



Note

Passive samplers of hydrophobic organic chemicals reach equilibrium faster in the laboratory than in the field

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ABSTRACT

The use of passive sampling methods for monitoring hydrophobic organic chemicals frequently requires the determination of equilibration times and partition coefficients in the laboratory. These experiments are often carried out by exposing passive samplers in a finite water volume, and errors are easily made when the obtained results are applied to the field, where water volumes are essentially infinite. The effect of water volume on the equilibration rate constant is discussed, using a mechanistic model. Application of this model to two literature reports illustrates that aqueous concentrations in the field may be underestimated by a factor of 10 or more, when the water volume effect is neglected. Finally, it is shown that the concept of “sorption capacity” (sampler mass times partition coefficient) allows for a more intuitive understanding of the passive sampling process in small and large water volumes, which may reduce the risk of laboratory-field extrapolation errors.

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1. Introduction

Passive sampling devices (PSDs) are valuable tools for measuring concentrations of freely dissolved hydrophobic organic chemicals (HOCs) in the aquatic environment, provided that these devices are properly calibrated (Vrana et al., 2005; Seethapathy et al., 2008). Laboratory calibrations of PSDs for determining sampling rates (R_s), equilibration times, and partition coefficients (K_{sw}) of HOCs are often based on the exposure of PSDs in a finite water volume, after applying a single contaminant dose, i.e. the “static exposure design”, with “static” not referring to the absence of water motion, but to the fact that there is no continuous supply of contaminants, as is the case in “flow through” designs (Booij et al., 2007). The calibration parameters can subsequently be used for estimating concentrations of freely dissolved HOCs in the environment, provided that the results of laboratory experiments are properly interpreted and translated to the field, where different flow and temperature conditions may prevail. However, problems with interpreting times to equilibrium in laboratory studies using static exposure designs is a recurring concern (Gustafson and Dickhut, 1997; Prest et al., 1998; Tucca et al., 2014), because equilibrium attainment for laboratory based exposures (closed systems) typically is much faster than for field exposures (open

systems). The reason for the shorter equilibration times can be qualitatively understood by considering that equilibrium attainment in a closed system is promoted by depletion of the water as well as by accumulation by the sampler. Phrased differently, in small water volumes a smaller amount of HOC needs to be transferred to the sampler before equilibrium is reached, resulting in a faster equilibrium attainment at a lower concentration level (Adams et al., 2007).

2. Theory

Following the addition of a PSD at $t = 0$, the evolution of HOC concentrations in water (C_w) and PSD (C_s) is given by Booij et al. (2007)

$$\frac{C_w - C_{w\infty}}{C_{w0} - C_{w\infty}} = \exp(-k_e t) \quad (1)$$

$$\frac{C_s - C_{s\infty}}{C_{s0} - C_{s\infty}} = \exp(-k_e t) \quad (2)$$

$$k_e = \left(1 + \frac{K_{sw}m}{V_w}\right) \frac{R_s}{K_{sw}m} \quad (3)$$

$$C_{w\infty} = \frac{V_w C_{w0} + m C_{s0}}{V_w + K_{sw}m} \quad (4)$$

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where k_e is the equilibration rate constant, C_{w0} is the aqueous concentration at $t = 0$, $C_{w\infty}$ is the equilibrium concentration in the water, C_{s0} and $C_{s\infty}$ are the initial and equilibrium concentrations in the sampler, V_w is the water volume, m is the sampler mass, K_{sw} is the sampler–water partition coefficient (volume per mass units, e.g. $L\ kg^{-1}$), R_s is the water sampling rate, and t is time. When K_{sw} is given in volume per volume units (e.g. $L\ L^{-1}$), sampler mass should be replaced by sampler volume (V_s). Similar equations are given by Kwon et al. (2009) for PSD exposures in suspensions, and by Lao et al. (2012) for the uptake of analytes that undergo first order degradation in water. In the derivation of Eqs. (1)–(4) it is assumed that there are no analyte losses due to hydrolysis, photolysis, vaporisation, biological transformation, or sorption on equipment surfaces. Further, it is assumed that R_s is independent of time. The latter assumption is valid for water boundary layer (WBL) controlled uptake kinetics, and only approximately valid for membrane controlled kinetics, where R_s only reaches a steady-state value after some time (Booij et al., 2007; Hong and Luthy, 2008). The important feature in Eqs. (1)–(3) is that the departure from equilibrium ($C_w - C_{w\infty}$ or $C_s - C_{s\infty}$) decays exponentially with time, with a rate constant k_e that increases when V_w decreases.

Two limiting cases are worth noting. For very large water volumes (open systems, $V_w \gg K_{sw}m$) Eq. (3) is reduced to

$$V_w \gg K_{sw}m: \quad k_e \approx \frac{R_s}{K_{sw}m} \quad (5)$$

which is commonly used for field-deployed samplers (Huckins et al., 2006). Since uptake rates of HOCs are generally controlled by the WBL, R_s is only weakly dependent on molecular size (Booij et al., 2003; Rusina et al., 2010), and k_e is inversely proportional to the HOC's sampler–water partition coefficient. By contrast, for very small water volumes (closed systems, $V_w \ll K_{sw}m$) Eq. (3) can be approximated by

$$V_w \ll K_{sw}m: \quad k_e \approx \frac{R_s}{V_w} \quad (6)$$

which implies that k_e is nearly independent of HOC properties, and inversely proportional to the water volume.

3. Application to literature data

The relevance of Eqs. (1)–(6) is confirmed by the results obtained by Gustafson and Dickhut (1997), who exposed SPMDs (surface area $36\ cm^2$, mass $0.36\ g$) in $3\ L$ spiked water in the laboratory. Application of Eqs. (1)–(4) to the C_s/C_w data shown in figure 3 of this publication yields k_e values from $2.8\ d^{-1}$ for fluorene ($\log K_{sw} = 4.7$) to $3.1\ d^{-1}$ for fluoranthene ($\log K_{sw} = 5.7$), in line with the expected behaviour of k_e at high values of $K_{sw}m/V_w$ (6.4 and 64, respectively). The mere fact that for field deployments $K_{sw}m/V_w = 0$ causes k_e to decrease by a factor of $1 + K_{sw}m/V_w$ (7.4 for fluorene, 65 for fluoranthene). As a result, the time to reach 95% equilibrium ($t_{95\%}$) in the sampler increases from 1 d in the laboratory to 7 d (fluorene) and 65 d (fluoranthene) in the field, and this increase is even stronger for the larger PAHs. Table 2 of this publication lists aqueous concentrations based on 4-d field deployments, assuming equilibrium, and concentrations obtained by batch water sampling. Good correspondence between passive sampling and batch sampling was observed for the 2- and 3-ring PAHs (mean ratio of 1.3), but SPMD based concentrations were 3 and 15 times lower for 4- and 5-ring PAHs, respectively. This can be qualitatively explained by the fact that equilibrium was not attained within 4 days for the latter compounds.

Similarly, Tucca et al. (2014) assumed that equilibration times obtained in the laboratory were the same as in the field. These authors studied the uptake of cypermethrin by $0.058\ cm^3$

poly(ethylene-co-vinylacetate) in the dark, using $1.5\ L$ ultra-pure water at $pH = 7$. Lao et al. (2012) report that cypermethrin hydrolysis half-life times are 4.97 d at $pH = 8.1$ and 274 d at $pH = 7$. The half-life time for photodegradation is reported to be 30 d (Schleier and Peterson, 2011). Adopting a 274 d half-life time in ultra pure water, cypermethrin hydrolysis can be estimated to be $<4\%$. Insignificant degradation is supported by the fact that C_w was constant between 9 and 15 d ($CV = 5\%$) and that the slope of C_w versus time was not significantly different from zero for this time period ($p > 0.9$). Adopting the authors' $\log K_{sw} = 5.6$ ($K_{sw} = 400,000\ L\ L^{-1}$) yields $K_{sw}V_s/V_w = 15$, which indicates that depletion of the water phase significantly increases the rate of equilibrium attainment. Modelling of the C_w data for this study, using Eq. (1), yielded $k_e = 0.51\ d^{-1}$. If the flow and temperature conditions in the field were the same as in the laboratory, then the k_e in the field would have been lower by a factor $1 + K_{sw}V_s/V_w = 16$, resulting in $k_e = 0.032\ d^{-1}$. This means that cypermethrin would have reached about 22% of its equilibrium concentration during the 7-d field deployments. As a result, aqueous cypermethrin concentrations in the field may have been underestimated by a factor of 5, but for a more reliable estimate the in-situ uptake kinetics of the sampler should have been calibrated, from the dissipation of performance reference compounds, or otherwise (Booij and Smedes, 2010).

4. Interpretation of the model

The concepts “sampling rate” and “sorption capacity” may be useful for a better understanding of PSD behaviour in closed and open systems. The sorption capacity of a sampler ($K_{sw}m$) has the dimension of a water volume, and equals the equivalent water volume that is extracted at equilibrium. Hence, a PSD may be visualised as a well-mixed water tank with volume $K_{sw}m$, that exchanges water with the outside environment at a rate R_s . The sorption capacity concept can be used to quickly calculate the aqueous concentration at equilibrium ($C_{w\infty}$) in a closed system, by considering that the initial amount ($V_wC_{w0} + mC_{s0}$) is distributed over a final equivalent water volume $V_w + K_{sw}m$.

$$C_{w\infty}(V_w + K_{sw}m) = C_{w0}V_w + mC_{s0} \quad (7)$$

which is the same as Eq. (4).

The sorption capacity concept is also useful for estimating the time needed to complete the sampling, by considering that a well-mixed water volume has to be flushed three times to exchange 95% of the water that was initially present. If $V_w \gg K_{sw}m$, then the transfer is nearly complete ($\sim 95\%$) when the tank is flushed three times by the external water, i.e. at $t_{95\%} = 3K_{sw}m/R_s$ (c.f., Eq. (5)). By contrast, if $V_w \ll K_{sw}m$, transfer is nearly complete when the external water volume is flushed three times by the water from the tank, i.e. $t_{95\%} = 3V_w/R_s$ (c.f., Eq. (6)). It is important, however, to distinguish “nearly complete transfer” from “near equilibrium”. For example, if the initial concentration is $100\ ng\ L^{-1}$ and the equilibrium concentration is $1\ ng\ L^{-1}$, then mass transfer is nearly complete when the concentration has dropped to $5\ ng\ L^{-1}$, but this would still be 5 times higher than the equilibrium level. Doubling the exposure time would bring the concentration in water to within 16% of its equilibrium value, in this case.

In conclusion, the concepts sampling rate (R_s) and sorption capacity (mK_{sw}) may be helpful for users of passive samplers of HOCs to obtain a more intuitive understanding of PSD behaviour in closed and open systems.

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