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Table of Contents

EXECUTIVE SUMMARY	3
1. INTRODUCTION.....	4
2. AVAILABLE MODELS FOR PERSISTENT ORGANIC POLLUTANTS.....	6
2.1. PARAMETERIZATION OF ATMOSPHERIC INPUTS	6
2.1.1. <i>Dry aerosol deposition</i>	6
2.1.2. <i>Diffusive air-water exchange</i>	7
2.1.3. <i>Parameterization of wet deposition</i>	8
2.2. UPTAKE AND PROCESSING OF POPS IN PLANKTONIC FOOD WEBS	9
2.3. PARAMETERIZATION OF POP UPTAKE IN PHYTOPLANKTON AND BACTERIA	11
2.3.1. <i>Accumulation in phytoplankton</i>	11
2.3.2. <i>Influence of microorganism size, or predicting the accumulation by bacteria</i>	12
2.4. PARAMETERIZATION OF POP UPTAKE IN ZOOPLANKTON.....	14
2.5. SEDIMENTS VERSUS ATMOSPHERIC INPUTS AS DRIVERS OF POP ACCUMULATION IN AQUATIC FOOD WEBS	17
2.6. INTERACTIONS BETWEEN ATMOSPHERIC DEPOSITION OF CONTAMINANTS AND TROPHIC STATUS	19
3. CONCLUSIONS	21
4. REFERENCES.....	22
ANNEXES	32
ANNEX I: PARAMETERIZATION OF DRY ATMOSPHERIC DEPOSITION OF POPS.	32
ANNEX II: PARAMETERIZATION OF WET DEPOSITION OF POPS.	35
ANNEX III: UPTAKE DYNAMICS OF POPS IN PHYTOPLANKTON AND BACTERIA.	37

List of Tables

Table 2.1: Uptake and depuration rate constants of PAHs for the different processes controlling the accumulation of PAHs in zooplankton.....	16
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List of Figures

Figure 1.1. Schematics of the processes driving the fate and accumulation of persistent organic pollutants in aquatic food webs.	5
Figure 2.2. Influence of microorganism size of bioconcentration factors for different PCB congeners.	14
Figure 2.3: Bioaccumulation factors of PAHs in phytoplankton (<i>Rhodomonas salina</i>), zooplankton due to diffusive uptake and zooplankton feeding on phytoplankton	17
Figure 2.4: Seasonal variability in the vertical profile of PCB 28 for a coastal water column of 50 m depth	18
Figure 2.5: Seasonal variability in the vertical profile of PCB 28 for a coastal water column 10 m depth	19
Figure 2.6. PCB concentrations in phytoplankton depending on the phytoplankton biomass (high and low). Results are compared with those obtained in a situation of equilibrium	20

Executive Summary

The objective of this deliverable is to review and report the available models for studying the coupling of atmospheric inputs of persistent organic pollutants and their accumulation in planktonic food webs. Atmospheric inputs are known to be the main input of pollutants to open sea marine environments and also be important in coastal environments. The modelling of these interactions is important because atmospheric inputs are very dynamic and variable with time and can induce temporally high concentrations in the water column. Therefore, the models needed for studying these interactions should be dynamic (not at equilibrium or steady state) in order to be able to predict the high observed environmental variability, and thus able to predict episodes where potential threshold values are obtained. Furthermore, these models should also be able to take into account the interactions between fate and impact of pollutants and trophic status, which allows studying together the two drivers considered within the Thresholds IP (nutrients and pollutants).

The models reviewed here are those of the three main atmospheric deposition processes; namely dry aerosol deposition, wet deposition and diffusive exchanges. Furthermore the current knowledge of the accumulation processes and cycling of organic pollutants in phytoplankton is reviewed. There are few reports of the quantification and parameterization of accumulation and cycling of POPs in bacteria and zooplankton. Here, novel results obtained for zooplankton within the threshold IP are presented which suggest an important role of these in POP cycling. It is identified that more research is needed on the role of bacteria in the impact of POPs in aquatic food webs.

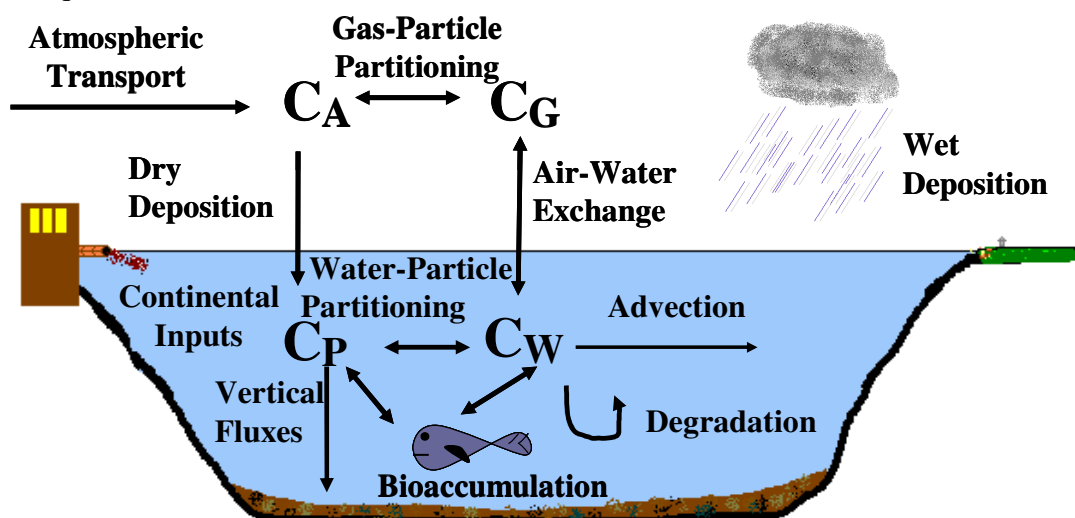
One of the issues that previous models were not able to assess is the relative importance of atmospheric inputs and inputs from sediments of POPs in food webs. Sediments are known to be a source of pollutants for benthic food webs, but their influence is not clear in the pelagic zone. The 1D model developed within Thresholds allows to elucidate the relative importance of these two sources of pollutants for the first time. It is shown that the atmosphere is the main contributor for the most part of the water column, except for very shallow ecosystems. Furthermore, some of the interactions between trophic status and atmospheric inputs as provided by models are also reviewed here.

The present review will allow in the next future to couple these models with toxicity models including the concepts of thresholds in order to identify whether points of no return and thresholds do happen in ecosystems due to pollutants as a driver.

1. Introduction

Atmospheric deposition is the main input of persistent organic pollutants in most marine systems, including high sea waters, many coastal ecosystems and other aquatic ecosystems (Iwata et al., 1993; Lakaschus et al., 2002; Jeremiason et al., 1999; Grimalt et al., 2001; Blais et al., 2001; Dachs et al., 2002; Blais et al., 2003; Bruhn et al., 2003). Once pollutants enter the aquatic environment, they can partition to organic matter phases, such as plankton, and in part sink to deep waters. Figure 1.1 shows schematics of the processes driving the fate and accumulation of POPs in aquatic food webs (Schwarzenbach et al., 2003). It has been shown that atmospheric deposition does control the occurrence of POPs in planktonic webs in several limnic and marine ecosystems (Jeremiason et al., 1999; Dachs et al., 1999a,b, 2000). Planktonic webs are the basis and first step for the introduction of POPs in the food web (Mailhot et al., 1987; Swackhamer et al., 1991; Skoglund et al., 1996); therefore, it is important to understand and be able to predict the processes driving the kinetics and the extend of these accumulation processes and their coupling with atmospheric deposition (Morrison et al., 1997; Dachs et al., 1999). Even though interactions between trophic status and pollutant fate and transport processes have received some attention, the field is still far from being able to understand these interactions in a comprehensive manner (Larsson et al., 1998; Dachs et al., 2000; Berglund et al. 2001).

Figure 1.1: Schematics of the processes driving the fate and accumulation of persistent organic pollutants in aquatic food webs.



POPs are hydrophobic chemicals, and thus have high tendency to associate to organic matter (Karickhoff et al., 1979). The planktonic food webs make up an important fraction of the water column

organic carbon and thus, the quantification of uptake and processing in plankton is also important to understand the fate and transport of POPs in the environment, and therefore, their impact (Skoglund et al., 1996; Morrison et al., 1997; Mackay 2001).

This deliverable aims at reviewing the work that has been done previously on the modeling of uptake of POPs in planktonic food webs and the coupling of these processes with atmospheric deposition. In addition to review the work reported in the literature it also describes the original work done within the THRESHOLDS project during the first 18 months of the project, which have been related to fill two of the gaps that were identified. One is the parameterization of the uptake of pollutants by zooplankton. The second is the role that vertical mixing in the water column has on levels of POPs in phytoplankton when all inputs are atmospherically driven. This allows now to discuss for the first time the relative importance of sediments and atmospheric inputs supporting water column concentrations. This work is explained in terms of its contribution to our understanding of the linking between atmospheric inputs of POPs and their accumulation in biota. The main text summarizes the models and current understanding, while specific details of the models are given in the annexes.

2. Available models for persistent organic pollutants

2.1. PARAMETERIZATION OF ATMOSPHERIC INPUTS

After being emitted or re-volatilised, persistent organic pollutants (POPs) partition between the gas and aerosol phases and are subject to Long Range Atmospheric Transport (LRAT) (Bidleman et al., 1988; Dachs and Eisenreich, 2000; Pankow 1994; Park et al., 2001; Eisenreich and Strachan, 1992). Semivolatile organic compounds may then be removed from the atmosphere to the ocean by three main processes: dry deposition of particulate-bound pollutants, diffusive gas exchange between the atmospheric boundary layer and the surface ocean and scavenging by rain (either from gas and particulate phases). Atmospheric depositional processes play a key role in the transport and fate of POPs at regional and global scale (Blais et al., 1998; Wania et al., 1993, 1996, 1998; Borghini et al., 2005). Furthermore, dry/wet deposition and diffusive air-water exchange can contribute to the impact of aquatic ecosystems and support POP accumulation in aquatic food webs (Dachs et al., 1999). Previous reports of comparison of the different removal mechanisms show that diffusive air-water exchange dominates over wet and dry particle deposition for POPs predominantly found in the gas phase, except in rainy regions and close to urban areas with high concentration of atmospheric particulate matter. Conversely, dry aerosol and wet deposition is important for chemicals that have a strong affinity to aerosols such as polycyclic aromatic hydrocarbons (PAHs) (Totten et al., 2001; Gigliotti et al., 2002, 2005; Jurado et al., 2005).

2.1.1. Dry aerosol deposition

In contrast to air-water exchange which is a fugacity driven process and thus it is bi-directional, dry deposition is a one direction transport process from the atmosphere to the surface, independent of the POP fugacity in the receiving medium (Bidleman, 1988; Slin and Slin, 1980). Experimental measures of dry deposition fluxes (F_{DD} , $\text{pg m}^{-2} \text{d}^{-1}$) are scarce and fluxes are often estimated by:

$$F_{DD} = v_D \cdot C_P \quad [1]$$

where v_D is the overall aerosol dry deposition velocity (m d^{-1}) and C_P is the POP aerosol-phase concentration (pg m^{-3}) (Jurado et al., 2004). v_D values are strongly dependent on aerosol size distribution, atmospheric turbulence (as influenced by wind speed) and at low wind speed by atmospheric stability. Pioneering studies that parameterized dry deposition velocities over natural surface waters, such as the models of Williams (1982) and Slinn (1980), still provide useful and widely used synopses for estimating v_D values (Shalatov et al. 2003; Jurado et al. 2004). In particular, within the Thresholds projects, dry deposition is estimated using the Williams' parameterization (Williams

1982), which determines v_D values as a function of aerosol diameter, wind speed and atmospheric stability. Additionally, it includes effects of spray formation under high wind speed conditions and particle growth due to high relative humidity. Previous studies have shown that dry deposition flux estimations from a distribution of aerosol size derived v_D values are more accurate than using a single overall v_D value (Ondov et al., 1994). Therefore, assuming the aerosol size distribution is known, the aerosol diameter range is divided into a number of intervals (i), so that the total flux is given by:

$$F_{DD} = \sum_i v_{D,i} \cdot C_{p,i} \quad [2]$$

where $C_{p,i}$ (pg m^{-3}) is the POP concentration in the aerosol phase of size i and $v_{D,i}$ (m d^{-1}) is the deposition velocity for the aerosol with a diameter in the midpoint of the interval i. The detailed procedure for estimation of $v_{D,i}$ values is given in Annex I.

2.1.2. Diffusive air-water exchange

Net diffusive gas-exchange is driven by the concentration gradient across the air-sea interface and depends strongly on wind speed, temperature and compound specific physical-chemical properties influence on the mass transfer coefficient (k_{AW} , m d^{-1}). Absorption (F_{AW_abs} , $\text{pg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) and volatilization fluxes (F_{AW_vol} , $\text{pg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) are computed respectively by:

$$F_{AW_abs} = k_{AW} \frac{C_G}{H'} \quad [3]$$

$$F_{AW_vol} = k_{AW} C_W \quad [4]$$

where C_W is the POP dissolved phase concentration (pg m^{-3}) and H' (dimensionless) is the temperature and salinity corrected Henry's law constant. The net air-water exchange flux (F_{AW} , $\text{pg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) is given by the difference of absorption and volatilization fluxes. k_{AW} is the air-water mass transfer rate (m d^{-1}). k_{AW} may be estimated as the result of transfer through two layers at each side of the air-water interface:

$$\frac{1}{k_{AW}} = \frac{1}{k_A H'} + \frac{1}{k_W} \quad [5]$$

where k_A and k_W are the POP mass transfer coefficients (m d^{-1}) in the air and water films, respectively. k_W may be calculated from the mass transfer coefficient of CO_2 in the water side (k_{w,CO_2} , m d^{-1}), which is a function of wind speed (U_{10} , m s^{-1}) (Wannikhof and McGillis 1999; Nigthingale2000).

$$k_{w,\text{CO}_2} = 0.24U_{10}^2 + 0.061U_{10} \quad [6]$$

$$k_W = k_{w,\text{CO}_2} \left(\frac{Sc_{POP}}{600} \right)^{-0.5} \quad [7]$$

where Sc_{POP} is the Schmidt number of the POP and 600 accounts for the Schmidt number of CO_2 at 298K, respectively. Similarly, k_A may be estimated from the mass transfer coefficient of H_2O in the air side (k_{A,H_2O} , $m\ d^{-1}$) that is also dependent on the wind speed,

$$k_{A,H_2O} = 0.2U_{10} + 0.3 \quad [8]$$

$$k_A = k_{A,H_2O} \left(\frac{D_{POP,a}}{D_{H_2O,a}} \right)^{0.61} \quad [9]$$

where $D_{POP,a}$ and $D_{H_2O,a}$ are the diffusivity coefficients of the POP and H_2O in air, respectively (Dachs et al., 2002). From equations 7-9, it is obvious that wind speed has a great influence on the magnitude of k_{AW} . On the other hand, temperature influences the magnitude of k_{AW} through its influence on diffusivities, Schmidt numbers and H' . Since the wind speed exerts a nonlinear influence, it is important to either use a high resolution wind speed time series, or average wind speed corrected by the appropriate parameters as discussed by Livingsgton and Imboden (1993), whose parameterization was updated by Simó and Dachs (2002).

2.1.3. Parameterization of wet deposition

The wet deposition flux (F_{WD} , $pg\ m^{-2}\ d^{-1}$) is given by the product of precipitation (p_0 , $m\ d^{-1}$) and the concentration of the chemical in rain (C_R , $pg\ m^{-3}$), which includes both the dissolved and particulate phases (Jurado et al., 2005).

$$F_{WD} = p_0 \cdot C_R \quad [10]$$

Here, p_0 ($m\ d^{-1}$) is the precipitation depth per day, which can be measured or derived from satellite values of monthly or weekly means. Since C_R is unknown, an empirical approach has been applied that makes use of an overall scavenging ratio (W_T , dimensionless), which is the ratio of concentrations in rain and in the atmosphere (C_A , $pg\ m^{-3}$), the latter including gas-phase (C_G , $pg\ m^{-3}$) and aerosol phase concentrations (C_P , $pg\ m^{-3}$).

W_T , also termed overall washout ratio, can alternatively be estimated by (Bidleman 1988; Ligocki et al. 1985):

$$W_T = W_G(1 - \phi) + W_P(\phi) \quad [11]$$

in which W_G and W_P are the gas and particle washout ratios respectively, and ϕ (dimensionless) is the fraction of aerosol-bound POPs to total atmospheric POP concentration ($C_P/C_P + C_G$). ϕ values for PCDD/F are determined using measured field C_G and C_P concentrations, while for PCBs it has been

necessary to estimate it from gas-particle partitioning models (Pankow 1994; Dachs and Eisenreich 2000) by:

$$\phi = \frac{K_p(TSP)}{1 + K_p(TSP)} \quad [12]$$

Details of the derivation of the particle-gas partition coefficient (K_p , $\text{m}^3 \text{kg}^{-1}$) and TSP (the total suspended particle matter, kg m^{-3}) from physico-chemical properties and remote sensing measurements, have been described elsewhere (Jurado et al., 1995).

In terms of ϕ , F_{WD} can be expressed by:

$$F_{WD} = (W_G(1-\phi) + W_P(\phi)) \cdot p_0 \cdot C_A = \left(W_G + \frac{W_P \cdot \phi}{(1-\phi)} \right) \cdot p_0 \cdot C_G \quad [13]$$

It is important to note that the previous equation accounts for the flux for an average day, which includes raining and non-raining periods. Additionally, it is useful to refer the wet deposition flux just to the time when the precipitation event is occurring (raining period); then the subscript *rain* is added to distinguish from the flux obtained above. F_{WD_rain} is given by dividing equation 13 by the fractional occurrence of rain (f).

$$F_{WD_rain} = \left(W_G + \frac{W_P \cdot \phi}{(1-\phi)} \right) \cdot \frac{p_0}{f} \cdot C_G \quad [14]$$

Annex II provides a detailed discussion on the estimation on wash-out ratios.

2.2. UPTAKE AND PROCESSING OF POPs IN PLANKTONIC FOOD WEBS

Phytoplankton plays a central role in the biogeochemical cycles of POPs in aquatic environments (Swackhamer et al., 1991; Swackhamer et al., 1993; Skoglund et al., 1996). There are several potential pathways for the introduction of POPs into food webs such as by interaction with the sediment, direct absorption during fish/organism respiration, etc, 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 (Morrison et al., 1997). Secondly, phytoplankton uptake of pollutants influences the transport, occurrence and distribution of POPs in aquatic environments (Skei et al., 2000; Dachs et al., 1997a,b). For example, vertical distribution of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) follow the vertical profile of phytoplankton biomass (Dachs et al., 1997). Furthermore, phytoplankton uptake and subsequent transfer to zooplankton drives the sinking fluxes of

POPs in the water column (Baker et al., 1991; Dachs et al., 1999; Dachs et al., 2002). 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 (Dachs et al., 2000; Skei et al., 2000; Berglund et al., 2001). In oligotrophic environments, heterotrophic bacteria may constitute an important fraction of organic matter in the water column (Gasol et al., 1997 ; Sobek et al. 2006). Uptake of POPs by bacteria may play an important role in some environments (Axelman et al., 1997) and have, for example, a potential 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 (Wallberg and Andersson 1999; Wallberg and Andersson 2000; Wallberg et al. 2001). Particularly, there is a lack of experimental uptake and depuration rate constants of POPs by bacteria that 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 (Del Vento and Dachs, 2002). Furthermore, bacteria may recycle particulate POPs from the particle-phase to the dissolved phase.

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 last decade on the experimental determination of uptake and depuration constants. Most of these studies focus on the exchange of PCBs between plankton and water (Skoglund et al. 1996; Wallberg and Andersson 1999). Uptake of nonionic persistent organic pollutants by phytoplankton and bacteria is a passive diffusive process that can be described by a two compartment model (Dachs et al., 1999; Del Vento and Dachs 2002). First there is fast adsorption to the phytoplankton surface followed by diffusion into the matrix in a partitioning like mechanism. The relative importance of these two sorption mechanisms as contributors to the total bioaccumulation of POPs by microorganisms is an issue of debate (Wallber and Andersson 1999). While for phytoplankton, absorption may dominate the total bioaccumulation potential (Skoglund et al.; 1996), the smaller size of bacteria and their higher specific surface area suggest that bacterial uptake may be dominated by surface adsorption (Axelman et al.; 1997). 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 (Dachs et al., 1997). This contrasts with the knowledge of the microbial metabolization processes of some POPs such as PAHs, which have been extensively studied in view of remediation strategies. Conversely, Zooplankton and other organisms, e.g. fish, can in addition to passive uptake, accumulate POPs through feeding on other organisms. While, these mechanisms must be the dominant route for most fish species, it is still not known whether diffusion or feeding dominates the accumulation of POPs in zooplankton.

Planktonic organisms do play a crucial role as a driver of the fate of persistent organic pollutants in aquatic environments (Wallberg et al., 2001; Skei et al., 2000), not only because they constitute the primary entrance of pollutants into the marine food web through processes such as accumulation or biomagnification, but also because they are key vectors for the cycling and settling of POPs in the water column. The potential routes of removal of POPs by planktonic organisms are i) sedimentation of phytoplankton dead cells, zooplankton fecal pellets, and debris (Swackhamer et al. 1991; Dachs et al., 2000), and ii) metabolization by bacteria and maybe zooplankton, even though this last process has not been documented so far. Therefore, the understanding of dynamics of accumulation of POPs in food webs is important for understanding the fate and impact of these in the environment and food webs.

2.3. PARAMETERIZATION OF POP UPTAKE IN PHYTOPLANKTON AND BACTERIA

2.3.1. Accumulation in phytoplankton:

POP uptake in phytoplankton and bacteria is a passive diffusive process. POP accumulation in phytoplankton and bacteria is given by the bioconcentration factors (BCFs),

$$BCF = \frac{C_p}{C_w} \quad [15]$$

where C_p is the POP concentration in phytoplankton (ng kg^{-1}) and C_w is the POP concentration in the dissolved phase (ng L^{-1}). Several authors have shown that BCFs in phytoplankton for PCBs and PAHs can be correlated to the octanol-water partition coefficient, and this is the most accepted methods to predict BCF values. However, there is still some discrepancy on the reasons that lead to a lack of correlation between BCF and K_{ow} for the most hydrophobic POPs. Skoglund et al. (1996) attributed this lack of correlation to kinetic limitations. Del Vento and Dachs also (2002) reported this observation and attributed it to low permeability of cellular membranes to large molecules (see Annex 3). However, other authors suggest that the BCF- K_{ow} correlations hold through all the range of K_{ow} values (Machlachlan et al., 2005).

BCF values do give an indication of the potential of organism to bioconcentrate POPs but do not tell anything on the kinetics of this process, which is what is needed for modelling purposes. The time-dependent accumulation of a chemical in phytoplankton or bacteria is given by:

$$\frac{dC_p}{dt} = k_u \cdot C_w - k_d \cdot C_p - k_g \cdot C_p \quad [16]$$

where k_u is the diffusive uptake rate ($\text{m}^3 \text{kg}^{-1} \text{d}^{-1}$), k_d is the diffusive depuration rate (d^{-1}), and k_g is the growth rate of phytoplankton (d^{-1}). Then, at steady state the BCF is given by:

$$BCF = \frac{k_u}{k_d + k_g} \quad [17]$$

Values for k_u and k_d for PCBs have been reported by Dachs et al. for *Isochrysis Galbana* (Dachs et al., 1999). Estimation for other chemicals or phytoplankton species, as well bacteria, is now possible following the work by Del Vento and Dachs (2002) that derived a set of equations for k_u and k_d in terms of chemical properties and microorganisms characteristics (see Annex 3 for details). Still, this methodology can not be applied to other organisms such as zooplankton, since for these, in addition to diffusive uptake and depuration; there are other processes that need to be considered.

2.3.2. Influence of microorganism size, or predicting the accumulation by bacteria

Due to the lack of measurements, and the very little knowledge on the role that bacteria play in the cycling of POPs, it is important to be able to estimate accumulation in bacteria. From the predictive equations for bioconcentration factors and rate constants derived in Annex 3, 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 , $\text{m}^2 \text{kg}^{-1}$) assuming a spherical shape depends on the microorganism radius (r , m).

$$S_p = \frac{3}{r \cdot \delta_{\text{phyto}}} \quad [18]$$

In case of cylindrical shape, like that shown for some bacteria species, S_p would be given by an equation analogous to equation [18] 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. From Equation 18, it can be derived that:

$$k_u = \frac{3D_p \zeta_{1,G}}{r \cdot e_p \zeta_{\text{Micro}}} BCF_M = \frac{3P \zeta_{1,G}}{r \delta_p \zeta_{\text{Micro}}} \quad [19]$$

$$k_d = \frac{3D_p}{r \cdot e_p} = \frac{3P}{r \delta_p BCF_M} \quad [20]$$

where $\zeta_{I,G}$ and ζ_{Micro} are the activity coefficient of the chemical in *Isochrysis galbana* and in a certain generic microorganism of size r , respectively. Equations 19 and 20 show that uptake and depuration kinetics is 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 1-3 of Annex 3 and BCF_M values for a different microorganisms need totake into account differences in activity coefficients. Even though differences in BCF_M are feasible between species (Skoglund et al., 1996), these are due to differences in composition of organic matter and not due 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 2-4 for *Isochrysis galbana* ($BCF_{S,IG}$) with a known value for the radius (r_{IG} , 2.7 μm) (Dachs et al., 1999).

$$BCF_S = BCF_{S,IG} \cdot \frac{r_{IG} a_{IG}}{ra} \quad [21]$$

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 *Isochrysis galbana* (reference data set). Assuming a spherical geometry, the thickness of the water film e_w equals to cell radius (Wolf-Gladrow and Riebesell, 1997) then the dependence of adsorption and desorption rate constants are given by Equations 22 and 23.

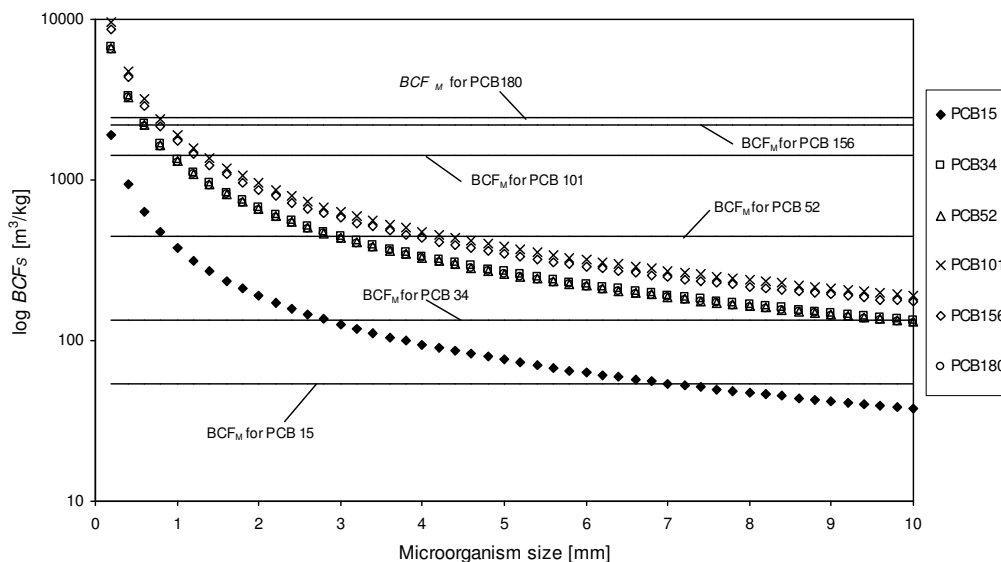
$$k_{ad} = \frac{3 \cdot D_w}{r^2 \cdot \rho_{phyto}} \quad [22]$$

$$k_{des} = \frac{3 \cdot D_w}{r^2 \cdot \rho_P BCF_S} = \frac{3 \cdot D_w \cdot a}{\rho_P \cdot r \cdot r_{IG} \cdot a_{IG} \cdot BCF_{S,IG}} \quad [23]$$

Equations 19-20 and 22-23 are for microorganism with spherical shape while those with cylindrical shape would be described by 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 37-42 is important in terms of uptake dynamics and as a key factor determining the dominant mechanism for accumulation into/onto the cell. Figure 2.2 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 19-23 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.

Figure 2.2. Influence of microorganism size of bioconcentration factors for different PCB congeners



2.4. PARAMETERIZATION OF POP UPTAKE IN ZOOPLANKTON

Even though, during the last decade, several studies have dealt with the bioconcentration of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in phytoplankton (Skoglund et al., 1996; Dachs et al., 1999; Reinfeld et al., 2003; Del Vento and Dachs 2002; McLachlan et al., 2005). However, much less knowledge is available on processes driving POP accumulation in zooplankton. Indeed, it is not clear whether zooplankton, and other heterotrophic organisms, accumulate POPs from feeding on phytoplankton or passively from surrounding waters. Recently, Sobek et al. (ETC 2006) have suggested that diffusive uptake dominates accumulation of PCBs in zooplankton. However, it is difficult to reach to these conclusions with a simple correlation

between a zooplankton-water partition constant vs. $\log K_{ow}$. Furthermore, so far, there is a lack of knowledge on dynamics of other POPs in zooplankton. Specially important is to determine the role of zooplankton in PAH cycling, since PAHs are known to accumulate in phytoplankton, and be metabolized by fish.

Once POPs accumulate into phytoplankton, their chemical fate is dominated by two processes, vertical transport to bottom waters and sediments by dead cells, debris, etc, and transfer into the food chain by zooplankton grazing (Swackhamer and Skoglund, 1991) and into the microbial loop through bacteria. While the first mechanism of settling POPs via phytoplankton dead cells, etc, has been reported before (Fowler et al., 1984; Bouloubassi et al., 2006), it still remains unclear whether these POPs introduced in zooplankton by dietary uptake biomagnificate, or on the contrary, zooplankton eliminates them through egestion of fecal pellets and potentially metabolization. Quantification of the transfer efficiency of POPs to fecal pellets has not been performed so far, even though, this would be important, since fecal pellets do transport efficiently PAHs, PCBs and other POPs down the water column (Prah and Carpenter 1979; Lipiatou et al., 1992). A correct understanding and parameterization of these processes would be important to determine the importance of the biologically mediated vertical flux mechanisms.

Therefore, in order to quantify (or model) the processing of POPs by zooplankton it is needed to have measurements and prediction methods for all the uptake and depuration constants. Unfortunately, even though it has been done for fish and phytoplankton in the past (Mackay 2001; Morrison et al., 1997), until now, there is not a single paper reporting them for zooplankton. As part of the threshold project, these uptake and depuration constants have been measured for PAHs uptake in zooplankton. Therefore it is now possible to model the accumulation of PAHs in zooplankton, the transfer of these PAHs to fecal pellets, and the role that zooplankton plays metabolizing POPs.

PAH accumulation in zooplankton is given by:

$$\frac{dC_{zoo}}{dt} = k_u \cdot C_w + k_{food} \cdot C_w - k_d \cdot C_p - k_{eg} \cdot C_p - k_{met} \cdot C_p \quad [24]$$

where k_u and k_d are the diffusive uptake and depuration rate constants, k_{food} is the uptake constant due to dietary uptake, k_{eg} is the depuration constant due to production of fecal pellets and k_{met} is the rate constant for the metabolization of POPs by zooplankton. These constants are now available from work performed within the threshold project. Briefly, they have been estimated from incubation experiments of zooplankton in varying conditions of PAH concentrations, food availability. In these experiments,

PAH concentrations in phytoplankton, zooplankton and fecal pellets have been measured, and therefore, it has been possible to estimate the parameters appearing in equation 24.

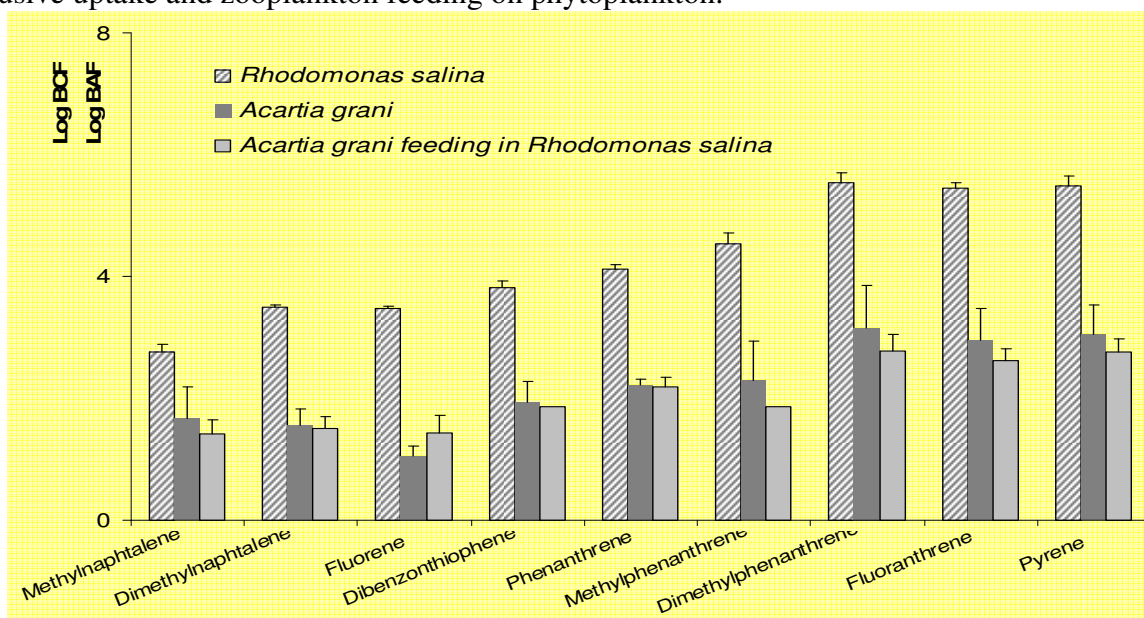
Table 2.1: Uptake and depuration rate constants of PAHs for the different processes controlling the accumulation of PAHs in zooplankton.

	METHYLNAPHTHALENE	DIMETHYLNAPHTHALENE	FLUORENE	DIBENZANTHROPHENE	PHENANTHRENE	METHYLPHENANTHRENE	DIMETHYLPHENANTHRENE	FLUORANTHRENE	PYRENE
Kfood	0,42	2,17	2,14	4,67	9,57	25,48	253,53	205,09	226,67
kup	0.30	3.11	2.92	4.46	58.69	24.37	132.58	223.80	219.31
keg	0,01	0,05	0,07	0,03	0,07	0,03	0,17	0,14	0,13
kmet	0,00	0,08	0,20	0,14	0,16	0,17	0,43	0,43	0,44
kdep	10.89	92.32	95.17	61.56	367.75	336.99	197.27	518.49	354.56

Table 2.1 shows the uptake and depuration constants for different PAHs. The results shows that passive uptake by diffusion is as fast as uptake due to ingest of phytoplankton, however, dietary uptake does not result in higher bioaccumulation factors since as shown in Figure 2.2 the accumulation factors in zooplankton accumulating from diffusion are significantly equal than those measured when zooplankton was feeding on phytoplankton. This is due to the low efficiency of zooplankton to incorporate PAHs to the body burden when these are feed on phytoplankton. Depuration constants in Table 2.1 show that there is a continuously cycling of PAHs between the dissolved phase and zooplankton as discerned from the high depuration rate constants which are 1 to 2 orders of magnitude higher than those reported for phytoplankton (Dachs et al., 1999). Therefore, PAHs are continuously getting into and out of zooplankton. Definitely, this process is faster than in phytoplankton due to their active respiration mechanisms. However, even though k_d are high, diffusive depuration does not eliminate the compound from the system, but just returns it to the dissolved phase. Conversely, k_{met} values are higher than k_{eg} , this mean that metabolization does play a role as a process removing PAHs from the environment. The high values reported in table – show that the half lives of PAHs due to

zooplankton metabolism are of 2 to 10 days, and points to zooplankton as a major driver of POPs in the biosphere.

Figure 2.3: Bioaccumulation factors of PAHs in phytoplankton (*Rhodomonas Salina*), zooplankton due to diffusive uptake and zooplankton feeding on phytoplankton.



2.5. SEDIMENTS VERSUS ATMOSPHERIC INPUTS AS DRIVERS OF POP ACCUMULATION IN AQUATIC FOOD WEBS

A topic that has received quite a lot of attention in the last two decades, is the issue of what controls and supports the accumulation of POPs in aquatic food webs. Traditionally, it has been suggested that the bioavailable fraction in sediments supports concentration and bioconcentration of POPs on the water column (Blais et al., 2003). Certainly, there is now field evidence that this happens for benthic organisms, but it is not clear for other food webs. Conversely, it has been shown that atmospheric deposition can support levels of water column POPs in atmospherically driven ecosystems such as remote lakes (Meijer et al., 2005). Traditional models for fate and transport of POPs could not respond to this question because even though they included most of the environmentally relevant processes (Mackay 2001; Meijer et al., 2005), they are 0-dimensional and thus assume that the water column is well mixed. However, the model developed within the Threshold project, that is able to model the vertical profiles allows now to answer this question. Figure 2.4 shows the seasonal variability in the vertical profiles for a PCB congener when the water column is 50 m depth. It is possible to distinguish

three zones. Deep water does show a huge influence from the influence, mainly due to sediment resuspension and diffusion of chemicals from the interstitial waters to the deep waters. Conversely, the surface waters are extremely sensible to atmospheric inputs with pulses of concentrations due to atmospheric deposition. The layer in the mid-depth water has low concentrations and reasonably constant all year round. Conversely, Figure 2.5 shows the concentrations for a water column of 10 m. The shallower water column allows it to be well mixed. In this case, the entire water column is influenced by the sediment, even though, the atmosphere can still in some cases exert a role.

Therefore, it seems that sediments are the source of POPs to the water column when this is remarkably shallow, otherwise, it will only affect benthic organisms. Conversely, for aquatic environments with water columns deeper than about 20 m, the atmospheric inputs control and support the concentrations in the water column.

Figure 2.4: Seasonal variability in the vertical profile of PCB 28 for a coastal water column of 50 m depth.

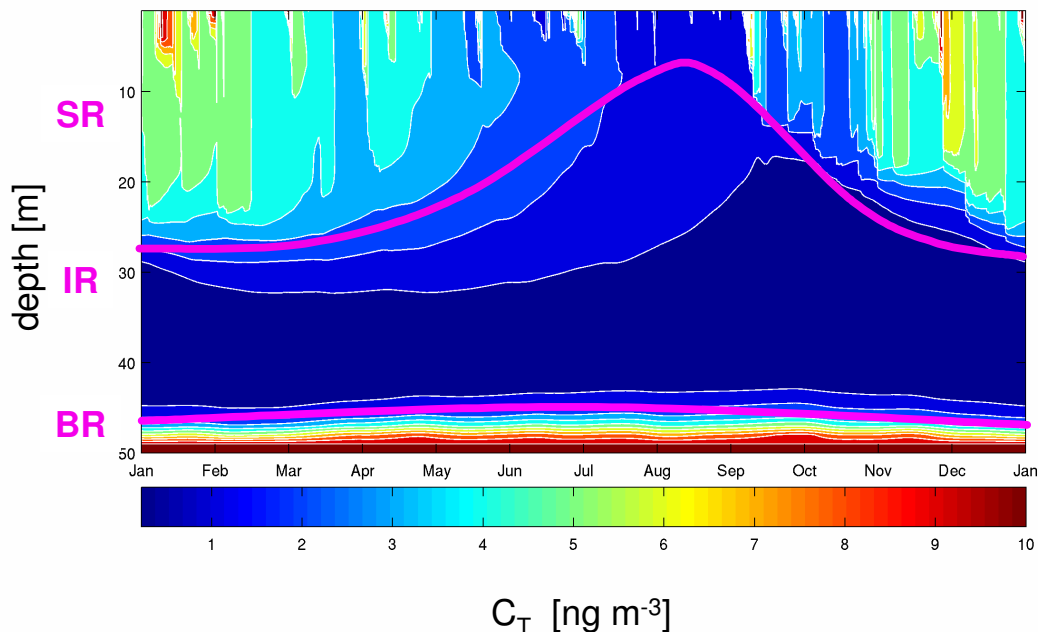
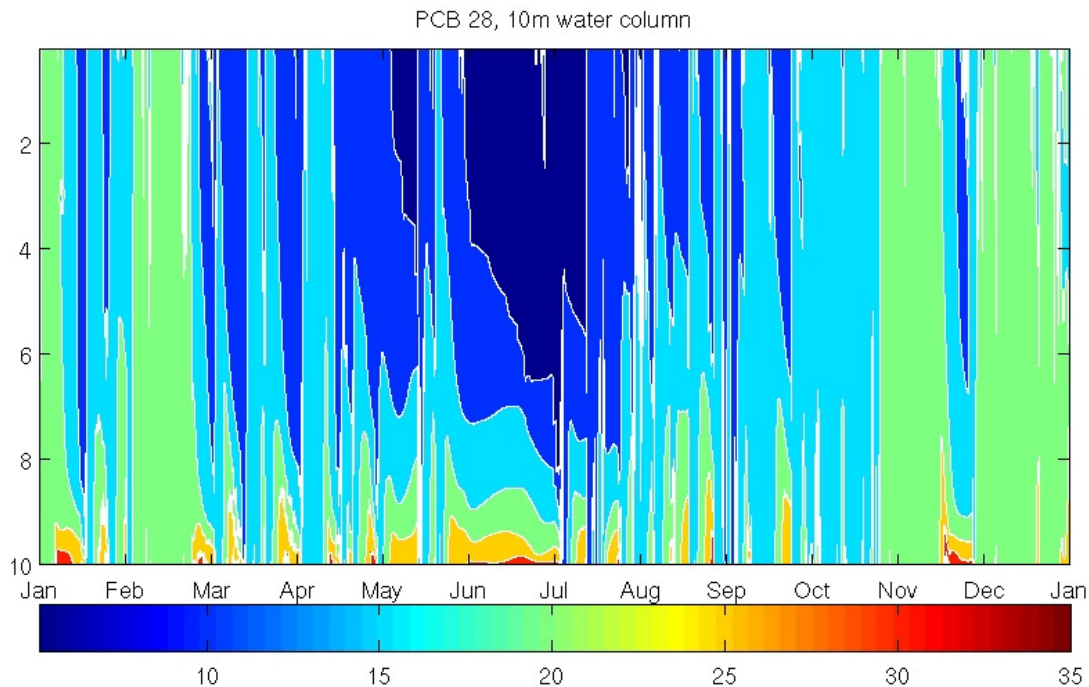


Figure 2.5: Seasonal variability in the vertical profile of PCB 28 for a coastal water column 10 m depth.

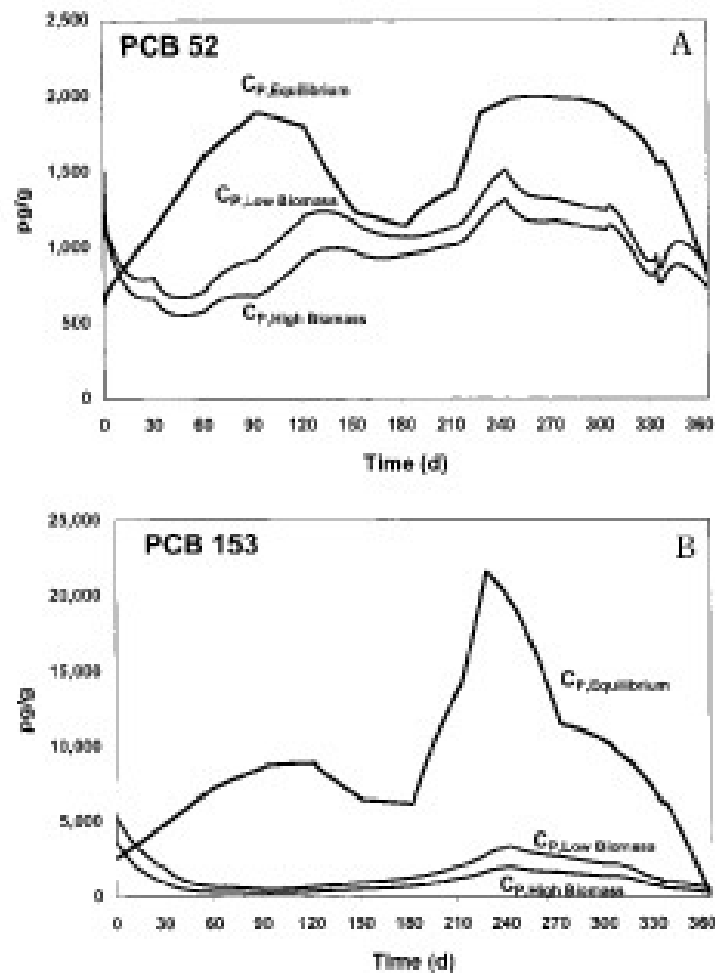


2.6. INTERACTIONS BETWEEN ATMOSPHERIC DEPOSITION OF CONTAMINANTS AND TROPHIC STATUS

Air-water-phytoplankton transfer: The coupling of atmospheric deposition, especially diffusive air-water exchange, and phytoplankton uptake results in a number of interactions that are important in order to understand the occurrence of POPs in the water column and aquatic food webs. These interactions do exist in the environment. For example, Millard et al. (1993) observed a decrease into the volatilization losses of PCBs at higher biomass. A similar trend has been observed by Jeremiason et al. (1999) in two well characterized lakes. Dachs et al. (2000) was able to model these trends with a simple model that took into account the air-water diffusive exchange and phytoplankton uptake of POPs, modeled as explained above. Furthermore, Taylor et al. (1991) has shown that PCB concentrations in plankton are lower in eutrophic environments. Lower concentrations at higher biomass can be explained by the fact that air-water exchange is not fast enough to support the phytoplankton uptake of POPs and the settling fluxes to deep waters. Dachs et al. (2000) has demonstrated that this situation can

be predicted with the models described here. Figure 2.6 shows that concentrations in the water column decrease at higher biomass (Dachs et al., 2000). These lower concentrations in the water column will induce as well lower concentrations in the organisms. In fact, because of this, phytoplankton uptake induces a difference in fugacity between the atmosphere and the water column. For the marine environment, these biogeochemical controls on air-water exchange are also important and play an important role at the oceanic scale (Dachs et al., 2002).

Figure 2.6. PCB concentrations in phytoplankton depending on the phytoplankton biomass (high and low). Results are compared with those obtained in a situation of equilibrium.



3. Conclusions

The present revision of the current models available for studying the coupling of atmospheric inputs and accumulation of POPs in biota has allowed identifying the best models that should be used in further assessing the impact of pollutants, and their interactions with eutrophication in aquatic ecosystems. The models need to be dynamic in order to be able to model the important environmental variability in POP concentrations.

- The state of the art models for dry deposition, diffusive air-water exchange and wet deposition allow to predict with known uncertainties the atmospheric inputs of POPs, and have been validated previously in published reports
- The bioconcentration of POPs in phytoplankton is relatively well known, and both magnitude and kinetics can be predicted adequately. However, effects are not well known.
- The accumulation and processing of POPs in zooplankton in bacteria are largely unknown, specially the kinetics.
- The experiments carried out within Thresholds, have allowed to parameterize uptake kinetics in zooplankton for the first time, showing the importance of zooplankton metabolizing some pollutants such as PAHs
- The current ecological models are incomplete in modelling the cycling of POPs in aquatic food webs. Especially, further research is needed to understand the role of bacteria.
- The relative role of the atmosphere as a source of POPs is now possible to model with the 1D model developed within Thresholds.
- Further research is needed to couple the available models with toxicity models in order to link atmospheric inputs of POPs and potential points of no return in ecosystems driven by pollutants.

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ANNEX I: PARAMETERIZATION OF DRY ATMOSPHERIC DEPOSITION

This section includes the method used to model dry deposition velocity to natural water surfaces, performed through an adaptation from Williams model (1982). This model includes the influence of spray formation enhancing entrainment of aerosols during high wind speed periods, effects of particle growth due to high relative humidity, the variation of turbulent transport with wind speed, and surface roughness. This approach separates the atmosphere below a reference height (10m) into two layers, as suggested previously by Slinn and Slinn (1980). The model parameterizes transport through an upper layer to an underlying laminar sublayer and provides different paths for smooth water and water broken by whitecaps.

Gravitational settling is superimposed on transport through both layers. The gravitational settling velocity v_s (cm s^{-1}), either referred to dry particle diameter (then v_{s_dry}) or wet particle diameter (then v_{s_wet}), is given by Stokes Law as:

$$v_s = \frac{1}{18} \frac{(D_p 10^{-4})^2 \rho_p g C_c}{\mu} \quad [25]$$

where D_p is the aerosol diameter (μm) either in dry conditions (D_{dry}) or in humid conditions (D_{wet}), ρ_p the particle density (g cm^{-3}), assumed constant and equal to 2 g cm^{-3} , g is the acceleration due to gravity (9.8 m s^{-2}), C_c is the Cunningham correction factor (dimensionless) and μ the dynamic viscosity of the air ($\text{g cm}^{-1} \text{ s}^{-1}$).

The Cunningham correction factor is:

$$C_c = 1 + \frac{2\lambda}{D_p} \left[1.257 + 0.4 \exp\left(-\frac{1.1D_p}{2\lambda}\right) \right] \quad [26]$$

where λ is the air mean free path ($7.63 \cdot 10^{-6} \text{ cm}$ at 298K). Conversely, the dynamic viscosity of the air (μ , $\text{g cm}^{-1} \text{ s}^{-1}$), for $T > 273\text{K}$ is given by:

$$\mu = (1.718 \times 10^{-5} + 0.0049 \times 10^{-5} \times (T - 273.15)) \times 10 \quad [27]$$

The wet particle diameter (D_{wet} , μm) results from the increase of the dry particle diameter (D_{dry} , μm) due to humidity, and it is estimated according to Fitzgerald's equation (Jurado et al., 2004), assuming a relative humidity around 70%:

$$D_{wet} = 2 \left(2.3489 \left(\frac{D_{dry}}{2} \right)^{1.00638} \right)$$

The aerodynamic or turbulent transfer coefficient (k_{ax} , cm s^{-1}) is used to characterize the turbulent transport in the overlying constant flux layer. Assuming neutral atmosphere, it is given by:

$$k_{ax} = \frac{\kappa u^*}{\ln\left(\frac{z}{z_{0x}}\right)} \quad [28]$$

where the subscript x is either s (then k_{as} , smooth surface transfer coefficient) or b (then k_{ab} , broken surface transfer coefficient), κ is von Karman's constant =0.4, u^* the friction velocity (cm s^{-1}), z is the reference height (taken=1000 cm), z_{0x} is the roughness length (assumed equal to 0.1 cm for broken open sea and 0.01 cm for calm open sea).

The friction velocity u^* is parameterized versus the mean wind speed retrieved by the satellite (u_{10} , cm s^{-1}) (Jurado et al., 2004):

$$u^* = u_{10} \sqrt{C_D} \quad [29]$$

where $C_D=1.3 \cdot 10^{-3}$ is the drag coefficient in a reference height of 10 m (Jurado et al., 2004).

Transport through the laminar layer (k_{xs} , cm s^{-1}) incorporates Brownian diffusion and inertial impaction. When referred to the smooth water surface it is characterized by the transfer coefficient k_{ss} , (cm s^{-1}) and the formulation is:

$$k_{ss} = \left(\frac{(u^*)^2}{\kappa u_{10}} \right) \left[10^{(-3/St)} + Sc^{(-1/2)} \right] \quad [30]$$

where St (dimensionless) is the Stokes number ($St = (u^*)^2 v_{s_wet} / g \nu$), ν ($\text{cm}^2 \text{s}^{-1}$) is the kinematic viscosity = $10^4 (\mu / \rho_{air})$, ρ_{air} (kg m^{-3}) the density of the air = $(10 \cdot 28.96 \cdot P) / (R \cdot 10^{-3} \cdot T)$, $R=0.082 \text{ atm} \cdot \text{L K}^{-1} \text{ mol}^{-1}$; Sc (dimensionless) is the Schmidt number = ν / D_c and D_c ($\text{cm}^2 \text{s}^{-1}$) is the diffusivity of the particles $\approx (2.38 \cdot 10^{-7} / D_{wet}) (1 + 0.163 / D_{wet} + 0.0548 \exp(-6.66 \cdot D_{wet} / D_{wet}))$. On the other hand, when referred to the broken surface transfer coefficient (k_{bs}) is assumed to be 10 cm s^{-1} .

Since wind speeds estimations by remote sensing are monthly averages, it is important to account for the short-term variability and nonlinear influence of wind speed on St and k_{ss} . It has been assumed an oceanic Weibull distribution of wind speed with a shape parameter of 2. Thus,

$$St_weibull = \frac{v_{s_wet} C_D}{g \nu \Gamma\left(1 + \frac{1}{2}\right)} u_{10}^2 \Gamma\left(1 + \frac{2}{2}\right) \quad [31]$$

$$k_{ss_weibull} = \frac{u_{10}^2 C_D \Gamma(2) \Gamma(0.5)}{\kappa u_{10} \Gamma(1.5)} \left[10^{(-3/St_weibull)} + Sc^{(-1/2)} \right] \quad [32]$$

Finally, the dry deposition velocity (v_D , cm s^{-1}) is obtained through the following equation, obtained by applying the resistance method with the transfer coefficients described above (Jurado et al., 2004):

$$v_D = \frac{A}{B} \left[(1 - \alpha)(k_{ss} + v_{s_wet}) + \frac{k_m \alpha (k_{bs} + v_{s_wet})}{k_m \alpha (k_{ab} + k_{bs} + v_{s_wet})} \right] + \frac{\alpha (k_{bs} + v_{s_wet}) \alpha (k_{ab} + v_{s_dry})}{k_m + \alpha (k_{ab} + k_{bs} + v_{s_wet})} \quad [33]$$

where

$$A = k_m [(1 - \alpha)k_{as} + \alpha k_{ab} + v_{s_dry}] + (1 - \alpha)(k_{as} + v_{s_dry}) \alpha (k_{ab} + k_{bs} + v_{s_wet}) \quad [34]$$

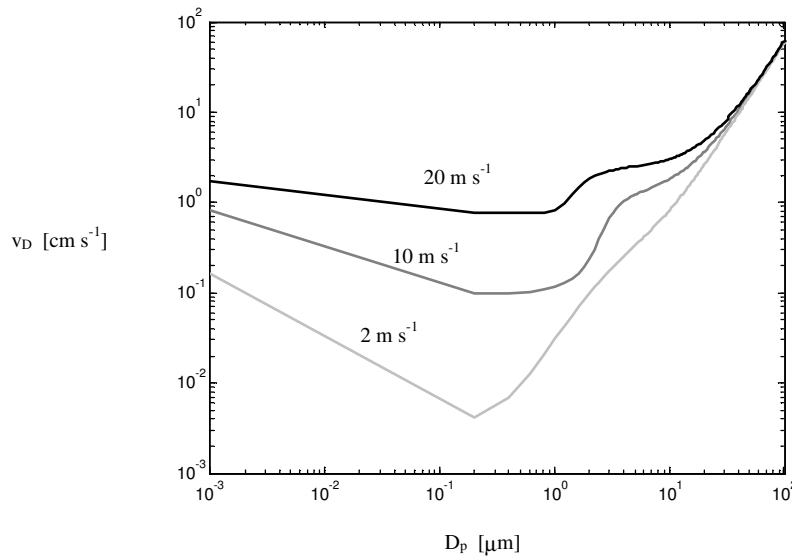
$$B = k_m [(1 - \alpha)(k_{as} + k_{ss}) + \alpha (k_{ab} + k_{bs}) + v_{s_wet}] + (1 - \alpha)(k_{as} + k_{ss} + v_{s_wet}) \alpha (k_{ab} + k_{bs} + v_{s_wet}) \quad [35]$$

The fraction of area that has a broken surface is represented by α . This value is strongly dependent on wind speed (u_{10} , cm s^{-1}) and can be calculated as:

$$\alpha = 1.7 \times 10^{-6} (u_{10} 10^{-2})^{3.75} \quad [36]$$

The lateral transfer coefficient (k_m , cm s^{-1}) is assumed equal k_{as} (Jurado et al., 2004).

Figure Annex 1.1: Dry deposition velocity versus wind speed. Assumptions: sea surface temperature of 298K, relative humidity about 80 %, aerosol density of 2 g cm^{-3} .



ANNEX II: PARAMETERIZATION OF WET DEPOSITION OF POPs

Traditionally W_G , defined as the ratio of the rain-dissolved phase to gas-phase POP concentrations, has been estimated using Henry's law constant (H , Pa m³ mol⁻¹), assuming that equilibrium is attained rapidly between the gas phase and the dissolved phase in a raindrop (Ligocki et al., 1984). However, field measured gas-washout of atmospheric POPs have found to be higher (Dickhut and Gustafson 1995; Poster et al., 1994; Poster et al., 1996; Roth et al. 2002). A recent study concluded that a better estimation of W_G is obtained when POP adsorption to the raindrop surface from the gas phase is considered (Simcik, 2004). Therefore, W_G is the sum of the absorption gas-phase washout (W_{G_diss}), and the gas-phase washout due to adsorption on the raindrop (W_{G_ads}):

$$W_G = W_{G_diss} + W_{G_ads} \quad [37]$$

$$W_{G_diss} = \frac{R \times T}{H} \quad [38]$$

$$W_{G_ads} = 2000 \times K_{ia} \times \Lambda \quad [39]$$

where T (K) and R (8.314 Pa m³ mol⁻¹ K⁻¹) are respectively the temperature and the ideal gas constant, K_{ia} (m³ m⁻²) the water interface/gas partitioning coefficient, described according to the sub-cooled liquid saturated vapor pressure in Simcik et al. (2004), and $\Lambda = 4.1 \cdot \left(\frac{1000 \cdot P_0}{24 \cdot f} \right)^{-0.21}$ (mm⁻¹) is a parameter of the exponential law proposed by Marshall and Palmer (1948) for the size distribution of raindrops. Temperature dependence of H has been estimated as suggested by Brunner et al. (1990). The inclusion of W_{G_ads} makes the parameterization of the gaseous removal of POPs by rain subject to the variability of the precipitation rate. This dependence has been observed in various studies (Mircea et al., 2000). Decreasing rainfall intensity increases W_{G_ads} because of the resulting increase of surface to volume ratio of the raindrop spectrum.

W_G values are in the range of 10^4 - $6 \cdot 10^4$ for PCDD/Fs and $5 \cdot 10^2$ - $3 \cdot 10^3$ for PCBs. They agree with field measurements such as $8 \cdot 10^3$ - $3 \cdot 10^6$ for PCDDFs in Eitzer and Hites (1989) in Bloomington U.S. (rural area), but overestimates up to an order of magnitude the range of $2 \cdot 10$ - $2 \cdot 10^2$ for PCBs measured by Van-Ry (2002) in coastal NW Atlantic ocean (Tuckerton, U.S., coastal area). It has been shown that the new parameterization (Eq. 39) has a stronger effect enhancing W_G for PCDD/Fs than for PCBs (Simcik 2003; Jurado et al. 2005). Since it improves the agreement with experimental data, the estimations reported here will be those given by Equation 39. Gas scavenging efficiency increases with the level of chlorination for both POPs.

Particle scavenging is the process by which rainfall removes aerosols and the compounds bound to those particles from the atmosphere (Franz and Eisenreich 1998; Nicholson et al. 1991; Koester and Hites, 1992; Mandalakis and Stephanou 2004). In contrast to gas scavenging, particle scavenging results not from equilibrium partitioning but rather from complex processes controlled by meteorological conditions, and physical-chemical properties of the aerosol. It is inferred that all the compounds bound to aerosols may be affected in a similar way (Ho et al., 1997). However, some authors as Franz et al. (1998) and Poster and Baker (1996) have measured higher particle washouts for the more volatile PCBs, suggesting that the lower molecular weight pollutants are associated with larger aerosols which are scavenged more easily. Such dependence can not be considered, since other studies that report size distribution of POPs suggest that these are mainly associated to small aerosols (Offenberg and Baker 2002). Reported average measured particle scavenging rates (W_p) are highly variable (Jurado et al., 2005). It can be explained by the complexity of the scavenging process and the natural variability of the aerosol population and meteorological conditions. In this line, Mircea et al. (2000) estimated scavenging coefficients that achieved maximums for urban aerosol and minimums for marine or continental aerosol, but almost no dependence on raindrop size distribution. Theoretically, scavenging rates are expected to increase with particle diameter (Poster et al. 1996; Koestler and Hites 1992), although to what extent is still not clear. Furthermore, there is not an evident dependence of the particle scavenging rate with the rainfall intensity (Radke et al., 1980). Therefore, in this modeling study an average value of $2 \cdot 10^5$ has been adopted, which is consistent with many reported measurements, and has been used in other modeling exercises (Jurado et al., 2005).

ANNEX III: UPTAKE DYNAMICS OF POPs IN PHYTOPLANKTON AND BACTERIA

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, 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.

$$F = -D \frac{dC}{dz} \quad [40]$$

where F is the flux of the chemical ($\text{ng m}^{-2} \text{d}^{-1}$), D is the molecular diffusivity and dC/dz is the gradient of the chemical concentration. Thus, the flux of a POP across the water-side layer ($F_{w,int}$, $\text{ng m}^{-2} \text{d}^{-1}$) is given by:

$$F_{w,int} = -D_w \frac{(C_w - C_{w,int})}{e_w} \quad [41]$$

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; D_w ($\text{m}^2 \text{d}^{-1}$) 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 ($F_{p,int}$, $\text{ng m}^{-2} \text{d}^{-1}$) can be described by Equation 42.

$$F_{p,int} = -D_p \cdot \delta_p \frac{(C_{p,int} - C_p)}{e_p} \quad [42]$$

where C_p (ng kg^{-1}) and $C_{p,int}$ (ng kg^{-1}) are the POP concentration in the phytoplankton matrix and at the phytoplankton-side of the interface, respectively; D_p ($\text{m}^2 \text{d}^{-1}$) 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 (BCF_M , $\text{m}^3 \text{kg}^{-1}$):

$$BCF_M = \frac{C_{p,int}}{C_{w,int}} \quad [43]$$

Since the flux through the water-side and phytoplankton-side must be equal (F_{P-W} , $\text{ng m}^{-2} \text{d}^{-1}$), from Equations 41-43 we obtain:

$$F_{P-W} = \frac{1}{\left(\frac{e_p}{D_p \cdot \delta_p \cdot BCF_M} + \frac{e_w}{D_w} \right)} \left(\frac{C_p}{BCF_M} - C_w \right) \quad [44]$$

Equation 44 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 BCF , 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 45 by the specific surface area of phytoplankton cells (S_p , $m^2 kg^{-1}$).

$$\frac{\partial C_p}{\partial t} = -k_u C_w + k_d C_p + k_G C_p + k_{meta} C_p \quad [46]$$

$$F_{P-W} = \frac{k_u}{S_p} \left(\frac{k_d + k_G + k_{meta}}{k_u} C_p - C_w \right) \quad [47]$$

where the BCF_M is also given by:

$$BCF_M = \frac{k_u}{k_d + k_G + k_{meta}} \quad [48]$$

where k_u ($m^3 kg^{-1} d^{-1}$) and k_d (d^{-1}) are the uptake and depuration rate constants, k_{meta} (d^{-1}) is the first order metabolization reaction rate and k_G (d^{-1}) 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 one day, it will have value of one.

Comparing Equations [45] and [48] 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:

$$k_d = \frac{S_p}{\left(\frac{e_p}{D_p \cdot \delta_p \cdot BCF_M} + \frac{e_w}{D_w} \right)} \cdot \frac{1}{BCF_M} \quad [49]$$

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

$$k_u = \frac{S_p}{\left(\frac{e_p}{D_p \delta_p BCF_M} + \frac{e_w}{D_w} \right)} \quad [50]$$

As determined by other studies, phytoplankton uptake is due to sorption into two different steps. 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

$$\frac{e_p}{D_p \cdot \delta_p \cdot BCF_M} \gg \frac{e_w}{D_w} \quad [51]$$

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

$$k_d = \frac{S_p \cdot D_p \cdot \delta_p}{e_p} \quad [52]$$

$$k_u = \frac{S_p \cdot D_p \cdot \delta_p \cdot BCF_M}{e_p} \quad [53]$$

The ratio k_u/S_p that appears in Equation 47 is the permeability (P , m d^{-1}) of the cell membrane, therefore, from Equation 52 an expression for permeability is derived (Equation 53). k_u and k_d can also be parameterized as a function of P (Equations 55 and 56).

$$P = \frac{D_p \delta_p BCF_M}{e_p} \quad [54]$$

$$k_d = \frac{S_p \cdot P}{BCF_M} \quad [55]$$

$$k_u = S_p \cdot P \quad [56]$$

So far, the development through Equations 10 to 56 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 45 and 47 by taking into account only the water-side boundary and substituting k_u , k_d and BCF_M by the adsorption (k_{ad} , $\text{m}^3 \text{kg}^{-1} \text{d}^{-1}$) and desorption (k_{des} , d^{-1}) rate constants and the bioconcentration factor at the surface (BCF_S , $\text{m}^3 \text{kg}^{-1}$). 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.

$$k_{des} = \frac{S_p \cdot D_w}{e_w \cdot BCF_S} \quad [57]$$

$$k_{ad} = \frac{S_p \cdot D_w}{e_w} \quad [58]$$

The expressions for uptake, depuration, adsorption and desorption rate constants allow to predict their values for a wide range of POPs, as well, 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.

Prediction of uptake and depuration rate constants: In order to use Equations 54-56 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 1025 kg m⁻³ (Jorgensen et al., 2000). 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 (Equation 59) (Reid et al., 1988).

$$D = \frac{7.4 \cdot 10^{-8} \cdot T(\phi_l M_l)^{1/2}}{\eta_l V_A^{0.6}} \quad [59]$$

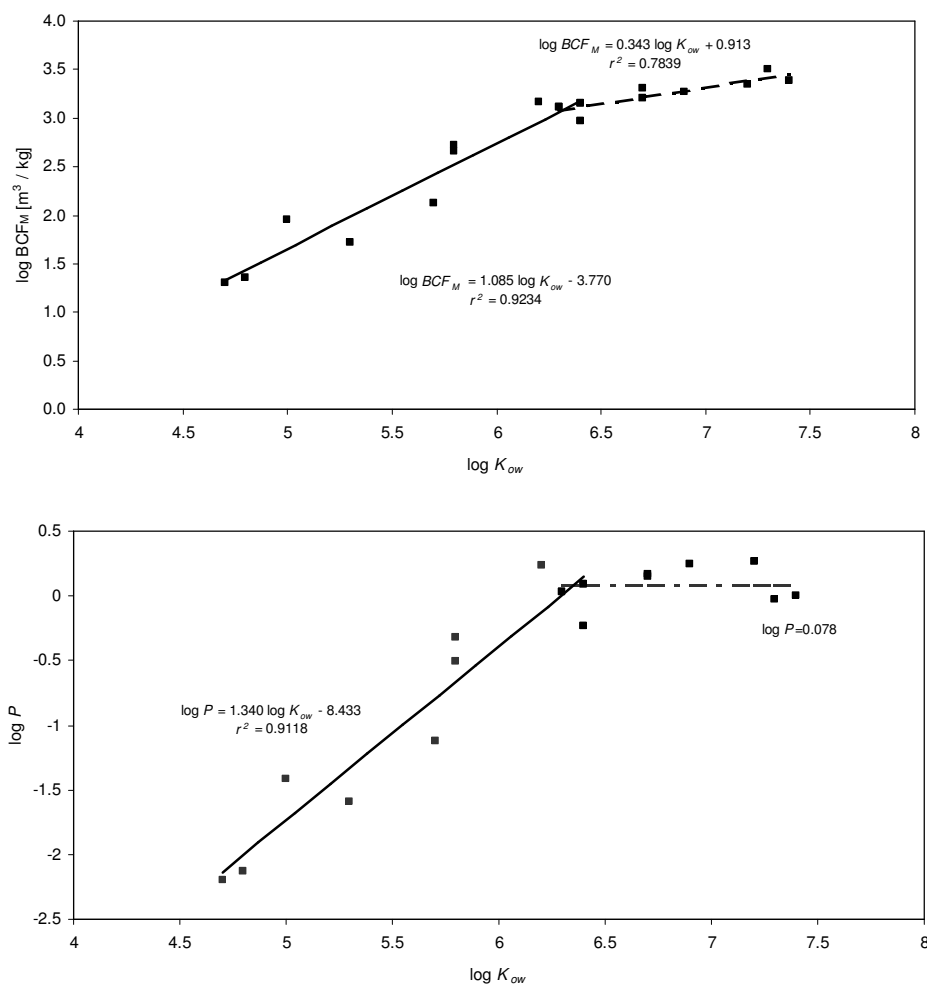
where T (K) is the temperature, M_l (g/mol) is the molecular weight of the solvent, ϕ is the association factor of the solvent (dimensionless), η_l (cP = 0.01 g s⁻¹ cm⁻¹) is the solvent viscosity and V_A (cm³ mol⁻¹) is the molar volume of chemical at its normal boiling temperature. However, the parameters used in this equation are largely unknown for the cellular membrane and therefore D_p can not be quantitatively predicted. Furthermore, BCF_M values have only been reported in few studies for PCBs (Skoglund et al., 1996; Wallberg and Andersson 1999), not for other POPs, and even very few of these report the numerical values (Dachs et al.; 1999). Since values for P and BCF_M for most POPs are largely unknown, in order to use Equations 55 and 56 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. (1999) which were obtained from uptake experiments by *Isochrysis galbana* done by Ko and coworkers (Table A3.1), BCF_M values were plotted against K_{ow} (Figure A3.1). As usually observed, there are two linear correlations between the logarithms of BCF_M and K_{ow} which can be fitted by least squares to the following equations depending on the hydrophobicity of the chemical (Swackhamer and Skoglund, 1991).

$$\log BCF_M = 1.085 \log K_{ow} - 3.770 \quad \text{for } \log K_{ow} < 6.4 \quad [60]$$

$$\log BCF_M = 0.343 \log K_{ow} + 0.913 \quad \text{for } \log K_{ow} \geq 6.4 \quad [61]$$

Figure A3.1. Dependence of the bioconcentrations factor (BCF_M) and permeability (P) on the physical-chemical properties of the chemical.



Equation 60 corresponds to chemicals with low to mid K_{ow} values which bioconcentrate in phytoplankton following well the hydrophobicity paradigm (Karickhoff et al., 1979) and is also similar to those reported by other studies of plankton bioconcentration of POPs (Rahman et al., 2001; Mailhot 1987). At high K_{ow} values there is a saturation of BCF_M values due to low solubility of the chemicals in the microorganism matrix and/or due to steric effects of large molecular size. 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 (Dachs et al.; 1999) by means of a QSAR that relates membrane permeability with the physical-chemical properties of the pollutant. Figure A3.1 shows the plot of permeability against K_{ow} and the obtained regressions which also depend of the compound physical-chemical properties.

$$\log P = 1.340 \log K_{ow} - 8.433 \quad \text{for } \log K_{ow} < 6.4 \quad [62]$$

$$\log P = 0.078 \quad \text{for } \log K_{ow} \geq 6.4 \quad [63]$$

The increase of permeability with the hydrophobicity of the chemical is consistent with reported trends for other non-ionic compounds and indicates a higher tendency of hydrophobic compounds to diffuse into the cell (Stein 1986). However, the saturation of the permeability for very hydrophobic molecules would indicate that molecules become either too large to diffuse into the cell or are not enough miscible in the microorganism matrix. BCF_M and P values estimated from Equations 59-62 allow to estimate the uptake and depuration rate constants for PCBs others than those reported elsewhere (Dachs et al., 1999) by means of Equations 55 and 56 (see Table A3.1). Furthermore, the present prediction procedure also allows predicting uptake for other POPs for which these properties are unknown. Tables A.3.2, A.3.3 and A.3.4 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.

Table A3.1. Physical-chemical properties and rate constants for polychlorinated biphenyls (PCBs). Italicize numbers are those reported elsewhere (Dachs et al., 1999) 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 microorganism with a radius of 2.7 μm .

<i>PCB</i>	<i>n^o</i> <i>Cl</i>	<i>log K_{ow}^a</i>	<i>TSA^a</i> (\AA^2)	<i>BCF_M</i> ($\text{m}^3 \text{kg}^{-1}$)	<i>P</i> (m d^{-1})	<i>k_u</i> ($\text{m}^3 \text{kg}^{-1} \text{d}^{-1}$)	<i>k_d</i> (d^{-1})	<i>BCF_S</i> ($\text{m}^3 \text{kg}^{-1}$)	<i>k_{ad}</i> ($\text{m}^3 \text{kg}^{-1} \text{d}^{-1}$)	<i>k_{des}</i> (d^{-1})
3	1	4.69	202.12	20	0.00711	8.2	0.41	24	3953	162.4
10	2	4.80	206.46	23	0.0100	9.7	0.43	38	3730	97.5
15	2	5.30	219.81	53	0.0467	33	0.62	83	3730	44.7
16	3	5.16	215.69	67	0.0303	39.2	0.58	118	3537	30.0
18	3	5.24	218.32	82	0.0388	50.1	0.61	139	3537	25.4
19	3	5.00	211.82	91	0.0185	50	0.55	90	3537	39.1
22	3	5.58	228.03	192	0.111	143.1	0.74	218	3537	16.2
28	3	5.67	230.83	241	0.146	188.9	0.78	241	3537	14.7
32	3	5.44	224.16	136	0.0720	92.9	0.69	187	3537	19.0
34	3	5.70	230.49	132	0.160	98	0.74	296	3537	12.0
37	3	5.83	235.42	359	0.240	309.5	0.86	278	3537	12.7
42	4	5.76	233.38	302	0.193	249.4	0.83	261	3369	12.9
43	4	5.75	233.21	294	0.187	241.8	0.82	260	3369	13.0
47	4	5.85	236.19	378	0.255	329.2	0.87	284	3369	11.9
48	4	5.78	234.10	317	0.205	265.3	0.84	267	3369	12.6
52	4	5.80	235.84	449	0.219	400	0.89	289	3369	11.7
56	4	6.11	243.63	723	0.569	734.4	1.02	344	3369	9.8
60	4	6.11	243.80	723	0.569	734.4	1.02	346	3369	9.7
64	4	5.95	239.04	485	0.347	448.2	0.92	307	3369	11.0
66	4	6.20	246.44	906	0.751	969.5	1.07	367	3369	9.2
74	4	6.20	246.43	906	0.751	969.5	1.07	367	3369	9.2
77	4	6.40	251.02	927	1.39	760	0.82	372	3369	9.1
82	5	6.20	246.36	906	0.751	969.5	1.07	367	3228	8.8
85	5	6.30	249.16	1163	1.022	1319.9	1.14	389	3228	8.3

89	5	6.07	242.48	654	0.503	649.1	0.99	335	3228	9.6
95	5	6.13	244.23	760	0.605	781.1	1.03	349	3228	9.2
97	5	6.30	248.99	1296	1.02	1400	1.08	369	3221	8.7
100	5	6.20	247.20	1477	0.751	2200	1.49	400	3221	8.1
101	5	6.40	251.62	1416	1.39	1600	1.13	421	3221	7.7
104	5	5.8	234.87	525	0.219	620	1.18	511	3221	6.3
105	5	6.70	259.41	1593	1.20	1800	1.13	400	3221	8.1
118	5	6.70	262.04	2021	1.20	1900	0.94	403	3221	8.0
123	5	6.74	262.04	1678	1.20	1544.9	0.92	396	3221	8.1
124	5	6.73	261.87	1665	1.20	1544.9	0.93	396	3228	8.2
126	5	6.90	266.63	1840	1.20	2300	1.25	421	3228	7.7
132	6	6.58	257.37	1479	1.20	1544.9	1.04	396	3089	7.8
136	6	6.22	246.95	1113	1.20	1544.9	1.39	396	3089	7.8
138	6	6.83	264.76	1801	1.20	1544.9	0.86	396	3089	7.8
141	6	6.82	264.59	1787	1.20	1544.9	0.86	396	3089	7.8
144	6	6.67	260.00	1587	1.20	1544.9	0.97	396	3089	7.8
147	6	6.64	259.29	1550	1.20	1544.9	1.00	396	3089	7.8
153	6	6.92	267.39	1934	1.20	1544.9	0.80	396	3089	7.8
156	6	7.20	275.01	2222	1.20	2400	1.08	382	3089	8.1
163	6	6.99	296.54	2044	1.20	1544.9	0.76	122	3089	25.4
170	7	7.30	277.74	3158	1.20	1200	0.38	292	2970	10.2
177	7	7.08	272.26	2195	1.20	1544.9	0.70	373	2970	8.0
180	7	7.40	280.37	2453	1.20	1300	0.53	285	2970	10.4
182	7	7.20	275.78	2413	1.20	1544.9	0.64	336	2970	8.8
185	7	7.11	272.98	2247	1.20	1544.9	0.69	365	2970	8.1
187	7	7.17	274.89	2356	1.20	1544.9	0.66	346	2970	8.6
190	7	7.46	283.40	2963	1.20	1544.9	0.52	258	2970	11.5
195	8	7.56	286.12	3206	1.20	1544.9	0.48	229	2863	12.5
201	8	7.62	287.87	3362	1.20	1544.9	0.46	211	2863	13.5
206	9	8.09	301.73	4873	1.20	1544.9	0.32	68	2766	40.7
208	9	7.71	290.59	3609	1.20	1544.9	0.43	183	2766	15.1

^a Hawker DW, Connell DW, 1988.

Table A3.2: Physical-chemical properties and predicted rate constants for polychlorinated dioxins (PCDD) and furans (PCDF) 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 .

	$n^\circ Cl$	$\log K_{ow}^a$	$TSA^{b,c}$ (\AA^2)	BCF_M ($\text{m}^3 \text{kg}^{-1}$)	P (m d^{-1})	k_u ($\text{m}^3 \text{kg}^{-1} \text{d}^{-1}$)	k_d (d^{-1})	BCF_S ($\text{m}^3 \text{kg}^{-1}$)	k_{ad} ($\text{m}^3 \text{kg}^{-1} \text{d}^{-1}$)	k_{des} (d^{-1})
PCDD	2	5.65	243.4*	229	0.138	178	0.8	342	3659	10.7
	3	6.35	272.8*	1317	1.193	1540	1.2	396	3475	8.8
	4	6.9	273.7	1904	1.196	1545	0.8	358	3315	9.2
	5	7.4	309	2826	1.196	1545	0.5	280	3172	11.3
	6	7.8	321	3875	1.196	1545	0.4	280	3045	10.9
	7	8.0	338	4538	1.196	1545	0.3	280	2931	10.5
	8	8.2	314.9	5315	1.196	1545	0.3	280	2828	10.1
	PCDF	2	5.0	216.6	46	0.019	25	0.5	125	3730
3		6.2 ^d	232	906	0.751	969	1.1	250	3537	14.1
4		7.7	247.7	3581	1.196	1545	0.4	378	3369	8.9
5		7.6	262.7	3309	1.196	1545	0.5	396	3221	8.1
6		7.7	274.7	3581	1.196	1545	0.4	347	3089	8.9
7		7.5	287.8	3058	1.196	1545	0.5	280	2970	10.6
8		7.6	300.4	3309	1.196	1545	0.5	280	2970	10.6

^aMackay et al., 1992; ^bDoucette and Andren, 1987; ^cDunn et al. 1986; ^dGovers and Krop, 1998; * evaluated from Doucette and Andren, 1987.

Table A3.3. 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 .

PAH	$\log K_{ow}^a$	TSA^b (\AA^2)	BCF_M ($\text{m}^3 \text{kg}^{-1}$)	P (m d^{-1})	k_u ($\text{m}^3 \text{kg}^{-1} \text{d}^{-1}$)	k_d (d^{-1})	BCF_S ($\text{m}^3 \text{kg}^{-1}$)	k_{ad} ($\text{m}^3 \text{kg}^{-1} \text{d}^{-1}$)	k_{des} (d^{-1})
Flourene	4.12	194.0	5	0.00122	1.58	0.32	24	4170	173.7
1-Methylfluorene	4.97	214.8	42	0.0169	21.8	0.52	110	3902	35.3
Phenanthrene	4.57	199.38	15	0.00491	6.34	0.41	24	4030	167.9
1-Methylphenanthrene	5.14	217.04	64	0.0285	36.8	0.57	128	3780	29.4
Anthracene	4.54	200.16	14	0.00448	5.78	0.40	24	4054	168.9
2-Methylanthracene	5.15	224.01	66	0.0294	38.0	0.58	185	3805	20.5
9-Methylanthracene	5.07	216.14	54	0.0230	29.7	0.55	121	3805	31.3
9,10-Dimethylanthracene	5.25	230.12	84	0.0400	51.7	0.61	235	3593	15.3
Pyrene	5.17	213.47	69	0.0313	40.4	0.58	100	3858	38.7
Flouranthene	5.17	218.63	69	0.0313	40.4	0.58	142	3826	27.0
Chrysene	5.84	240.15	368	0.247	319	0.87	316	3506	11.1
Benzo[a]anthracene	5.84	244.32	368	0.247	319	0.87	350	3531	10.1
Benzo[b+k]fluoranthene	6.44	262.87	1324	1.20	1545	1.17	396	3364	8.5
Benzo[a]pyrene	6.44	228.6	1324	1.20	1545	1.17	222	3409	15.3
Benzo[e]pyrene	6.44	227.78	1324	1.20	1545	1.17	216	3409	15.8
Perylene	6.44	251.46	1324	1.20	1545	1.17	396	3409	8.6

^aMackay et al., 1992; ^bPearlman et al., 1984; *evaluated from Doucette and Andren, 1987.

Table A3.4. 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 .

		$\log K_{ow}^a$	TSA^b (\AA^2)	BCF_M ($\text{m}^3 \text{kg}^{-1}$)	P (m d^{-1})	k_u ($\text{m}^3 \text{kg}^{-1} \text{d}^{-1}$)	k_d (d^{-1})	BCF_S ($\text{m}^3 \text{kg}^{-1}$)	k_{ad} ($\text{m}^3 \text{kg}^{-1} \text{d}^{-1}$)	k_{des} (d^{-1})
PBDE	# Br									
	3	5.5	237.1	158	0.087	112	0.7	396	3447	8.7
	4	6.0	258.7	570	0.424	548	1.0	396	3247	8.2
	5	6.8	291.9	1766	1.196	1545	0.9	280	3098	11.0
	6	7.4	315.8	2770	1.196	1545	0.6	280	2965	10.6
NP		4.5	195.0	13	0.004	5	0.4	24	3130	130

^aAlcock et al, 1999; *evaluated from Doucette and Andren, 1987.

Prediction of adsorption and desorption rate constants:

Prediction of adsorption and desorption rate constants (Equation 16-17) needs of 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 A3.2 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 \AA^2 .

$$BCF_S = 8.11TSA - 1631.33 \quad \text{for } TSA < 250 \text{ \AA}^2 \quad [64]$$

$$BCF_S = 396 \quad \text{for } 250 \leq TSA \leq 270 \text{ \AA}^2 \quad [65]$$

$$BCF_S = -10.34TSA + 3187.85 \quad \text{for } TSA > 270 \text{ \AA}^2 \quad [66]$$

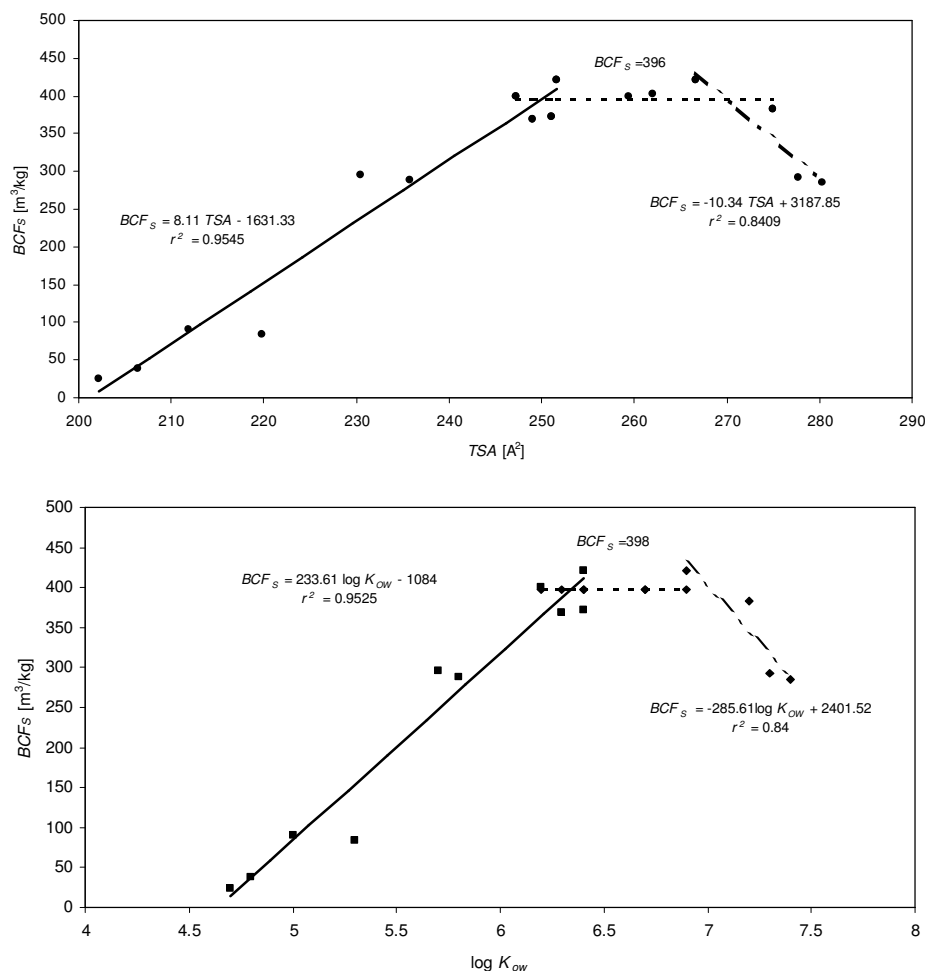
There is a strong correlation between TSA and K_{ow} for most POPs (Schwarzenbach et al., 2003), therefore BCF_S can also be predicted from K_{ow} values.

$$BCF_S = 233.61 \log K_{ow} - 1084.05 \quad \text{for } \log K_{ow} \leq 6.3 \quad [67]$$

$$BCF_S = 398 \quad \text{for } 6.3 \leq \log K_{ow} \leq 7.0 \quad [68]$$

$$BCF_S = -285.61 \log K_{ow} + 2401.52 \quad \text{for } \log K_{ow} \geq 7.0 \quad [69]$$

Figure A3.2: Dependence of the bioconcentration factor (BCF_S) on the physical-chemical properties of the chemical



Equations 60-61 are analogous to Equations 62-63 and representative of higher tendency to adsorption for chemicals with lower water solubility (higher K_{ow}) and at saturation for molecules with a higher TSA . However, for adsorption onto the surface, there is a decrease of BCF_S for compounds with very high K_{ow} values. This trend has also been reported by other phytoplankton species (Skoglund et al., 1996) and may be due to steric hindrance at the active sorption sites at the cellular surface. Equations 67-69 allow 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, 2 and 3). In order to predict the adsorption and desorption rate constants using Equations 49 and 50, D_W and e_W need to be estimated. Diffusivity in water can be estimated using Equation 59. 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, then e_W equals the radius of the microorganism (Wolf-Gladrow and Riebesell 1997). Tables A3.1-A3.4 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 A3.1 are different than those reported elsewhere (Dachs et al., 1999) 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 A3.1-A3.4 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 *Isochrysis 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, then large differences in temperatures are found which affects the environmental fate of POPs, and may effect 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 (Swackhamer et al., 1993), due to 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 (Equations 14-18) and $BCFs$, both for the matrix and the surface, depend on temperature due to changes in the activity coefficient in the organic phase.

$$\frac{BCF(T)}{BCF(298)} = \exp\left[\frac{\Delta H_s}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right] \quad [70]$$

where ΔH_s (KJ mol^{-1}) and R ($\text{KJ mol}^{-1} \text{K}^{-1}$) 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 (Schwarzenbach et al., 2003). In the present study, we assume an enthalpy of sorption of 35 KJ mol^{-1} for all the compounds (Shiu et al., 1997).

Given the uptake, depuration, adsorption and desorption rate constants at 25°C reported in Tables A3.1-A3.4, 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 71 and 72.

$$k_{ad}(T) = \frac{\eta_{H_2O}(298)}{\eta_{H_2O}(T)} \frac{T}{298} k_{ad}(298) \quad [71]$$

$$k_{des}(T) = \frac{\eta_{H_2O}(298)}{\eta_{H_2O}(T)} \frac{T}{298} \frac{BCF_S(298)}{BCF_S(T)} k_{des}(298) \quad [72]$$

Water viscosity is evaluated from the following empirical relationships depending on the temperature value (Lide, 2001):

For $273 < T < 293$

$$\log_{10} \eta_T = \frac{1301}{998.333 + 8.1855(T - 293) + 0.00585(T - 293)^2} - 3.30233 \quad [73]$$

For $293 < T < 373$

$$\log_{10} \frac{\eta_T}{\eta_{20}} = \frac{1.3272(293 - T) - 0.001053(T - 293)^2}{T - 168} \quad [74]$$

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

$$k_u(T) = \frac{\eta_P(298)}{\eta_P(T)} \frac{T}{298} \frac{BCF_M(T)}{BCF_M(298)} k_u(298) \quad [75]$$

$$k_d(T) = \frac{\eta_P(298)}{\eta_P(T)} \frac{T}{298} k_d(298) \quad [76]$$

Since phytoplankton viscosity (η_P) is unknown, we assume 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 75 and 76. The viscosity of octanol can be calculated by the Lewis-Squires empirical relationship (Reid et al., 1988).

$$\eta_P^{-0.2661}(T) = \eta_P^{-0.2661}(298) + \frac{T - 298}{233} \quad [77]$$

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 (Reid et al., 1988).

Figure A3.3 shows the temperature dependence of the rate constants in the 0-30C range. Depuration, desorption and adsorption rate constants increase with temperature due to enhanced diffusivity. Thus, uptake kinetics will be significantly faster in warm environments than in cold areas. Conversely, uptake rate constants show a constant or slightly decrease due to the influence of temperature on the BCF s which counteracts the influence of temperature on diffusivity.

Figure A3.3. Dependence of uptake (k_u), depuration (k_d), adsorption (k_{ad}) and desorption (k_{des}) rate constants on temperature.

