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PREDICTION OF UPTAKE DYNAMICS OF PERSISTENT ORGANIC POLLUTANTS BY BACTERIA AND PHYTOPLANKTON

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Abstract—Phytoplankton and bacteria play an important role on the biogeochemical cycles of persistent organic pollutants (POPs). However, experimental data and quantitative knowledge of the kinetics of uptake and depuration of most POPs by bacteria and phytoplankton are scarce. In the present paper, a procedure to predict the sorption kinetics to bacteria and phytoplankton is developed. The prediction method is the combination of a mechanistic model for sorption and quantitative structure–activity relationships relating bioconcentration factors and membrane permeability to the chemical physical-chemical properties. The model consists of two compartments where the first compartment is the cellular surface and the second compartment is the cell biomass or matrix. Equations for estimating uptake and depuration rate constants into the matrix and adsorption and desorption rate constants onto the surface are obtained. These expressions depend on the physical-chemical properties of the chemical, the environmental temperature, the microorganism size, and species-specific quality of organic matter. While microorganism shape has a secondary influence on uptake dynamics, microorganism size and chemical hydrophobicity arise as the key factors controlling the kinetics of POP incorporation into bacteria and plankton. Uptake, depuration, adsorption, and desorption rate constants are reported for POPs such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dioxins and furans (PCDD/Fs), and POPs of emerging concern, such as polybrominated diphenyl ethers (PBDEs). Finally, implications of uptake and depuration dynamics on the biogeochemical cycling of POPs are discussed.

Keywords—Uptake Depuration Bacteria Phytoplankton Persistent organic pollutants

INTRODUCTION

Phytoplankton plays a central role in the biogeochemical cycles of POPs in aquatic environments [1–3]. Several potential pathways exist for the introduction of POPs into food webs, such as by interaction with the sediment, direct absorption during fish respiration, and so on, but since phytoplankton is the first step of the food web, phytoplankton uptake is thought to be a key process in the transfer of pollutants from water to fish [4]. Second, phytoplankton uptake of pollutants influences the transport, occurrence, and distribution of POPs in aquatic environments [5–7]. For example, vertical distribution of PCBs and PAHs follow the vertical profile of phytoplankton biomass [5,6]. Furthermore, phytoplankton uptake and subsequent transfer to zooplankton drives the sinking fluxes of POPs in the water column [8,9]. Recently, it has been suggested that trophic status may influence the sinking fluxes, the air–water exchange, and water column concentrations of POPs due to coupling of atmospheric deposition processes, such as air–water diffusive exchange with phytoplankton uptake [9,10]. In oligotrophic environments, heterotrophic bacteria may constitute an important fraction of organic matter in the water column [11]. Uptake of POPs by bacteria may play an important role in some environments and have, for example, a potentially important role for the degradation of POPs in the environment. In the present paper, we refer as uptake to the transfer of a certain pollutant from the surrounding water to the microorganism biomass and not to the process of active pollutant metabolization. In fact, the role of bacteria in the cycling of POPs in the environment, specifically, the influence on the transport of POPs, has not been assessed in detail besides some pioneering studies on transfer into food webs [3,12,13]. Particularly, a lack of experimental uptake and depuration rate constants of POPs by bacteria complicates the environmental modeling of processes involving bacteria. However, bacterial uptake could contribute, as phytoplankton does, to enhancing air–water fluxes by uptake-driven depletion of dissolved POPs and to transfer of pollutants to the food web, especially in low primary productivity areas, such as open ocean regions, with an important influence to regional and global cycling of POPs.

Since quantitative knowledge of uptake dynamics is needed in order to understand and predict the environmental fate of POPs, several studies have focused during the past decade on the experimental determination of uptake and depuration constants. Most of these studies focus on the exchange of PCBs between plankton and water. Uptake of nonionic persistent organic pollutants is a passive diffusive process that can be described by a two-compartment model [13–16]. First, fast adsorption to the phytoplankton surface is followed by diffusion into the matrix in a partitioning-like mechanism. The relative importance of these two sorption mechanism as contributors to the total bioaccumulation of POPs by microorganisms is an issue of debate [12–16]. While for phytoplankton absorption may dominate the total bioaccumulation potential [14], the smaller size of bacteria and their higher specific surface area suggest that bacterial uptake may be dominated by surface adsorption [12]. All these studies have focused on the uptake of PCBs, and little is known about the diffusive uptake of PAHs and PCDD/F, even though their accumulation in phytoplankton has been proved in some cases [5]. This contrasts with the knowledge of the metabolization processes of some POPs, such as PAHs, which have been extensively studied in view of remediation strategies.

The goal of the present paper is to further develop previous modeling efforts of diffusion of POPs onto/into bacteria and

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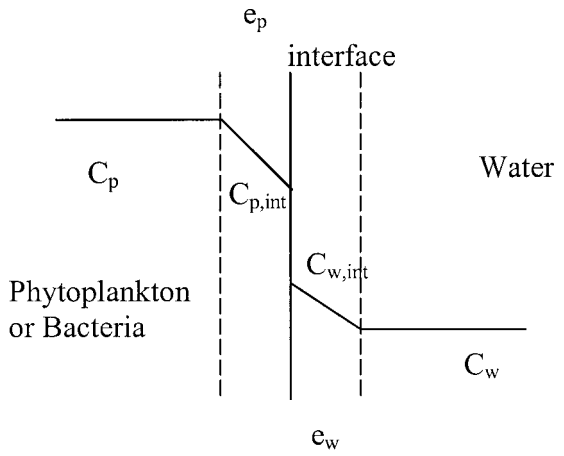

Fig. 1. Schematics of the water–microorganism exchange model. e_p and e_w are the thickness of the microorganism and water films, respectively. Both C_p and C_w are the persistent organic pollutants (POP) concentration in the bulk organism and water, respectively, and $C_{p,int}$ and $C_{w,int}$ are the POP concentrations at the microorganism and water side of the interface.

phytoplankton in order to obtain predictive equations to estimate quantitatively uptake, depuration, adsorption, and desorption rate constants for a wide range of POPs, including PCBs, PAHs, and PCDD/Fs. The bioaccumulative potential of some pollutants of emerging concern [17,18], such as polybrominated diphenyl ethers and nonylphenols (NPs), will also be evaluated. Furthermore, the implications of the obtained results are reviewed in terms of the potential role of bacteria and phytoplankton on the fate and transport of POPs in aquatic environments.

MODEL DESCRIPTION

Uptake of POPs by phytoplankton can be evaluated by modeling the water–phytoplankton exchange assuming a stagnant two-film model at the microorganism–water interface (Fig. 1), in effect, with a microorganism and a water stagnant boundary layer adjacent to the interface. The flux of a particular POP through each one of these layers can be calculated from Fick's first law:

$$F = -D\frac{dC}{dz} \tag{1}$$

where F is the flux of the chemical (ng/m^2/d), D is the molecular difussivity, and dC/dz is the gradient of the chemical concentration. Thus, the flux of a POP across the water-side layer ($F_{w,int}$, ng/m^2/d) is given by

$$F_{w,int} = -D_w\frac{(C_w - C_{w,int})}{e_w} \tag{2}$$

where C_w (ng/m^3) and $C_{w,int}$ (ng/m^3) are the POP concentrations in bulk water and at the water side of the interface, respectively. The D_w (m^2/d) is the POP molecular diffusion coefficient in water, and e_w is the thickness of the water-side boundary layer. Similarly, the flux across the phytoplankton-side boundary layer ($F_{p,int}$, ng/m^2/d) can be described by Equation 3:

$$F_{p,int} = -D_P\cdot\delta_P\frac{(C_{p,int} - C_p)}{e_p} \tag{3}$$

where C_p (ng/kg) and $C_{p,int}$ (ng/kg) are the POP concentration in the phytoplankton matrix and at the phytoplankton side of the interface, respectively. The D_p (m^2/d) is the POP molecular diffusion coefficient in phytoplankton, e_p is the thickness of the phytoplankton boundary film, and δ_p is the phytoplankton density (kg/m^3). The water-side and phytoplankton-side concentrations at the interface, $C_{w,int}$ and $C_{p,int}$, are assumed to be at equilibrium, and thus their ratio is given by the bioconcentration factor in the microorganism matrix (BCF_M, m^3/kg):

$$BCF_M = \frac{C_{p,int}}{C_{w,int}} \tag{4}$$

Since the flux trough the water side and phytoplankton side must be equal (F_{P-W}, ng/m^2/d), from Equations 2 to 4 we obtain

$$F_{P-W} = \frac{1}{\left(\frac{e_p}{D_P\cdot\delta_P\cdot BCF_M} + \frac{e_w}{D_w}\right)}\left(\frac{C_p}{BCF_M} - C_w\right) \tag{5}$$

Equation 5 gives the flux of a POP between phytoplankton and water per square meter of phytoplankton area. Therefore, phytoplankton–water exchange depends only on the physical-chemical properties of the compound, such as the bioconcentration factor (BCF) and diffusivity, and on some variables dependent on the phytoplankton species. An alternative method to derive a different equation for F_{P-W} is by considering the uptake and depuration rate constants by dividing Equation 6 by the specific surface area of phytoplankton cells (S_p, m^2/kg):

$$\frac{\partial C_P}{\partial t} = -k_uC_w + k_dC_P + k_GC_P + k_{meta}C_p \tag{6}$$

$$F_{P-W} = \frac{k_u}{S_p}\left(\frac{k_d + k_G + k_{meta}}{k_u}C_p - C_w\right) \tag{7}$$

where the BCF_M is also given by

$$BCF_M = \frac{k_u}{k_d + k_G + k_{meta}} \tag{8}$$

where k_u (m^3/kg/d) and k_d (per day) are the uptake and depuration rate constants, k_{meta} (per day) is the first-order metabolization reaction rate, and k_G (per day) is the growth rate of phytoplankton community or biomass: For a self-sustained biomass, it will have a value of zero, while for a phytoplankton community that doubles its biomass in 1 d, it will have value of one.

Comparing Equations 5 and 8 and assuming $C_w = 0$, $k_G = 0$, and a metabolization rate much slower than sorption kinetics ($k_{meta} \ll k_d$), we obtain a predictive equation for the depuration rate constant:

$$k_d = \frac{S_p}{\left(\frac{e_p}{D_P\cdot\delta_P\cdot BCF_M} + \frac{e_w}{D_w}\right)}\cdot\frac{1}{BCF_M} \tag{9}$$

Similarly, assuming $C_p = 0$, we derive the equation for the uptake rate constant:

$$k_u = \frac{S_p}{\left(\frac{e_p}{D_P\delta_P BCF_M} + \frac{e_w}{D_w}\right)} \tag{10}$$

As determined by other studies, phytoplankton uptake is due to sorption to two differentiated compartments [10,14,15]. The first step is a fast adsorption to the cellular surface followed by a slower absorption into the cellular matrix. Diffusion through the water-side boundary layer is much faster than diffusion through the phytoplankton-side boundary layer.

Therefore, water–phytoplankton exchange into the cellular matrix is limited by diffusion through the phytoplankton layer, and we can assume that

$$\frac{e_p}{D_P \cdot \delta_P \cdot BCF_M} \gg \frac{e_w}{D_w}$$

which yields the following expressions for the uptake and depuration rate constants:

$$k_d = \frac{S_p \cdot D_P \cdot \delta_P}{e_P} \quad (11)$$

$$k_u = \frac{S_p \cdot D_P \cdot \delta_P \cdot BCF_M}{e_P} \quad (12)$$

The ratio k_u/S_p that appears in Equation 7 is the permeability (P, m/d) of the cell membrane; therefore, from Equation 12, an expression for permeability is derived (Eqn. 13). The k_u and k_d can also be parameterized as a function of P (Eqns. 14 and 15):

$$P = \frac{D_P \delta_P BCF_M}{e_P} \quad (13)$$

$$k_d = \frac{S_p \cdot P}{BCF_M} \quad (14)$$

$$k_u = S_p \cdot P \quad (15)$$

So far, the development through Equations 1 to 15 has been for uptake and bioconcentration into the phytoplankton matrix. The assessment of sorption onto the cellular surface can be done in a similar way. Indeed, we could derive similar expressions for Equations 5 and 7 by taking into account only the water-side boundary and substituting k_u, k_d, and BCF_M by the adsorption (k_{ad}, m^3/kg/d) and desorption (k_{des}, per day) rate constants and the bioconcentration factor at the surface (BCF_S, m^3/kg). Adsorption is assumed to be limited by diffusion through the water-side boundary layer, and the following expressions for adsorption and desorption rate constants are obtained:

$$k_{des} = \frac{S_p \cdot D_w}{e_w \cdot BCF_S} \quad (16)$$

$$k_{ad} = \frac{S_p \cdot D_w}{e_w} \quad (17)$$

The expressions for uptake, depuration, adsorption, and desorption rate constants allow one to predict their values for a wide range of POPs as well as to study the influence of the microorganism size and environmental variables, such as temperature. The model has been developed by phytoplankton but could equally be applied to bacteria.

RESULTS AND DISCUSSION

Prediction of uptake and depuration rate constants

In order to use Equations 13 to 15 to estimate uptake and depuration rate constants for POPs, it is necessary to know the values of all the variables used in the equations. Specific surface area can be estimated by assuming spherical shape and a known radius of the microorganism or cylindrical shape as appropriate for some bacteria species. Density of phytoplankton is taken as of 1,025 kg/m^3 [19]. Assuming that the cellular membrane is a liquid-like phase, diffusivity of a POP in the phytoplankton could be predicted from the Wilke–Chang correlation (Eqn. 18) [20]:

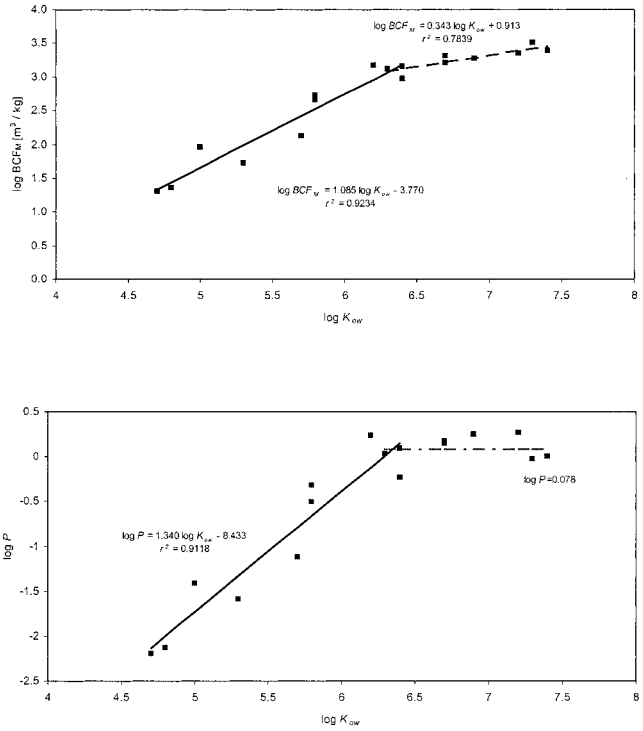

Fig. 2. Dependence of the bioconcentration factor in the microorganism matrix (BCF_M), and permeability (P) on the physical-chemical properties of the chemical.

$$D = \frac{7.4 \cdot 10^{-8} \cdot T(\phi_l M_l)^{1/2}}{\eta_l V_A^{0.6}} \quad (18)$$

where T (K) is the temperature, M_l (g/mol) is the molecular weight of the solvent, ϕ_l is the association factor of the solvent (dimensionless), η_l (cP = 0.01 g/s/cm) is the solvent viscosity, and V_A (cm^3/mol) is the molar volume of chemical at its normal boiling temperature. However, the parameters used in this equation are largely unknown for the cellular membrane, and therefore D_P cannot be quantitatively predicted. Furthermore, BCF_M values have been reported in only a few studies for PCBs [14,15], not for other POPs, and even very few of these report the numerical values [10]. Since values for P and BCF_M for most POPs are largely unknown, in order to use Equations 14 and 15 it is necessary to relate BCF_M and P to physical-chemical properties of the compounds, such as octanol–water partition coefficient (K_{ow}).

Taking as a reference the uptake and depuration rate constants for a number of PCBs reported by Dachs et al. [10] that were obtained from uptake experiments by *Isochrysis galbana* done by Ko [21] (Table 1), BCF_M values were plotted against K_{ow} (Fig. 2). As usually observed, two linear correlations exist between the logarithms of BCF_M and K_{ow} that can be fitted by least squares to the following equations depending on the hydrophobicity of the chemical [22]:

$$\log BCF_M = 1.085 \log K_{ow} - 3.770 \quad \text{for } \log K_{ow} < 6.4 \quad (19)$$

$$\log BCF_M = 0.343 \log K_{ow} + 0.913 \quad \text{for } \log K_{ow} \geq 6.4 \quad (20)$$

Equation 19 corresponds to chemicals with low to mid-K_{ow} values that bioconcentrate in phytoplankton following well the hydrophobicity paradigm [23] and is also similar to those reported by other studies of plankton bioconcentration of POPs [18,24]. At high K_{ow} values, a saturation of BCF_M values occurs

Table 1. Physical-chemical properties and rate constants for polychlorinated biphenyls (PCBs). Italicized numbers are those reported elsewhere [10] and were used for development of the predictive equations. Uptake (k_u), depuration (k_d), adsorption (k_{ad}), and desorption (k_{des}) rate constants are at 298 K and for a microorganisms with a radius of 2.7 μm. TSA = total surface area; BCF_M = bioconcentration factor in the microorganism matrix; BCF_S = bioconcentration factor at the surface

PCB	n^o Cl	log K_{ow}[a]	TSA[a] (Å^2)	BCF_M (m^3/kg)	P (m/d)	k_u (m^3/kg/d)	k_d (per day)	BCF_S (m^3/kg)	k_{ad} (m^3/kg/d)	k_{des} (per day)
3	*1*	*4.69*	*202.12*	*20*	*0.00711*	*8.2*	*0.41*	*24*	*3,953*	*162.4*
10	*2*	*4.80*	*206.46*	*23*	*0.0100*	*9.7*	*0.43*	*38*	*3,730*	*97.5*
15	*2*	*5.30*	*219.81*	*53*	*0.0467*	*33*	*0.62*	*83*	*3,730*	*44.7*
16	3	5.16	215.69	67	0.0303	39.2	0.58	118	3,537	30.0
19	*3*	*5.00*	*211.82*	*91*	*0.0185*	*50*	*0.55*	*90*	*3,537*	*39.1*
22	3	5.58	228.03	192	0.111	143.1	0.74	218	3,537	16.2
28	3	5.67	230.83	241	0.146	188.9	0.78	241	3,537	14.7
32	3	5.44	224.16	136	0.0720	92.9	0.69	187	3,537	19.0
34	*3*	*5.70*	*230.49*	*132*	*0.160*	*98*	*0.74*	*296*	*3,537*	*12.0*
37	3	5.83	235.42	359	0.240	309.5	0.86	278	3,537	12.7
42	4	5.76	233.38	302	0.193	249.4	0.83	261	3,369	12.9
43	4	5.75	233.21	294	0.187	241.8	0.82	260	3,369	13.0
47	4	5.85	236.19	378	0.255	329.2	0.87	284	3,369	11.9
48	4	5.78	234.10	317	0.205	265.3	0.84	267	3,369	12.6
52	*4*	*5.80*	*235.84*	*449*	*0.219*	*400*	*0.89*	*289*	*3,369*	*11.7*
56	4	6.11	243.63	723	0.569	734.4	1.02	344	3,369	9.8
60	4	6.11	243.80	723	0.569	734.4	1.02	346	3,369	9.7
64	4	5.95	239.04	485	0.347	448.2	0.92	307	3,369	11.0
66	4	6.20	246.44	906	0.751	969.5	1.07	367	3,369	9.2
74	4	6.20	246.43	906	0.751	969.5	1.07	367	3,369	9.2
77	*4*	*6.40*	*251.02*	*927*	*1.39*	*760*	*0.82*	*372*	*3,369*	*9.1*
82	5	6.20	246.36	906	0.751	969.5	1.07	367	3,228	8.8
85	5	6.30	249.16	1,163	1.022	1,319.9	1.14	389	3,228	8.3
89	5	6.07	242.48	654	0.503	649.1	0.99	335	3,228	9.6
95	5	6.13	244.23	760	0.605	781.1	1.03	349	3,228	9.2
97	*5*	*6.30*	*248.99*	*1,296*	*1.02*	*1,400*	*108*	*369*	*3,221*	*8.7*
100	*5*	*6.20*	*247.20*	*1,477*	*0.751*	*2,200*	*1.49*	*400*	*3,221*	*8.1*
101	*5*	*6.40*	*251.62*	*1,416*	*1.39*	*1,600*	*1.13*	*421*	*3,221*	*7.7*
104	*5*	*5.8*	*234.87*	*525*	*0.219*	*620*	*1.18*	*511*	*3,221*	*6.3*
105	*5*	*6.70*	*259.41*	*1,593*	*1.20*	*1,800*	*1.13*	*400*	*3,221*	*8.1*
118	*5*	*6.70*	*262.04*	*2,021*	*1.20*	*1,900*	*0.94*	*403*	*3,221*	*8.0*
123	5	6.74	262.04	1,678	1.20	1,544.9	0.92	396	3,221	8.1
124	5	6.73	261.87	1,665	1.20	1,544.9	0.93	396	3,228	8.2
126	*5*	*6.90*	*266.63*	*1,840*	*1.20*	*2,300*	*1.25*	*421*	*3,228*	*7.7*
132	6	6.58	257.37	1,479	1.20	1,544.9	1.04	396	3,089	7.8
136	6	6.22	246.95	1,113	1.20	1,544.9	1.39	396	3,089	7.8
138	6	6.83	264.76	1,801	1.20	1,544.9	0.86	396	3,089	7.8
141	6	6.82	264.59	1,787	1.20	1,544.9	0.86	396	3,089	7.8
144	6	6.67	260.00	1,587	1.20	1,544.9	0.97	396	3,089	7.8
147	6	6.64	259.29	1,550	1.20	1,544.9	1.00	396	3,089	7.8
153	6	6.92	267.39	1,934	1.20	1,544.9	0.80	396	3,089	7.8
156	*6*	*7.20*	*275.01*	*2,222*	*1.20*	*2,400*	*1.08*	*382*	*3,089*	*8.1*
163	6	6.99	296.54	2,044	1.20	1,544.9	0.76	122	3,089	25.4
170	*7*	*7.30*	*277.74*	*3,158*	*1.20*	*1,200*	*0.38*	*292*	*2,970*	*10.2*
177	7	7.08	272.26	2,195	1.20	1,544.9	0.70	373	2,970	8.0
180	*7*	*7.40*	*280.37*	*2,453*	*1.20*	*1,300*	*0.53*	*285*	*2,970*	*10.4*
182	7	7.20	275.78	2,413	1.20	1,544.9	0.64	336	2,970	8.8
185	7	7.11	272.98	2,247	1.20	1,544.9	0.69	365	2,970	8.1
187	7	7.17	274.89	2,356	1.20	1,544.9	0.66	346	2,970	8.6
190	7	7.46	283.40	2,963	1.20	1,544.9	0.52	258	2,970	11.5
195	8	7.56	286.12	3,206	1.20	1,544.9	0.48	229	2,863	12.5
201	8	7.62	287.87	3,362	1.20	1,544.9	0.46	211	2,863	13.5
206	9	8.09	301.73	4,873	1.20	1,544.9	0.32	68	2,766	40.7
208	9	7.71	290.59	3,609	1.20	1,544.9	0.43	183	2,766	15.1

[a] Hawker and Connell [34].

because of low solubility of the chemicals in the microorganism matrix and/or because of steric effects of large molecular size. Both k_u and k_d can also be predicted from P values provided that these are known. No correlation between P values and physical-chemical properties has been published for POPs. However, P values can be estimated from the k_u and BCF_M values reported elsewhere [11,21] by means of a quantitative structure–activity relationship (QSAR) that relates membrane permeability with the physical-chemical properties of the pollutant. Figure 2 shows the plot of permeability against K_{ow} and the obtained regressions, which also depend of the compound physical-chemical properties:

$$\log P = 1.340 \log K_{ow} - 8.433 \quad \text{for } \log K_{ow} < 6.4 \quad (21)$$

$$\log P = 0.078 \quad \text{for } \log K_{ow} \geq 6.4 \quad (22)$$

The increase of permeability with the hydrophobicity of the chemical is consistent with reported trends for other nonionic compounds and indicates a higher tendency of hydrophobic compounds to diffuse into the cell [25]. However, the satu-

Table 2. Physical-chemical properties and predicted rate constants for polychlorinated dioxins (PCDDs) and furans (PCDFs) depending on the number of chlorines. Uptake (k_u), depuration (k_d), adsorption (k_{ad}), and desorption (k_{des}) rate constants are at 298 K and for a microorganism with a radius of 2.7 μm; TSA = total surface area; BCF_M = bioconcentration factor in the microorganism matrix; BCF_S = bioconcentration factor at the surface

	n^o *Cl*	log K_{ow}[a]	*TSA*[b,c] (Å²)	BCF_M (m³/kg)	*P* (m/d)	k_u (m³/kg/d)	k_d (per day)	BCF_S (m³/kg)	k_{ad} (m³/kg/d)	k_{des} (per day)
PCDD	2	5.65	243.4[d]	229	0.138	178	0.8	342	3,659	10.7
	3	6.35	272.8[d]	1,317	1.193	1,540	1.2	396	3,475	8.8
	4	6.9	273.7	1,904	1.196	1,545	0.8	358	3,315	9.2
	5	7.4	309	2,826	1.196	1,545	0.5	280	3,172	11.3
	6	7.8	321	3,875	1.196	1,545	0.4	280	3,045	10.9
	7	8.0	338	4,538	1.196	1,545	0.3	280	2,931	10.5
	8	8.2	314.9	5,315	1.196	1,545	0.3	280	2,828	10.1
PCDF	2	5.0	216.6	46	0.019	25	0.5	125	3,730	29.9
	3	6.2[e]	232	906	0.751	969	1.1	250	3,537	14.1
	4	7.7	247.7	3,581	1.196	1,545	0.4	378	3,369	8.9
	5	7.6	262.7	3,309	1.196	1,545	0.5	396	3,221	8.1
	6	7.7	274.7	3,581	1.196	1,545	0.4	347	3,089	8.9
	7	7.5	287.8	3,058	1.196	1,545	0.5	280	2,970	10.6
	8	7.6	300.4	3,309	1.196	1,545	0.5	280	2,970	10.6

[a] Mackay et al. [35].
[b] Doucette and Andren [36].
[c] Dunn et al. [37].
[d] Evaluated from Doucette and Andren [36].
[e] Govers and Krop [38].

ration of the permeability for very hydrophobic molecules would indicate that molecules either become too large to diffuse into the cell or are not miscible enough in the microorganism matrix. The BCF_M and *P* values estimated from Equations 18 to 21 allow estimating the uptake and depuration rate constants for PCBs other than those reported elsewhere [10] by means of Equations 14 and 15 (see Table 1). Furthermore, the present prediction procedure also allows one to predict uptake for other POPs for which these properties are unknown. Tables 2 to 4 show the predicted uptake and depuration constants for PCDD/Fs, PAHs, PBDEs, and NPs. These values are, to the best of our knowledge, the only available data of these important physical-chemical properties for PCDD/Fs, PBDEs, NP, and most PAHs.

Prediction of adsorption and desorption rate constants

Prediction of adsorption and desorption rate constants (Eqns. 16 and 17) need the knowledge of BCF_S values and its dependence on the chemical properties. Being sorption at the cellular membrane an interface phenomenon, BCF_S values can be related both to hydrophobic character (K_{ow}) and to total surface area (*TSA*) of the chemical. Figure 3 contains the plot of BCF_S versus *TSA* and versus log K_{ow}. Throughout the *TSA* and log K_{ow} interval, it is possible to identify three different relationships; two linear relationships between BCF_S and *TSA* for $TSA < 250$ and $TSA > 270$, respectively, and a constant value when *TSA* ranges between 250 and 270 A²:

Table 3. Physical-chemical properties and predicted rate constants for polycyclic aromatic hydrocarbons (PAHs). Uptake (k_u), depuration (k_d), adsorption (k_{ad}), and desorption (k_{des}) rate constants are at 298 K and for a microorganism with a radius of 2.7 μm; TSA = total surface area; BCF_M = bioconcentration factor in the microorganism matrix; BCF_S = bioconcentration factor at the surface

PAH	log K_{ow}[a]	*TSA*[b] (Å²)	BCF_M (m³/kg)	*P* (m/d)	k_u (m³/kg/d)	k_d (per day)	BCF_S (m³/kg)	k_{ad} (m³/kg/d)	k_{des} (per day)
Fluorene	4.12	194.0	5	0.00122	1.58	0.32	24	4,170	173.7
1-Methylfluorene	4.97	214.8	42	0.0169	21.8	0.52	110	3,902	35.3
Phenanthrene	4.57	199.38	15	0.00491	6.34	0.41	24	4,030	167.9
1-Methylphenathrene	5.14	217.04	64	0.0285	36.8	0.57	128	3,780	29.4
Anthracene	4.54	200.16	14	0.00448	5.78	0.40	24	4,054	168.9
2-Methylanthracene	5.15	224.01	66	0.0294	38.0	0.58	185	3,805	20.5
9-Methylanthracene	5.07	216.14	54	0.0230	29.7	0.55	121	3,805	31.3
9,10-Dimethylanthracene	5.25	230.12	84	0.0400	51.7	0.61	235	3,593	15.3
Pryene	5.17	213.47	69	0.0313	40.4	0.58	100	3,858	38.7
Flouranthene	5.17	218.63	69	0.0313	40.4	0.58	142	3,826	27.0
Chrysene	5.84	240.15	368	0.247	319	0.87	316	3,506	11.1
Benzo[*a*]anthracene	5.84	244.32	368	0.247	319	0.87	350	3,531	10.1
Benzo[*b*+*k*]fluoranthene	6.44	262.87	1,324	1.20	1545	1.17	396	3,364	8.5
Benzo[*a*]pyrene	6.44	228.6	1,324	1.20	1545	1.17	222	3,409	15.3
Benzo[*e*]pyrene	6.44	227.78	1,324	1.20	1545	1.17	216	3,409	15.8
Perylene	6.44	251.46	1,324	1.20	1545	1.17	396	3,409	8.6

[a] Mackay et al. [35].
[b] Pearlman et al. [39].
[c] Evaluated from Doucette and Andren [36].

$$BCF_S = 8.11TSA - 1631.33 \quad \text{for } TSA < 250 \text{ Å}^2 \tag{23}$$

$$BCF_S = 396 \quad \text{for } 250 \leq TSA \leq 270 \text{ Å}^2 \tag{24}$$

$$BCF_S = -10.34TSA + 3187.85 \quad \text{for } TSA > 270 \text{ Å}^2 \tag{25}$$

A strong correlation exists between *TSA* and K_{ow} for most POPs [26]; therefore, BCF_S can also be predicted from K_{ow} values:

$$BCF_S = 233.61 \log K_{ow} - 1084.05 \quad \text{for } \log K_{ow} \leq 6.3 \tag{26}$$

$$BCF_S = 398 \quad 6.3 \leq \log K_{ow} \leq 7.0 \tag{27}$$

$$BCF_S = -285.61 \log K_{ow} + 2401.52 \quad \text{for } \log K_{ow} \geq 7.0 \tag{28}$$

Equations 26 and 27 are analogous to Equations 19 to 20 and representative of a higher tendency to adsorption for chemicals with lower water solubility (higher K_{ow}) and a saturation for molecules with a higher *TSA*. However, for adsorption onto the surface, a decrease of BCF_S occurs for compounds with very high K_{ow} values. This trend has also been reported by other phytoplankton species [14] and may be due to steric hindrance at the active sorption sites at the cellular surface. Equations 23 to 28 allow one to predict BCF_S for all PCBs and for a wide range of persistent organic pollutants, such as PCDD/Fs and PAHs (see Tables 1 to 3). In order to predict the adsorption and desorption rate constants using Equations 16 and 17, D_W and e_W need to be estimated. Diffusivity in water can be estimated using Equation 18. The thickness of the water-side boundary layer (e_W) can be estimated if we assume a certain geometry of the microorganism. Assuming a spherical shape, e_W equals the radius of the microorganism [27]. Tables 1 to 4 report the predicted values of adsorption and desorption rate constants for all major PCBs, PCDD/Fs, PAHs, PBDEs, and NPs. The desorption rate constants reported for PCBs in Table 1 are different than those reported elsewhere [10], but this is due to the assumptions done by that study. Anyway, in both cases desorption is a very fast process, and therefore, for modeling purposes, equilibrium between microorganisms surface and water can be assumed. The values of k_u, k_d, k_{ad}, and k_{des} reported in Tables 1 to 4 are useful for being used in dynamic environmental models taking into account the role of phytoplankton and/or bacteria. The values reported in these tables are at 298 K and for a microorganism of the size of *I. galbana* with a radius of 2.7 μm. When modeling processes at a different temperature and for microorganisms of different size, a correction for these variables is needed.

Influence of temperature

When determining the seasonal trends of cycling of POPs in aquatic environments and/or cycling at the global scale, large differences in temperatures are found that affect the environmental fate of POPs and may affect in particular its bioaccumulation and uptake kinetics by microorganisms. The influence of temperature on uptake and depuration by bacteria and phytoplankton has been largely omitted so far, besides some exceptions [28], because of practical constrains during experimental studies. The k_u, k_d, k_{des}, and k_{ad} rate constants depend on temperature due to the temperature dependence of diffusivity (Eqns. 14–18), and bioconcentration factors for both the matrix and the surface (*BCFs*) depend on temperature due to changes in the activity coefficient in the organic phase [26]:

$$\frac{BCF(T)}{BCF(298)} = \exp\left[\frac{\Delta H_S}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right] \tag{29}$$

where ΔH_S (kJ/mol) and R (kJ/mol/K) are the enthalpy of sorption and the gas constant, respectively. To the best of our knowledge, sorption enthalpies in bacteria or phytoplankton have never been determined under controlled conditions, but for what is known for sorption into organic matter, they may be low [26]. In the present study, we assume an enthalpy of sorption of 35 kJ/mol for all the compounds [29].

Given the uptake, depuration, adsorption, and desorption rate constants at 25°C reported in Tables 1 to 3, the rate constants at a different temperature can be estimated by considering differences in diffusivity and *BCFs*. The influence of temperature on adsorption and desorption rate constants are thus given by Equations 30 and 31:

$$k_{ad}(T) = \frac{\eta_{H_2O}(298)}{\eta_{H_2O}(T)} \frac{T}{298} k_{ad}(298) \tag{30}$$

$$k_{des}(T) = \frac{\eta_{H_2O}(298)}{\eta_{H_2O}(T)} \frac{T}{298} \frac{BCF_S(298)}{BCF_S(T)} k_{des}(298) \tag{31}$$

Water viscosity is evaluated from the following empirical relationships depending on the temperature value [30]:

$$273 < T < 293$$

$$\log_{10}\eta_T = \frac{1301}{998.333 + 8.1855(T - 293) + 0.00585(T - 293)^2} - 3.30233 \tag{32}$$

$$293 < T < 373$$

$$\log_{10}\frac{\eta_T}{\eta_{20}} = \frac{1.3272(293 - T) - 0.001053(T - 293)^2}{T - 168} \tag{33}$$

For the uptake and depuration rate constants, differences in diffusivity in phytoplankton need to be considered:

$$k_u(T) = \frac{\eta_P(298)}{\eta_P(T)} \frac{T}{298} \frac{BCF_M(T)}{BCF_M(298)} k_u(298) \tag{34}$$

$$k_d(T) = \frac{\eta_P(298)}{\eta_P(T)} \frac{T}{298} k_d(298) \tag{35}$$

Since phytoplankton viscosity (η_P) is unknown, we assume that the influence of temperature on octanol viscosity is representative of the phytoplankton viscosity dependence of temperature. Even though the absolute value may be more than one order of magnitude different, its relative variability with temperature may still be a good approximation, which is enough for the use of Equations 34 and 35. The viscosity of octanol can be calculated by the Lewis–Squires empirical relationship [20]:

$$\eta_P^{-0.2661}(T) = \eta_P^{-0.2661}(298) + \frac{T - 298}{233} \tag{36}$$

where $\eta_P(T)$ is assumed to equal the octanol viscosity at T and $\eta_P(298)$ is the known value of octanol viscosity at 298 K, which is 7.21 cP [20].

Figure 4 shows the temperature dependence of the rate constants in the 0 to 30°C range. Depuration, desorption, and adsorption rate constants increase with temperature because of enhanced diffusivity (Fig. 4). Thus, uptake kinetics will be significantly faster in warm environments than in cold areas. Conversely, uptake rate constants show a constant or slight

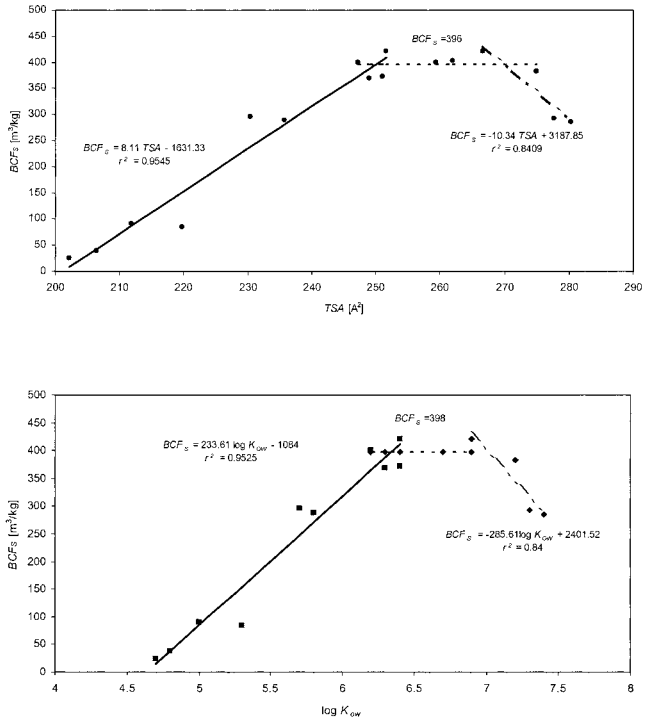

Fig. 3. Dependence of the bioconcentration factor on the surface (BCF_S) at the physical-chemical properties of the chemical.

decrease because of the influence of temperature on the *BCFs* that counteracts the influence of temperature on diffusivity.

Influence of microorganism size

From the predictive equations for bioconcentration factors and rate constants derived here, it is possible to quantify the role of microorganism size on the uptake, depuration, and bioaccumulation of POPs. The specific surface area of phytoplankton or bacteria (S_p, m^2/kg), assuming a spherical shape, depends on the microorganism radius (r, m):

$$S_p = \frac{3}{r \cdot \delta_{phyto}} \tag{37}$$

In case of cylindrical shape, like that shown for some bacteria species, S_P would be given by an equation analogous to Equation 37 but with a term of 2 instead of 3. Knowing the dependence of S_P on the microorganism size, we can predict the dependence of uptake and depuration constants on the microorganism radius. Introducing Equation 37 in Equations 7 and 8 yields

$$k_u = \frac{3D_p\zeta_{I,G}}{r \cdot e_p \zeta_{Micro}} BCF_M = \frac{3P\zeta_{I,G}}{r\delta_P \zeta_{Micro}} \tag{38}$$

$$k_d = \frac{3D_p}{r \cdot e_p} = \frac{3P}{r\delta_P BCF_M} \tag{39}$$

where $\zeta_{I,G}$ and ζ_{Micro} are the activity coefficient of the chemical in *I. galbana* and in a certain generic microorganism of size r, respectively. Equations 38 and 39 show that uptake and depuration kinetics are inversely proportional to the microorganism size. Therefore, the larger the microorganism, the slower the transfer of pollutants between water and phytoplankton and bacteria. However, BCF_M are the reference values given in Tables 1 to 3, and BCF_M values for a different microorganism need to take into account differences in activity coefficients. Even though differences in BCF_M are feasible between species [22], these are due to differences in composition of organic matter and not to different microorganism size. Conversely, for adsorption onto the cell membrane, the BCF_S depends on the number of sites of the phytoplankton surface where molecules can adsorb to; therefore, BCF_S is proportional to the specific surface area (S_P) multiplied by the number of active surface sites per unit of area (a, sites/m^2). We can take into account the dependence on the number of active surface sites by comparing the BCF_S of a microorganism of radius r with the BCF_S of reference, which for this study are the BCF_S reported in Tables 2 to 4 for *I. galbana* ($BCF_{S,IG}$) with a known value for the radius ($r_{IG,}$ 2.7 μm) [18]:

$$BCF_S = BCF_{S,IG} \cdot \frac{r_{IG} a_{IG}}{ra} \tag{40}$$

where BCF_S, r, and a are the bioconcentration factor at surface, radius, and number of active sites for a certain phytoplankton or bacteria species, respectively, and $BCF_{S,IG}$, r_{IG}, and a_{IG} are bioconcentration factor at surface, radius, and number of surface active sites for *I. galbana* (reference data set). Assuming a spherical geometry, the thickness of the water film e_w equal to cell radius [27], the dependence of adsorption and desorption rate constants is given by Equations 41 and 42:

$$k_{ad} = \frac{3 \cdot D_w}{r^2 \cdot \rho_{phyto}} \tag{41}$$

$$k_{des} = \frac{3 \cdot D_w}{r^2 \cdot \rho_P BCF_S} = \frac{3 \cdot D_w \cdot a}{\rho_P \cdot r \cdot r_{IG} \cdot a_{IG} \cdot BCF_{S,IG}} \tag{42}$$

Equations 38 to 39 and 41 to 42 are for microorganism with spherical shape, while those with cylindrical shape would be described by an analogous equation but with a term of 2 instead of 3. This shows that microorganism shape has a secondary influence, less than 50%, on the uptake dynamics in comparison with other variables, such as chemical hydrophobicity or microorganism size. Indeed, the role of microorganism size as discerned from Equations 37 to 42 is important in terms of uptake dynamics and as a key factor determining the dominant mechanism for accumulation into/onto the cell. Figure 5 shows the comparison of BCF_M and BCF_S for a number of PCBs with different physical-chemical properties depending on the microorganism size. Since BCF_M is independent of microorganism size while BCF_S is inversely proportional to it, the relative importance of membrane surface and cellular material depends on the size, being surface adsorption dominant for small microorganisms (bacteria), while absorption is dominant for most phytoplankton species. Equations 37 to 42 also show that uptake, depuration, adsorption, and desorption rate constants are inversely proportional to the radius or the radius to the second potency, and thus uptake in small organisms is significantly faster than in larger phytoplankton cells. In fact, bioconcentration by bacteria, as shown in this study, must be virtually instantaneous, and environmental models taking into account bacteria can assume equilibrium conditions between water and bacteria.

Implications for the biogeochemical cycles of POPs

Since phytoplankton and bacteria play an important role on the cycles of POPs, the dependence of uptake dynamics on temperature and microorganism size may have important implications for the biogeochemical cycles of POPs in aquatic environments. For example, sorption to small organisms (bacteria) is dominated by surface adsorption to a great extent

Table 4. Physical-chemical properties and predicted rate constants for polybrominated biphenyl ethers (PBDEs) and nonylphenols (NPs). Uptake (k_u), depuration (k_d), adsorption (k_{ad}), and desorption (k_{des}) rate constants are at 298 K and for a microorganism with a radius of 2.7 μm; TSA = total surface area; BCF_M = bioconcentration factor in the microorganism matrix; BCF_S = bioconcentration factor at the surface

	log K_{ow}[a]	TSA[b] (Å^2)	BCF_M (m^3/kg)	P (m/d)	k_u (m^3/kg/d)	k_d (per day)	BCF_S (m^3/kg)	k_{ad} (m^3/kg/d)	k_{des} (per day)
PBDE # Br									
3	5.5	237.1	158	0.087	112	0.7	396	3,447	8.7
4	6.0	258.7	570	0.424	548	1.0	396	3,247	8.2
5	6.8	291.9	1,766	1.196	1,545	0.9	280	3,098	11.0
6	7.4	315.8	2,770	1.196	1,545	0.6	280	2,965	10.6
NP	4.5	195.0	13	0.004	5	0.4	24	3,130	130

[a] Alcock et al. [40].
[b] Evaluated from Doucette and Andren [36].

[12,13]. Therefore, it is a fast process with characteristic response times of a few minutes at temperatures of environmental relevance. On the contrary, uptake by phytoplankton is dominated by absorption into the cell, and the response times are significantly larger (a few hours to days) [10,14,15]. In real environments, where mixtures of bacteria and phytoplankton populations are present, the water–microorganism partitioning dynamics will depend on the predominance of bacteria and phytoplankton. In coastal and high productivity areas, phytoplankton biomass dominates bacterial biomass [11], and therefore the overall kinetics of sorption will be slower than in areas dominated by bacterial biomass. This is the case of oligotrophic seas and oceans, where an efficient recycling of organic matter, and presumably of POPs, occurs in the photic zone because of intensive heterotrophic activity [11]. The important role of bacteria at low primary productivity areas of the ocean may have other important implications. Bacteria are susceptible to be able to degrade certain POPs by means of exoenzymes that could degrade the chemicals onto the cellular surface. Thus, the degradation potential would be higher in environments where bacterial biomass is dominant or accounts for an important fraction of total biomass since most of particle-phase POPs would be associated to bacterial surface. The low sinking fluxes of POPs observed at open sea [31] would be the result of a low fraction of POPs sorbed to large cells in addition, of course, to the low export ratio in these areas. Finally, the concurrent accumulation of bacteria and POPs at the sea surface microlayer may exert an influence on the air–water exchange, as has already been suggested for phytoplankton [10,32,33]. Since sorption to bacteria is faster than air–water exchange and sinking of large particulate matter [9], bacteria uptake will never be the limiting step dominating the dynamics of the environmental fate of POPs in aquatic environments. In fact, models that take into account bacteria may assume that bacteria–water partitioning of POPs is in equilibrium at temperatures of environmental relevance, which is not true for phytoplankton [10,28].

The predicted rate constants shown in Tables 1 to 4 are for *I. galbana*, and some uncertainly is present when these results are extrapolated to other phytoplankton and bacteria species besides the consideration of microorganism size. Different phytoplankton and bacteria species may have organic matter with different affinity for POPs. The cellular surface, and thus the number of adsorption active sites, may also be species dependent. The present model takes into account the species dependence by means of the ratios $\zeta_{I,G}/\zeta_{Micro}$ and a_{IG}/a. Further research would need to focus on determining whether these ratios are equal to one since species specificity may also play a role in the biogeochemical cycling. Extrapolation of Equations 19 to 29 obtained from PCB data to other POPs may also have some uncertainly associated, and therefore much research on uptake for POPs other than PCBs is needed.

The increase of depuration and desorption rate constants at high temperatures indicates that the transfer of POPs is faster in warm environments and less efficient in cold environments. Therefore, one would expect conditions closer to equilibrium when high temperatures are dominant. Since phytoplankton uptake is a key step for the sinking of pollutants to deep waters and sediments, the slower uptake kinetics would imply potential lower sinking fluxes of POPs during winter and in cold

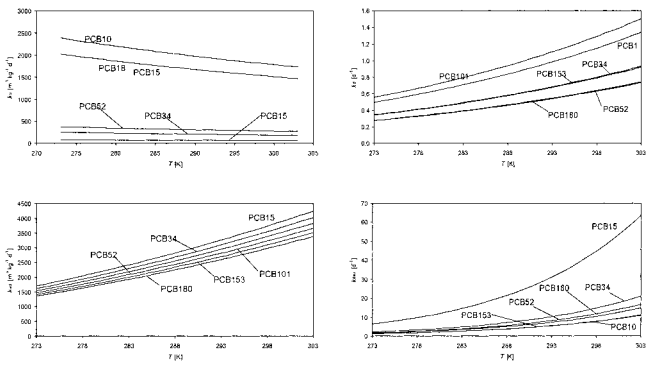

Fig. 4. Dependence of uptake (k_u), depuration (k_d), adsorption (k_{ad}), and desorption (k_{des}) rate constants on temperature (T) polychlorinated biphenyl (PCB).

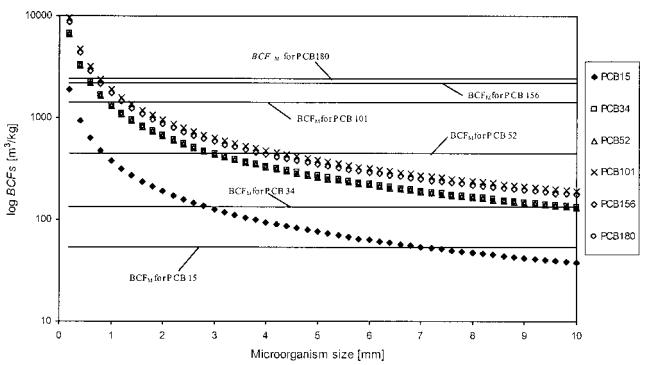

Fig. 5. Dependence of bioconcentration factors (BCF_M and BCF_S) on microorganism size, depending on the polychlorinated biphenyl (PCB) congener.

environments, assuming that all the other variables affecting the vertical fluxes remain equal.

As a summary, a prediction procedure for estimating uptake, depuration, adsorption, and desorption rate constants has been developed. The mechanistic and predictive nature of this procedure has allowed the prediction of the rate constants for a wide range of POPs for which no experimental data are available. Furthermore, a predictive method to quantify the influence of temperature and microorganism size is also presented. All this provides valuable information and methods for environmental modelers, which otherwise would be impossible to determine by means of experimental work. However, further work is needed to validate the predicted values in this work for POPs other than PCBs and understand better the influence of bacteria and phytoplankton on the biogeochemical cycles of POPs as well as species-specific differences in uptake dynamics and bioaccumulation of POPs by aquatic microorganisms.

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