Critical Review

Dynamic Exposure of Organisms and Passive Samplers to Hydrophobic Chemicals

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An insight into the dynamic aspects of the accumulation process is essential for understanding bioaccumulation as well as effect studies of hydrophobic organic chemicals. This review presents an overview of kinetic studies with organisms (fish, bivalve, crustacean, insect, worm, algae, and protozoan) as well as passive samplers (solid and liquid phase microextraction, semipermeable membrane device, polymer sheet, solid-phase extraction, Chemcatcher, etc.) for the uptake of neutral nonpolar chemicals from the aqueous phase. Information about uptake rates, elimination rates, and 95% equilibration times was collected and analyzed with diffusion based models. The present literature review suggests that the surface to volume ratio appears to be a critical parameter for the uptake rate of the more hydrophobic chemicals both for samplers and organisms. In addition, as a very first approximation, the combination of the first-order kinetic model with the assumption that diffusion through the aqueous boundary layers is rate limiting, gives a reasonable description of the experimental kinetic data. In this way, the presented model might be used to estimate uptake and elimination rate constants of chemicals by organisms or passive samplers.

Introduction

The analysis of processes in the environment is often performed at an equilibrium situation (*1, 2*). The fugacity theory, for example, represents a well-known concept to study and analyze the equilibrium status of environmental systems (*3*). However, the equilibration between phases in the environment such as geosorbents, organisms, and water takes time and, in several circumstances, both in the laboratory and in the field, equilibrium is not reached.

Various processes such as biological and chemical degradation, sequestration (*4*), dispersion, and changing environmental conditions may prevent that a thermodynamic equilibrium is established and a pseudo equilibrium or steady state situation may occur. For example, if a chemical is discharged in the environment, due to a disaster or a pesticide application, the peak concentration will drop by dispersion, sorption, and degradation (*5*). Consequently, not only the equilibrium situation but also the dynamic aspects of the accumulation process are essential for a correct ecological risk assessment of hydrophobic organic chemicals in the environment, because it determines the response of an organism to fluctuating concentrations of a chemical in the environment. Gaps in the understanding of uptake kinetics may then lead to an incorrect interpretation of bioaccumulation studies, toxicity testing, and field monitoring. For example, Jonker et al. (*6*) showed how insufficient equilibration can lead to underestimation of bioaccumulation factors.

In recent decades, the use of passive samplers has emerged to assess exposure of organisms in the laboratory and field (*7*−*9*). Passive sampling is, for example, applied to measure freely dissolved concentrations or chemical activity in water, soil, or sediments (*10*), or to mimic accumulation into organisms (biomimetic extractions) (*11*). The determination of the freely dissolved concentrations is preferably performed by equilibrating the sampler with its environment (a test system, sample, or field location), because that will generally result in more robust data than kinetic measurements (*12*). Bioaccumulation also receives attention nowadays in effect studies because the internal concentration is a more intrinsic dose parameter than external concentrations, and circumvents complications in the exposure assessment caused by differences in bioavailability (*13*−*16*).

In a highly dynamic environmental system, internal concentrations in the organism do not follow the changing environmental concentrations closely. Especially, larger organisms integrate exposure concentrations over a large time window because their exchange kinetics are slow. Subsequently, their internal concentrations will slowly respond to fluctuating environmental concentrations. On the other hand, smaller organisms such as algae will respond much faster to these fluctuations. This gives an additional reason why risk assessment based on internal concentrations is more appropriate than an assessment based on concentration in the exposure media itself. Thus, in the field of bioaccumulation, ecotoxicology, and environmental risk assessment, it is essential to have knowledge about the dynamic characteristics of exchange processes of organisms and passive samplers. This is the key issue of this critical review. One additional reason to analyze these dynamic characteristics is related to the topic of biomimetic extractions. The objective of biomimetic extraction is to simulate the accumulation into organisms via a chemical-partition based extraction. This implies that the accumulation rate of the sampler and organisms of interest should be similar, and that, in some cases, both the sampler and organism are not equilibrated with the test system.

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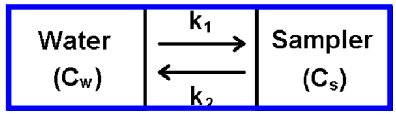

FIGURE 1. Two-compartment model.

The uptake kinetics of organisms and passive samplers are affected by the physicochemical properties of the compound(s) of interest, the environmental matrix, the mixing conditions, and the size, age, geometry, behavior, physiology, habitat, and niche of the organisms (*17*). Aqueous boundary layers often act as a rate-limiting step in the mass transfer of hydrophobic organic chemicals in aquatic organisms such as fish and macro-invertebrates (*18, 19*). These aqueous boundary layers are considered as stagnant. Consequently, the transport over these layers is limited by diffusion. For less hydrophobic chemicals, the diffusion in the sampler or organism itself may become rate limiting.

This review presents an overview of kinetic studies with organisms as well as passive samplers. The data are analyzed with diffusion based models. The kinetic properties are related to physicochemical properties of the chemicals and characteristics of the biota and sampler such as surface/volume ratios. A first section will describe the theory of accumulation and elimination kinetics of chemicals in both passive samplers and organisms. Then, the uptake kinetics of a wide range of neutral organic substances (log $K_{ow} = 0.7-8.3$) were collected and compared to theoretical models. The analysis was focused on neutral and nonpolar organic contaminants, including polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), dioxins, and furans, and various organophosphorous and organochlorine pesticides. The uptake kinetics of chemicals to organisms and samplers are compared to see whether certain samplers can mimic accumulation of chemicals in certain classes of organisms. Strengths and limitations of the various samplers are highlighted and directions for future research are indicated.

Theory

Passive Samplers. In the two-compartment model (Figure 1), uptake and elimination of neutral and nonpolar chemicals are assumed to follow first-order kinetics, resulting in the following relationship:

$$\frac{dC_s(t)}{dt} = k_1 \cdot C_w(t) - k_2 \cdot C_s(t) \quad (1)$$

where $C_w(t)$ and $C_s(t)$ are the concentration (function of time) in the aqueous phase and sampler phase, respectively; k_1 and k_2 are the uptake and elimination rate constants, respectively. The unit of k_1 is in [(volume of water/volume of sampler) × time^{-1}], e.g., [$L_w \cdot L_s^{-1} \cdot$hour^{-1}] (L_w = liter of water; L_s = liter of sampler). k_2 is expressed in [time^{-1}], e.g., [hour^{-1}]. From the elimination rate constant, it is simple to derive t_{95}, i.e. the time to reach 95% of the equilibrium concentration in the sampler:

$$t_{95} = \frac{-\ln(0.05)}{k_2} = \frac{3.00}{k_2} \quad (2)$$

At equilibrium, the sampler−water partition coefficient, K_{sw}, is related to kinetic parameters:

$$K_{sw} = \frac{k_1}{k_2} \quad (3)$$

Considering that $C_w(t)$ is constant with time (noted as C_w^*), the combination of the first order (eq 1) and the diffusion models (see Supporting Information, Appendix A) leads to the following general expression for samplers:

$$k_1 = \frac{A}{V} \times \frac{1}{\frac{\delta_w}{D_w} \cdot \frac{r}{\delta_w + r} + \frac{1}{m_t K_{sw}}} \quad (4)$$

where A represents the surface area of sampler/water interface, V is the volume of the sampler, δ_w is the diffusion layer thickness in water, r is the radius of curvature of the sampler surface, D_w is the diffusion coefficient of the analyte in water, and m_t is the mass transfer coefficient in the sampler. For flat samplers, $r \gg \delta_w$, so that the term $r/(r+\delta_w)$ in eq 4 tends to 1. Then, combination of eqs 3 and 4 gives:

$$k_2 = \frac{A}{V \cdot K_{sw}} \cdot \frac{1}{\frac{\delta_w}{D_w} \cdot \frac{r}{\delta_w + r} + \frac{1}{m_t \cdot K_{sw}}} \quad (5)$$

From the above equations, it immediately appears that factors such as convection or water flow-rate, temperature, (bio)fouling, which may influence δ_w, D_w, and m_t, will therefore influence the uptake and elimination rates. Temperature will also influence K_{sw}. These aspects will be discussed in detail later in the manuscript.

The general trends of k_1, k_2, and t_{95} as a function of K_{sw} are presented in Figure 2. At lower K_{sw}, i.e., when mass transfer is limited by diffusion inside the sampler/organism, k_1 will increase with K_{sw}, whereas k_2 and t_{95} are relatively constant. At higher K_{sw}, i.e., when mass transfer is limited by aqueous diffusion, k_1 reaches a plateau (k_{1max}) or might even decrease slightly with K_{sw} (*6*), whereas k_2 decreases rapidly with K_{sw}. Such profiles have been reported in the literature (*20−25*). The transition stage, or "breaking point" (*18*) where the mass transfer in the sampler switches from diffusion limiting step/organism to diffusion in the aqueous diffusion layer, as reported in the literature, are listed in Table 1. This breaking point is generally presented as a critical log K_{ow} value (noted $(K_{ow})_c$ in the present paper), because individual sampler/water partition coefficients are not available for all chemicals. Convection and water flow-rate will influence $(K_{ow})_c$.

Theoretically, the maximum uptake kinetics (k_{1max}) of a sampler exposed to an aqueous phase is determined by the diffusion of the chemical in the aqueous phase. In this manuscript, k_{1max} is defined as the maximum uptake rate. For flat samplers ($r \gg \delta_w$), k_{1max} is obtained from eq 4 when $\delta_w/D_w \gg (m_t \times K_{sw})^{-1}$:

$$k_{1max} = \frac{A}{V} \cdot \frac{D_w}{\delta_w} \quad (6)$$

Aquatic Organisms. Modeling the uptake and elimination of hydrophobic organic chemicals in organisms is more challenging than in samplers since physiological parameters such as metabolism (e.g., active clearance, biotransformation) and uptake via food will affect the apparent uptake and elimination rates. Nevertheless, as a very first approximation, the model described in the previous section can be applied to organisms, by just replacing the C_S for the concentration in the organism (C_B). In contrast to most passive samplers, concentrations in organisms are generally reported per wet weight (ww), dry weight (dw), or lipid weight (lw), and not per volume. Therefore, the unit of the uptake rate (k'_1), and organism/water partitioning coefficient (K_{BW}) for organisms needs to be adjusted into kg$_{ww} \cdot$L$_w^{-1} \cdot$hour^{-1} and kg$_{ww} \cdot$L$_w^{-1}$ respectively, and the volume (V) will be replaced by the wet weight (W). Note that the density of organism is often close to 1, so that values of k'_1 (organisms) and k_1 (samplers) are comparable.

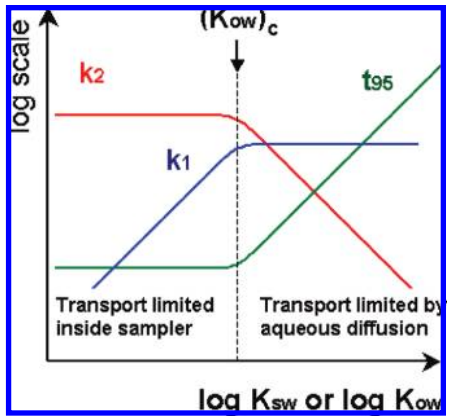

FIGURE 2. Relation between uptake rate constant (k_1) or elimination rate constant (k_2) and sampling-water partition coefficient (K_{sw}) or the octanol−water partition coefficient (K_{ow}) as a more general measure for the hydrophobicity.

The uptake rate constant can then be expressed by:

$$k'_1 = \frac{A}{W} \times \frac{1}{\frac{\delta_w}{D_w} \cdot \frac{r}{\delta_w + r} + \frac{1}{m_t \cdot K_{Bw}}} \quad (7)$$

On gill surfaces of fish, diffusion layers, δ_w, of 1−10 μm have been estimated from distance between gill lamellae (*18*) and planar diffusion occurs ($r \gg \delta_w$). Active movements and respiration will influence convection and water flow at the surface of exchange, and therefore δ_w. The elimination rate constant is expressed as follows:

$$k'_2 = \frac{A}{W \cdot K_{Bw}} \cdot \frac{1}{\frac{\delta_w}{D_w} \cdot \frac{r}{\delta_w + r} + \frac{1}{m_t \cdot K_{Bw}}} \quad (8)$$

From the above equations, it immediately appears that growth will influence *A*, *W* (and possibly K_{BW}, m_t,...) and therefore the uptake and elimination rates. Internal distribution inside the organism may limit the overall uptake rate, and this is included in the m_t parameter. As before, k'_1 is eventually limited by the diffusion of the compound in the aqueous phase:

$$k'_{1max} = \frac{A}{W} \cdot \frac{D_w}{\delta_w} \cdot \frac{\delta_w + r}{r} \quad (9)$$

Materials and Methods

Methodology. This review discusses the uptake kinetics of organic chemicals in aquatic organisms and passive samplers exposed in the aqueous phase. Uptake rate constants (k_1 and k'_1) were obtained from accumulation studies. Elimination rate constants (k_2 and k'_2) and 95% equilibration times (t_{95} and t'_{95}) were obtained from both accumulation and elimination (depuration) studies. Theoretically, both methods should lead to identical k_2 or t_{95} values (*26*). However, experimental parameters (insufficient exposure time, variation of exposure concentration, metabolic degradation of chemicals) may lead to discrepancies between rate constants (*27*). The k_1 data for passive samplers were normalized to [$L_w \cdot L_s^{-1} \cdot hour^{-1}$] as in eq 4. For organisms, the concentrations were almost exclusively presented per mass, therefore k'_1 data were normalized as [$L_w \cdot kg_{ww}^{-1} \cdot hour^{-1}$] as in eq 7. For both passive samplers and organisms, the chosen unit of k_2 was [$hour^{-1}$].

The data were selected to reflect exposure via the aqueous phase only, so accumulation from food and sediment/soil were not considered. Additionally, accumulation data in media containing large amounts of dissolved (organic) matrixes were also neglected because these dissolved materials might facilitate transport of especially hydrophobic substances (*28*−*30*). This restriction implies that only exposure experiments (mainly in the laboratory) in aqueous media free of dissolved organic matter (DOM) were included in the overview.

The chemicals for which data on uptake kinetics were available include PAHs, PCBs, dioxins/furans, pesticides and herbicides, octyl- and nonyl-phenols, and chlorobenzenes. log K_{ow} values of these organic chemicals range from 0.69 to 8.27. Octyl- and nonyl-phenols were included in this study as they are mostly not ionized in most natural waters. In general, neutral hydrophobic organic chemicals were selected because they bioaccumulate and can be sampled by a hydrophobic phase of a passive sampler. The selected octanol−water partition coefficients of the chemicals are listed in Table S1 and S2 of the Supporting Information. log K_{ow} was often used as a surrogate measurement of hydrophobicity, because robust partition coefficients and bioconcentration factors were not always available for sampler materials and organisms, respectively.

Stirring varied from stagnant systems to ultrasonication. Test temperatures ranged from 2 to 37 °C, with most studies conducted between 19 and 25 °C (see Tables S1 and S2).

Passive Samplers. The number of passive sampler designs has been growing in recent decades (*7*−*9*). To compute k_1 and k_2, this paper used uptake and elimination profiles of various passive samplers that were applied in a nondepletive manner. Depletive extraction techniques were not considered because this does not reflect the uptake of samplers or organisms in the field, and can not be described by a one-compartment model as presented in the theoretical section (eq 2, Appendix A in the Supporting Information). A short description of the passive samplers for which kinetic data were available is presented in Appendix B.

Organisms. This paper summarizes uptake and elimination studies of various aquatic organisms, including fish, bivalves, crustaceans, insects, worms, unicellular algae, and protozoans. Similar to selected data of the passive samplers, the organisms should be exposed to constant aqueous concentrations and the uptake should not lead to a depletion of the aqueous phase. Furthermore, organisms were not considered to eliminate via feces (*31*).

Experimental data for organisms were selected according to these criteria. A description of the approximations (size/weight) for the various organisms is presented in Appendix C.

Results and Discussion

All together, a few thousand data on uptake/elimination rates were collected in the literature (see Supporting Information).

Uptake Rates. Uptake rate constants (k_1) for passive samplers, as reported in the selected literature, range from 0.55 to 2.6 × 10^6 $L_w \cdot L_s^{-1} \cdot hour^{-1}$ (Table 1). Figure 3a shows the relationship between k_1 and the area/volume ratio (*A*/*V*, mm^{-1}) of the passive samplers. Overall, k_1 values seem to increase with *A*/*V*. The largest k_1 values were obtained for samplers with the largest area/volume ratio (fibers with a 7 μm thin PDMS coating) that were agitated in solutions by ultrasonication (*32*). The k_1 values for SPMDs ranged from 2.3 to 2193 $L_w \cdot L_s^{-1} \cdot hour^{-1}$. Highest uptake rates for SPMDs were measured by Booij et al. (*22*), at a flow velocity of 90 $cm \cdot s^{-1}$, and rates decrease by 1−2 orders of magnitude for lower agitation. Booij et al. (*22*) reported that sampling rates, and therefore k_1, were overall similar for SPMDs and low-density PE, i.e., SPMD with no triolein.

Similarly, Figure 3b shows the k'_1 values for organisms, plotted against the area (of the gills) to wet weight ratio (*A*/*W*; $m^2 \cdot kg_{ww}^{-1}$). k'_1 values range from 0.33 to 10^7

TABLE 1. Summary of Kinetic Data Reviewed from Literature

passive samplers	A/V range (mm^{-1})	k_1 range (n) ($L_w \cdot L_s^{-1} \cdot hour^{-1}$)	k_2 range (n) ($hour^{-1}$)	t_{95} range (hour)	$\log(K_{ow})_c$
PDMS SPME[a] fiber	4−160	33−2604000 (92)	1.1×10^{-2}−2.2×10^{2}(38)	0.01−280	0−1(*36*)
PA SPME[b] fiber	17−37	7−8475 (25)	1.1×10^{-2}−1.1 × 10 (25)	0.3−280	2−3.5(*24, 25, 65*)
SPMD [c]	8−14	2.3−2193 (362)	1.3×10^{-4}−7.6×10^{-2} (114)	39−23000	3.6(*66*) 4.4 low flow velocity(*20*) 5.7 high flow velocity(*22*)
LDPE[d]	11	224−2101 (41)	5.3×10^{-4}-2.9×10^{-2} (19)	103−5700	n.a.
PDMS sheet	5	478−4395 (18)	n.a.	n.a.	
LPME[e]	33	174−1300 (11)	n.a.	n.a.	n.a.
C18 disk	3−4	161−6110 (20)	1.2×10^{-2}−8.2×10^{-2} (14)	36−260	n.a.
Chemcatcher	12	0.55−96 (134)	2.0×10^{-4}−4.7×10^{-3} (31)	640−15000	n.a.
TECAM[f]	22	6−507 (18)	2.1×10^{-3}−2.3×10^{-1} (22)	13−1400	n.a.

organism	A/W range ($m^2 \cdot kg_{ww}^{-1}$)	k'_1 range (n) ($L_w \cdot kg_{ww}^{-1} \cdot hour^{-1}$)	k'_2 range (n) ($hour^{-1}$)	t'_{95} range (hour)	$\log(K_{ow})_c$
fish	0.2−1	0.33−750 (211)	5.8×10^{-5}−2.0×10^{-1} (88)	15−51400	3−4(*21*) 7.38(*67*)
bivalve	0.4−8	0.4−1680 (59)	1.5×10^{-4}−7.0×10^{-2} (153)	43−19000	n.a.
crustacean	1.7−18	0.85−346 (45)	1.1×10^{-3}−1.2 (55)	2.6−2700	n.a.
insect	3−11	16.4−584 (20)	3.2×10^{-3}−1.9 (20)	1.6−920	<3(*61*)
algae/protozoan	9−1240	18−10^7 (15)	3.1×10^{-2}−23 (15)	0.13−96	n.a.
worm	1.7−14	0.61−110 (5)	3.2×10^{-3}−2.5 (3)	1.2−940	n.a.

[a] Polydimethylsiloxane solid-phase microextraction. [b] Polyacrylate solid-phase microextraction. [c] Semipermeable membrane. [d] Low-density polyethylene.l [e] Liquid phase microextraction. [f] Triolein-embedded celullose acetate membrane.

$L_w \cdot kg_{ww}^{-1} \cdot hour^{-1}$ (Table 1). Among organisms, the highest k'_1 values were obtained for algae, the organisms with the highest A/W ratio (*33, 34*). Small fish ($A/W \geq 1$ $m^2 \cdot kg_{ww}^{-1}$) showed higher uptake rates than larger ones ($A/W \leq 1$ $m^2 \cdot kg_{ww}^{-1}$). Similar relations were observed for bivalves, where the smaller bivalve *D. polymorpha* (*35*), with shell length ≤20 mm and $A/W \geq 4$ $m^2 \cdot kg_{ww}^{-1}$, displayed higher uptake rates than larger bivalves ($A/W \leq 1$ $m^2 \cdot kg_{ww}^{-1}$).

The lines plotted in Figure 3a and b represent the theoretical maximum uptake rate constants (k_{1max} and k'_{1max}) for various stirring conditions corresponding to different δ_w values. Lines were computed according to eqs 6 and 9, for a typical organic pollutant with an average aqueous diffusion coefficient $D_w = 5 \times 10^{-10}$ $m^2 \cdot s^{-1}$. The selected aqueous diffusion layer thicknesses δ_w were equal to 1 μm (dotted line), 10 μm (dash line), 100 μm (thin plain line), and 400 μm (thick plain line). These δ_w values correspond to a wide range of laboratory/environmental conditions as 1 μm might be regarded as the diffusion layer thickness for highly agitated systems (*36*), 10−100 μm is expected for systems under strongly to mildly mixed conditions (*37, 38*), and 400 μm may be considered as an upper value corresponding to quiescent conditions in laboratory experiments (*39*).

Mass Transfer Limitations for Samplers and Organisms. As mentioned earlier, the mass transfer of chemicals from an aqueous phase to a hydrophobic phase can be limited by either diffusion through the aqueous boundary layers or diffusion in the hydrophobic absorbent itself, as described in eqs 4 and 7 (see Figure 2). Which process is rate limiting largely depends on the partition coefficient between the aqueous and hydrophobic phase (passive sampler or organism), the ratio of diffusivity in the aqueous phase and sampler or organism phase, and the mixing conditions of the aqueous phase. As discussed in the Theory section, $(K_{ow})_c$ represents the value of K_{ow} below which the diffusion in the hydrophobic phase is rate limiting and above which the diffusion in the aqueous phase becomes rate limiting. $(K_{ow})_c$ values reported in the literature are listed in Table 1. It can be observed that this transition range can vary largely between passive samplers: log $(K_{ow})_c$ of SPME fibers ranges from 0 to 3.5, while it ranges from 3.6 to 5.7 for SPMDs. log $(K_{ow})_c$ also vary largely for organisms, even though only limited information was available. Aqueous diffusion layers often act as the rate limiting barriers for the mass transfer of hydrophobic organic chemicals in aquatic organisms such as fish and macroinvertebrates (*18, 19*). For most samplers and organisms the log $(K_{ow})_c < 5$.

The data on uptake rates of chemicals with log $K_{ow} \geq 5$ can be considered as maximum, aqueous phase limited, uptake rate constants (k_{1max}, see Figure 2). For these chemicals, the maximum k_1 and k'_1 values reported were plotted versus the A/V (sampler) or A/W (organism) ratio in Figure 4. As can be seen in Figure 4, the experimental maximum values of k_1 and k'_1 generally fall within the range of k_{1max} and k'_{1max} predicted by the simple aqueous diffusion based model of eqs 6 and 9 with a δ_w ranging from 1 to 400 μm. With the approximation that the density of organisms is equal to 1 (and therefore $W = V$), organisms and passive samplers seem to cover different A/V ranges (m^2/L) ratio. For all data of samplers and organisms, the slope of log (maximum k_1) versus log (A/V) was equal to 1.00 ± 0.16 (correlation coefficient = 0.94), demonstrating that the maximum k_1 values were linearly proportional to A/V. Consequently, the A/V or A/W parameter appears to be a critical parameter for uptake rate constants of the more hydrophobic chemicals both for samplers and organisms.

From this observation, it can be deduced that data points in Figure 3 below the thick plain line corresponding to aqueous boundary layer thickness of 400 μm are probably limited by diffusion inside the sampler material or slow distribution within the organism. By comparing Figure 3a and b, organisms seem to be more often under aqueous diffusion limiting transfer than the passive samplers. This makes sense because diffusion in some sampler materials can be several orders of magnitude slower than in water (*40*), while the diffusion through biological membranes is rather close to aqueous diffusion (*21*). Additionally, the distribution of chemicals within organisms is facilitated by internal convection, such as the circulation of blood trough the tissues, which does not exist in passive samplers.

Observed Variability in Uptake Rate Constants. There are several reasons, besides the possible limitation of the mass transport between the aqueous and sorbent by distribution in the sorbing phase (sampler or organism), that

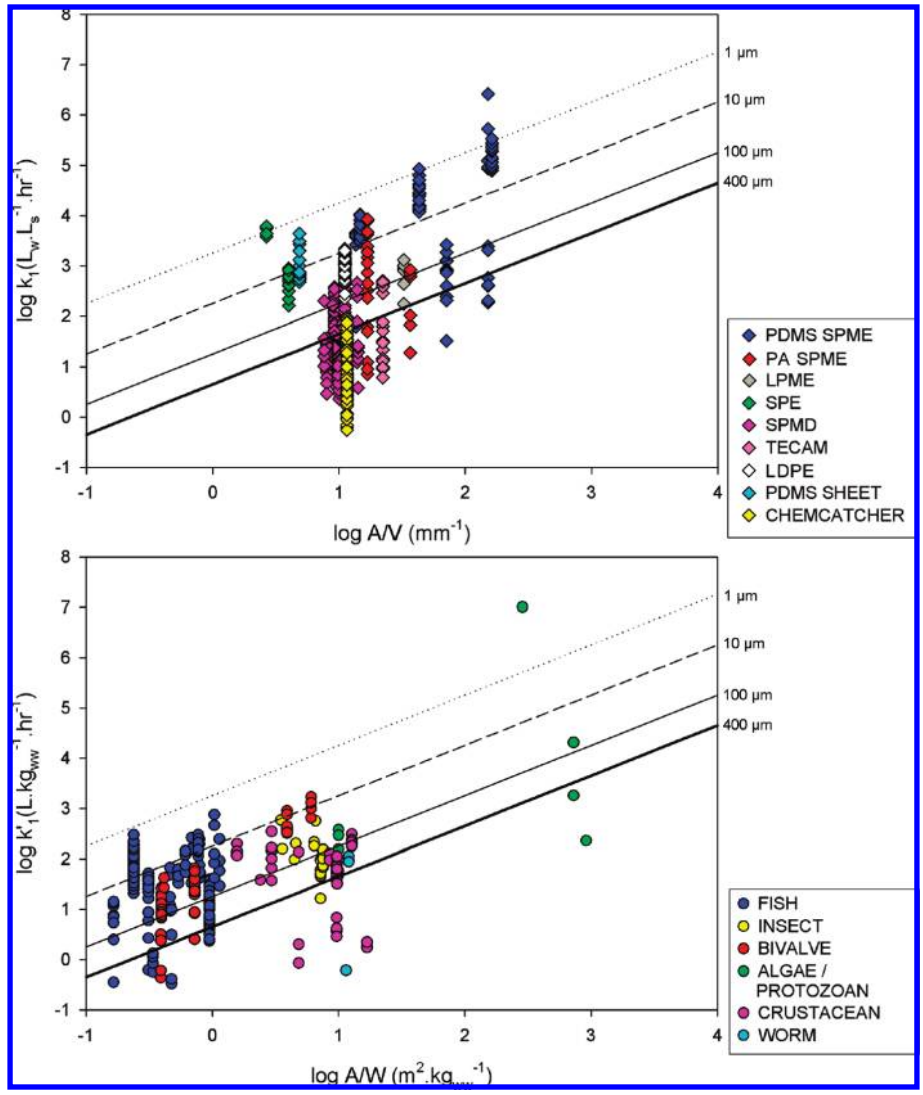

FIGURE 3. Log−log plot of experimental uptake rate constant k_1 versus *A/V* for passive samplers (a) and versus *A/W* for organisms (b). Lines represent the maximum uptake rate constant assuming that transport is limited by diffusion in the aqueous diffusion layer with a thickness of 1 μm (dotted line), 10 μm (dash line), 100 μm (thin plain line), and 400 μm (thick plain line), for a typical organic pollutant with an average aqueous diffusion coefficient $D_w = 5 \times 10^{-10}$ $m^2 \cdot s^{-1}$.

can explain the rather large variability that is observed in the relationships between the surface volume ratio and the uptake rate contant (Figures 3 and 4). Some of these reasons are listed below.

The first reason is that the temperature is not constant. The temperature in the test systems varied from 2 to 37 °C (Tables S1 and S2). Diffusion coefficients in water increase with temperature by 2.78−2.99% per °C (*41*), i.e., and thus by a factor of 2.8 between 2 and 37 °C. Similar relationships can be expected for organic phases such as passive sampler materials and organism tissue. In addition, differences in temperature will also have an effect on the ventilation volume and metabolism of organisms. The systematic influence of temperature on the uptake rates was reported in the literature for passive samplers, such as SPMDs (*22*) or C18 disks (*42*). Booij et al. (*22*), for example, showed that uptake rates of SPMDs increased by an average factor of 2.8 between 2 and 30 °C.

Second, agitation of the aqueous phase can reduce the thickness of the aqueous boundary layer, and can thereby increase the uptake rate of organic chemicals by organisms or passive samplers (eqs 4 and 7). The variation of agitation was especially large for the reported laboratory exposed passive samplers. Agitation varied from stagnant to ultrasonicated systems, where the sampler was agitated in the aqueous solution at a frequency of 50 Hz (*32*). The design of the passive sampler might also affect the thickness of the diffusion layer at the interface with the aqueous phase. For example, with the Chemcatcher system, Vrana et al. (*43*) estimated that the diffusion layer thickness varied between 200 and 1000 μm, even though smaller values would be expected under their relatively turbulent flow conditions. They conclude that the Teflon body around the sampler reduced agitation in the vicinity of the extracting membrane (*44*). For organisms, usually stagnant test systems are used (e.g., aquarium). However, organisms create agitation by moving and by ventilating their gills. These movements are affected by environmental conditions such as temperature (*45*), light, and oxygen concentration. For example, a study (*46*) with a worm showed that decreasing the oxygen concentration in the aqueous phase led to an increase of the uptake of an organic chemical due to behavioral changes to increase oxygen uptake.

Third, values of k_1 and k'_1 computed in Figure 3a and b are based on planar diffusion. This is valid as long as $r \gg \delta_w$ in eqs 4 and 7. However, some systems (unicellular algae in particular), may not fit these criteria. Algae, such as *Chlorella spp.*, typically have a diameter of 2−10 μm, which is smaller or similar to typical aqueous boundary layer thicknesses. Under these conditions, the model involving radial diffusion,

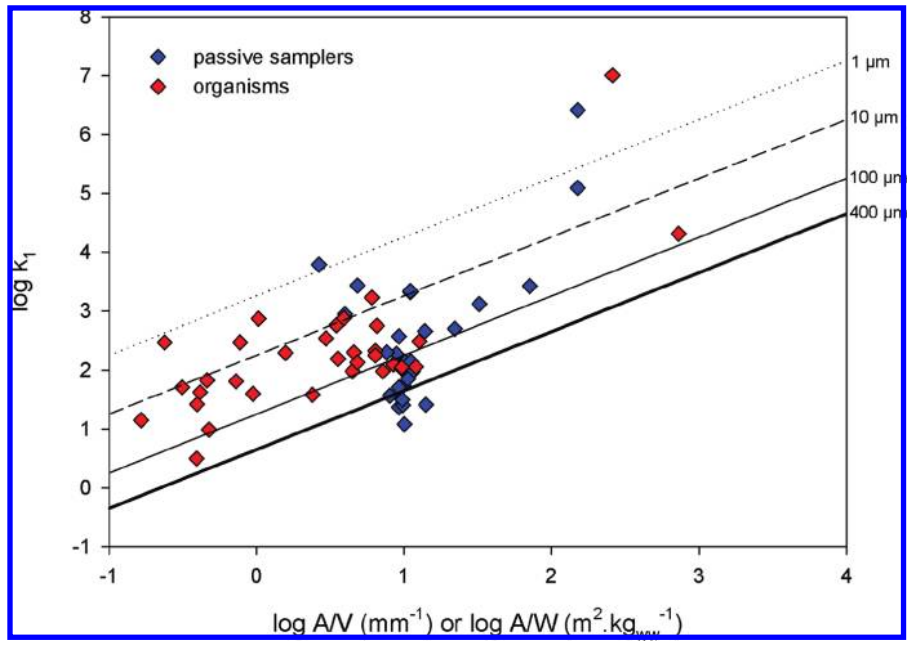

FIGURE 4. Log−log plot of maximum uptake rate constant k_1 versus A/V for passive samplers and k'_1 versus A/W for organisms for each of the reviewed studies. Lines represent the maximum uptake rate constant assuming that transport is limited by diffusion in the aqueous diffusion layer with a thickness of 1 μm (dotted line), 10 μm (dash line), 100 μm (thin plain line), and 400 μm (thick plain line), for a hypothetical compound with an average aqueous diffusion coefficient $D_w = 5 \times 10^{-10}$ m^2·s^{-1}.

as described in the Theory section, could be inserted (*47*). In this case, uptake rates are independent of δ_w and only depends on r. However, information on r was not always available and, therefore, the maximum error on k'_{1max} is equal to δ_w / r.

A fourth reason is that hydrophobic contaminants can associate with dissolved or particulate phases in water such as humic acids (*48*), clays (*49*), or cells (*50*). These colloids can influence the uptake rate. Numerous studies have examined the binding of organic chemicals to these colloids (*48*), but only a limited number of studies investigated their influence on kinetics (*51*). In the presence of a complexant forming inert complexes, eq 4 would become (see Supporting Information Appendix A):

$$k_1 = \frac{A}{V \cdot \alpha} \times \frac{1}{\frac{\delta_w}{D_w} \cdot \frac{r}{\delta_w + r} + \frac{1}{m_t \cdot K_{sw}}} \qquad (10)$$

where α is the degree of complexation of the organic chemical in the solution, i.e., the ratio of the total over free concentrations of this chemical (note: α significantly increases with the compound hydrophobicity). This equation shows that under these specific conditions, k_1 would decrease when α increases, and such relationship was reported in the literature (*51*). When the association−dissociation kinetics of complexation are fast enough, k_1 is less influenced by α (*52*−*55*), even though it may also decrease when the complexant is colloidal (small diffusion coefficient). The present uptake rates were selected from studies in which the quantity of natural aquatic colloid and particles was limited (i.e., α∼1). It is of course, impossible to claim that these systems were completely free of suspended and dissolved phases. Especially organisms exposed in an aqueous phase generate some particulate and dissolved organic materials (e.g., feces, mucus) in the aqueous phase, which might affect apparent uptake rates.

Finally, it is important to note that, besides variability among experimental conditions, measurement of uptake and elimination rates are affected by (bio)fouling, growth dilution, transfer through reproduction, and biotransformation. Biotransformation of the parent chemical may create a bias in the observed uptake or clearance rates if the burden of metabolized compounds is not taken into account. The degree of biotransformation is known to vary between species. For example, oysters are generally selected instead of fish to monitor PAHs because of their limited ability to metabolize these compounds (*56*).

Elimination Rate Constant k_2 and Time to Reach 95% of Equilibrium t_{95}. The net uptake of a compound is determined by the uptake and the elimination rate. This section discusses the elimination rate constants, k_2 and k'_2, and the related time to reach 95% of the equilibrium in the samplers and organisms (eqs 5 and 8). k_2 ranged from 1.3×10^{-4} to 2.2×10^2 hour^{-1} for passive samplers, and k'_2 ranged from 5.8×10^{-3} to 23 h^{-1} for organisms (Table 1). The time to reach 95% of the equilibrium concentration, t_{95}, ranged from 0.01 to 2.3×10^4 hour for passive samplers, and t'_{95}, for organisms, ranged from 0.13 to 5.1×10^4 hour (Table 1). Among the samplers, solid-phase microextraction fibers (PDMS and PA) generally reach 95% of equilibrium within several days (even for the most hydrophobic chemicals, see details in Appendix D), while the other samplers often need more than a month to reach equilibrium. Among organisms, the few available data suggest that algae and protozoans will generally reach 95% of equilibrium in less than 1 day, while fish and bivalves would require more than a month for some of the more hydrophobic chemicals (log $K_{ow} > 5.5$). Insects/worms have intermediate equilibration times. The rest of the discussion below will focus on time to reach 95% of equilibrium.

Figure 5a shows the relation between t_{95} and the A/V ratio of the samplers divided by the octanol−water partition coefficient (K_{ow}) (eqs 2 and 5). Figure 5b shows the relation between t'_{95} and the A/W ratio of the organisms divided by K_{ow} (eq 8). In both cases, K_{ow} is used as a surrogate measure of sampler−water and organism−water distribution coefficients. It can be observed that the time to equilibrium is inversely proportional to the $A/(V \times K_{ow})$ or $A/(W \times K_{ow})$ (Figure 5). The lines plotted in Figure 5a and b represent the theoretical time to reach 95% of equilibrium limited by diffusion in the test solution phase (considering planar

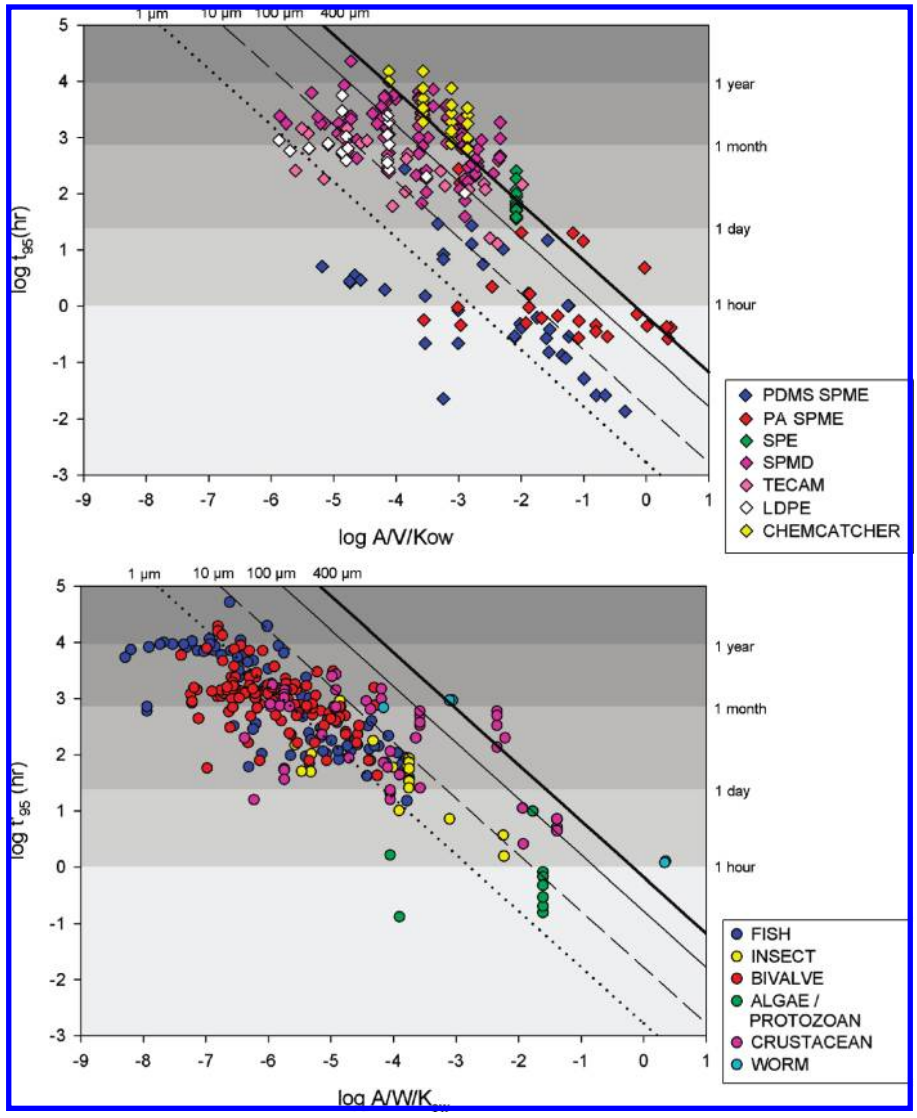

FIGURE 5. Log−log plot of the time to reach 95% of the equilibrium concentration versus $A/V/K_{ow}$ for passive samplers (a) and versus $A/W/K_{ow}$ for organisms (b). Lines represent the time to reach 95% of the equilibrium assuming that transport is limited by diffusion in the aqueous diffusion layer with a thickness 1 μm (dotted line), 10 μm (dash line), 100 μm (thin plain line), and 400 μm (thick plain line), for a hypothetical compound with an average aqueous diffusion coefficient $D_w = 5 \times 10^{-10}$ m^2·s^{-1}.

diffusion) for various stirring conditions corresponding to different δ_w values. Lines were computed (combination of eqs 2, 5, and 8), for a typical organic pollutant with an average aqueous diffusion coefficient $D_w = 5 \times 10^{-10}$ m^2·s^{-1}. The selected aqueous diffusion layer thicknesses δ_w were equal to 1 μm (dotted line), 10 μm (dash line), 100 μm (thin plain line), and 400 μm (thick plain line).

For passive samplers, the model (combination of eqs 2, 5, and 8) for a typical test compound gives a good description of experimental t_{95} (and therefore k_2) data reported in the literature, although the different samplers do not show exactly the same trend (Figure 5a). Besides factors such as temperature, agitation, and limitation of uptake by diffusion in samplers and distribution in organisms, as discussed in the section Explaining Observed Variability in Uptake Rate Constants, the discrepancies can also be explained by different affinities of sampler material for the chemicals. Rusina et al. (*40*) showed, for example, large differences of the partition coefficients of some PAHs among polymers for passive sampling. The use of a single hydrophobicity parameter (K_{ow}) as a surrogate of K_{sw} also introduces variability in the model.

For organisms, the model for a typical test compound generally fits the data from literature well (Figure 5b). However, the equilibration times (t'_{95}) of very hydrophobic chemicals in fish and bivalves are often lower than predicted by the model. This deviation might be attributed to some experimental artifacts (*6*), such as insufficient equilibration times or depletion of the system by the organisms. If the organisms deplete the test system, the uptake and elimination rate constants obtained by fitting a one-compartment model (that assumes constant exposure concentrations) will overestimate the true rate constants. In this situation, a two-compartment model (eq 1) should be fitted to describe the changing concentrations of the aqueous phase and organisms (*51*). The trend observed for the organism seems to display less variability than that for passive samplers (Figure 5b). This might be attributed to a lower variability in exposure conditions; e.g., no stirring or shaking was applied in the tests with organisms. Furthermore lipid is generally considered to be the main sorption phase for hydrophobic organics, even though recent studies have pointed out that the sorptive capacity of proteins might play a role in lean tissues (*57*). The property of these lipids is probably less variable than the different materials used in passive samplers. Sijm and Van der Linde (*18*) included the lipid content in the modeling of uptake and elimination rate constants for fish and showed that "exchange surface and lipid content are the

main fish properties that determine bioconcentration kinetics". In the present review, a correction for the lipid content could not be made because the lipid content was not always given in the literature.

Discussion and Outlook

Predicting Internal Concentration and Equilibration Times. The present literature review suggests that, as a very first approximation, the combination of the first-order kinetic modeling with the assumption that diffusion through the aqueous boundary layers is rate limiting, gives a satisfactory description of experimental kinetic data. Even though the model does not correct for the lipid content of organisms, and the octanol−water partition coefficient is used as a generic measure of chemical hydrophobicity, the model describes the data reasonably well. In this way, the model might be used to make a rough estimate of uptake and elimination rate constants (and therefore t_{95}) of chemicals by organisms or passive samplers for which the mass transfer of the chemical is limited by diffusion in the test solution.

These predictions are useful for the evaluation of internal concentrations under nonequilibrium conditions. Furthermore, these predictions are also useful to design laboratory or field monitoring experiments and estimate the time to equilibrium in the samplers/organisms (for compounds whose transport is limited by diffusion in the test solution). This is relevant, in particular because the presented data show that equilibration can take a long time, especially when the A/V is rather small. Some systems may never reach equilibrium for the most hydrophobic compounds, because equilibration times are larger than practical deployment times of samplers and organisms in test systems, or because concentrations in the environment or laboratory test system change in time or space (*5*). For example, for fish or bivalves and various samplers such as SPMDs, Chemcatcher, and LDPEs, an exposure period below 1 month is insufficient to reach equilibrium for the more hydrophobic chemicals (see Table 1). If this is not tested or even not acknowledged, and equilibrium is assumed, this will likely lead to underestimation of bioconcentration factors and sampler−water partition coefficients (*6*). Contrastingly, PDMS fibers and microorganisms such as algae and protozoa appear to reach equilibrium rather quickly. Consequently, these organisms and samplers will often be in equilibrium with the test system. Passive samplers or organisms with high surface/volume ratio (such as microextraction devices and unicellular algae) might be suitable systems when quick response is required. For field-monitoring studies that need to integrate contamination over a long period of time, passive samplers or organisms with low elimination rates and larger sampling volumes are more suitable.

Comparison of Samplers and Organisms. Several studies have analyzed similarities or differences between passive samplers and organisms in their ability to accumulate hydrophobic compounds. For example, Meadows et al. (*58*) and Lu and Wang (*59*) have compared uptake rates of SPMDs and trouts, Richardson et al. (*60*) reported the comparison of SPMDs and mussels in a field deployment in Hong Kong, and Leslie et al. (*61*) studied the uptake kinetics of chlorobenzenes in midge larvae and SPME fibers. The models presented in the present paper show that uptake is a complex mechanism involving numerous parameters. Comparable behavior between samplers and organisms can be achieved, provided that they display similar combinations of A/V ratio, partition coefficients, and internal mass transfer coefficients.

To use a passive sampler as a biomimetic tool under equilibrium conditions, one should know the partition coefficient to the sampler material and the organism (lipid) for a suite of chemicals. However, organisms and samplers are not always equilibrated with their environment because exchange kinetics are slow or exposure concentrations vary in time (*62*). Consequently, exchange rates of organisms should also be mimicked by the sampler for a better assessment of the exposure of organisms and the related risk under dynamic exposure conditions. For that purpose, equilibration kinetics of the sampler and organism should be similar. Furthermore, the critical hydrophobicity corresponding to the transition from internal diffusion limited kinetics to "external" diffusion limited kinetics should be similar as well when a suite of chemicals with different properties are considered. Nevertheless, the kinetic similarities between samplers and organisms will always remain circumstantial to a certain extent because organisms are not passive. Various behavioral responses might affect uptake or elimination rates. For example, exposure to a contaminant can lead to modification of gill surface or absorption efficiency (*63*), passivity of the organism, selective feeding, and escaping behavior from a contaminated environment (*64*).

Future Needs. The application of passive samplers as biomimetic tools needs detailed knowledge on uptake and elimination rates. For this purpose, the following parameters should be known:

- A/V (A/W) for the passive sampler (organism)
- the size r of spherical microorganism or sampler
- K_{ow} (or ideally K_{sw} and/or K_{Bw}) and D_w of the test compound
- the diffusion layer thickness δ_w for the system (average values over time and the total sampler surface can be obtained)
- the degree of complexation α.

Additional information is also necessary on the critical hydrophobicity breaking-point, $(K_{ow})_c$, to assess the applicability for a suite of chemicals. In particular, the relationship between $(K_{ow})_c$ and parameters such as the diffusivity in the sampler phase or organism tissue, A/V or A/W ratios, or the agitation of the aqueous phase should be validated, as too few data are available to identify clear trends.

In conclusion, this review shows that the range for uptake and elimination rates is rather large and that the surface-to-volume or surface-to-weight ratios are critical parameters. The data agree reasonably well with the theoretical model and represent a strong basis for the understanding of bioavailability and exchange kinetics of hydrophobic chemicals.

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Supporting Information Available

Theoretical background, a short description of the passive samplers and organisms, and detailed data. This information is available free of charge via the Internet at http://pubs.acs.org.

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