

# Supporting Information

*to Activity-based Concept for Transport and Partitioning of Ionizing Organics*

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This SI contains additional information on how equations and parameters were derived, all input data and intermediate results.

## Table of Contents

Alternative definition of activity

Permeability

$K_{OC}$  of organic ionics

$\log D$  - apparent  $\log K_{OW}$ .

Bioconcentration factor fish, empirical method

Permeability

Table with environmental data (Table SI1)

Table with compound properties (Table SI2)

Input data for the calculation of bulk activity capacity  $B$  of compartments (Table SI3)

Additional Literature cited in SI

## Alternative definition of activity

An alternative, well-known definition of activity uses molar fraction as concentration unit and the pure compound as reference state. The dimensionless activity  $a^*$  of a compound in solution is basically defined via the chemical potential  $\mu$  ( $\text{J mol}^{-1}$ )

$$\mu = \mu^0 + RT \ln a^* \quad (\text{A1})$$

where  $\mu^0$  is the standard potential at the reference state. If the concentration of components in ideal or non-ideal mixtures is described by the molar fraction  $x$  ( $\text{mol mol}^{-1}$ ), then, the most practical reference state for activity is the pure compound, i.e.

$$\mu = \mu^0 + RT \ln(x \gamma_x) \quad (\text{A2})$$

and the relation of activity to the molar fraction,  $x$  ( $\text{mol mol}^{-1}$ ), is

$$x \gamma_x = \frac{a^*}{x} \quad (\text{A3})$$

$\gamma_x$  is a dimensionless factor, the so-called activity coefficient, which accounts for deviations from ideal behaviour (the superscript  $x$  indicates that this coefficient is related to molar fraction), with the constraint for the pure compound that

$$\lim_{x \rightarrow 1} x \gamma_x = \lim_{x \rightarrow 1} \frac{a^*}{x} = 1 \quad (\text{A4a})$$

$$\text{or } x \gamma_x \rightarrow 1 \text{ for } x \rightarrow 1 \quad (\text{A4b})$$

Compare this to the equations when concentration is given as molarities  $C$  ( $\text{mol L}^{-1}$  or  $\text{mol m}^{-3}$ ). Then, the relation between chemical potential and activity is

$$\mu = \mu^0 + RT \ln(c \gamma_c C) \quad (\text{A5})$$

An activity coefficient related to molar fraction,  $\gamma_x$ , differs in its numerical value from the activity coefficient related to molarity,  $\gamma_c$  (SI):

$$^c\gamma \rightarrow 1 \text{ for } C \rightarrow 0 \quad (\text{A6})$$

In infinitely diluted aqueous solutions ( $C$  of all electrolytes is 0), activity  $a$  defined this way is identical to the truly dissolved aqueous concentration,  $C_w$ . Therefore, it is important to define clearly the reference state when calculating with activities. Equation A4 has been referred to as the Raoult's Law convention and eq. A6 as Henry's Law convention.

## **$K_{OC}$ of organic ionics**

The partition coefficient organic carbon to water  $K_{OC}$  ( $\text{L kg}^{-1}$ ) (here soil-water partition coefficient normalized to organic carbon) is calculated using new regression equations of Franco and Trapp (49) for organic ionics:

$$\text{for acids, neutral molecules: } \log K_{OC} = 0.54 \times \log K_{OW,n} + 1.11 \quad (\text{A7a})$$

$$\text{for acids, anion: } \log K_{OC} = 0.11 \times \log K_{OW,n} + 1.54 \quad (\text{A7b})$$

$$\text{for bases, neutral molecules: } \log K_{OC} = 0.37 \times \log K_{OW,n} + 1.70 \quad (\text{A7c})$$

$$\text{for bases, cation (1): } \log K_{OC} = 0.42 \times \log K_{OW} + 2.19 \quad (\text{A7d})$$

$$\text{for bases, cation (2): } \log K_{OC} = pK_a^{0.65} \times f^{0.14} \quad (\text{A7e})$$

where  $\log K_{OW,n}$  is the octanol-water partition coefficient of the neutral molecule, and  $f$  is calculated from the apparent  $K_{OW}$  at pH 7 (the  $D_{\text{pH}=7}$ ):  $f = D/(D + 1)$ . The calculation of  $\log D$  is described below. For cations, two different approaches were developed:

- (1) is a regression obtained by log-linear regression. It considers only lipophilic interaction.
- (2) is a method obtained by non-linear fit to the data. It weighs more the electrical properties of the cation and was used in this study. The authors apologize for mistyping the  $K_{OC}$ -regression of the acid in the second paper (50), even in the erratum.

The  $K_d$  results from the multiplication of  $K_{OC}$  with organic carbon content and density (Eqn. 41). This approach was used in all compartments, except for the adsorption of neutral molecules to aerosols (solids in air compartment), which was calculated by a method derived from Harner and Bidleman (S/2) and corrected as recommended by Götz et al. (S/3):

$$K_{d,n,A} = 0.54 \times K_{OW} \times OC \times \rho_{S,A} \quad (\text{A7f})$$

where  $K_{d,n,A}$  is the partition coefficient between aerosols and water in air ( $\text{m}^3 \text{m}^{-3}$ ).

## Log $D$ apparent log $K_{ow}$

The lipophilicity of ionics at a given pH is often described by the apparent  $K_{ow}$ , also named  $D$ , which is composed of the contribution of the neutral molecule,  $K_{ow,n}$  and the contribution of the ionic molecule,  $K_{ow,i}$

$$D = \phi_n \times K_{ow,n} + \phi_i \times K_{ow,i} \quad (A8)$$

From experimental values, the average relation between  $\log K_{ow,n}$  and  $\log K_{ow,i}$  was found to be  $\log K_{ow,i} = \log K_{ow,n} - 3.5$  (37).

## Bioconcentration factor fish, empirical method

The bioconcentration factor (BCF) is the ratio of total concentration in fish  $C_{t,F}$  to truly dissolved concentration in water  $C_{free,W}$ . In dilute solutions, such as freshwater systems, the truly dissolved concentration of a chemical in water is approximately equal to its activity,  $a_{t,W}$  (the difference in our example with  $I$  is 0.003 mol L<sup>-1</sup> is 6% for the monovalent ion and 0.2% for the neutral species), therefore

$$C_{t,F}(\text{empirical}) \cong a_{t,W} \times BCF(\text{empirical}) \quad (A9)$$

An empirical regression for the BCF stems from *Veith* (14). For ionics, the  $\log D$  at given pH was successfully used as parameter for prediction (40):

$$\log BCF = 0.85 \times \log D - 0.70 \quad (A10)$$

## Permeability $P$

If the layer or the membrane is uncharged, then

$$J = P(a_o - a_i)$$

where  $J$  [ $\text{kg m}^{-2} \text{s}^{-1}$ ] is the net flux per unit area from outside into the compartment, and  $P$  [ $\text{m s}^{-1}$ ] is the permeability, which is defined as

$$P = \frac{K \times D}{\Delta x}$$

where  $K$  is the partition coefficient between the phase, in which the transport occurs, and the phase to which the activity is related (water),  $D$  is the effective diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ ) and  $\Delta x$  (m) is the thickness of the boundary layer.

### Example: Transfer between water and air

Diffusion between water and air is usually described by the two-film theory. To come from water to air (and vice versa), a molecule needs to diffuse first through a stagnant water film, and then through a stagnant air film. At the boundary is local equilibrium, both activities are equal.

**Water-side.** The flux  $J$  through the water-side boundary layer is:

$$J_W = P_{n,W}(a_{n,W} - a_{n,W}^*) + P_{i,W}(a_{i,W} - a_{i,W}^*)$$

where the index \* indicates the activity directly at the boundary between air and water. The diffusion coefficient of the neutral compound and that of the ion in water are approximately equal, and the partition coefficient between water and water is unity. Thus, the permeabilities of neutral molecule and ion can be set equal, and

$$J_W = P_W(a_{n,W} + a_{i,W} - a_{n,W}^* - a_{i,W}^*)$$

$P_W$  is identical with the well-known liquid side transfer velocity  $k_l$ .

The *Henderson-Hasselbalch* equation describes the activity ratio of ionic molecules to neutral ones,  $D_W$ .

$$J_W = P_W (a_{n,W} + D_W \times a_{n,W} - a_{n,W}^* - D_W \times a_{n,W}^*)$$

or

$$J_W = P_W (1 + D_W)(a_{n,W} - a_{n,W}^*)$$

With  $\frac{1}{\phi_n} = 1 + D_W$  ( $\phi_n$  being the neutral fraction) we get

$$J_W = \frac{P_W}{\phi_n}$$

**Air-side.** The activity of the ion in air was set to zero, and the flux through the air-side resistance is only of the neutral molecule:

$$J_A = P_A (a_{n,A} - a_{n,A}^*)$$

At the interface, the diffusion is in local equilibrium, but only for the neutral activity, thus

$$J_A = P_A (a_{n,A} - a_{n,W}^*)$$

The permeability  $P_A$  for the air boundary layer is

$$P_A = \frac{K_{AW} \times D_G}{z_A} = K_{AW} \times k_g$$

where  $D_G$  is the diffusion coefficient in the gas phase,  $z_A$  is the thickness of the laminar layer (air-side),  $k_g$  [ $\text{m s}^{-1}$ ] is the well-known air-side transfer resistance and  $K_{AW}$  is the partition coefficient between air and water [ $\text{L L}^{-1}$ ].

**Overall flux.** The gradient for the flux is in both equations to  $a_{n,W}^*$  which means the fluxes can be added. Both layers are in series. *Kirchhoff's Law* requires that resistances in series are added. The resistance  $r$  [ $\text{s m}^{-1}$ ] is the inverse of the permeability  $P$  [ $\text{m s}^{-1}$ ], thus the overall permeability for transfer from water to air,  $P_{WA}$  [ $\text{m s}^{-1}$ ] is

$$P_{WA} = \frac{1}{\frac{\phi_{n,W}}{P_W} + \frac{1}{P_A}}$$

or, in traditional nomenclature

$$P_{WA} = \frac{1}{\frac{\phi_{n,W}}{P_W} + \frac{1}{P_A}} = \frac{1}{\frac{\phi_{n,W}}{k_l} + \frac{1}{K_{AW} \times k_g}}$$

The overall flux from water to air (or vice versa) is

$$J_{WA} = P_{WA} \{a_{n,W} - a_{n,A}\}$$

Only the neutral molecule exchanges, and in equilibrium, the neutral activities will be equal. The contribution of the ions in water is to increase the velocity of transfer on the water side.

#### **Compatibility with traditional approach.**

The relation between activity and concentration is

$$a = C / B$$

where  $B_W$  (pure water) was  $1/\gamma_n$  (for ideal behaviour = 1), and  $B_A$  (pure gas phase) was  $K_{AW}$ . This into the equation

$$J_{WA} = P_{WA} (a_{n,W} - a_{n,A})$$

gives

$$J_{WA} = P_{WA} \left( C_{n,W} - \frac{C_{n,A}}{K_{AW}} \right)$$

The activity approach leads to the same result as the traditional, concentration-based approach, if non-ideal behaviour and dissociation are excluded. More permeabilities are derived in reference (34), SI. The permeability approach was also used in (S/4).

## Table with environmental data

**Table SI1.** Data of environmental compartments (analogous to (42), except volume, pH and I).

Compartment	Volume (m <sup>3</sup> )	Gas (L/L)	Water (L/L)	Solids (L/L)	OC (kg/kg)	$\rho_s$ (kg/L)	pH	I (mol/L)
Freshwater	$3 \times 10^6$	0	1	$6 \times 10^{-6}$	0.1	2.5	6 to 9	0.003
Air	$5 \times 10^8$	1	$2 \times 10^{-7}$	$2 \times 10^{-11}$	0.1	2.0	5.6	$2 \times 10^{-4}$
Sediment	$3 \times 10^4$	0	0.8	0.2	0.05	2.5	5.4 to 8.4 <sup>a</sup>	0.003
Fish	1	0	0.95	0.05	-	-	7.0	0.3

<sup>a</sup> The pH in the aqueous phase of the sediment is the same as the pH in lake water, but the pH in the organic matter of sediment (solid phase) is in average 0.6 units lower (49).

## Table with compound properties

**Table SI2.** Data of example compounds (45);  $\log K_{OW}$  is partition coefficient octanol to water;  $S$  is solubility in water;  $p_s$  is saturation vapor pressure at 12°C;  $K_{AW}$  is partition coefficient between air and water, calculated from  $S$  and  $p_s$ . All four properties are for the neutral molecule species.

Name	$z$	$pK_a$	$\log K_{OW}$ (L/L)	$S$ (mol/m <sup>3</sup> )	$p_s$ (Pa)	$K_{AW}$ (L/L)
Trimethoprim	+1	7.20	0.79	1.31	$2.35 \times 10^{-10}$	$7.34 \times 10^{-14}$
Ibuprofen	-1	4.41	3.72	0.32	$3.4 \times 10^{-3}$	$4.37 \times 10^{-6}$



## Input data for the calculation of bulk activity capacity $B$ of compartments

Results of pre-calculations for activity capacities  $B$  at pH 6 and pH 9 are shown in Table SI3.

**Table SI3.** Calculated values of neutral and ionic fraction  $\phi$ , activity coefficient  $\gamma$ , partition coefficient to organic carbon  $K_{OC}$  and sorption to lipids in fish  $L \times K_{OW}$  for neutral (n) and ionic (i) molecules of trimethoprim and ibuprofen at pH 6 and pH 9. W is water; A is air; S is sediment; SS is solids in sediment.

Parameter	Trimethoprim	Trimethoprim	Ibuprofen	Ibuprofen
	lake pH 6	lake pH 9	lake pH 6	lake pH 9
$\phi_{n,W}$	0.06	0.98	0.025	$2.6\times 10^{-6}$
$\phi_{i,W}$	0.94	0.02	0.975	1
$\phi_{n,A}$	0.025		0.06	
$\phi_{i,A}$	0.975		0.94	
$\phi_{n,SS}^a$	0.016	0.94	0.09	$10^{-4}$
$\phi_{i,SS}^a$	0.984	0.06	0.91	1
$\phi_{n,F}$	0.39		$2.5\times 10^{-3}$	
$\phi_{i,F}$	0.61		0.9975	
$\gamma_{n,W}$ and $\gamma_{n,S}$	1.0			
$\gamma_{i,W}$ and $\gamma_{i,S}$	0.94			
$\gamma_{n,AW}$	1.0			
$\gamma_{i,AW}$	0.98			
$\gamma_{n,F}$	1.23			
$\gamma_{i,F}$	0.74			
$K_{d,n,A}$ aerosols	2.55		2172	
$K_{OC,n}$ (L kg <sup>-1</sup> )	98		1 315	
$K_{OC,i}$ (L kg <sup>-1</sup> )	2726		89	
$L\times K_{OW,n}$ (L L <sup>-1</sup> )	0.3		262	
$L\times K_{OW,i}$ (L L <sup>-1</sup> )	$10^{-4}$		0.1	

<sup>a</sup> a dissociation in the water phase of sediment,  $\phi_{SW}$ , is identical to that in lake water,  $\phi_{WW}$ . Dissociation in the solid phase of sediment,  $\phi_{SS}$ , was calculated for a pH which is 0.6 units lower than the pH in the lake and in the aqueous solution of sediment (49).

## Additional Literature Cited in SI

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