Three-Compartment Model for Contaminant Accumulation by Semipermeable Membrane Devices

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Passive sampling of dissolved hydrophobic contaminants with lipid (triolein)-containing semipermeable membrane devices (SPMDs) has been gaining acceptance for environmental monitoring. Understanding of the accumulation process has employed a simple polymer film-control model of uptake by the polymer-enclosed lipid, while aqueous film control has been only briefly discussed. A more complete three-compartment model incorporating both aqueous film (turbulent-diffusive) and polymer film (diffusive) mass transfer is developed here and is fit to data from accumulation studies conducted in constant-concentration, flow-through dilutors. This model predicts aqueous film control of the whole device for moderate to high K_{ow} compounds, rather than polymer film control. Uptake rates for phenanthrene and 2,2′,5,5′-tetrachlorobiphenyl were about 4.8 and 4.2 L/day/standard SPMD, respectively. Maximum 28 day SPMD concentration factors of 30 000 are predicted for solutes with log K_{ow} values of >5.5. Effects of varying aqueous and polymer film thicknesses and solute diffusivities in the polymer film are modeled, and overall accumulation by the whole device is predicted to remain under aqueous film control, although accumulation in the triolein may be subject to polymer film control. The predicted half-life and integrative response of SPMDs to pulsed concentration events is proportional to log K_{SPMD}.

Introduction

Passive monitors are rapidly gaining wide acceptance for assessing integrated, or time-weighted concentrations of organic chemicals in aquatic systems. One category of passive sampler, the lipid-containing semipermeable membrane device (SPMD), has been extensively studied in the laboratory and utilized in the field. The development and applications of SPMDs have been recently reviewed (*1*). As conventionally configured, an SPMD consists of a 1 m length of 2.5−5 cm wide 50−100 μm wall-thickness low-density polyethylene lay-flat tubing with a thin (~40 μm) layer of triolein between the two polyethylene layers. In this study, a 1 m long by 2.5 cm wide by 75−100 μm thick (wall) section of polyethylene tubing containing 1 g of triolein will be referred to as a standard SPMD, or simply as an SPMD.

The basic principle underlying the SPMD as a passive sampler has been discussed in detail, and a one-compartment model developed (*2*, *3*), in which it was hypothesized that

dissolved hydrophobic compounds in water are transported to the aqueous boundary by turbulence (mixing), diffuse through the aqueous and polymer films, and partition into the inner lipid reservoir. This one-compartment model greatly simplifies the uptake phenomenon by assuming that the overall control of the accumulation process is a single rate-limiting step: solute diffusion through the polyethylene (and accumulation into only the triolein phase), resulting in a first-order uptake equation. A provision for independent and additive resistances to mass transfer by incorporating aqueous diffusion was included for completeness, although mass transfer through the aqueous film was assumed to be much faster than through the polyethylene film, and it was concluded that polyethylene resistance generally controls the uptake rate. In practice, SPMD sampling rates are usually determined empirically and expressed in terms of the volume of water completely extracted by the entire device over the exposure interval.

The one-compartment model does not emphasize turbulent mass transfer to the device or diffusive mass transfer through the aqueous film, nor does it account for solute concentrations in the polyethylene, which are recovered along with residues in the triolein by dialysis of the whole SPMD. A large proportion of the SPMD consists of polyethylene (76% v/v), having a solute partition coefficient versus water (K_{pw}) similar to that of the inner triolein reservoir (K_{Tw}); $K_{pw} \approx 0.1-0.5\ K_{Tw}$. Polyethylene has been shown to contain a significant portion of the total amount of solute accumulated by an SPMD, often as much as 50% (*1−3*). Therefore, a model which considers accumulation by both the polymer and the inner lipid, but that does not assume polymer control of the accumulation rate of all chemicals, is necessary for completeness.

The objectives of this study were to develop a compartmental model incorporating both turbulent-diffusive (aqueous film) and diffusive (polymer film) mass-transfer terms for accumulation by SPMDs and then to predict concentrations in the polyethylene and triolein compartments of the SPMD as a function of time using the model. These predictions would be applied to three exposure scenarios: constant water concentrations, single application exposure experiments, and pulsed-event sampling where integrated water concentrations of chemicals are sought.

Model Development

A general approach to the study of transport kinetics is to compartmentalize various regions (or discrete parts) of a system into a set of ideal volumes between which chemicals (solutes) move based on kinetic laws (*4*, *5*). The sequence of turbulent mixing, diffusive, and partitioning processes by which SPMDs accumulate freely dissolved hydrophobic organic chemicals (depicted in Figure 1A) was used to construct the three-compartment (3C) model shown in Figure 1B. Equilibration rates of all partitioning steps were considered to be much faster than any diffusive step and were neglected in this derivation, reducing the steps in accumulation to (1) the turbulent approach of a dissolved chemical in the bulk aqueous phase to the aqueous diffusion film, (2) diffusion through the aqueous film and partitioning into an infinitely thin volume of polyethylene at the surface of the SPMD, and (3) diffusion through the polymer film and partitioning between it and the triolein, which is assumed to be well mixed. Clearance is described as the reverse of this set of processes.

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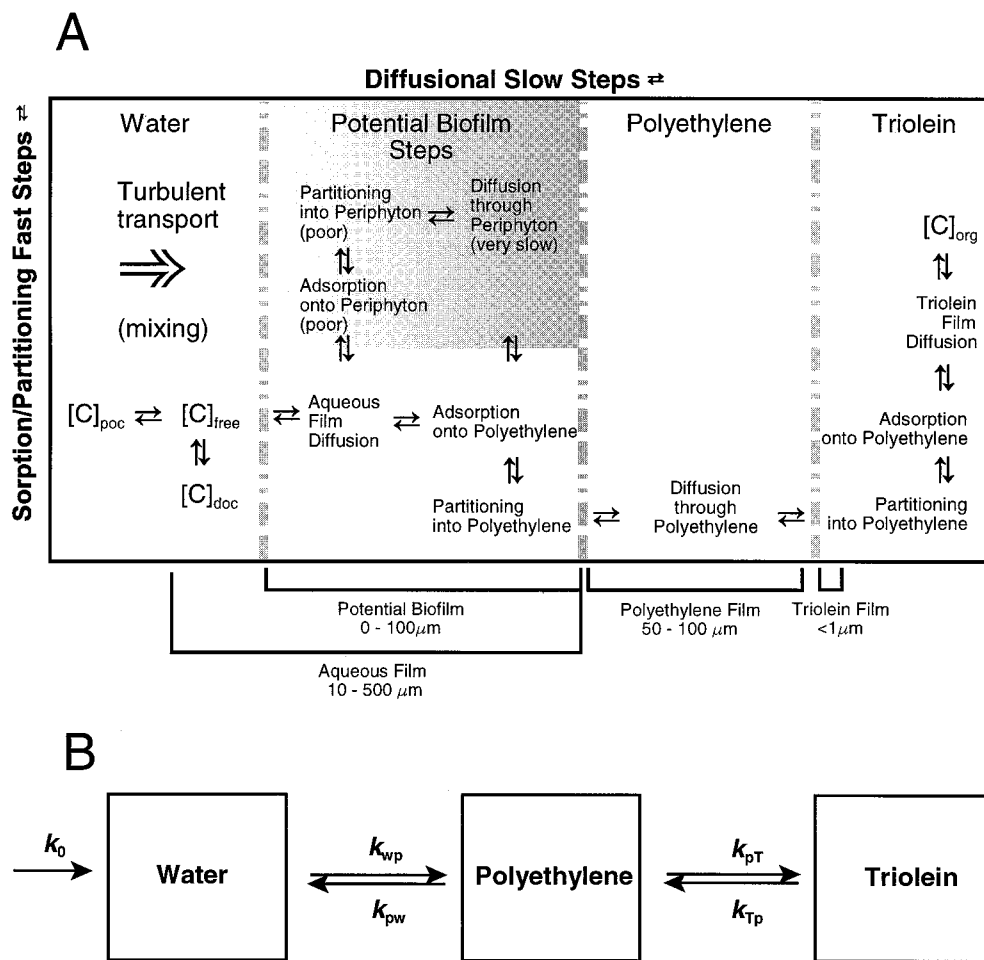
A

Diffusional Slow Steps ⇄

B

FIGURE 1. (A) Proposed passive sampling steps for SPMD accumulation. Contaminants are transported to the aqueous diffusion film via turbulent mixing and diffuse through the aqueous and polyethylene films into, first, the polyethylene layer and, second, the triolein layer of the SPMD. The sorption and partitioning steps (fast) are stacked, while the diffusion (slow) steps progress from left to right. [The additional sequence of steps resulting from potential growth of a periphytic (biofilm) layer is shown in the shaded area, but is not considered in the 3C model.] (B) The 3C model, consisting of three compartments (water, polyethylene, and triolein), and three mass-transfer steps. Rate constants for input into the water (k_0), accumulative mass transfer from water to polyethylene (k_{wp}), from polyethylene to triolein (k_{pT}), and the corresponding clearance rate constants for mass transfer from water to polyethylene (k_{wp}) and from polyethylene to triolein (k_{pT}) are shown with their respective arrows.

The set of simultaneous linear differential equations associated with this 3C model shown in Figure 1B are

water:
$$V_w \frac{dC_w}{dt} = k_0 - \beta_{wp} A_p C_w + \beta_{pw} A_p C_p \qquad (1)$$

polyethylene:
$$V_p \frac{dC_p}{dt} = \beta_{wp} A_p C_w - \beta_{pw} A_p C_p -$$
$$\beta_{pT} A_p C_p + \beta_{Tp} A_p C_T \qquad (2)$$

triolein:
$$V_T \frac{dC_T}{dt} = \beta_{pT} A_p C_p - \beta_{Tp} A_p C_T \qquad (3)$$

where C_w, C_p, and C_T and V_w, V_p, and V_T are the solute concentrations and volumes of the water, polyethylene, and triolein compartments, respectively. A_p is the area of the water−polyethylene and the polyethylene−triolein interfaces, and k_0 is the zero-order rate constant for input into water, and β_{pT} and β_{wp} are the mass-transfer coefficients for the movement of chemicals from the polyethylene into triolein and from water into polyethylene, respectively. The first-order mass-transfer coefficients for the reverse processes are

clearance from triolein:
$$\beta_{Tp} = \frac{\beta_{pT}}{K_{Tp}} \qquad (4)$$

clearance from polyethylene:
$$\beta_{pw} = \frac{\beta_{wp}}{K_{pw}} \qquad (5)$$

where K_{Tp} and K_{pw} are the respective triolein−polyethylene and polyethylene−water partition coefficients.

The first and second compartments are separated by the aqueous film. Aqueous film theory hypothesizes a gradient of turbulent-diffusive transport extending from the interface (6), with the first molecular layer adjacent to the interface having no movement (diffusive transport only) and subsequent layers increasing in turbulent transport until conditions in the bulk aqueous solution are attained. This gradient is simplified by assuming only turbulent transport in the bulk solution up to a fictitious distance δ_w from the interface (aqueous film thickness), and only diffusive transport of a solute through this film to the interface. The aqueous phase mass-transfer coefficient at steady state is then

$$\beta_{wp} = \frac{D_w}{\delta_w} \qquad (6)$$

where D_w is the molecular diffusion coefficient of the solute in water and is inversely proportional to molecular mass and to molecular volume (7, 8). Turbulence (mixing) decreases aqueous film thickness and the mass-transfer coefficient is proportional to the rate of flow adjacent to the interface. This is not shown explicitly, but rather contained in β_{wp}, because of the complexity of separately estimating the contribution of the turbulence term.

The first and third compartments are separated by the polymer film comprising the second compartment. Assuming negligible differences in solute diffusivities in either surface layer of the polyethylene compared to the bulk polymer, a constant solute diffusion coefficient D_p may be used and the mass-transfer coefficient expressed as

$$\beta_p = \frac{D_p}{\delta_p} \tag{7}$$

Solute diffusion coefficients in polyethylene are more difficult to predict than aqueous diffusion coefficients because of complex interactions with the polymer. D_p is estimated from delay times (t_d) for the solute's appearance in triolein by diffusion (3, 9). The delay time is the intercept extrapolated from the linear portion of the triolein accumulation curve. The polyethylene diffusion coefficient of a solute is related to the delay time by

$$D_p \approx \frac{\delta_p^2}{6t_d} \tag{8}$$

The polyethylene-to-triolein and water-to-polyethylene mass-transfer coefficients may be expressed in terms of film thicknesses, interfacial areas, and diffusivities by combining eqs 6–8, yielding overall rate constants for mass transfer to each compartment:

$$k_{pT} = \beta_{Tp}A_p = \frac{\delta_p A_p}{6t_d} \tag{9}$$

$$k_{wp} = \beta_{wp}A_p = \frac{D_w A_p}{\delta_w} \tag{10}$$

Substituting rate constants (eqs 9 and 10) for mass-transfer coefficients in eqs 1–3 and expressing clearance processes as the ratios of uptake rate constants to partition coefficients (eqs 4 and 5) yield a modified set of simultaneous linear differential equations adjusted for system volumes and interfacial areas (from βs to ks), with constants that can be estimated experimentally:

water: $\quad dC_w = \left[k_0 - k_{wp}\left(C_w + \dfrac{C_p}{K_{pw}}\right)\right]\dfrac{dt}{V_w} \tag{11}$

polyethylene: $\quad dC_p = \left[k_{wp}\left(C_w - \dfrac{C_p}{K_{pw}}\right) - k_{pT}\left(C_p - \dfrac{C_T}{K_{Tp}}\right)\right]\dfrac{dt}{V_p} \tag{12}$

triolein: $\quad dC_T = k_{pT}\left(C_p - \dfrac{C_T}{K_{Tp}}\right)\dfrac{dt}{V_T} \tag{13}$

Simultaneous linear differential equations (11–13) do not yield a simple closed-form solution; consequently, a computer was used to obtain numerical solutions of the 3C model (10). Contributions of individual parameters such as film thickness and partition coefficient were investigated by differential modeling, i.e., parametric variation.

The 3C model suggests accumulation in SPMDs may be controlled by either: (1) polymer film diffusion ($D_p K_{pw}/\delta_p \ll D_w/\delta_w$) for large molecules with low polymer diffusivity, or accumulation at lower temperatures, where steady-state solute concentrations in polyethylene and water are reached before they are attained in polyethylene and triolein; (2) aqueous film diffusion ($D_w/\delta_w \ll D_p K_{pw}/\delta_p$) for small, highly polymer-diffusive molecules, where steady-state solute concentrations in triolein and polyethylene are reached before those in the whole device (polyethylene + triolein), and the whole-device concentration approaches steady state with the water; (3) a combination of aqueous and polymer film diffusion ($D_p K_{pw}/\delta_p \approx D_w/\delta_w$), where solute concentrations in polyethylene and triolein reach a relatively constant ratio (but not necessarily the final steady-state value), and the steady-state concentration between these compartments and the water is approached. This third control mode has been observed for many of the contaminants investigated.

Results

3C Model Fit to SPMD Data. The 3C model was fit to the complete data set of dilutor studies provided by J. Huckins, U. S. Geological Survey, Columbia, MO. Some of this data was previously reported (3). The uptake studies utilized ^{14}C-labeled phenanthrene or 2,2′,5,5′-tetrachlorobiphenyl (PCB-52) for exposures at water concentrations of approximately 1, 10, and 100 ng L^{-1}. Solute concentrations in the triolein and polyethylene were determined at 1, 3, 7, 14, 21, and 28 days.

Triolein–water partition coefficients (K_{Tw}) were taken from Chiou (11). Reported values of K_{Tw} are significantly different from and less than K_{ow} values when values greater than 10^5 are compared, resulting in a 35% lower value of K_{Tw} than K_{ow} for PCB-52. However, K_{Tw} values are not widely available, limiting their usefulness for modeling. Values of the polyethylene–water partition coefficient K_{pw} and the triolein–polyethylene partition coefficient K_{Tp} are even less available. The values of K_{Tp} used here were calculated using the solute triolein–polyethylene concentration ratio at longer exposure times, where the ratios attained nearly constant values. The value of K_{Tp} for PCB-52 calculated from these dilutor exposures is significantly less than that reported previously from single application exposure measurements (3), though the value for phenanthrene is in good agreement with these measurements.

The physical parameters of the SPMDs used in the dilutor exposures, solute delay times, aqueous diffusivity values, and values of K_{Tw}, K_{pw}, and K_{Tp} are reported in Table 1. The best-fit values for the aqueous film thicknesses, polyethylene diffusivities, aqueous and polyethylene film mass-transfer coefficients (β_{wp} and β_{pT}), and rate constants (k_{pT} and k_{wp}) are reported in Table 2. Figure 2 shows the best fits of the 3C model to the dilutor data. The independence of SPMD concentration factors (CFs) from aqueous solute concentrations was previously demonstrated (1–3); therefore, CFs were used to express the data in Figure 2 and show accumulation from all water concentrations simultaneously. Figure 2, panels A and B, shows accumulation of phenanthrene and PCB-52 by the SPMD and triolein and polyethylene constituting the SPMD. Figure 2C also shows accumulation of PCB-52 by polyethylene alone with the same volume and thickness, but twice the surface area of the polyethylene used in the SPMDs.

Estimated aqueous film thicknesses for the SPMDs exposed to phenanthrene and PCB-52 (350 versus 400 μm) were the same within the experimental error of the exposure data. After 28 day exposures to phenanthrene and PCB-52, the standard SPMDs sampled an estimated 133 and 118 L of water ($k_{wp}t$) and solutes in 45 and 108 L were retained ($C_{SPMD}V_{SPMD}/C_w$), respectively, while solutes in 88 and 11 L

TABLE 1. Physical Parameters of SPMDs Used in the Dilutor Studies

physical input values for the three-compartment model	phenanthrene SPMD	PCB-52 SPMD	PCB-52 polyethylene only
area^{a,b} A_P (cm^2)	200 ± 10	200 ± 10	400 ± 20
polyethylene film thickness^b			
δ_p (cm)	(8.7 ± 3) × 10^{-3}	(7.4 ± 0.2) × 10^{-3}	(7.4 ± 0.2) × 10^{-3}
V_p^c (cm^3)	2.00 ± 0.05	1.70 ± 0.05	1.70 ± 0.05
V_T^d (cm^3)	0.50 ± 0.02	0.50 ± 0.02	
t_d^b (delay time, h)	<1	9 ± 1	
diffusivity in water^e D_w (cm^2 s^{-1})	(5.4 ± 0.2) × 10^{-6}	(4.3 ± 0.2) × 10^{-6}	(4.3 ± 0.2) × 10^{-6}
log K_{Tw}^f (triolein-water)	4.5 ± 0.1	5.6 ± 0.1	
$K_{Tp}^{g,h}$ (triolein-polyethylene)	6.5 ± 0.5	4.0 ± 0.5	
partition coefficient values (3)			
(for comparison only)			
log K_{ow} (1-octanol-water)	4.46 ± 0.02	5.82 ± 0.02	
log K_{Tw} (triolein-water)	5.0 ± 0.1	5.6 ± 0.1	
log K_{pw} (polyethylene-water)	4.2 ± 0.1	4.6 ± 0.1	4.6 ± 0.1
K_{Tp}^h (triolein-polyethylene)	6.3 ± 0.5	10 ± 1	

^{a} Surface area contacting water, total polyethylene-SPMD surface area 232 ± 5 cm^2. ^{b} Taken from Huckins, et al. (3). ^{c} Density of polyethylene ~0.92 g cm^{-3} at 25 °C. ^{d} Density of triolein 0.91 g cm^{-3} at 25 °C. ^{e} Estimated from ref 7. ^{f} Taken from Chiou (11). ^{g} Calculated from later dilutor data in ref 3. ^{h} Note: these are not logarithmic values.

TABLE 2. Three-Compartment Model Best-Fit Values for SPMDs and Polyethylene-Only Samplers Used in the Dilutor Studies

	phenanthrene SPMD	PCB-52 SPMD	PCB-52 polyethylene only
aqueous film thickness δ_p (cm)	(4.0 ± 0.5) × 10^{-2}	(3.5 ± 0.5) × 10^{-2}	(3.5 ± 0.5) × 10^{-2}
diffusivity in polyethylene D_p^a (cm^2 s^{-1})	(>3 ± 0.5) × 10^{-9}	(4 ± 0.5) × 10^{-10}	(4 ± 0.5) × 10^{-10}
aqueous film mass transfer coefficient β_{wp} (cm s^{-1})	(1.4 ± 0.2) × 10^{-4}	(1.2 ± 0.2) × 10^{-4}	(1.2 ± 0.2) × 10^{-4}
polyethylene film mass transfer coefficient β_{pT}^a (cm s^{-1})	(>3.4 ± 0.5) × 10^{-7}	(5.4 ± 0.5) × 10^{-8}	(5.4 ± 0.5) × 10^{-8}
aqueous film rate constant k_{wp} (cm^3 day^{-1})	4800 ± 200	4200 ± 200	4200 ± 200
polyethylene film rate constant k_{pT}^a (cm^3 s^{-1})	>12 ± 4	1.9 ± 0.4	1.9 ± 0.4

^{a} Estimate of linear diffusion time through polymer.

were cleared ($k_{wp}t - C_{SPMD}V_{SPMD}/C_w$), resulting in concentration factors of 10 000 and 27 000, respectively. Under the experimental conditions used, a maximum theoretical 28 day concentration factor of about 30 000 was predicted for chemicals with log K_{ow} values of >5.5. This CF was approached for exposures to PCB-52. Polyethylene used alone reached approximately twice the concentration factor for PCB-52 of an SPMD (55 000 versus 27 000) in 28 days. This was expected, as a result of having twice the surface area of the SPMD. However, at steady state, the total capacity of the polyethylene-only sampler would be only about 50% that of the SPMD, and if ambient concentrations fell, desorptive losses would be twice as great.

The aqueous uptake rate constants (k_{wp}) for phenanthrene and PCB-52 were 4.8 and 4.2 L day^{-1}/standard SPMD and were the same within experimental error. The value of k_{wp} for accumulation of PCB-52 by polyethylene alone was about 8.4 L day^{-1}/device (obtained by doubling the surface area) or twice that of an SPMD. The experimentally observed values of K_{Tp} for triolein-containing SPMDs increase with time, asymptotically reaching a steady-state value (J. Huckins, personal communication). This behavior is also indicated by the 3C model, and the predicted values of the ratio (approaching K_{Tp}) correspond well to the experimental measurements.

Discussion

Aqueous Film Thickness and Diffusivity. Molecular diffusivities of hydrophobic molecules in water are approximately inversely proportional to the square root of molecular mass and vary about 2-fold (about $7 \times 10^{-6} - 4 \times 10^{-6}$ cm^2 s^{-1}), for molecular masses ranging from 100 to 400 Da (7). Interpolated values for phenanthrene (5.4×10^{-6} cm^2 s^{-1}) and PCB-52 (4.3×10^{-6} cm^2 s^{-1}) differ by only about 20%. Diffusive mass transfer in water, without turbulent mixing,

is calculated to be only 300−400 mL day^{-1}/standard SPMD (8, 12). This value is more than 10-fold less than experimentally measured values and may indicate the importance of turbulent transport. Insufficient data are available for differentiating aqueous mixing from diffusive transport; therefore, the combined (turbulent-diffusive) transport is modeled as a single instance.

Aqueous film thicknesses on the order of 100 μm are expected from the relatively quiescent dilutor system, while thicknesses of 10 μm were considered possible in well-stirred systems (6, 13−15). Yet, assuming aqueous diffusivities were appropriately estimated, aqueous film thicknesses of 350−400 μm were required to provide sufficiently low aqueous uptake rates to fit the experimental data.

Biofouling—the growth of a periphytic layer or biofilm on the exterior polyethylene surface—was noted to some extent in these dilutor exposures and was most noticeable in polyethylene-alone studies (Figure 2C), in which the polyethylene-only samplers fouled more rapidly and to a greater extent than triolein-containing SPMDs (J. Huckins, personal communication). Though not included in the 3C model, slowing of uptake by a small biofilm could explain the greater than expected aqueous film thicknesses necessary to account for decreased uptake rates. The lesser fouling of lipid-containing SPMDs is due, in part, to the formation of a thin film of methyl oleate and oleic acid on the exterior surface which initially slows colonization (16). Significant biofouling during environmental exposures has been observed, and SPMDs previously biofouled by environmental exposure then placed in dilutors were demonstrated to have accumulation rates reduced as much as 70% for solutes with K_{ow} values greater than 10^6 (17). This suggests that rate control may switch to the biofilm as the SPMD becomes fouled.

Polyethylene Film Thickness and Diffusivity. The 3C model was used to investigate the effects of varying solute
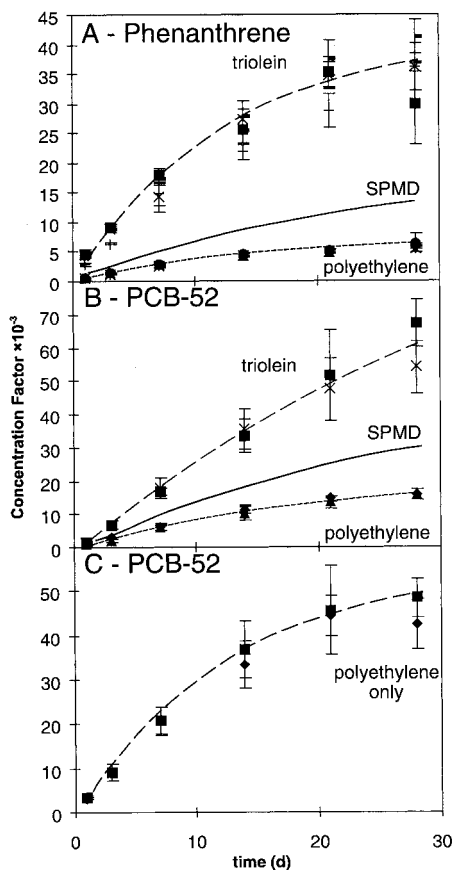
FIGURE 2. Best fits of the 3C model to experimental accumulation data (concentration factors) provided by James Huckins, U. S. Geological Survey-Columbia, Missouri, for (A) phenanthrene, SPMDs; (B) PCB-52, SPMDs; and (C) PCB-52 using polyethylene alone (PE-only) as a sampler. Concentration factors were calculated from exposure data at water concentrations of approximately 1, 10, and 100 ng L^{-1}. Experimental parameters are reported in Table 1, and best-fit values resulting from the 3C model are reported in Table 2.

diffusivity and polyethylene film thickness on accumulation by SPMDs. Decreasing polyethylene film thickness (δ_p) from 1000 to 10 μm is predicted to increase in the total amount of PCB-52 accumulated by the whole device by <10% in 28 days. Under these conditions, aqueous film control would almost completely dominate whole-SPMD accumulation. Nearly constant values of K_{Tp} (constant ratios of solute concentrations in triolein and polyethylene) are predicted before the end of a 28 day exposure.

The 28 day solute concentration in SPMDs is predicted to decrease <5% between solute–polyethylene diffusivities of ∼4 × 10^{-9}–4 × 10^{-12} cm^2 s^{-1} ($t_d \approx 0.9$ to 900 h, equivalent to diffusivities ranging from 10-fold faster to 100-fold slower than that for PCB-52). Polyethylene film control of accumulation in triolein is predicted by the 3C model for solute–polyethylene diffusivities less than that of PCB-52; however, overall accumulation in the whole device is predicted to remain under aqueous film control.

Approach to Steady State. The percentages of the steady-state SPMD concentrations as a function of the logarithm of K_{ow} for several sampling times were predicted with the 3C model and are shown in Figure 3A. (The 1-octanol–water partition coefficient K_{ow} will be used to approximate K_{SPMD} in the remainder of the discussion.) The volume of water requiring extraction to achieve this SPMD concentration is shown as the upper axis. Constant sampling rates (linear portion of the curves) are predicted for SPMD concentrations

less than about 50% of the steady-state values. As steady state is approached, mass transfer from the SPMD into water becomes significant, with subsequent decreases in overall accumulation. Substantial concentration factors (10^4–10^5) can be achieved in the SPMD with sampling periods of 7–90 days.

Predicted SPMD concentration factors as a function of exposure time and partition coefficient are shown in Figure 3B. The long-term accumulation profiles presented in Figure 3 are hypothetical; the longest reported sampling times are only about 90 days (1). In the environment, and to a lesser extent in dilutor studies, initial accumulation rates may not be maintained due to biofouling (17).

At constant water concentrations, chemicals with log K_{ow} values of <4.0 are predicted to reach steady state during a 28 day exposure, and their steady-state CFs and times-to-steady state would be proportional to the logarithm of their partition coefficients. Chemicals with log K_{ow} values of >5.5 would have similar 28 day CFs, as uptake rates ($k_{wp}C_w$) of most hydrophobic organic compounds are similar and are much greater than the clearance rates ($k_{wp}C_{SPMD}/K_{ow}$) early in the accumulation curve. The importance of the aqueous boundary layer in controlling overall uptake by SPMDs may help to explain the narrow range (∼an-order-of-magnitude) of accumulation rates for polycyclic aromatic hydrocarbons (18) with K_{ow} values varying by 10^5.

Single Application and Constant Concentration Exposures. Accumulation under single application conditions was investigated with the 3C model and compared with accumulation under constant-concentration conditions. Single application exposures in closed systems, such as microcosms, use only small amounts of chemical and aqueous volumes of a few liters, and are often employed to simulate larger-scale exposure. These exposures are conducted without further input of chemical ($k_0 = 0$), unlike flow-through dilutors or static renewal systems (where serial exposures to multiple volumes of water containing solute are used to simulate constant aqueous solute concentrations). Accumulation in single application exposures is greatly influenced by the rapidly decreasing aqueous solute concentration (see eq 1). SPMDs exposed under these conditions may have sufficient capacities and adequate aqueous uptake rates to deplete the solute, thereby decreasing the time required for the system to approach steady state (2–3, 19, 20). Solute depletion is an important consideration in extrapolating single application exposure results to predict kinetics in larger systems or environmental situations.

Experimental data from Gustafson et al. (20) for pyrene accumulation in 7 cm SPMD segments in a stirred, 3 L single application system were converted from triolein–water partition coefficients (reported values) to SPMD and water concentrations and compared with predictions from the 3C model (Figure 4A). The 3C model was able to fit the data well, though a much smaller aqueous film value was needed than that used for the dilutor exposures (25 vs 400 μm). Predicted SPMD accumulation in constant concentration flow-through dilutor and 3 L stirred-single application exposures are compared in Figure 4B, using the previously fitted aqueous film thicknesses (dilutor, 400 μm; single application, 25 μm). The aqueous uptake rate constant in the single application system was predicted to be 2.7 L day^{-1}/7 cm SPMD segment, or 35 L day^{-1}/standard SPMD. This is in marked contrast with a predicted uptake rate of 4.3 L day^{-1} for the dilutor exposure (3), and with the 6–8 L day^{-1}/SPMD reported for priority pollutant PAHs in flow-through dilutor studies (18). Differences in the 3C model-fitted uptake rates of single application versus flow-through systems may reside in the aqueous film thicknesses used to fit the accumulation data. The 350–400 μm film thicknesses required to fit the experimental values of 4–5 L day^{-1} for the
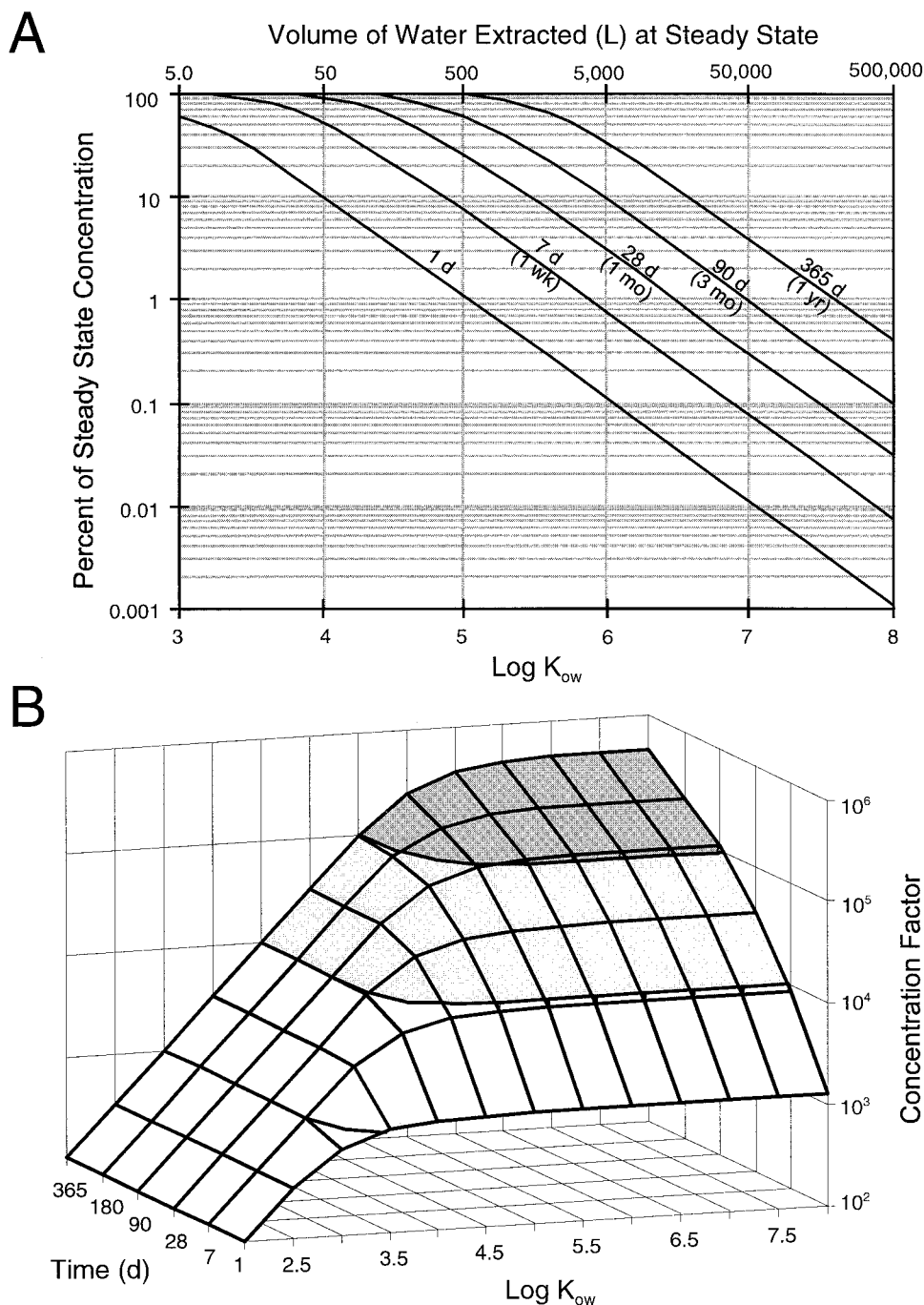
FIGURE 3. (A) Percentages of steady-state concentrations as a function of log K_{ow} predicted for five sampling times. Volumes of water extracted to reach the steady-state SPMD concentrations are shown as the upper axis and are proportional to log K_{ow} and percent of steady-state reached. (B) Predicted concentration factors attainable for standard SPMDs as a function of log K_{ow} for several sampling times. Note: the time axis is incremental rather than scalar.

flow-through dilutor exposures were much greater than anticipated. Aqueous films on the order of about 50−100 μm are expected from poorly mixed solutions (13) similar to those occurring in the dilutor, while an aqueous film of about 400 μm is indicative of a nearly stagnant system (21).

Pulsed Concentration Events. SPMDs are often deployed in the field as integrative samplers of dissolved hydrophobic contaminants and are considered to respond well to varying water concentrations of a solute by accumulating and retaining the chemical. The 3C model was used to examine the integrative sampling characteristics of SPMDs.

Assuming aqueous film control (i.e., similar uptake rate constants for many solutes for the whole device), integrative

sampling will be controlled predominately by the SPMD−water partition coefficient. The integrative sampling ability of the SPMD can then be expressed in terms of a characteristic response-time or half-life $\tau_{1/2}$ for the device:

$$\tau_{1/2} = 0.693 \frac{K_{ow} V_{SPMD}}{k_{wp}} \tag{14}$$

where K_{ow} is used to approximate the partition coefficient of the whole device, V_{SPMD} is the device volume, and k_{wp} is the aqueous uptake rate constant. (The actual partition coefficient K_{SPMD} of the whole device is equivalent to the volume-weighted average of the partition coefficients of the poly-
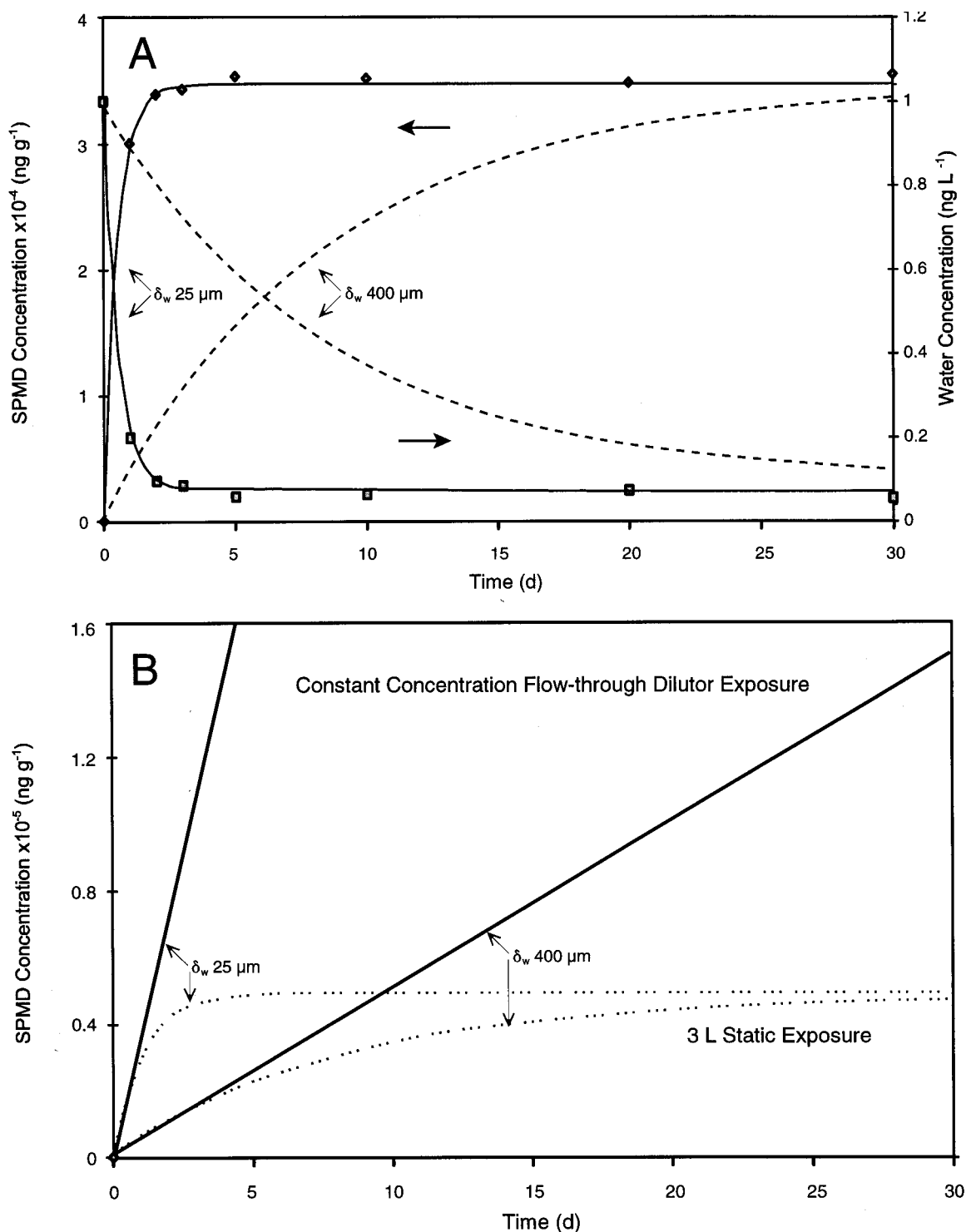
FIGURE 4. (A) Pyrene concentrations [from Gustafson et al. (*20*)] in 7 cm segments of SPMDs and in water exposed in a stirred, 3 L single application system, and the predicted concentration curves with an aqueous film thickness of 25 μm fit to these data. Predicted concentrations using an aqueous film thickness of 400 μm (dilutor data provided by James Huckins, USGS, Columbia, Missouri) are shown for comparison. (B) Predicted concentration profiles for pyrene in both the stirred, 3 L single application system and in a constant concentration flow-through dilutor system using their respective fitted aqueous film thicknesses (25 and 400 μm).

ethylene and the triolein compartments.) The 3C model developed here suggests that SPMDs sample integratively only in the linear region of the accumulation curve, and, for a changing concentration event, over times that are less than the solute half-life ($\tau_{1/2}$) in the device. Errors in integrated water concentrations for $t < \tau_{1/2}$ would be <10%, while errors of <25% would result from $t < 2\tau_{1/2}$.

The SPMD's ability to integrate varying water concentrations was demonstrated by considering accumulation over

a 28 day sampling period, with a unit background concentration of solute and with a two-day-long pulsed event of 10-fold greater concentration beginning on day 10. The 3C model was used to predict integrated water concentrations (C_{iw}) for three solutes, naphthalene, phenanthrene, and PCB-52, exhibiting a broad range of measured clearance rates (*17, 18*). Modeled SPMD accumulation profiles are shown in Figure 5A, actual and predicted integrated water concentrations in Figure 5B, and the errors predicted from assuming
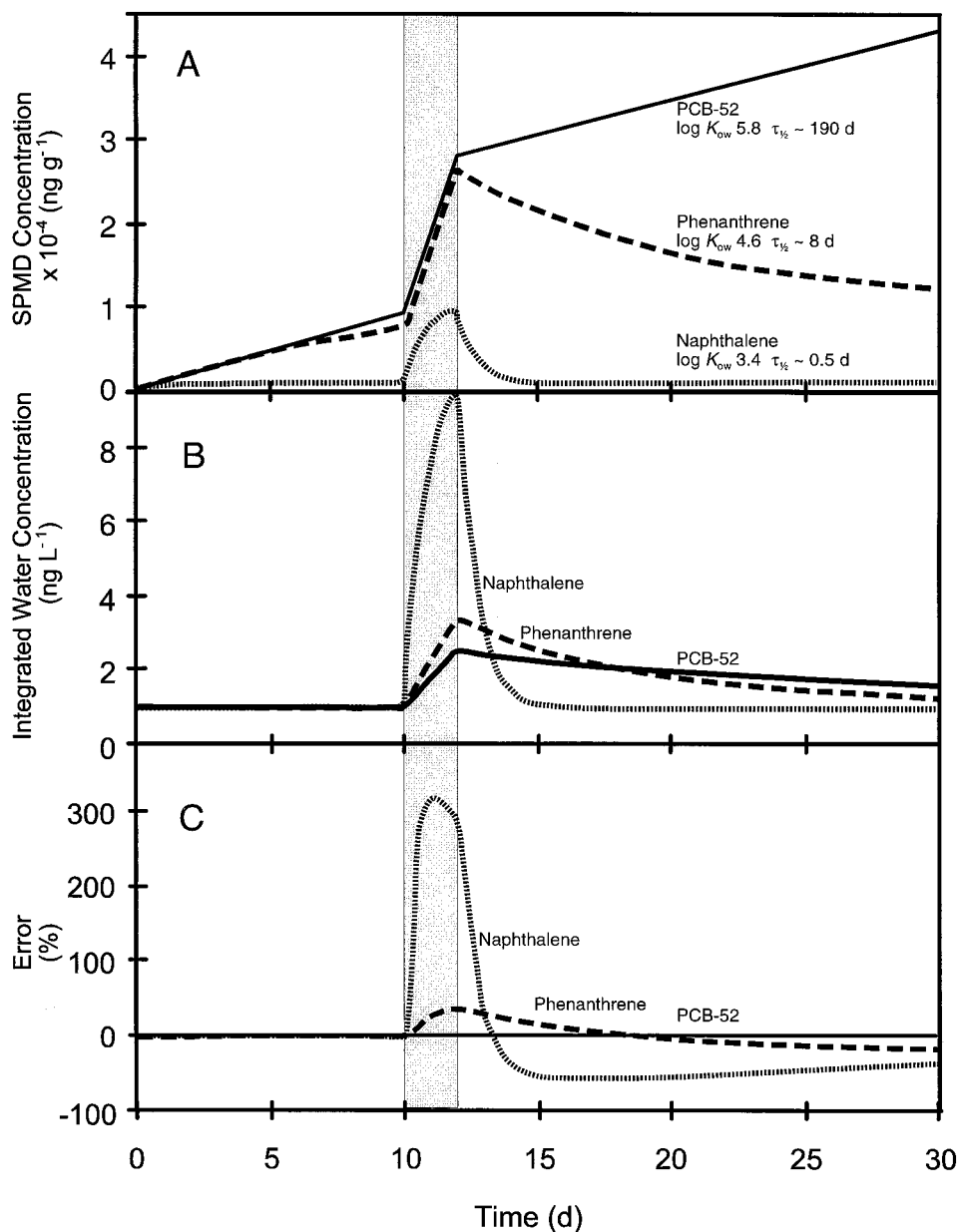
FIGURE 5. Simulation of the accumulation (and retention) of naphthalene, phenanthrene, and PCB-52 for standard SPMDs exposed to a constant water concentration of 1 ng L^{-1}, with a two day, 10-fold pulse in water concentration (10 ng L^{-1}) beginning at day 10 (shaded time window). (A) Predicted SPMD concentrations; (B) integrated water concentrations (C_{iw}). The actual values of C_{iw} are superimposed on the calculated values for PCB-52. (C) Errors in estimated C_{iw}.

complete integration of the water concentration (negligible clearance) in Figure 5C. Predicted concentrations of naphthalene (log K_{ow} = 3.45, $\tau_{1/2} \approx 0.5$ day) are poorly integrated over the period past the pulsed event due to rapid clearance from the SPMD. Predicted phenanthrene (log K_{ow} = 4.6, $\tau_{1/2}$ $\approx$ 8 day) concentrations are moderately well integrated overall, and clearance from the SPMD is slow enough to provide a more accurate integration of the pulsed event. Integration of the pulse is improved over that of naphthalene since the half-life for phenanthrene is now several times the width of the event and is approaching the width of the sampling period. Water concentrations for PCB-52 (log K_{ow} = 5.8, $\tau_{1/2} \approx 190$ day) are well integrated, which is the result of both the event time and the sampling period being much less than the half-life of the device (2 and 28 days $\ll 2\tau_{1/2}$.). Accumulation of solutes with K_{ow} values less than 10^4 have been increased using dispersed sorbents, such as activated carbon, in triolein (22), which increase the effective partition (adsorption) coefficient of the solute.

Evaluation of the 3C Model. The 3C model fitted data from single application and dilutor exposures of SPMDs well and suggests turbulent-diffusive aqueous transport may control the accumulation of many chemicals in SPMDs. The model predicts that uptake rate constants should vary less than about 2-fold when under aqueous boundary layer control. The observed importance of the polyethylene as a solute reservoir in SPMDs is accounted for by the 3C model, and the polyethylene film is predicted to be less important than the aqueous boundary layer in controlling accumulation in the whole device. Passive samplers with high surface area and low capacity, such as the polyethylene-alone examined in this study, tended to have faster response times but proportionally faster clearance times, and greater tendency to biofoul, making them poor choices for integrative long-term (weeks-to-months) monitoring. Accurate predictions of dissolved concentrations of hydrophobic organic contaminants in water are limited by the ability to control the aqueous film thickness, and biofouling. These limits may

be addressed by the use of permeability reference compounds (*17*).

Acknowledgments

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