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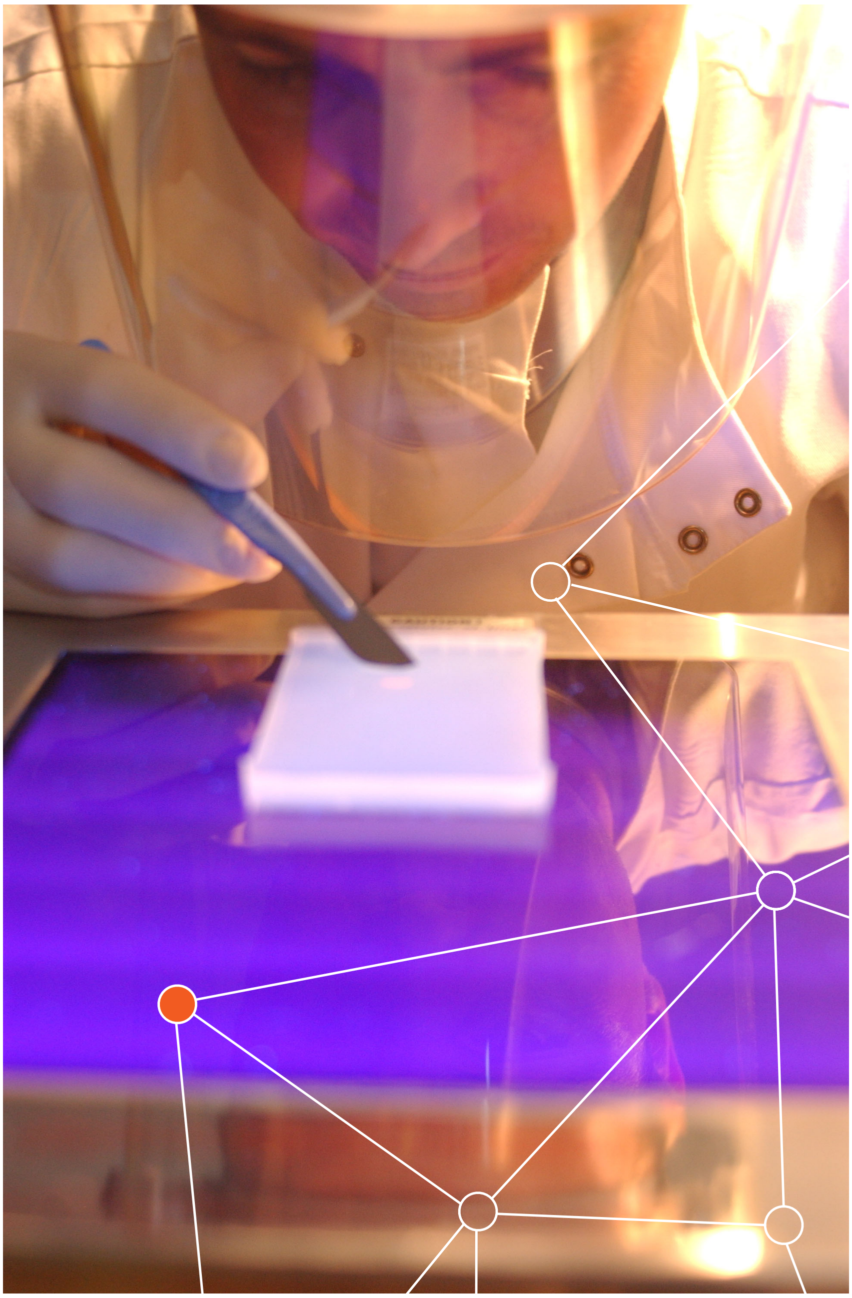

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Guidelines for determining polymer-water and polymer-polymer partition coefficients of organic compounds

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Correspondence about the details of any method or procedure should be directed to the author(s).

This series presents detailed descriptions of methods and procedures relating to chemical and biological measurements in the marine environment. Most techniques described have been selected for documentation based on performance in ICES or other intercalibration or intercomparison exercises: they have been carefully evaluated and demonstrated to yield good results when correctly applied. They have also been subject to review by relevant ICES working groups, but this is not to be construed as constituting official recommendation by the Council.

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Contents

Abstract

Methods for the experimental determination of polymer-water partition coefficients (K_{pw}) and polymer-polymer partition coefficients (K_{p1p2}) are reviewed with the aim to improve the quality of passive sampling-based monitoring of organic compounds. Mechanistic models are used for optimizing the experimental design of K_{pw} measurements with respect to scaling (polymer mass, water volume, concentration levels) and equilibration times. It is shown that the polymer-water phase ratio has a profound effect on the rate of equilibrium attainment. Experimental artefacts are discussed and quality control measures for quantifying uncertainties in the reported K_{pw} values are suggested. Examples of experimental design modelling are provided. Experimental methods for determining K_{p1p2} are not fully developed yet and several suggestions for the further development of K_{p1p2} measurements are included. It is expected that this guideline will be useful for investigators who seek to improve their experimental procedures for determining polymer-water and polymer-polymer partition coefficients, or to assess the quality of literature values of these partition coefficients.

Keywords: passive sampling, chemical monitoring, hydrophobic organic compounds, quality assurance, quality control

1 Introduction

The availability of accurate polymer-water partition coefficients (K_{pw}) is important for a successful application of passive samplers for monitoring the freely dissolved concentrations of organic compounds in the aquatic environment. Passive samplers for these compounds typically consist of a single polymer, such as low-density polyethylene (LDPE), poly(oxymethylene) (POM), or silicone (Booij *et al.*, 2016), with the exception of semipermeable membrane devices (SPMDs), which consist of an LDPE lay-flat tubing that is filled with triolein (Huckins *et al.*, 2006). The present guideline focuses on single-phase polymers but many considerations also apply to the determination of SPMD-water partition coefficients.

When the uptake rates are limited by transport through the water boundary layer, aqueous concentrations of freely dissolved organic compounds (C_w) in the environment are calculated from the amounts (N) that are accumulated by field-exposed samplers using

$$C_w = \frac{N}{mK_{pw}\left[1 - \exp\left(-\frac{R_s t}{mK_{pw}}\right)\right]} \tag{1}$$

where m is the polymer mass, K_{pw} is the polymer-water partition coefficient, R_s is the equivalent water sampling rate, and t is time. To appreciate the effect of inaccuracies in K_{pw} on the calculated C_w of a particular compound, it is instructive to consider the limiting cases for long and short exposure times. In the long-time limit (equilibrium sampling stage, $t \gg mK_{pw}/R_s$) equilibrium is approached, and Equation (1) reduces to

$$C_w \approx \frac{N}{mK_{pw}} \tag{2}$$

which shows that the accuracy of the C_w of a particular compound strongly depends on the accuracy of its K_{pw}. In the short-time limit (kinetic sampling, $t \ll mK_{pw}/R_s$), Equation (1) reduces to

$$C_w \approx \frac{N}{R_s t} \tag{3}$$

Equation (3) shows that the errors in C_w are independent of the errors in K_{pw}, but instead depend on the accuracy of R_s, which may be estimated from the dissipation of performance reference compounds (PRCs) that are spiked into the sampler before exposure. With the PRC method, R_s is estimated from the fraction of retained PRCs (f) as a function of their K_{pw} using nonlinear least squares (Booij and Smedes, 2010)

$$f = \exp\left(-\frac{R_s t}{mK_{pw}}\right) \tag{4}$$

which illustrates that the accuracy of R_s is highly dependent on the accuracy of the K_{pw} of the PRCs.

In some cases, sampler-water exchange rates are completely or partially controlled by diffusion in the polymer. This may occur for the sampling of compounds with small K_{pw} values at high flow conditions. In these cases, Equation (1) is no longer exact, and more complex models need to be used (Tcaciuc *et al.*, 2015). Further details are provided in sections 3.1 and 3.2.

K_{pw} values can be determined by allowing a chemical to reach its equilibrium distribution between water and polymer ($K_{pw} = C_p/C_w$). A distinction can be made between methods that aim to keep C_w constant during the experiment, and methods that allow C_w to change with time, following a single dose. The former methods are limited to absorption experiments while the latter include both absorption and desorption studies.

A thermodynamic method for determining K_{pw} is based on the consideration that partition coefficients can be calculated from the ratio of compound solubilities in the respective phases (Grant *et al.*, 2016). Although this method has its merits and is a useful addition to the passive sampling literature, it focuses on the measurement of solubilities in polymers and therefore falls outside the scope of this guideline.

K_{pw} values can also be derived by measuring the mass flux from a spiked sampler (donor) to an unspiked sampler (acceptor) that are separated by a stirred water phase (Kwon *et al.*, 2007). This method is based on the consideration that the mass flux between the sheets is inversely proportional to K_{pw}. It can only be applied when the transport resistance of the polymer can be neglected. The experimental setup has to be calibrated using reference compounds with accurately known K_{pw} values. This method has not been extensively used in other studies. In addition, the difference between the $\log K_{pw}$ values from the desorption experiments and the kinetic method used by Kwon *et al.* (2007) increased from −0.1 at $\log K_{pw} = 3.5$ to 0.3 at $\log K_{pw} = 6$. Because of this bias, this method is not yet recommended for routine application.

The fact that different concentration scales are used for the polymer and water phases may cause ambiguity in the reported K_{pw}. Amount per litre is recommended for expressing concentrations in the water phase because $\log K_{pw}$ values are used to obtain concentrations in water on a volume basis. Amount per kg is recommended for the concentrations in the polymer because the mass of a polymer is more conveniently measured than its volume. An exception is the case of solid phase micro extraction fibres, where the amount of polymer has to be calculated from the diameter of the fibre core and the film thickness reported by the manufacturer. In any case, the units of K_{pw} should be clearly specified and the adopted polymer density should be given whenever polymer volume was calculated from polymer mass or vice versa.

Documentation of manufacturer name, product name, product number, and batch number is useful for future reference, e.g., when a certain polymer batch yields deviating K_{pw} values. Information on type and content of fillers and additives may also prove useful for future reference. Polymer pre-extraction methods should be documented because the residual oligomer content may have an effect on the K_{pw}.

A number of experimental artefacts may result in erroneous K_{pw} values. The presence of analyte aggregates and sorption to dissolved organic matter can cause an overestimation of dissolved-phase concentrations, particularly for the more hydrophobic compounds (Hermans *et al.*, 1992; Smedes *et al.*, 2009; Choi *et al.*, 2013). Inclusion of analytes that are sorbed to container walls during the extraction of the water phase may result in overestimating C_w and the reverse may occur in the case of analyte losses by evaporation and photodegradation/biodegradation. Analyte losses may be minimized by the use of sealed incubation vessels, amber glassware (Reitsma *et al.*, 2013), and the addition of 50 mg L^{-1} sodium azide (Jonker *et al.*, 2015). Insufficiently long incubation times may cause measured concentrations to deviate from their equilibrium values. Aqueous concentrations should be below the analyte's solubility limit and above its method detection limit.

Insufficient temperature control may also result in deviating K_{pw} values since partition coefficients generally decrease with increasing temperature. The temperature effect ($\Delta \log K_{pw}/\Delta T$) can be estimated from

$$\frac{\Delta \log K_{\text{pw}}}{\Delta T} = \frac{\Delta H_{\text{pw}}}{2.303RT^2} \tag{5}$$

where ΔH_{pw} is the compound's enthalpy of phase transfer from water to the polymer, R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature. ΔH_{pw} values typically are in the range −10 to −60 kJ mol^{-1} (Muijs and Jonker, 2009; Lohmann, 2012; Jonker *et al.*, 2015), which results in a change in $\log K_{pw}$ of −0.01 to −0.04°C^{-1} (i.e. a 2–10% decrease in K_{pw} per °C). This means that experimental temperatures should be kept constant to within 1°C, and that specifications like "ambient temperature" are not sufficiently accurate.

The inter-laboratory variability of $\log K_{pw}$ was estimated by Lohmann *et al*. (2012) as 0.18 for LDPE, 0.21 for SPMDs, and 0.45 for silicones. In addition, Difilippo and Eganhouse (2010) reported that published poly(dimethylsiloxane)-water partition coefficients for the same compound can differ by up to four orders of magnitude. These values are larger than the uncertainties of 0.01 to 0.1 log units that are typically reported for individual studies (Smedes *et al.*, 2009; e.g., Hale *et al.*, 2010; Jonker and Muijs, 2010; Pintado-Herrera *et al.*, 2016). This suggests that reported uncertainties for individual experiments underestimate the true uncertainties. It is therefore desirable that laboratories base their uncertainty estimates on intermediate precision (e.g. different experiments, instruments, analysts) rather than on (within-experiment) repeatability (Ellison and Williams, 2012). For example, three consecutive experiments yield a more realistic uncertainty estimate than a single experiment that is carried out in triplicate because more sources of variability are included in the former case.

The determination of polymer-polymer partition coefficients (K_{p1p2}) is useful for improving data quality of passive sampling of organic compounds. First, K_{p1p2} can be used to compare K_{pw} values across different polymers (p1, p2), or to generate K_{pw} values for uncalibrated polymers using

$$K_{p1w} = K_{p2w}\, K_{p1p2} \tag{6}$$

which allows to better assess the variability of reported K_{pw} values. Second, K_{p1p2} can be used to assess between-batch variability and between-manufacturer variability of K_{pw} values for a particular polymer type.

The purpose of the present document is to provide guidance for the measurement of K_{pw} and K_{p1p2}, aiming to improve quality of newly generated data and to assess the quality of literature values. To this end, existing methods and their mechanistic basis are reviewed, potential artefacts are identified, and quality assurance and control measures to reduce the effects of these artefacts are outlined.

2 Parameters for experimental design modelling

Initial modelling of the exposure system is useful to properly design K_{pw} determination experiments with respect to scaling (i.e. sampler mass, water volume, spike level) and incubation times. Most importantly, concentrations in polymer and water at equilibrium should fall within the calibrated range of the analytical equipment and incubation time should be sufficiently long to ensure equilibrium attainment. Typical incubation times range from 4 to 13 weeks and polymer/water phase ratios range between 0.001 and 1 g L^{-1} (Adams *et al.*, 2007; Cornelissen *et al.*, 2008; Muijs and Jonker, 2009; Smedes *et al.*, 2009; Choi *et al.*, 2013; Reitsma *et al.*, 2013; Jonker *et al.*, 2015). Considering the wide range of incubation times and polymer/water phase ratios, it is difficult to recommend default values for these parameters, particularly because unexpected disequilibrium was observed in several studies (Cornelissen *et al.*, 2008; Reitsma *et al.*, 2013; Jonker *et al.*, 2015). Instead, it is recommended that these parameters are optimized in advance. Required parameters for the modelling are the diffusion coefficient in the polymer (D_P), the mass transfer coefficient of the water boundary layer (k_w), and an initial best estimate of K_{pw}. An initial estimate of K_{pw} is needed to determine the spike levels that are required for an accurate determination of the concentrations at equilibrium. Knowledge of k_w and D_p is needed to estimate the rate at which equilibrium is attained. The best available practice for estimating these parameters is discussed in this section.

2.1 Polymer-water partition coefficients

Initial estimates of K_{pw} can be obtained from published values for the target compound. For nonpolar compounds, K_{pw} can also be estimated from correlations with $\log K_{ow}$ for LDPE (Sacks and Lohmann, 2012), silicone (Difilippo and Eganhouse, 2010), and POM (Endo *et al.*, 2011)

LDPE $\quad \log K_{pw}$ (L kg^{-1}) $= 1.08 \log K_{ow} - 0.67$ (7)

$R^2 = 0.93$, $n = 93$, (s not specified)

Silicone $\quad \log K_{pw}$ (L L^{-1}) $= 0.86 \log K_{ow} - 0.13$ (8)

$R^2 = 0.78$, (s and n not reported)

POM $\quad \log K_{pw}$ (L kg^{-1}) $= 1.01 \log K_{ow} - 0.60$ (9)

$R^2 = 0.94$, $s = 0.49$, $n = 110$

$\log K_{pw}$-$\log K_{ow}$ relationships that are based on a specific compound group (e.g., PCBs, PAHs) may yield more accurate estimates compared with the more generic Equations (7)–(9) (U.S. EPA/SERDP/ESTCP, 2017). It should also be noted that not all silicones are pure poly(dimethylsiloxane), but instead may contain functional groups and fillers which may result in differences in $\log K_{pw}$ values up to 0.5 log units for nonpolar and polar compounds (Smedes *et al.*, 2009; Martin *et al.*, 2016).

Poly-parameter linear free energy relationships (pp-LFERs) use multiple compound descriptors to model partition coefficients: excess molar refraction (E), dipolarity/polarizability (S), hydrogen bond acidity (A), hydrogen bond basicity (B), and molar volume divided by 100 (V) (Endo and Goss, 2014). These relationships yield better estimates of $\log K_{pw}$ for both polar and nonpolar compounds. Descriptors for many compounds can be obtained from www.ufz.de/lserd. Endo *et al.* (2011) summarized pp-LFERs for several polymers, and suggested that the pp-LFER for hexadecane-water may be used to estimate the $\log K_{pw}$ for LDPE

POM $\log K_{pw}$ (L/kg) $= -0.37 + 0.39E + 0.28S - 0.46A - 3.98B + 2.98V$ (10)

$n = 116$, $s = 0.24$, $R^2 = 0.99$

silicone $\log K_{pw}$ (L/L) $= 0.27 + 0.60E - 1.42S - 2.52A - 4.11B + 3.64V$ (11)

n = 170, $s = 0.17$, $R^2 = 0.99$

LDPE $\log K_{pw}$ (L/L) $= 0.09 + 0.67E - 1.62S - 3.59A - 4.87B + 4.43V$ (12)

$n = 370$, $s = 0.12$, (R^2 not reported)

Alternatively, the K_{pw} of a structurally similar compound may be adopted when no further information is available.

2.2 Diffusion coefficients in the polymer

Knowledge of D_P is needed for cases where diffusion in the polymer phase is rate-limiting for the sampler-water exchange kinetics. When experimental values of D_P are not available, an initial estimate can be obtained from correlations with known compound properties. D_P has been correlated with molecular surface area and volume (Hong and Luthy, 2008; Rusina *et al.*, 2010a; Lohmann, 2012). Molecular weight is considered to be a poor predictor of D_P, while surface area calculations require specialized software. For the purpose of these guidelines D_P were correlated with the McGowan molar volume (Abraham and McGowan, 1987; Schwarzenbach *et al.*, 2003), which is more easily calculated than the LeBas molar volume, particularly for compounds that contain multiple ring structures, C-C bridges, or oxygen. The McGowan method yields smaller molar volume estimates, but McGowan/LeBas ratios of molar volumes for these methods do not vary much among compound groups: 0.73 for PAHs, 0.67 for PCBs, 0.72 for polybrominated diphenyl ethers, and 0.63 for bridged organochlorine pesticides, (e.g., aldrin, endosulfan, heptachlor). Experimental D_P values of PAHs, PCBs, and hexachlorobenzene, reported for LDPE (Lohmann, 2012), silicone (Rusina *et al.*, 2010a), and POM (Hong and Luthy, 2008) could be modelled by

LDPE $\log D_P\ (m^2\ s^{-1}) = -\ 0.0145\ V_{McGowan} - 10.43$ (13)

$R^2 = 0.64$, $s = 0.30$, $n = 75$

silicone $\log D_P\ (m^2\ s^{-1}) = -\ 0.0073 V_{McGowan} - 9.13$ (14)

$R^2 = 0.74$, $s = 0.13$, $n = 56$

POM $\log D_P\ (m^2\ s^{-1}) = -0.0119 V_{McGowan} - 12.27$ (15)

$R^2 = 0.93$, $s = 0.07$, $n = 7$

Diffusion coefficients in LDPE, silicone, and POM are markedly different. For example, the D_P of PCB52 ($V_{McGowan}$ = 181 $cm^3\ mol^{-1}$) in silicone is approximately $3.5{\cdot}10^{-11}\ m^2\ s^{-1}$, and its D_P in LDPE and POM is lower by a factor of 400 and 10,000, respectively. The effect of molecular size is less pronounced: D_P values of acenaphthene ($V_{McGowan}$ = 126 $cm^3\ mol^{-1}$) are three to six times larger than those of PCB52, while the D_P values of PCB194 ($V_{McGowan}$ = 230 $cm^3\ mol^{-1}$) are two to five times smaller. The regression equation for POM should be applied with caution since it is based on only a few measurements for relatively small molecules up to fluoranthene ($V_{McGowan}$ = 158 $cm^3\ mol^{-1}$). Equation (15) predicts $D_P = 2{\cdot}10^{-15}\ m^2\ s^{-1}$ for benzo[a]pyrene, but Rusina *et al.* (2007) report a value of $<10^{-16}\ m^2\ s^{-1}$. Exceptionally small D_P values have been observed for some polybrominated diphenyl ethers ($<10^{-16}\ m^2\ s^{-1}$) and organophosphates ($<10^{-15}\ m^2\ s^{-1}$) in LDPE (Narvaez Valderrama *et al.*, 2016; Pintado-Herrera *et al.*, 2016), and for triphenyl phosphate ($3{\cdot}10^{-15}\ m^2\ s^{-1}$) in silicone (Pintado-Herrera *et al.*, 2016).

2.3 Mass transfer coefficient of the water boundary layer

Knowledge of k_w is required when transport through the water boundary layer is rate limiting, which is commonly the case for hydrophobic organic compounds with $\log K_{ow}$ values larger than about five (Huckins *et al.*, 2006; Booij *et al.*, 2007). Its value is often expressed in terms of an equivalent boundary layer thickness (δ_w)

$$k_w = \frac{D_w}{\delta_w} \quad (16)$$

where D_w is the diffusion coefficient in water (approximately $6{\cdot}10^{-10}$ m² s⁻¹ = 600 µm² s⁻¹ for organic compounds at 20°C). Lohmann (2012) suggested δ_w values between 500 and 10 µm for quiescent and turbulent flows, respectively (k_w = 1 to 50 µm s^{-1}), in line with observed k_w values between 2 to 30 µm s^{-1} at stirring rates between 60 and 600 min^{-1} (Tcaciuc *et al.*, 2015; Booij *et al.*, 2017). Considering that investigators aim for intense mixing, a k_w value between 10 and 50 µm s^{-1} appears to be a safe estimate. Experimental values of k_w can be determined for a specific exposure system, using the dissolution rates of alabaster or benzoic acid (Booij *et al.*, 2017). Alternatively, k_w estimates may be obtained by modelling the time evolution of concentrations for a test compound with boundary layer controlled exchange rates, for which accurate K_{pw} values are available (Reitsma *et al.*, 2013; Tcaciuc *et al.*, 2015). The use of PAHs with three and four aromatic rings may be convenient for this purpose because relatively high initial concentrations can be used, which allows for frequent subsampling of small water volumes. In addition, literature values of K_{pw} generally agree within 0.1 log unit for these compounds (Lohmann, 2012).

Although 10 to 50 µm s^{-1} may be a fair guess for freshwater at room temperature, lower values can be expected at lower temperatures and higher salinities. Reitsma *et al.* (2013) confirmed equilibrium attainment in 28 days for benzo[a]pyrene at 20°C in freshwater, but report 1% equilibrium at −15°C and a salinity of 245 PSU. These authors attributed this effect to a sixfold increase in viscosity, causing a 50-fold decrease in k_w. The unexpectedly low K_{pw} values that were reported by Jonker *et al.* (2015) at 4°C and 12°C, compared with the values obtained at 20°C and 30°C, may also be caused by viscosity effects on k_w. Viscosities of pure water are 1.6 times higher at 4°C than at 20°C, which results in a 1.7 times smaller aqueous diffusion coefficient. In addition, higher viscosities may result in smaller flow velocities for the same settings of the stirring or shaking device. Hence, adopting k_w = 3 to 15 µm s^{-1} may be a safe choice for experiments at 0°C.

When the polymer-water exchange kinetics is fully controlled by the water boundary layer, R_s is related to k_w by

$$R_s = A\, k_w \quad (17)$$

where A is the sampler area that is exposed to the water. Hence, k_w can be interpreted as a surface area normalized sampling rate, with units of L dm^{-2} d^{-1}. The numerical values of k_w in µm s^{-1} and in L dm^{-2} d^{-1} are nearly equal

$$1\ \mu m\ s^{-1} = 0.864\ L\ dm^{-2}\ d^{-1} \quad (18)$$

which is helpful for the modelling of K_{pw} experiments (section 3).

2.4 Membrane controlled versus boundary layer controlled kinetics

The relative importance of the transport resistance of the polymer (I_p) and the water boundary layer (I_w) can be estimated from (Huckins *et al.*, 2006; Booij *et al.*, 2007; Hong and Luthy, 2008; Lohmann, 2012; Tcaciuc *et al.*, 2015)

$$\frac{I_{\mathrm{p}}}{I_{\mathrm{w}}} = \frac{k_{\mathrm{w}}\,L}{D_{\mathrm{p}} K_{\mathrm{pw}} \rho} \qquad (19)$$

where ρ is the density of the polymer, and L is the volume to area ratio of the polymer, i.e., its half-thickness when both sides are exposed to water, or its thickness, when one side is exposed to water. Fully membrane controlled exchange can be expected when $I_{\mathrm{p}}/I_{\mathrm{w}}$>>1, which may occur at high water flow rates (high k_{w}), low K_{pw}, and low D_{p}.

As an example, consider the uptake of phenanthrene by a silicone sheet of 0.5 mm thickness with a density of 1.2 g cm^3. Phenanthrene's D_{p} in silicone is about $6{\cdot}10^{-11}$ m^2 s^{-1} = 60 µm^2 s^{-1} and its logK_{pw} value is 4.11. For highly turbulent flow (k_{w} = 50 µm s^{-1}), the ratio $I_{\mathrm{p}}/I_{\mathrm{w}}$ equals

$$\frac{I_{\mathrm{p}}}{I_{\mathrm{w}}} = \frac{50\ \mu\mathrm{m\ s}^{-1} \times 250\,\mu\mathrm{m}}{60\ \mu\mathrm{m}^2\mathrm{s}^{-1} \times 10^{4.11}\ \mathrm{L\ kg}^{-1} \times 1.2\ \mathrm{kg\ L}^{-1}} = 0.013 \qquad (20)$$

indicating water boundary layer controlled exchange in this case. By contrast, phenanthrene uptake by 500 µm POM strips (density 1.38 kg L^{-1}) under similar flow conditions would be membrane controlled ($I_{\mathrm{p}}/I_{\mathrm{w}} \approx 600$), since phenanthrene's D_{p} is 6000 times smaller, its K_{pw} is eight times smaller than in silicone, and the POM density is 1.15 times larger (Hong and Luthy, 2008).

3 Equilibration methods

In determinations of K_{pw} by equilibration the choice can be made to maintain constant aqueous concentrations (constant C_w design) or to allow these concentrations to change over time (single dose design). Difilippo and Eganhouse (2010) considered methods in which C_w was not kept constant to be of questionable quality but the reason for this is unclear. Instead, K_{pw} should be evaluated from the concentrations in both phases at equilibrium. The question of whether or not the equilibrium concentration in water differs from the initial concentration is irrelevant.

3.1 Constant C_w design

The negligible depletion design is a straightforward method to ensure constant C_w during the experiments. Sampler mass and water volume should be chosen such that the volume of water (V_w) is much larger than the sorption capacity of the sampler ($m\ K_{pw}$) (Vaes *et al.*, 1996)

$$V_w >> K_{pw}\ m \qquad (21)$$

This design is limited by the largest water volume and the smallest sampler mass that can be practically handled in the laboratory. For example, determining a $\log K_{pw}$ of 6 with a polymer mass of 1 mg requires a water volume that is much larger than 1 L.

In flow-through designs, a constant C_w is obtained by flushing the exposure chamber with spiked water that is prepared by mixing water with a stock solution in a water miscible solvent such as acetone or methanol (Kingston *et al.*, 2000; Vrana and Schuurmann, 2002; Wennrich *et al.*, 2003). Organic solvent concentrations in the exposure chamber are typically kept below 1% by volume. Generator columns (Booij *et al.*, 2003) and dialysis membranes (Ouyang *et al.*, 2006) have also been used to prepare spiked water of constant concentration.

In sampler-doser designs, depletion of the water phase is prevented by delivery from a large amount of dosing material that is spiked with the target compound. C18 extraction disks (Mayer *et al.*, 2000; Witt *et al.*, 2009) and silicone (Rusina *et al.*, 2010b) have been used as dosing materials.

For water boundary layer controlled uptake rates, the fraction of equilibrium (f_{eq}) follows from Equations (1) and (17)

$$f_{eq} = \frac{C_p}{C_w K_{pw}} = 1 - \exp\left(-\frac{k_w A t}{m K_{pw}}\right) \qquad (22)$$

and the time needed to attain equilibrium within 5% (t_{eq}) is given by

$$t_{eq} = \frac{-\ln(0.05)}{\left(\frac{k_w A}{m K_{pw}}\right)} = \frac{-\ln(0.05)}{\left(\frac{k_w}{K_{pw} \rho L}\right)} \qquad (23)$$

where ρ is the density of the polymer, and L is its volume to area ratio. In the constant C_w design, for a polymer of given thickness, t_{eq} is independent of sampler mass, since the surface area is linearly proportional to the mass of the polymer.

The fraction of attained equilibrium for membrane controlled uptake is given by (Crank, 1975, Equation 4.18)

$$f_{\mathrm{eq}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(-\frac{(2n+1)^2 \pi^2 D_{\mathrm{p}} t}{4L^2}\right) \tag{24}$$

For estimating the time to reach equilibrium within 5%, the terms with $n \geq 1$ can be neglected

$$t_{\mathrm{eq}} = -\frac{4L^2}{\pi^2 D_{\mathrm{p}}} \ln\left(\frac{0.05\pi^2}{8}\right) \approx 1.13 \frac{L^2}{D_{\mathrm{p}}} \tag{25}$$

For example, a compound with typical D_{P} value in LDPE of 10^{-13} m^2 s^{-1} = 0.1 µm^2 s^{-1} (e.g., PCB52, V_{McGowan} = 181 cm^3 mol^{-1}) would reach equilibrium with a 50 µm thick LDPE sheet in $1.13 \times 25^2 \div 0.1 = 7063$ s = 2 h.

Equation (19) can be used to determine whether t_{eq} is to be estimated for membrane controlled kinetics (Equation 25) or water boundary layer controlled kinetics (Equation 23). In case the kinetics are partially controlled by the membrane and partially by the water boundary layer, it is suggested that equilibration times are estimated for both cases, and that the larger of the two estimates is adopted for the purpose of experimental design. Alternatively, exact models for the case of mixed rate control can be used, e.g., Equation (4.53) from Crank (1975) and Equations (8) and (9) from Tcaciuc *et al.* (2015). These models are computationally more demanding and not easily incorporated in spreadsheet calculations.

3.2 Single dose design

With the single dose design, a fixed amount of the target compound is spiked into the water phase (absorption) or into the sampler (desorption). When the exchange kinetics is fully controlled by the water boundary layer, the time required to bring $C_{\mathrm{P}}/C_{\mathrm{w}}$ to within 5% of K_{pw}, is given by

$$\text{absorption:} \quad t_{\mathrm{eq,abs}} = \frac{-1}{\left(1 + \frac{mK_{\mathrm{pw}}}{V_{\mathrm{w}}}\right) \frac{k_{\mathrm{w}} A}{mK_{\mathrm{pw}}}} \ln\left(\frac{0.05}{1 + 0.95 \frac{mK_{\mathrm{pw}}}{V_{\mathrm{w}}}}\right) \tag{26}$$

$$\text{desorption:} \quad t_{\mathrm{eq,des}} = \frac{-1}{\left(1 + \frac{mK_{\mathrm{pw}}}{V_{\mathrm{w}}}\right) \frac{k_{\mathrm{w}} A}{mK_{\mathrm{pw}}}} \ln\left(\frac{0.05}{1.05 + \frac{V_{\mathrm{w}}}{mK_{\mathrm{pw}}}}\right) \tag{27}$$

A derivation of Equations (26) and (27) is provided in Annex 1.

To illustrate how equilibration times depend on m, V_{w}, and K_{pw}, some examples are shown in Figure 1, adopting m = 0.5 g, V_{w} = 2 L, K_{pw} = 10^5 L kg^{-1}, k_{w} = 10 µm s^{-1} (8.64 L dm^{-2} d^{-1}), a polymer density of 1.2 kg L^{-1}, and a polymer thickness of 500 µm. For this scenario, the dimensionless phase ratio $m\, K_{\mathrm{pw}}/V_{\mathrm{w}}$ = 25, which means that at equilibrium 96% of the chemical will be in the polymer and 4% in the water. Equilibration times are inversely proportional to sampler mass (Figure 1, left panel), because for a given polymer sheet, a higher polymer mass implies a higher sampling rate, and hence faster equilibrium attainment. Equilibration times steadily increase with increasing water volume (Figure 1, middle panel), because the sampling rate is the same, but a higher water volume has to be sampled, which takes longer. To appreciate the longer equilibration times for the absorption scenario, it should be

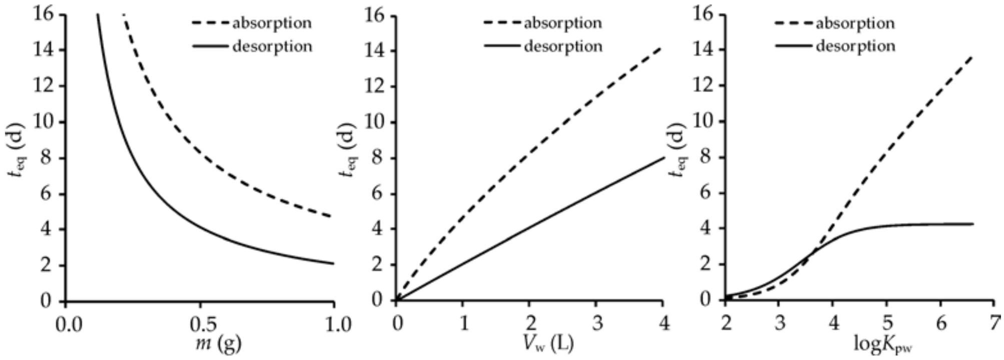

Figure 1. Equilibration times (t_{eq}) required for C_P/C_W to be within 5% of K_{pw} for water boundary layer controlled kinetics as a function of sampler mass (m, left), water volume (V_w, middle) and sampler-water partition coefficient (K_{pw}, right). Parameters are varied around central values of m = 0.5 g, V_w = 2 L, and K_{pw} = 10^5 L kg^{-1}. Polymer density = 1.2 kg L^{-1}, thickness = 500 μm, surface area normalized sampling rate = 8.64 L dm^{-2} d^{-1}.

considered that the water phase has to be more extensively depleted when the K_{pw} is higher. For example, when the initial concentration is 100 ng L^{-1} and the equilibrium concentration is 4 ng L^{-1}, then a 5% deviation from equilibrium corresponds to a C_w of 4.2 ng L^{-1}, which is 0.2 ng L^{-1} higher than the equilibrium value. Hence, 99.8% of the initial concentration difference has to be bridged before the C_w is within 5% of its equilibrium value. With increasing logK_{pw}, the equilibrium C_w gets smaller and total mass transfer has to be closer to 100% in order to bring C_w to within 5% of its equilibrium value. Equilibration times for the desorption scenario reach a plateau when K_{pw} increases because C_w is always within 5% of the equilibrium value when 95% of the initial concentration difference is bridged.

When the exchange kinetics are not limited by the water boundary layer but by the membrane instead, no analytical solution exists for estimating equilibration times for the single dose design. However, a limited number of numerical solutions is sufficient to estimate t_{eq} for a wide range of parameters. Specifically, the parameter group $D_P t_{eq}/L^2$ is a unique function of the phase ratio mK_{pw}/V_w. (Table 1. See Annex 1 for further details.) As an example of the use of Table 1, consider a desorption experiment with 1 g of a 50 μm thick polymer in 1 L water, and a compound with a D_P of 10^{-15} m^2 s^{-1} = 10^{-3} μm^2 s^{-1} and a K_{pw} of 10^4 L kg^{-1}. In this case, mK_{pw}/V_w = 10, and $D_P t_{eq}/L^2$ = 0.18. The equilibration time would then be estimated as t_{eq} = 0.18 L^2/D_P = 112 500 s = 1.3 d.

The effect of polymer mass, water volume, and K_{pw} is further illustrated in Figure 2, where these parameters are varied around central values of m = 0.5 g, V_w = 2 L, logK_{pw} = 5. The effect of changes in polymer mass and water volume are similar to the effects with boundary layer controlled kinetics, except that t_{eq} levels off to a constant value for absorption experiments at high polymer mass or small water volumes (Figure 2, left and middle panel). The reason for this is that it takes a certain minimum time for the compounds to become evenly distributed within the polymer. Another difference with water boundary layer controlled kinetics is that t_{eq} decreases with increasing K_{pw} (Figure 2, right panel). This can be explained by considering that the sampling rates with membrane controlled kinetics increase with increasing K_{pw}, which causes t_{eq} to decrease. However, it should be noted that sampling rates cannot increase beyond the values that are permitted by the water boundary layer. Therefore, t_{eq} should always be evaluated for both membrane controlled and boundary layer controlled exchange, and the largest value should be adopted for the purpose of experimental design.

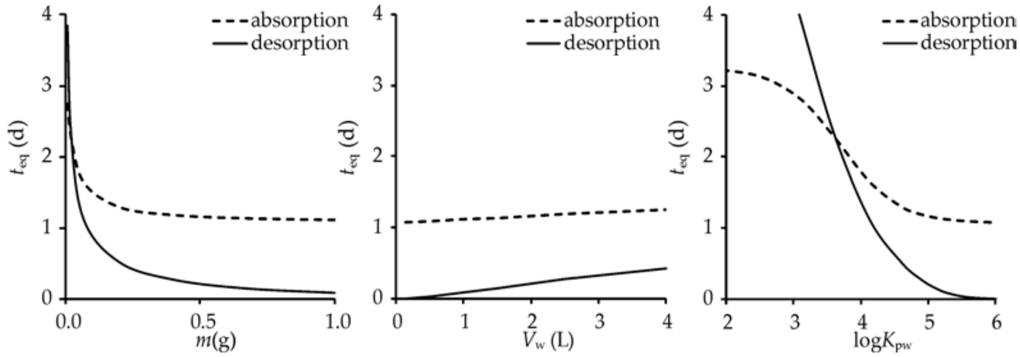

Figure 2. Equilibration times (t_{eq}) for membrane controlled kinetics as a function of sampler mass (m, left), water volume (V_w, middle) and sampler-water partition coefficient (K_{pw}, right). Parameters are varied around central values of m = 0.5 g, V_w = 2 L, and K_{pw} = 10^5 L kg^{-1}. Polymer thickness = 100 µm, $D_P = 10^{-14}$ m^2 s^{-1}.

Table 1. Values of $D_P t_{eq}/L^2$ as a function of mK_{pw}/V_w for desorption and absorption, for membrane controlled exchange kinetics with the single dose design. Equilibration times (t_{eq}) are estimated from the listed values of $D_P t_{eq}/L^2$ and the applicable values of D_P and L.

	desorption	absorption
mK_{pw}/V_w	$D_P t_{eq}/L^2$	$D_P t_{eq}/L^2$
0.0010	3.93	1.13
0.0033	3.43	1.13
0.010	2.97	1.12
0.033	2.45	1.11
0.10	1.94	1.07
0.33	1.33	0.97
1.0	0.80	0.79
3.3	0.39	0.57
10.0	0.18	0.45
33	0.051	0.39
100	0.010	0.38
333	0.0011	0.37
1000	0.00013	0.37

3.3 Cosolvent method

The cosolvent method is based on the observation that the addition of a water miscible organic solvent causes the polymer-solvent partition coefficients (K_{px}) to decrease. Cosolvent models were originally developed for modelling the effect of organic cosolvents on the solubility of organic compounds (Yalkowsky *et al.*, 1976; Li and Andren, 1995) and were later applied to the study of polymer water partition coefficients (Yates *et al.*, 2007; Smedes *et al.*, 2009; Pintado-Herrera *et al.*, 2016). Methanol appears to be exclusively used as a cosolvent in the latter applications.

With the cosolvent method, logK_{px} is plotted as a function of the fraction of organic solvent and K_{pw} is obtained by linear extrapolation to pure water (Yates *et al.*, 2007; Smedes *et al.*, 2009). There is no definite theoretical basis for choosing the units of concentration in the dissolved phase: amount per volume, amount per mass, amount per mole have all been used. Nor is there a definite theoretical basis for deciding whether the cosolvent content should be expressed as a mass, volume, or mole fraction. However, for PAHs, PCBs, and hexachlorobenzene there is a strong empirical basis for choosing mole fraction (x) as a cosolvent concentration, over the range $0 \le x \le 0.3$ (Smedes *et al.*, 2009)

$$\log K_{\mathrm{px}} = \log K_{\mathrm{pw}} - a\,x \tag{28}$$

where K_{px} is given in units of kg kg^{-1}. The slope (a) of the logK_{px} vs. x plot depends on the compound and the cosolvent type. The slope may also depend on the polymer type, which suggests that methanol also has an effect on the compound's chemical activity in the polymer phase (Smedes, unpublished data). Cosolvent concentrations of $x > 0.3$ are not recommended because logK_{px} vs. x deviates from linearity at these higher mole fractions. Plotting logK_{px} vs. volume fraction or mass fraction of methanol results in deviations from linearity at low cosolvent fractions, and the use of volume fractions and mass fractions in Equation (28) is therefore not recommended (Smedes *et al.*, 2009). The cosolvent method is generally applied using a single dose to either the sampler or the aqueous phase.

Equation (28) is useful for assessing data quality of K_{pw} measurements, and helps to evaluate the occurrence of experimental artefacts such as binding to dissolved organic matter and insufficient equilibration times. Binding to dissolved organic matter can be diagnosed when the K_{pw} that is measured in pure water is systematically smaller than the extrapolated value and when this difference increases with increasing logK_{pw}. Insufficiently long incubation times may result in similar (absorption) or opposite deviations (desorption).

An estimate of logK_{px} is needed for estimating the required equilibration times and spike levels. The following rule of thumb can be used for this purpose: the logK_{px} at x = 0.3 is approximately half of the logK_{pw} (Yates *et al.*, 2007; Smedes *et al.*, 2009; Pintado-Herrera *et al.*, 2016). For example, when logK_{pw} = 6, then a logK_{px} = 3 can be expected at x = 0.3.

At least four, and preferably five, methanol-water mixtures in the mole fraction range 0 to 0.3 should be used (e.g. x = 0, 0.06, 0.12, 0.18, 0.24, 0.30 which corresponds to nominal volume fractions of approximately 0.1, 0.2, 0.3, 0.4, 0.5). Concentrations in the polymer and in the solvent are expressed in amount per mass for convenience. The resulting logK_{px} are plotted versus the cosolvent mole fraction. Subsequently, the intercept (logK_{pw}) and its standard deviation are evaluated based on all methanol mole fractions > 0 (i.e. exclude the data for pure water). The extrapolated logK_{pw} and its standard deviation are then compared with the experimental logK_{pw}. When the difference is not significant, the experimental logK_{pw} is included in the regression and a new logK_{pw} estimate is obtained from the intercept. This K_{pw} has units of kg kg^{-1}, which can be replaced by L kg^{-1}, because the density of water is very close to 1 (less than 0.5% difference for temperatures between 0°C and 30°C).

3.4 Spike level requirements

The aqueous concentrations should be below the compound's solubility (S_w) and amounts present in a water sample should be above the method detection limit (MDL). For the constant C_w design, the following conditions should therefore apply

$$C_{\mathrm{w}} < \frac{S_{\mathrm{w}}}{10} \tag{29}$$

$$V_{\mathrm{w}} C_{\mathrm{w}} > 10 \text{ MDL} \tag{30}$$

In addition, the amounts present in the polymer phase should fall within the calibrated range of the analytical equipment.

For the single dose design, $C_{w,\infty}$ can be calculated from the mass balance

$$V_{\mathrm{w}} C_{\mathrm{w},0} + m C_{\mathrm{p},0} = V_{\mathrm{w}} C_{\mathrm{w},\infty} + m C_{\mathrm{p},\infty} \tag{31}$$

where $C_{p,0}$ is the initial concentration in the polymer. The requirements with respect to S_w and MDL for the single dose design can be expressed as

$$C_{\mathrm{w},\infty} = \frac{V_{\mathrm{w}} C_{\mathrm{w},0} + m C_{\mathrm{p},0}}{V_{\mathrm{w}} + m K_{\mathrm{pw}}} < \frac{S_{\mathrm{w}}}{10} \tag{32}$$

$$V_{\mathrm{w}} C_{\mathrm{w},\infty} = V_{\mathrm{w}} \frac{V_{\mathrm{w}} C_{\mathrm{w},0} + m C_{\mathrm{s},0}}{V_{\mathrm{w}} + m K_{\mathrm{pw}}} > 10 \text{ MDL} \tag{33}$$

The optimum spiking level can be found by trial and error, by first choosing convenient values for $C_{p,0}$ (desorption experiments) or $C_{w,0}$ (absorption experiments) and then testing this choice against Equations (32) and (33). Alternatively, the total spike amount (N_{total}) can be calculated from the required amount in the water (N_w) and the group mK_{pw}/V_w

$$\frac{N_{\mathrm{w},\infty}}{N_{\mathrm{total}}} = \frac{1}{1 + \dfrac{m K_{\mathrm{pw}}}{V_{\mathrm{w}}}} \tag{34}$$

For example, when $mK_{pw}/V_w = 9$, then 10% of the total spike amount will be in the water phase at equilibrium.

3.5 Sampling and analysis

At the end of the incubation, the water phase is poured into a separate extraction device to prevent extraction of chemicals that are adsorbed to the container walls and stirrers. Polymer and water are extracted and analysed using validated methods. Container walls, stirrers, and any water that remained in the exposure vessel are also analysed for the purpose of mass balance calculations. Procedure blanks and recoveries of spiked samples are included in the chemical analysis. To minimize detector nonlinearity issues, appropriate dilutions of the polymer extracts are made to ensure that the concentrations in the extracts of water and polymer samples prior to instrumental analysis do not differ by more than a factor of 10. This requirement could be relaxed if detector linearity is demonstrated by plotting the response factors (response per injected amount) versus injected amount, which should yield a horizontal line for truly linear detectors. All samples are analysed in the same analysis batch to minimize the effects of changes in detector sensitivity.

3.6 Quality assurance and quality control

Concentrations in polymer and water are calculated and checked against the requirements with respect to solubility and MDL (Equations 29, 30, 32, 33). With the single dose design, the mass balance is evaluated from the initial amounts that are spiked into the exposure system and the final amounts that are recovered from polymer, water, and exposure equipment. The mass balance should be satisfied to within 80–120%. The results for procedure blanks and recoveries of spiked samples should be within the required limits.

Experimental evidence should be provided to show that the equilibration times were sufficiently long. This can be done by comparing the logK_{pw} values from desorption and absorption measurements, which should be the same within experimental error. Alternatively, the experiment can be repeated using an equilibration time that is twice as long or a polymer thickness that is twice as large or small.

A convenient way of including a desorption experiment is to first carry out the absorption experiment and to use part of the sampler for the desorption experiment. Alternatively, the sampler for the desorption experiment may be spiked separately by incubating this sampler 24 h in spiked methanol/water 80/20 (v/v), increasing the water content in 10% steps (24 h) to 90%, followed by a washing step in ultrapure water (24 h) to remove traces of methanol from the sampler (Smedes and Booij, 2012). Reitsma *et al*. (2013) elegantly combined the adsorption and desorption design in single experiments by exposing samplers that were spiked with deuterated compounds to water that was spiked with non-deuterated analogues.

The inclusion of compounds for which multiple literature values of logK_{pw} exist is highly recommended as this provides a measure of the between-laboratory variability of logK_{pw} values. PAHs (e.g., phenanthrene, pyrene, chrysene) or frequently analysed PCBs (e.g., PCB52, PCB101, PCB153) may be suitable candidates for this purpose.

The final reported mean logK_{pw} and standard error is preferably based on at least two separate experiments with two or three replicates each. Confidence in the reported values can be enhanced by using various experimental conditions such as concentration level, incubation time, stirring rates, and direction of the mass transfer (desorption versus absorption).

3.7 Design modelling

Initial modelling of the exposure systems with respect to polymer mass, water volume, concentration levels, and incubation times can be achieved through spreadsheet calculations. This allows the effect of changes in the experimental conditions and uncertainties in the initial estimates of K_{pw}, D_p, and k_w to be evaluated. The optimal values of polymer mass and water volume are determined by trial and error as changes in these parameters have an effect on both the equilibration times and the concentration levels at equilibrium. Calculation examples are shown for the measurement of the LDPE-water partition coefficients of benzo[a]pyrene (Box 1, boundary layer controlled kinetics) and triclosan (Box 2, membrane controlled or boundary layer controlled kinetics).

In Step 1 of Box 1, properties are collected for the target compound (solubility, logK_{ow}, molar volume) and the polymer (thickness, area/mass ratio, density). In addition, an estimate of k_w is made. A default value of 10 μm s^{-1} for moderate stirring may be adopted when no further information from previous experiments is available.

Estimates of logK_{pw} and D_p are needed to determine if the exchange kinetics is controlled by the water boundary layer or the polymer (Box 1, Step 2). These estimates will often be approximate. The sensitivity of the model to uncertainties in these parameters can be evaluated by adopting values that are 0.5 log units higher or lower, for example. In the example of Box 1, the exchange kinetics is likely controlled by the water boundary layer, even when K_{pw} or D_p are an order of magnitude smaller than assumed.

A reasonable estimate of the phase ratio (mK_{pw}/V_w) is needed to ensure that detectable amounts can be found in the water and polymer phases at equilibrium (Box 1, Step 3).

It is desirable to have at least 1% of the total spike amount in either phase. For highly hydrophobic compounds, $\log K_{pw} > 6$, this may not be feasible.

Box 1, Step 4 demonstrates that application of the constant C_w design results in long equilibration times of almost 500 d. The single dose design, with a polymer mass of 10 mg and a water volume of 1 L, results in expected equilibration times of 18.4 d and 7.9 d for absorption and desorption experiments, respectively.

A total amount of 1000 ng that is spiked into the exposure setup yields C_w estimates that are below solubility and above the detection limit (Box 1, Step 5).

The experimental design can be further modified and checked against the requirements for a particular study. For example, decreasing the polymer mass to 1 mg causes an increase in the equilibrium amounts in the water phase (137 ng), but also results in an increase of t_{eq} to 112 d (absorption) and 72 d (desorption). These longer equilibration times may or may not be acceptable depending on the time that is available. Further, equilibration times may be decreased by enhanced agitation of the water. This could result in higher k_w values but probably not beyond 50 µm s^{-1} (section 2.3). Errors in the adopted $\log K_{pw}$ have only a minor effect on t_{eq} in this example. If the actual $\log K_{pw}$ equals 7.3, the t_{eq} increases to 21.6 d for absorption and 8.0 d for desorption experiments.

Box 1. Experimental design modelling for boundary layer controlled kinetics: Benzo[*a*]pyrene sorption by LDPE.

Step 1: Information on polymer, compound, exposure system, and analysis

LDPE properties: thickness 50 µm, density 0.91 kg L^{-1}, half-thickness L = 25 µm. One gramme of this polymer has a volume $V_P = m/\rho = 0.001/0.91 = 0.00110$ dm^3 and an area $A = V_P/L = 0.00110/0.000250 = 4.40$ dm^2.

Benzo[a]pyrene properties: $V_{McGowan} = 195.36$ $cm^3\,mol^{-1}$, $\log K_{ow} = 6.05$, $S_w = 3.8$ µg L^{-1}.

Adopted k_w (for moderate stirring): 10 µm s^{-1} = 8.64 L $dm^{-2}\,d^{-1}$

MDL = 0.5 ng per sample, prior to analysis

Step 2: Estimates of $\log K_{pw}$, D_P, and I_P/I_w

Calculated $\log K_{pw}$ values are 5.86 (Equation 7) and 5.83 (Equation 12). Experimental values are 6.81 (Reitsma *et al.*, 2013), and 6.75 (Smedes *et al.*, 2009). $\log K_{pw} = 6.8$ is adopted as the best available estimate.

From Equation (13): $\log D_P$ ($m^2\,s^{-1}$) = −0.0145 × 195.36 − 10.43= −13.26, in fair agreement with the experimental value of −13.72 (Rusina *et al.*, 2010a). The experimental value is adopted as best available estimate: $D_P = 1.9\ 10^{-14}\ m^2\,s^{-1} = 0.019\ \mu m^2\,s^{-1}$.

The importance of membrane controlled kinetics is calculated from Equation (19):

$$\frac{I_P}{I_w} = \frac{k_w L}{D_P K_{pw} \rho} = \frac{10\ \mu m\ s^{-1} \times 25\ \mu m}{0.019\ \mu m^2 s^{-1} \times 10^{6.8}\ L\,kg^{-1} \times 0.91\ kg\,L^{-1}} = 0.002$$

This indicates boundary layer controlled kinetics.

Step 3: Approximate phase ratio

A polymer mass of (for example) 100 mg in 1 L water results in a mK_{pw}/V_w value of 631, which means that 0.16% of the compound would be found in the water phase at equilibrium (Equation 34). A polymer mass of 10 mg on 1 litre of water is therefore a better choice. This polymer mass has a surface area of 4.40 × 0.010 = 0.0440 dm^2.

(continued on next page)

Box 1 (continued)

Step 4: Equilibration times

The required equilibration time for the constant C_w design (Equation 23) equals

$$t_{eq} = \frac{-\ln(0.05)}{\left(\frac{k_w A}{m K_{pw}}\right)} = \frac{-\ln(0.05)}{\left(\frac{8.64\ \mathrm{L\ dm^{-2} d^{-1}} \times 0.0440\,\mathrm{dm^2}}{10 \cdot 10^{-6}\,\mathrm{kg} \times 10^{6.8}\,\mathrm{L\ kg^{-1}}}\right)} = \frac{-\ln(0.05)}{0.00602\,\mathrm{d^{-1}}} = 498\,\mathrm{d}$$

This equilibration time is too long in most cases, so the single dose design may be a better alternative.

To simplify the calculations, it is convenient to first calculate the parameter groups $k_w A/(mK_{pw})$ and mK_{pw}/V_w.

$$\frac{k_w A}{m K_{pw}} = \frac{8.64\ \mathrm{L\ dm^{-2} d^{-1}} \times 0.0440\,\mathrm{dm^2}}{10 \cdot 10^{-6}\,\mathrm{kg} \times 10^{6.8}\ \mathrm{L\,kg^{-1}}} = 0.00602\ \ \mathrm{d^{-1}}$$

$$\frac{m K_{pw}}{V_w} = \frac{10 \cdot 10^{-6}\ \mathrm{kg} \times 10^{6.8}\ \ \mathrm{kg\,L^{-1}}}{1\ \mathrm{L}} = 63.1$$

The equilibration times for absorption (Equation 26) and desorption experiments (Equation 27) are

$$t_{eq,abs} = \frac{-1}{\left(1 + \frac{mK_{pw}}{V_w}\right)\frac{k_w A}{m K_{pw}}} \ln\left(\frac{0.05}{1 + 0.95\frac{mK_{pw}}{V_w}}\right)$$

$$= \frac{-1}{(1 + 63.1) \cdot 0.00602\ \mathrm{d^{-1}}} \ln\left(\frac{0.05}{1 + 0.95 \cdot 63.1}\right) = 18.4\,\mathrm{d}$$

$$t_{eq,des} = \frac{-1}{\left(1 + \frac{mK_{pw}}{V_w}\right)\frac{k_w A}{m K_{pw}}} \ln\left(\frac{0.05}{1.05 + \frac{V_w}{mK_{pw}}}\right)$$

$$= \frac{-1}{(1 + 63.1) \cdot 0.00602\,d^{-1}} \ln\left(\frac{0.05}{1.05 + \frac{1}{63.1}}\right) = 7.9\ \mathrm{d}$$

Step 5: Optimal spike levels

A spiked amount of 1000 ng results in an expected amount in the water phase of

$$N_{w,\infty} = \frac{N_{total}}{1 + \frac{m K_{pw}}{V_w}} = \frac{1000\ \mathrm{ng}}{1 + 63.1} = 15.6\ \mathrm{ng}$$

which is above the MDL. The concentration in the water phase at equilibrium (15.6 ng L^{-1}) is below the solubility (3800 ng L^{-1}). The initial concentration in the water for the absorption experiment (1000 ng L^{-1}) is also below the solubility. The amount in the polymer phase would be 984 ng which is much larger than the amount in the water.

Therefore, a dilution of the polymer extract by a factor of 10, for example, is required to bring the concentrations or polymer and water extracts to the same level prior to instrumental analysis.

Box 2 shows the example of triclosan sorption by 50 μm thick LDPE. Compared with benzo[a]pyrene, triclosan has a much smaller K_{pw} and a somewhat higher D_p, which causes the kinetics to be partially membrane controlled and partially boundary layer controlled ($I_p/I_w = 0.48$, Box 2, Step 2).

With 10 mg LPDE in 1 L water, mK_{pw}/V_w equals 0.02 (Box2, Step 3). This is within the recommended limits (0.01–99) but a value 10 times higher would be beneficial for the equilibrium amounts in the polymer. A water volume of 0.1 L is therefore a better choice.

Equilibration times of 0.15 d (absorption) and 0.22 d (desorption) are found for boundary layer controlled kinetics (Box 2, Step 4). For membrane controlled kinetics, t_{eq} is 0.028 d (absorption) and 0.045 d (desorption). Therefore, the estimates based on boundary layer controlled kinetics are selected.

A total spike amount of 1000 ng yields amounts of 820 ng in the water phase and 180 ng in the polymer (Box 2, Step 5). These values meet the requirements with respect to S_w and MDL.

Box 2 Experimental design modelling for membrane controlled kinetics: Triclosan sorption by LDPE.

Step 1: Information on polymer, compound, exposure system, and analysis

LDPE properties: thickness 50 μm, density 0.91 kg L^{-1}, half-thickness L = 25 μm. One gramme of this polymer has a volume $V_p = m/\rho = 0.001/0.91 = 0.00110$ dm^3 and an area $A = V_p/L = 0.00110/0.000250 = 4.40$ dm^2.

Triclosan properties: $V_{McGowan}$ = 180.88 cm^3 mol^{-1}, $\log K_{ow}$ = 4.76, S_w = 10 000 μg L^{-1}.

Adopted k_w (for moderate stirring): 10 μm s^{-1} = 8.64 L dm^{-2} d^{-1}

MDL = 3 ng per sample, prior to analysis.

Step 2: Estimates of $\log K_{pw}$, D_p, and I_p/I_w

Initial estimate of $\log K_{pw}$: 4.47 (from $\log K_{ow}$, Equation 7), 2.87 (from pp-LFER, Equation 12). The experimental value is 3.34 (Sacks and Lohmann, 2011), which is adopted in the calculations below.

From Equation (13): $\log D_p$ (m^2 s^{-1}) = − 0.0145 × 180.88 − 10.43= −13.05, in fair agreement with the experimental value of −12.58 (Pintado-Herrera *et al.*, 2016). The experimental value is adopted as best available estimate: $D_p = 2.6 \cdot 10^{-13}$ m^2 s^{-1} = 0.26 μm^2 s^{-1}.

$$\frac{I_p}{I_w} = \frac{k_w L}{D_p K_{pw} \rho} = \frac{10\ \mu\text{m s}^{-1} \times 25\ \mu\text{m}}{0.26\ \mu\text{m}^2\text{s}^{-1} \times 10^{3.34}\ \text{L kg}^{-1} \times 0.91\ \text{kg L}^{-1}} = 0.48$$

which indicates partial membrane control and partial boundary layer control. This means that equilibration times for both cases have to be evaluated.

Step 3: Approximate phase ratio

A polymer mass of 10 mg in 1 L water results in a mK_{pw}/V_w value of 0.022 which means that 98% of the compound would be found in the water phase at equilibrium. A water volume of 0.1 L is therefore adopted instead (~82% in the water, ~18% in the polymer). The surface area of 10 mg polymer equals A = 4.40 × 0.010 = 0.0440 dm^2.

Step 4: Equilibration times

For convenience, the parameter groups $k_w A/(mK_{pw})$ and mK_{pw}/V_w are calculated first.

$$\frac{k_w A}{mK_{pw}} = \frac{8.64\ \text{L dm}^{-2}\text{d}^{-1} \times 0.044\ \text{dm}^2}{10 \cdot 10^{-6}\ \text{kg} \times 10^{3.34}\ \text{L kg}^{-1}} = 17.4\,\text{d}^{-1}$$

(continued on next page)

Box 2 (continued)

$$\frac{mK_{\mathrm{pw}}}{V_{\mathrm{w}}} = \frac{10 \cdot 10^{-6}\ \mathrm{kg} \times 10^{3.34}\ \mathrm{kg\,L^{-1}}}{0.1\ \mathrm{L}} = 0.22$$

Equilibration times for boundary layer controlled kinetics are

$$t_{\mathrm{eq,abs}} = \frac{-1}{\left(1+\frac{mK_{\mathrm{pw}}}{V_{\mathrm{w}}}\right)\frac{k_{\mathrm{w}}A}{mK_{\mathrm{pw}}}} \ln\left(\frac{0.05}{1+0.95\frac{mK_{\mathrm{pw}}}{V_{\mathrm{w}}}}\right)$$

$$= \frac{-1}{(1+0.22)\cdot 17.4\ \mathrm{d}^{-1}} \ln\left(\frac{0.05}{1+0.95\cdot 0.22}\right) = 0.15\,\mathrm{d}$$

$$t_{\mathrm{eq,des}} = \frac{-1}{\left(1+\frac{mK_{\mathrm{pw}}}{V_{\mathrm{w}}}\right)\frac{k_{\mathrm{w}}A}{mK_{\mathrm{pw}}}} \ln\left(\frac{0.05}{1.05 + \frac{V_{\mathrm{w}}}{mK_{\mathrm{pw}}}}\right)$$

$$= \frac{-1}{(1+0.22)\cdot 17.4\,\mathrm{d}^{-1}} \ln\left(\frac{0.05}{1.05 + \frac{1}{0.22}}\right) = 0.22\ \mathrm{d}$$

Equilibration times for membrane controlled kinetics are obtained from Table 1. For absorption, $D_{\mathrm{p}}t_{\mathrm{eq}}/L^2$ is between 1.07 (at $mK_{\mathrm{pw}}/V_{\mathrm{w}}$ =0.1) and 0.97 (at $mK_{\mathrm{pw}}/V_{\mathrm{w}}$ = 0.33). The interpolated value (1.02) yields an equilibration time of

$$t_{\mathrm{eq,\,abs}} = 1.02\frac{L^2}{D_{\mathrm{p}}} = 1.02\frac{25^2\ \mu\mathrm{m}^2}{0.26\ \mu\mathrm{m}^2\ \mathrm{s}^{-1}} = 2452\ \mathrm{s} = 0.028\,\mathrm{d}$$

For desorption, $D_{\mathrm{p}}t_{\mathrm{eq}}/L^2$ is between 1.94 (at $mK_{\mathrm{pw}}/V_{\mathrm{w}}$ = 0.1) and 1.33 (at $mK_{\mathrm{pw}}/V_{\mathrm{w}}$ = 0.33). The interpolated value at $mK_{\mathrm{pw}}/V_{\mathrm{w}}$ = 0.22 equals 1.62

$$t_{\mathrm{eq,\,des}} = 1.62\frac{L^2}{D_{\mathrm{p}}} = 1.62\frac{25^2\ \mu\mathrm{m}^2}{0.26\ \mu\mathrm{m}^2\ \mathrm{s}^{-1}} = 3894\ \mathrm{s} = 0.045\,\mathrm{d}$$

The highest t_{eq} estimates for absorption (0.15 d) and desorption (0.22 d) are adopted.

Step 5: Optimal spike levels

A total spike amount of 1000 ng results in an amount in the water phase of 820 ng and 180 ng in the polymer phase. These amounts are above the MDL and concentrations in the water phase are below the solubility. The amounts in the polymer and water are of similar magnitude and no dilution of either phase is required before analysis.

Adopting a 0.5 log units higher logK_{pw} results in larger t_{eq} estimates: 0.38 d (absorption) and 0.42 d (desorption) for the case of boundary layer controlled kinetics.

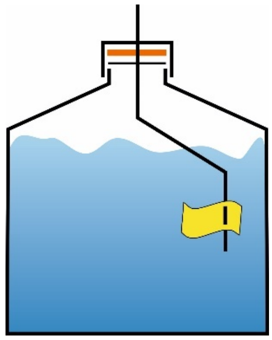

Figure 3. Sampler on S-shaped rod that is fixed to the lid.

3.8 Shaking in single dose exposures

Since passive samplers are polymers, the exposure system should not contain competing polymeric material. Teflon coated stir bars are therefore not recommended for mixing. Glass coated stir bars cause wear to the glass surface and the glass particles that are created form a third phase that may result in an overestimation of aqueous concentrations and underestimation of K_{pw}. Overhead stirring is an alternative but is technically more difficult. Tumblers and orbital shakers provide sufficiently turbulent conditions, provided that 10–20% headspace is allowed for. Simply adding the sampler to the water will not necessarily create a sufficiently high flowrate at the sampler surface as the sampler moves through the bottle at approximately the same rate and in the same direction as the water. An efficient method is to fix the polymer as a flag to an S-shaped stainless steel rod that is held in place by the lid (Figure 3). Typical speed settings for orbital shakers are 100 min^{-1} for 10 L bottles and up to 200 min^{-1} for 0.1 L bottles.

4 Polymer-polymer partition coefficients

The determination of polymer-polymer partition coefficients (K_{p1p2}) is a relatively new research field that is important for the quality assurance of passive sampling data. First, K_{p1p2} data are needed to assess between-batch and between-manufacturer variability of polymers. Second, this data can be used to convert K_{pw} values that are obtained from one polymer to another polymer, for example when a certain polymer type is taken out of production by manufacturers. The challenge with K_{p1p2} determinations is to establish polymer-polymer mass transfer rates that are high enough to reach equilibrium at acceptable time scales. This can be accomplished by the use of an intermediate solvent (section 4.1) or by direct contact experiments (section 4.2).

4.1 Intermediate solvent method

The use of an intermediate solvent of moderate polarity serves to lower the solvent-polymer partition coefficients, which enhances the transport rate between the polymers. Gilbert *et al*. (2016) incubated different polymers in 60/40 (v/v) methanol/water mixtures under continuous shaking for time periods between 10 days and 6 months. These authors estimated the effect of methanol on K_{p1p2} to be 0.1 to 0.2 log units on average. This is confirmed by unpublished data from the study by Smedes *et al*. (2009), which indicates that the K_{p1p2} in 60/40 (v/v) methanol water can be up to 0.3 log units smaller compared with the values in pure water.

4.2 Direct contact method

Equilibrating two polymers in direct contact under enhanced pressure is an alternative way of eliminating the transport resistance of the water boundary layer without the use of intermediate solvents. Such experiments are similar to measurements of diffusion coefficients in polymers using the film stacking method (Rusina *et al.*, 2007, 2010a; Narvaez Valderrama *et al.*, 2016; Pintado-Herrera *et al.*, 2016). In the latter experiments a spiked polymer sheet is sandwiched between (or overlain with) several unspiked sheets under a pressure of 0.5 to 1 kg cm^{-2}. Incubation times are chosen so that concentrations significantly increase in the outer sheet while avoiding a uniform (equilibrium) distribution of concentrations. The models that are used for film stacking experiments comprise an infinite series of error functions (Narvaez Valderrama *et al.*, 2016). Models for transport between different polymers should account for a concentration jump at the polymer-polymer interface and for differences in diffusion coefficients in the two polymers. To our knowledge, these models are not readily available but numerical integration of the diffusion equations in composite media (Crank, 1975, Section 8.8) may be considered.

Meanwhile, it can be considered that typical incubation times for the measurement of diffusion coefficients are 3–5 h for stacks of 3 to 5 silicone sheets of 500 µm thickness, or LDPE sheets of 70 µm thickness. This implies that 3 to 5 h is sufficient to reach a measurable, yet not complete, degree of equilibrium and that incubation times of the order of days are probably sufficient to reach essentially complete equilibrium for chemicals with D_p values in the order of 10^{-11} m^2 s^{-1} for 500 µm thick silicones and 10^{-13} m^2 s^{-1} for 70 µm thick LDPE. Because D_p values in POM are two orders of magnitude smaller than in LPDE, it can be expected that significantly longer equilibration times are needed for K_{p1p2} determinations using this polymer and the same holds for chemicals with high molar volumes (e.g., polybrominated diphenyl ethers) in LDPE (Narvaez Valderrama *et al.*, 2016).

The suggested incubation time of several days is an indicative value only and equilibrium should be experimentally demonstrated. A possible experimental scenario for providing the evidence is to sandwich an unspiked sheet of polymer 1 between a spiked and an unspiked sheet of polymer 2. When equilibrium exists between the outer sheets (i.e., equal concentrations) then equilibrium must also exist between polymer 1 and polymer 2.

5 Acknowledgements

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Annex 1: Equilibration times

Constant C_w design, boundary layer controlled kinetics

For water boundary layer controlled uptake rates, the fraction of equilibrium (f_{eq}) follows from Equations (1) and (17)

$$f_{eq} = \frac{C_p}{C_w K_{sw}} = 1 - \exp\left(-\frac{k_w A t}{K_{pw} m}\right) \quad \text{(A1)}$$

From Equation (A1) it follows that the time to reach equilibrium within 5% (f_{eq} = 0.95) is given by

$$t_{eq} = \frac{-\ln(0.05)}{\left(\frac{k_w A}{K_{pw} m}\right)} \quad \text{(A2)}$$

Constant C_w design, membrane controlled kinetics

The fraction of attained equilibrium for membrane controlled uptake is given by (Crank, 1975, Equation 4.18)

$$f_{eq} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(-\frac{(2n+1)^2 \pi^2 D_p t}{4L^2}\right) \quad \text{(A3)}$$

For estimating the time to reach equilibrium within 5%, the terms with $n \geq 1$ can be neglected

$$t_{eq} = -\frac{4L^2}{\pi^2 D_p} \ln\left(\frac{0.05\pi^2}{8}\right) \approx 1.13 \frac{L^2}{D_p} \quad \text{(A4)}$$

Single dose design, boundary layer controlled kinetics

For water boundary layer controlled uptake, the evolution of concentrations in polymer (C_p) and water (C_w) following a single dose are given by (Booij *et al.*, 2007; Booij and Tucca, 2015)

$$\frac{C_w - C_{w,\infty}}{C_{w,0} - C_{w,\infty}} = \exp\left(-\left(1 + \frac{m K_{pw}}{V_w}\right) \frac{k_w A t}{K_{pw} m}\right) \quad \text{(A5)}$$

$$\frac{C_p - C_{p,\infty}}{C_{p,0} - C_{p,\infty}} = \exp\left(-\left(1 + \frac{m K_{pw}}{V_w}\right) \frac{k_w A t}{K_{pw} m}\right) \quad \text{(A6)}$$

$$V_w C_{w,0} + m C_{p,0} = V_w C_{w,\infty} + m C_{p,\infty} \quad \text{(A7)}$$

$$C_{p,\infty} = K_{pw} C_{w,\infty} \quad \text{(A8)}$$

where the subscripts 0 and ∞ refer to the initial and final (equilibrium) concentrations. Equation (A7) is an expression of the mass balance (initial amounts = final amounts).

The fraction of attained equilibrium (f_{eq}) follows from Equations (A5) and (A6), for absorption ($C_{p,0}$ = 0) and desorption ($C_{w,0}$ = 0) experiments

$$\text{absorption:} \quad f_{eq} = \frac{C_p}{C_w K_{pw}} = \frac{1 - \exp(-k_e t)}{1 + \frac{m K_{pw}}{V_w} \exp(-k_e t)} \quad \text{(A9)}$$

desorption: $$f_{\mathrm{eq}}=\frac{C_{\mathrm{p}}}{C_{\mathrm{w}}K_{\mathrm{pw}}}=\frac{1+\dfrac{V_{\mathrm{w}}}{mK_{\mathrm{pw}}}\exp\left(-k_{\mathrm{e}}t\right)}{1-\exp\left(-k_{\mathrm{e}}t\right)} \tag{A10}$$

where k_e is given by

$$k_{\mathrm{e}}=\left(1+\frac{mK_{\mathrm{pw}}}{V_{\mathrm{w}}}\right)\frac{k_{\mathrm{w}}A}{K_{\mathrm{pw}}m} \tag{A11}$$

The deviation from equilibrium is 5% for absorption experiments at f_{eq} = 0.95 and for desorption experiments at f_{eq} = 1.05. The equilibration times are given by rearranging Equations (A9) and (A10)

absorption: $$t_{\mathrm{eq,abs}}=\frac{-1}{\left(1+\dfrac{mK_{\mathrm{pw}}}{V_{\mathrm{w}}}\right)\dfrac{k_{\mathrm{w}}A}{mK_{\mathrm{pw}}}}\ln\left(\frac{0.05}{1+0.95\dfrac{mK_{\mathrm{pw}}}{V_{\mathrm{w}}}}\right) \tag{A12}$$

desorption: $$t_{\mathrm{eq,des}}=\frac{-1}{\left(1+\dfrac{mK_{\mathrm{pw}}}{V_{\mathrm{w}}}\right)\dfrac{k_{\mathrm{w}}A}{mK_{\mathrm{pw}}}}\ln\left(\frac{0.05}{1.05+\dfrac{V_{\mathrm{w}}}{mK_{\mathrm{pw}}}}\right) \tag{A13}$$

Single dose design, membrane controlled kinetics

The evolution of concentrations in polymer and water for membrane controlled exchange in a closed system is given by

$$\frac{C_{\mathrm{p}}-C_{\mathrm{p},\infty}}{C_{\mathrm{p},0}-C_{\mathrm{p},\infty}}=\sum_{\mathrm{n}=1}^{\infty}\frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2q_{\mathrm{n}}^2}\exp\left(-\frac{q_{\mathrm{n}}^2D_{\mathrm{p}}t}{L^2}\right) \tag{A14}$$

$$\frac{C_{\mathrm{w}}-C_{\mathrm{w},\infty}}{C_{\mathrm{w},0}-C_{\mathrm{w},\infty}}=\sum_{\mathrm{n}=1}^{\infty}\frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2q_{\mathrm{n}}^2}\exp\left(-\frac{q_{\mathrm{n}}^2D_{\mathrm{p}}t}{L^2}\right) \tag{A15}$$

$$\alpha=\frac{V_{\mathrm{w}}}{mK_{\mathrm{pw}}} \tag{A16}$$

where q_n are the non-zero positive roots of

$$\tan q_{\mathrm{n}}=-\alpha\, q_{\mathrm{n}} \tag{A17}$$

The mass balance condition (Equation A7) and the equilibrium condition (Equation A8) are also applicable in this case. The special case of absorption with membrane controlled kinetics is given by Crank (1975, Equation 4.37).

The fraction of attained equilibrium is obtained from Equations (A14) and (A15) for absorption ($C_{p,0}$ = 0) and desorption ($C_{w,0}$ = 0)

absorption: $$f_{\mathrm{eq}}=\frac{C_{\mathrm{p}}}{C_{\mathrm{w}}K_{\mathrm{pw}}}=\frac{1-\displaystyle\sum_{\mathrm{n}=1}^{\infty}\frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2q_{\mathrm{n}}^2}\exp\left(-\frac{q_{\mathrm{n}}^2D_{\mathrm{p}}t}{L^2}\right)}{1+\dfrac{1}{\alpha}\displaystyle\sum_{\mathrm{n}=1}^{\infty}\frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2q_{\mathrm{n}}^2}\exp\left(-\frac{q_{\mathrm{n}}^2D_{\mathrm{p}}t}{L^2}\right)} \tag{A18}$$

$$\text{desorption: } f_{\mathrm{eq}} = \frac{C_{\mathrm{p}}}{C_{\mathrm{w}} K_{\mathrm{pw}}} = \frac{1 + \alpha \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(-\frac{q_n^2 D_{\mathrm{p}} t}{L^2}\right)}{1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(-\frac{q_n^2 D_{\mathrm{p}} t}{L^2}\right)} \tag{A19}$$

An analytical expression for the equilibration times is not possible because the values of q_n have to be obtained numerically from Equation (A17), and because the higher order terms ($n \geq 2$) in the summation cannot always be neglected. Instead, equilibration times were estimated numerically from Equations (A18) and (A19) for a range of α values between 0.001 and 1000 (Table 1, Figure A1).

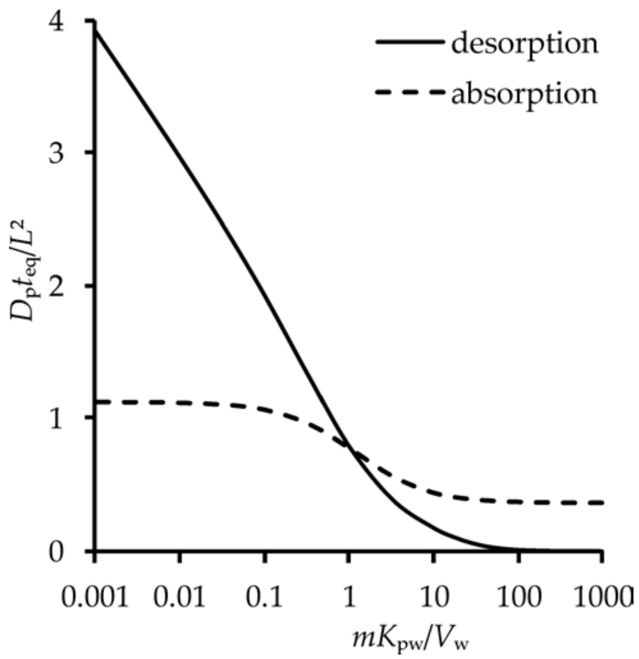

Figure A1. Equilibration times (t_{eq}) for desorption and absorption experiments as a function of mK_{pw}/V_w for membrane controlled exchange kinetics with the single dose design.

Abbreviations and technical terminology

a	slope of the logK_{px} vs. x plot
A	sampler area that is exposed to water
C_w	concentration in water
C_p	concentration in polymer
$C_{w,0}$	initial concentration in water
$C_{w,\infty}$	equilibrium concentration in water
$C_{p,0}$	initial concentration in the polymer
$C_{p,\infty}$	equilibrium concentration in the polymer
D_p	diffusion coefficient in the polymer
D_w	diffusion coefficient in water
f	fraction of retained PRCs
f_{eq}	fraction of equilibrium that is attained
I_p	transport resistance of the polymer
I_w	transport resistance of the water boundary layer
k_w	mass transfer coefficient of the water boundary layer
K_{p1p2}	polymer-polymer partition coefficient
K_{pw}	polymer-water partition coefficient
K_{px}	polymer-solvent partition coefficient
K_{ow}	octanol-water partition coefficient
L	polymer half-thickness (polymer exposed on two sides) or polymer thickness (polymer exposed on one side)
LDPE	low-density polyethylene
m	polymer mass
MDL	method detection limit
n	number of observations
N	amount
POM	poly(oxymethylene)
PRC	performance reference compound
R	gas constant (8.314 J mol^{-1} K^{-1})
R_s	equivalent water sampling rate
R^2	coefficient of determination
s	standard deviation
S_w	aqueous solubility
SPMD	Semipermeable membrane device
T	absolute temperature
t	time
t_{eq}	time to reach equilibrium within 5%
V_p	polymer volume
V_w	water volume
x	mole fraction
δ_w	equivalent boundary layer thickness
ρ	polymer density
ΔH_{pw}	enthalpy of phase transfer from water to polymer

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