$

In Eq. (3), small letters $l_{16,P}$, s_P, a_P, b_P and v_P refer to sorption

properties of the PUF, capital letters $L_{16,i}$, S_i, A_i, B_i and V_i are descriptors of the sorbing compound ("solute parameters") and c is a constant. $L_{16,i}$ is the dimensionless hexadecane-air partition coefficient, S_i is the dipolarity/polarizability descriptor, A_i characterizes the "acidic" hydrogen bond donor (or electron acceptor) capability, B_i is the "basic" hydrogen bond acceptor (or electron donor) property, and V_i is the McGowan molar volume. The pp-LFER equation at 15 °C for a polyether-type foam (manufacturer's number LM2033) with a density of 0.020 g cm^{-3} was (the b_P descriptor was not significantly different from zero):

$$Log K_{PA}/mLg^{-1} = (0.71\pm0.02)L_{16,i} + (1.69\pm0.05)S_i + (3.66\pm0.05)A_i$$
$$+ (0.36\pm0.09)V_i - (0.15\pm0.05)$$
$$(4)$$

Eq. (4) fitted experimental data with $r^2 = 0.997$ and a standard error less than 0.1 log unit. In comparison, a log-log plot of K_{PA} versus liquid-phase vapor pressure gave a poorer fit and divergence of different compound classes. Further, by measuring K_{PA} at different temperatures, Kamprad and Goss (2007) were able to derive a similar relationship for the enthalpy of PUF-to-air desorption (ΔH_{PA}, kJ mol^{-1}) for LM2033 (note: sign changed from enthalpy of sorption in the original paper):

$$\Delta H_{PA}\left(kJ\ mol^{-1}\right) = (4.3\pm1.0)L_{16,i} + (17.6\pm2.3)S_i + (46.6\pm4.0)A_i$$
$$+ (12.8\pm4.0)V_i - (2.7\pm2.6)$$
$$(5)$$

$$Log\ K_{PA}/mL\ g^{-1} = \frac{10^3 \Delta H_{PA}}{2.3RT} + b_{PA} \quad (6)$$

where $R = 8.31$ J mol^{-1} K^{-1}.

PUF-air partition coefficients have not been determined for OCPs and it has been assumed that they can be predicted from their K_{OA} (Gouin et al., 2005; Harner et al., 2004; He and Balasubramanian, 2010; Pozo et al., 2006). In this paper we describe field experiments to investigate gas-phase partitioning between PUF and air for hexachlorobenzene (HCB) and alpha-hexachlorocyclohexane (α-HCH), anthropogenic compounds which have been measured in northern Baltic air (Bidleman et al., 2015), and the natural brominated compounds 2,4-dibromoanisole and 2,4,6-tribromoanisole (2,4-DiBA and 2,4,6-TriBA), which are produced by marine algae and volatilize from the Baltic (Bidleman et al., 2014, 2015). Resulting K_{PA} are compared to those predicted by K_{OA} (Eq. (2)) and using the Kamprad-Goss pp-LFER approach (Eqs. (4) and (5)). A second paper explores the consequences of uncertainties in K_{PA} on PUF disk air sampling rates and results from a passive sampling network in the northern Baltic (Bidleman et al., 2016).

2. Experimental methods

High-volume air samples were taken at the island Holmön (63.792 N, 20.839E) in the northern Baltic Sea by pumping air through a 20 × 25-cm glass fiber filter (GFF) followed by two plugs of polyether-type PUF, each 7.5 cm diameter × 7.5 cm thick, density 0.025 g cm^{-3}. Flow rates were 0.45–0.57 m^3 min^{-1}. Sampling methods and flow rate monitoring are described further by Bidleman et al. (2014, 2015). Six experiments were conducted between May–August 2012 and three in April 2015. Mean event temperatures ranged from 1.9 to 17.5 °C. Two sets of collections were done within a few days of each other, "short" samples of 2–4 h to measure air concentrations and "long" samples of 24–98 h