

Teasing out the Non-Linearity in the POPs-Phytoplankton Bioconcentration Processes

Mayumi SETO and Itsuki C. HANDOH

*Centre for Marine Environmental Studies (CMES), Ehime University,
Bunkyo-cho 2-5, Matsuyama 790-8577, Japan*

(Received 13 January 2009; accepted 9 March 2009)

Abstract—Phytoplankton play a vital role in determining the fate and transport of persistent organic pollutants (POPs). Phytoplankton lipids could accumulate POPs, and equilibrium partitioning of such chemicals between lipid and water can be deduced from the octanol/water partition coefficient (K_{ow}). However, there is much uncertainty about correlations between the bioconcentration factor (BCF) and K_{ow} , and also mathematical reasoning of the correlations has been lacking. Using two models for phytoplankton-driven bioconcentration, we examined previously-recognized non-linear relationship between K_{ow} and BCF . Our modelling study suggests that the non-linearity of K_{ow} - BCF relationship could be attributed to the apparent BCF (BCF estimated at non steady-state) that results from phytoplankton's slow uptake rate of chemicals with higher molecular volume, or higher K_{ow} .

Keywords: bioconcentration, persistent organic pollutants, two-film model, octanol-water coefficient, phytoplankton

INTRODUCTION

Phytoplankton play a vital role in determining the fate and transport of persistent organic pollutants (POPs) in aquatic systems (Swackhamer and Skoglund, 1991; Schwarzenbach *et al.*, 1993). Phytoplankton-driven POPs bioconcentration is followed by biomagnification through higher trophic-level organisms grazing activity and a persistent sink to the deeper oceans (Dachs *et al.*, 1999, 2000, 2002). Therefore, to better understand and quantify the phytoplankton-driven bioconcentration is of primary importance in order to predict both biomagnification and the ultimate fate of POPs in the marine ecosystems.

It is generally accepted that POPs are accumulated in organism lipids. Equilibrium partitioning of these chemicals between organism lipids and water can be deduced from the octanol-water partition coefficient (K_{ow}). The quantitative measure of bioconcentration for phytoplankton is the bioconcentration factor (BCF), which is defined by

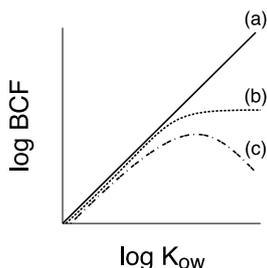


Fig. 1. Previously-reported K_{ow} - BCF relationships: (a) linear, (b) level off (non-linear), and (c) decrease (non-linear).

$$BCF = \frac{\text{POPs concentration in phytoplankton at steady state}}{\text{POPs concentration in dissolved phase at steady state}}. \quad (1)$$

If POPs concentrations are assumed to be in thermodynamic equilibrium, BCF should, by definition, be given by K_{ow} , i.e.,

$$BCF = K_{ow}. \quad (2)$$

However, previous experimental and field studies (Swackhamer and Skoglund, 1993; Stange and Swackhamer, 1994; Koelmans *et al.*, 1999; Gerofke *et al.*, 2005) suggested some non-linear relationships between K_{ow} and BCF . While a K_{ow} - BCF linearity is confirmed at $K_{ow} < 10^6$, $\log K_{ow}$ - $\log BCF$ relationship at $K_{ow} > 10^6$ could take one of the following three shapes: (a) linear, (b) level off (non-linear), and (c) decrease (non-linear) (Fig. 1). This could in part be due to the fact that the permeabilities of cell membranes and lipid bilayers appear to exhibit a steep dependence on molecular volume of solute which passes through the membranes (Opperhuizen *et al.*, 1985; Gobas *et al.*, 1988; Xiang and Anderson, 1994). For example, some steric hindrance effects for molecular weight >350 g/mol (Connell, 1990) or molecular volume >0.25 nm³ (Shaw and Connell, 1984) were observed in higher-trophic level organisms such as trout and mullet (Shaw and Connell, 1984; Opperhuizen *et al.*, 1985; Niimi and Oliver, 1988; Connell, 1990).

In the present study, using simple mathematical models that represent the phytoplankton-driven POPs bioconcentration processes, we examine two models to clarify the molecular size-dependent non-linearity of BCF against K_{ow} .

MATERIAL AND METHODS

Following Del Vento and Dachs (2002), here we introduce the two-film model and the first-order differential equations model, in Subsection “Two-film model” and “First-order differential equations model”, respectively.

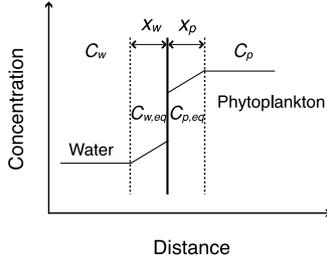


Fig. 2. Schematics of the two-film model. The symbols are summarized in Table 1. See also Del Vento and Dachs (2002).

Two-film model

The two-film model (Liss and Slater, 1974; Schwartzenbach *et al.*, 1993; Del Vento and Dachs, 2002) is used to describe the water-phytoplankton exchange that is influenced by size-dependent permeability in water and phytoplankton side interfaces (Fig. 2). The model assumes that chemical mass transfer is limited by the rate of molecular diffusion through thin films of water and phytoplankton cell on either side of the surface. The POPs fluxes through water and phytoplankton side layers, F_w and F_p (both $\text{ng m}^{-3} \text{d}^{-1}$), respectively, can be calculated from Fick's first law:

$$F_w = -D_w \frac{C_w - C_{w,eq}}{x_w} \quad (\text{water side}), \quad (3)$$

$$F_p = -D_p \frac{\delta(C_{p,eq} - C_p)}{x_p} \quad (\text{phytoplankton side}), \quad (4)$$

where D_w and D_p are the molecular diffusion coefficients of POPs in water and lipid bilayer membranes (both $\text{m}^2 \text{d}^{-1}$). C_w and $C_{w,eq}$ are the POPs concentrations in water and at the water side of the interface (both ng m^{-3}). C_p and $C_{p,eq}$ are the POPs concentrations in phytoplankton and at the phytoplankton side of interface (both ng kg^{-1}). x_w and x_p are the thicknesses of water and phytoplankton side layers. δ is the phytoplankton density (kg m^{-3}). The symbols are summarized in Table 1.

First-order differential equations model

To obtain an apparent *BCF* (i.e., C_p/C_w at both steady state and non-steady state), POPs uptake and depuration processes of phytoplankton is modelled by differential equations. It is common practice to assume that the POPs transport to and desorption from phytoplankton are first-order processes. Assuming that

Table 1. The variables and parameters used in the two-film model and the first-order differential equations model.

Symbol	Definition	Unit
Variables		
C_w	POPs concentration in water	ng m^{-3}
C_p	POPs concentration in phytoplankton	ng kg^{-1}
Parameters		
F_w	POPs flux through water side layer	$\text{ng m}^{-3} \text{d}^{-1}$
F_p	POPs flux through phytoplankton side layer	$\text{ng m}^{-3} \text{d}^{-1}$
D_w	Molecular diffusion coefficient of POPs in water	$\text{m}^2 \text{d}^{-1}$
D_p	Molecular diffusion coefficient of POPs in lipid bilayer membranes	$\text{m}^2 \text{d}^{-1}$
$C_{w,eq}$	POPs concentrations at the water side of the interface	ng m^{-3}
$C_{p,eq}$	POPs concentrations at the phytoplankton side of the interface	ng kg^{-1}
x_w	Thickness of water side layer	m
x_p	Thickness of phytoplankton side layer	m
δ	Phytoplankton density	kg m^{-3}
f_u	Uptake rate of chemicals by phytoplankton	$\text{m}^3 \text{kg}^{-1} \text{d}^{-1}$
f_d	Depuration rate of chemicals by phytoplankton	d^{-1}
r	Radius of the microorganism	m
D^0	Constant dependence on the molecular viscosity of solvent	$\text{m}^2 \text{d}^{-1}$
V	Molecular volume of the diffusing chemicals	Å
n_w	Size-dependent partitioning coefficient in water	—
n_p	Size-dependent partitioning coefficient in lipid bilayer membranes	—
a	Size-dependent diffusion coefficient in lipid bilayer membranes	—
S_p	Specific surface area of phytoplankton	$\text{m}^2 \text{kg}^{-1}$

POPs in the system occur in either phytoplankton or their surrounding media, the governing equations are,

$$\frac{dC_w}{dt} = -f_u C_w + f_d \delta C_p, \quad (5)$$

$$\frac{dC_p}{dt} = f_u C_w - f_d \delta C_p, \quad (6)$$

where t is time (d), f_u ($\text{m}^3 \text{kg}^{-1} \text{d}^{-1}$) and f_d (d^{-1}) are the uptake and depuration rates.

RESULTS AND DISCUSSION

Using the above-mentioned mathematical models, in this section, we provide new insights into K_{ow} -dependent bioconcentration processes.

K_{ow} dependence of chemical transfer at the interface

For the two-film model, the POPs concentrations at the interface are

assumed to be in thermodynamic equilibrium:

$$\frac{\delta C_{p,eq}}{C_{w,eq}} = K_{ow}. \quad (7)$$

The net flux of POPs between water and phytoplankton, F_{pw} ($\text{ng m}^{-2} \text{d}^{-1}$) is then given by Eqs. (3), (4) and (7):

$$F_{pw} = K_{pw} \left(\frac{\delta C_p}{K_{ow}} - C_w \right), \quad (8)$$

$$K_{pw} = \frac{1}{\frac{x_p}{D_p K_{ow}} + \frac{x_w}{D_w}}, \quad (9)$$

where K_{pw} (m d^{-1}) is the net phytoplankton-water transfer coefficient.

Although the parameters used in Eq. (9) are largely unknown, we can quantify them from previously-reported theoretical and empirical equations. Assuming a spherical shape for phytoplankton, the thickness of the water side (x_w) equals the radius of the microorganism, r (m) (Wolf-Glandrow and Riebesell, 1997). For a continuous liquid medium like water, an equation having the form of the Stokes-Einstein relation is used for the diffusion coefficient as

$$D_w = D^0 V^{-n_w}, \quad (10)$$

where D^0 is a constant depending on the viscosity and V is the molecular volume of the diffusing chemicals (Xiang and Anderson, 1994). Hildebrand (1977) suggested that the size-dependent partitioning coefficient, n_w , depends mainly on the cross-sectional area of the molecules, or simply $n_w = 2/3$ (see also Wilk and Change (1955) who suggested that n_w is close to 0.6). Total molecular volume data of PCBs by Opperhuizen *et al.* (1988) shows a linear relationship with logarithms of K_{ow} ,

$$V = 11.6 \ln(K_{ow}) + 100.82. \quad (11)$$

Having substituted Eq. (11) into Eq. (10), we yield D^0 from a fit of diffusivities of PCBs calculated from Schmids Numbers (Hornbuckle *et al.*, 1994) to D_w ($D^0 = 6.47 \times 10^{-5} \text{ m d}^{-1}$ at 0°C (wind speed 1.34 m s^{-1}) and $D^0 = 1.03 \times 10^{-4} \text{ m d}^{-1}$ at 15°C (wind speed 1.34 m s^{-1})). Following Xiang and Anderson (1994), the diffusion coefficient-size dependency in lipid bilayer is described as

$$D_p = D^0 e^{-\alpha V} V^{-n_p}, \quad (12)$$

with $a = 0.0053$ and $n_p = 0.8$. a is the size-dependent diffusion coefficient.

K_{ow} dependence of the apparent BCF

The net flux of POPs between water and phytoplankton is alternatively obtained by dividing Eq. (5) by the specific surface area, S_p ($\text{m}^2 \text{kg}^{-1}$):

$$F_{pw} = \frac{f_u}{S_p} \left(\frac{f_d}{f_u} \delta C_p - C_w \right), \quad (13)$$

$$K_{pw} = \frac{f_u}{S_p}. \quad (14)$$

Assuming a spherical shape to phytoplankton, S_p is given by dividing the surface area by the weight,

$$S_p = \frac{4\pi r^2}{\delta \times \frac{4}{3}\pi r^3} = \frac{3}{\delta r}. \quad (15)$$

Setting Eq. (5) to 0, we obtain the equilibrium condition of this model:

$$\frac{\delta C_{p,eq}}{C_{w,eq}} = \frac{f_u}{f_d} = K_{ow}. \quad (16)$$

f_u is given as the function of K_{ow} by combining Eqs. (9)–(12) and (14)–(16):

$$f_u = \frac{3}{\delta r} \times \frac{D^0 K_{ow}}{x_p e^{\alpha V} V^{n_p} + r V^{n_w} K_{ow}}. \quad (17)$$

Then, the apparent BCF, BCF_a , is obtained from solving Eqs. (5) and (6):

$$BCF_a = \frac{f_u \left(\delta C_p^0 + C_w^0 \left(1 - e^{-(f_u + f_d)t} \right) \right) + f_d \delta C_p^0 e^{-(f_u + f_d)t}}{f_d \left(C_w^0 + \delta C_p^0 \left(1 - e^{-(f_u + f_d)t} \right) \right) + f_d C_w^0 e^{-(f_u + f_d)t}}, \quad (18)$$

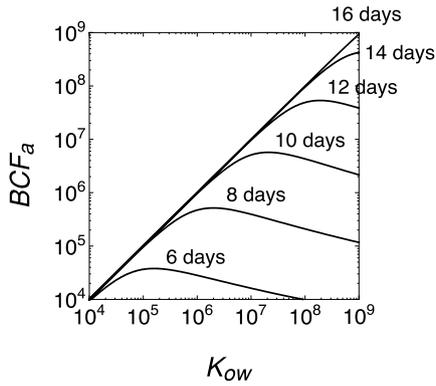


Fig. 3. Apparent BCF_a for various K_{ow} at each time step (days). The parameters used here are $r = 8 \times 10^{-5}$, $D^0 = 1.03 \times 10^{-4}$, $a = 0.05$, $n_w = 0.6$, $n_p = 0.8$.

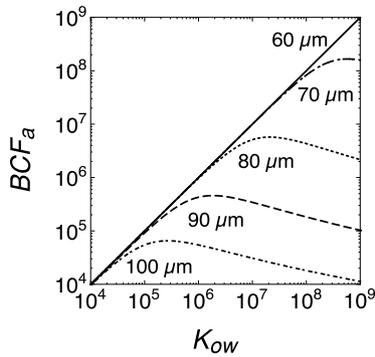


Fig. 4. Apparent BCF_a against K_{ow} for various r (proxy for phytoplankton size). The parameters used here are $t = 10$ days, $D^0 = 1.03 \times 10^{-4}$, $a = 0.05$, $n_w = 0.6$, $n_p = 0.8$.

where C_p^0 and C_w^0 are the initial POPs concentrations in phytoplankton and their surrounding media, respectively. Assuming $C_p^0 = 0$ and $1 + 1/K_{ow} \approx 1$, BCF_a is reduced to

$$BCF_a \approx \frac{K_{ow}(1 - e^{-f_a t})}{1 + K_{ow}e^{-f_a t}}. \tag{19}$$

Differentiating BCF_a with respect to K_{ow} yields

$$\frac{dBCF_a}{dK_{ow}} = \frac{1 - e^{-f_u t} + e^{-f_u t} f_u' K_{ow} (1 + K_{ow}) t}{(1 + e^{-f_u t} K_{ow})^2}. \quad (20)$$

Since f_u' can be both positive and negative depending on the parameters, the apparent BCF may be capable of explaining the decreasing pattern in Fig. 1.

The effect of steric hindrance on non-linearity of the apparent BCF against K_{ow}

Combining Eqs. (17) and (19) allows us to numerically predict the response of apparent BCF to K_{ow} , provided the assumption of $x_p = r$, which is shown in Fig. 3. The chemicals with lower K_{ow} , or lower molecular volume, are quickly equilibrated because of the rapid uptake rate of such chemicals through cell membrane. However, the uptake rate of chemicals with higher K_{ow} is too slow to attain the equilibrium, which can reproduce the previously-observed K_{ow} - BCF non-linear relationships (Fig. 1). Laboratory experiments on the phytoplankton-driven POPs bioconcentration demonstrated that the equilibration time varies from a few minutes or hours (Sijm *et al.*, 1998; Koelmans *et al.*, 1999; Halling-Sørensen *et al.*, 2000; Gerofke *et al.*, 2005) to several days or weeks (Swackhamer and Skoglund, 1993; Stange and Swackhamer, 1994).

The equilibration time depends on not only the property of chemicals but also size of phytoplankton. Figure 4 shows the non-steady BCF against K_{ow} for various r at $t = 10$ days, which demonstrates that the larger phytoplankton require longer equilibration time. This might also indicate that the system is not at equilibrium.

In conclusion, the longer equilibration time can be required for chemicals with higher K_{ow} because of the phytoplankton's slow uptake rate due to the size-dependent permeability of chemicals through the lipid bilayer of phytoplankton. Thus, previously-observed K_{ow} - BCF non-linear relationships are likely to be attributed to the apparent BCF at non-steady state. Our modelling study has provided mathematical insights into the non-linearity in POPs-phytoplankton bioconcentration processes. In order to evaluate further on the model parameters we have adopted, further laboratory and field investigations into phytoplankton-driven POPs bioconcentration processes are needed.

REFERENCES

- Connell, D. W. (1990): *Bioaccumulation of Xenobiotic Compounds*. CRC, Boca Raton, FL, U.S.A.
- Dachs, J., S. J. Eisenreich, J. E. Baker, F.-C. Ko and J. D. Jeremiason (1999): Coupling of phytoplankton uptake and air-water exchange of persistent organic pollutants. *Environ. Sci. Technol.*, **33**, 3653–3660.
- Dachs, J., S. J. Eisenreich and R. M. Hoff (2000): Influence of eutrophication on air-water exchange, vertical fluxes, and phytoplankton concentrations of persistent organic pollutants. *Environ. Sci. Technol.*, **34**, 1095–1102.
- Dachs, J., R. Lohmann, W. A. Ockenden, L. Méjanelle, S. J. Eisenreich and K. C. Jones (2002): Oceanic biogeochemical controls on global dynamics of persistent organic pollutants. *Environ. Sci. Technol.*, **36**, 4229–4237.

- Del Vento, S. and J. Dachs (2002): Prediction of uptake dynamics of persistent organic pollutants by bacteria and phytoplankton. *Environ. Toxicol. Chem.*, **21**, 2099–2107.
- Gerofke, A., P. Komp and M. S. McLachlan (2005): Bioconcentration of persistent organic pollutants in four species of marine phytoplankton. *Environ. Toxicol. Chem.*, **24**, 2908–2917.
- Gobas, F. A. P. C., J. M. Lahittete, G. Garofalo, W. Y. Shiu and D. Mackay (1988): A novel method for measuring membrane-water partition coefficients of hydrophobic organic chemicals: comparison with 1-octanol-water partitioning. *J. Pharm. Sci.*, **77**, 265–272.
- Halling-Sørensen, B., N. Nyholm, K. O. Kusk and E. Jacobsson (2000): Influence of nitrogen status on the bioconcentration of hydrophobic organic compounds to *Selenastrum capricornutum*. *Ecotoxicol. Environ. Saf.*, **45**, 33–42.
- Hildebrand, J. H. (1977): *Viscosity and Diffusivity*. John Wiley & Sons., New York.
- Hornbuckle, K. C., J. D. Jeremiason, C. W. Sweet and S. J. Eisenreich (1994): Seasonal Variations in Air-Water Exchange of Polychlorinated Bisphenyls in Lake Superior. *Environ. Sci. Technol.*, **28**, 1491–1501.
- Koelmans, A. A., H. van der Woude, J. Hattling and D. J. M. Niesten (1999): Long-term bioconcentration kinetics of hydrophobic chemicals in *Selenastrum capricornutum* and *Microcystis aeruginosa*. *Environ. Toxicol. Chem.*, **18**, 1164–1172.
- Liss, P. S. and P. G. Slater (1974): Flux of gases across the air-sea interface. *Nature*, **247**, 181–184.
- Niimi, A. J. and B. G. Oliver (1988): Influence of molecular weight and molecular volume on dietary adsorption efficiency of chemicals by fishes. *Can. J. Fish Aquat. Sci.*, **45**, 222–227.
- Opperhuizen, A., E. W. van de Velde, F. A. P. C. Gobas, D. A. K. Liem and J. M. D. van der Steen (1985): Relationship between bioconcentration of hydrophobic chemicals in fish and steric factor. *Chemosphere*, **15**, 1871–1896.
- Opperhuizen, A., F. A. P. C. Gobas and J. M. D. Van der Steen (1988): Aqueous solubility of polychlorinated biphenyls related to molecular structure. *Environ. Sci. Technol.*, **22**, 638–646.
- Schwartzenbach, R. P., P. M. Gschwend and E. M. Imboden (1993): *Environmental Organic Chemistry*. Wiley-Interscience, New York.
- Shaw, G. R. and W. Connell (1984): Physicochemical properties controlling polychlorinated biphenyl (PCB) concentrations in aquatic organisms. *Environ. Sci. Technol.*, **18**, 18–23.
- Sijm, D. T. H. M., K. W. Broersen, D. F. de Roode and P. Mayer (1998): Bioconcentration kinetics of hydrophobic chemicals in different densities of *Chlorella pyrenoidosa*. *Environ. Toxicol. Chem.*, **17**, 1695–1704.
- Stange, K. and D. L. Swackhamer (1994): Factors affecting phytoplankton species-specific differences in accumulation of 40 polychlorinated biphenyls (PCBs). *Environ. Toxicol. Chem.*, **13**, 1849–1860.
- Swackhamer, D. L. and R. S. Skoglund (1991): *Organic Substances and Sediments in Water, Vol. II*. Lewis Publishers, Boca Raton, FL, U.S.A.
- Swackhamer, D. L. and R. S. Skoglund (1993): Bioaccumulation of PCBs by algae: kinetics versus equilibrium. *Environ. Toxicol. Chem.*, **12**, 831–838.
- Wilke, C. R. and P. Change (1955): Correlation of diffusion coefficients in dilute solutions. *AIChE J.*, **1**, 264–270.
- Wolf-Glandrow, D. and U. Riebesell (1997): Diffusion and reactions in the vicinity of plankton: A refined model for inorganic carbon transport. *Mar. Chem.*, **59**, 17–34.
- Xiang, T.-X. and B. D. Anderson (1994): The relationship between permeant size and permeability in lipid bilayer membranes. *J. Membrane Biol.*, **140**, 111–122.