

Accessory publication

FLUXY: a simple code for computing steady-state metal fluxes at consuming (bio)interfaces, in natural waters

Zeshi Zhang,^A Jacques Buffle,^{A,B} Konstantin Startchev^A and Davide Alemani^A

^AAnalytical and Biophysical Environmental Chemistry (CABE), University of Geneva, Sciences II, 30 quai E. Ansermet, 1211 Geneva 4, Switzerland.

^BCorresponding author. Email: jacques.buffle@cabe.unige.ch

The reaction layer approximation (FLUXY-RLA)

The version 3.0 (used in the present paper) of *FLUXY-RLA* has been improved, compared with the algorithm described in ref [18], to include a more general expression of the reaction layer thickness, *r.l.t.* The basic expression for the latter is given by ref [9]:

$$r.l.t. = \sqrt{D_M \times \tau} \quad (A1)$$

where D_M is the diffusion coefficient of free M, and τ the life-time of free M. The *r.l.t.* is thus the maximum distance that can be covered by M to reach the consuming interface before recombining with L, to form ML. Conventionally, it is expressed as μ (Eqn A2^[3,9,10]), under conditions of most laboratory experiments, i.e. (i) for sufficiently strong complexes ($K[L] = [ML]/[M] \gg 1$, which also corresponds to $k_a[L] \gg k_d$); (ii) for $D_{ML} \approx D_M$; and (iii) for $\mu \ll \delta$ (Fig. 1).

$$\mu = \sqrt{\frac{D_M}{k_a[L]}} \quad (A2)$$

where k_a = association rate constant of ML, and $[L]$ = concentration of free L. In the algorithm discussed in ref [18], each complex is characterised by a specific value of μ , corresponding to its specific value of $k_a[L]$.

It has been shown, however^[11], that in environmental systems where $k_a[L]$ is not necessarily much larger than k_d (weak complexes) and/or where D_{ML} may be much smaller than D_M (complexes with colloidal complexants), the reaction layer of a complex ML is given by the more general expression, λ :

$$\lambda = \sqrt{\frac{D_M}{k_a[L] + k_d \varepsilon^{-1}}} \quad (A3)$$

where $\varepsilon = D_{ML}/D_M$. In addition, it has also been shown^[11] that when the reaction layer is not much smaller than the diffusion layer, λ should be corrected by $\tanh(\delta/\lambda)$ and becomes: $\lambda \times \tanh(\delta/\lambda)$. When $\delta/\lambda \rightarrow \infty$, $\lambda \times \tanh(\delta/\lambda) \rightarrow \lambda$, and when $\delta/\lambda \rightarrow 1$, $\lambda \times \tanh(\delta/\lambda) \rightarrow \delta$.

By comparing Eqns A1 and A3, one gets:

$$\tau = \frac{1}{k_a[L] + k_d \varepsilon^{-1}} \quad (\text{A4})$$

In a mixture of m ligands, iL , each one reacting with M to form a semi- or non-labile complex, M^iL , M has only one single lifetime given by:

$$\tau = \frac{1}{\sum_{i=1}^m ({}^i k_a [{}^i L] + {}^i k_d \varepsilon^{-1})} \quad (\text{A5})$$

to which corresponds a ‘composite’ reaction layer, $\bar{\lambda}$:

$$\bar{\lambda} = \sqrt{\frac{D_M}{\sum_{i=1}^m ({}^i k_a [{}^i L] + {}^i k_d \varepsilon^{-1})}} \quad (\text{A6})$$

In *FLUXY* version 3.0, the computation of the metal flux in a mixture of n ligands, numbered 1 to n forming 1/1 complexes M^iL , considers the existence of n composite reactions layers, and a diffusion layer, δ . The reactions layers are sorted from the thinner (${}^1\bar{\lambda}$) to the thicker (${}^n\bar{\lambda}$). According to the reaction layer approximation, between the distances $x = {}^n\bar{\lambda}$ and $x = \delta$, all complexes are supposed to be fully labile, i.e. their formation and dissociation rates are supposed to be instantaneous. Between $x = {}^{n-1}\bar{\lambda}$ and $x = {}^n\bar{\lambda}$, only the complex M^nL behaves in a semi- or non-labile manner and must be considered for the computation of the lifetime of M . Reactions with other ligands are instantaneous and do not play a role on τ . Thus

$$\begin{aligned} {}^n\bar{\lambda} &= \sqrt{\frac{D_M}{{}^n k_a [{}^n L] + {}^n k_d \varepsilon^{-1}}} \\ &= \sqrt{\frac{D_M}{{}^n \kappa}} \end{aligned} \quad (\text{A7})$$

Between $x = {}^{n-2}\bar{\lambda}$ and $x = {}^{n-1}\bar{\lambda}$, only the complexes M^nL and $M^{n-1}L$ behave in a semi- or non-labile manner. Thus:

$$\begin{aligned} {}^{n-1}\bar{\lambda} &= \sqrt{\frac{D_M}{{}^{n-1} k_a [{}^{n-1} L] + {}^{n-1} k_d \varepsilon^{-1} + {}^n k_a [{}^n L] + {}^n k_d \varepsilon^{-1}}} \\ &= \sqrt{\frac{D_M}{{}^{n-1} \kappa + {}^n \kappa}} \end{aligned} \quad (\text{A8})$$

The general expression for the composite reaction layer j is thus:

$${}^j\bar{\lambda} = \frac{D_M}{\sqrt{\sum_{i=j}^n {}^i\kappa}} \quad (\text{A9})$$

with ${}^i\kappa$ sorted out in decreasing order, from 1 to n . Each value of ${}^j\bar{\lambda}$ is then corrected by the term $\tanh(\delta/{}^j\bar{\lambda})$ for the reason explained above, and used as the successive reaction layers in the algorithm of *FLUXY*, as explained in ref [18].

Complementary results

Table A1. Conditions of ligand/metal ratios used to evaluate the error due to the assumption of ligand excess (*Limitation due to non excess of ligand section*)

$$\log K = 7$$

Conditions	$[L]_t$ (mol L ⁻¹)	$[M]_t$ (mol L ⁻¹)	$[M]$ (mol L ⁻¹)	$[L]$ (mol L ⁻¹)	$[ML]$ (mol L ⁻¹)	$[ML]/[L]$
1	0.00101	0.001	6.15×10^{-6}	1.62×10^{-5}	9.94×10^{-4}	61.53
2	0.0011	0.001	9.89×10^{-7}	1.01×10^{-4}	9.99×10^{-4}	9.892
3	0.002	0.001	1.00×10^{-7}	0.001	0.001	0.9998
4	0.011	0.001	1.00×10^{-8}	0.01	0.001	0.1

Table A2. Association rate constants and diffusion coefficients used in the modified Aquil culture medium

Association rate constants are computed by using the generalised Eigen mechanism as explained in ref [4]. Diffusion coefficients are also taken from ref [4]

Species	k_a (M ⁻¹ s ⁻¹)			D (m ² s ⁻¹)		
	Cd ^{II}	Pb ^{II}	Zn ^{II}	Cd ^{II}	Pb ^{II}	Zn ^{II}
MOH ⁺		6.05×10^9	3.55×10^7		9.45×10^{-10}	7.03×10^{-10}
MCl ⁺	1.78×10^8	5.22×10^9	3.55×10^7	1.13×10^{-9}	1.13×10^{-9}	1.13×10^{-9}
MCl ₂ ⁰	7.86×10^7	2.62×10^9		1.13×10^{-9}	1.13×10^{-9}	1.13×10^{-9}
MCl ₃ ⁻	3.33×10^7	1.19×10^9		1.13×10^{-9}	1.13×10^{-9}	1.13×10^{-9}
MCl ₄ ²⁻		4.97×10^8			1.13×10^{-9}	1.13×10^{-9}
MCO ₃ ⁰		1.10×10^{10}	1.27×10^8		9.45×10^{-10}	7.03×10^{-10}
MCO ₄ ⁰	6.34×10^8	1.15×10^{10}	1.27×10^8	7.19×10^{-10}	9.45×10^{-10}	7.03×10^{-10}

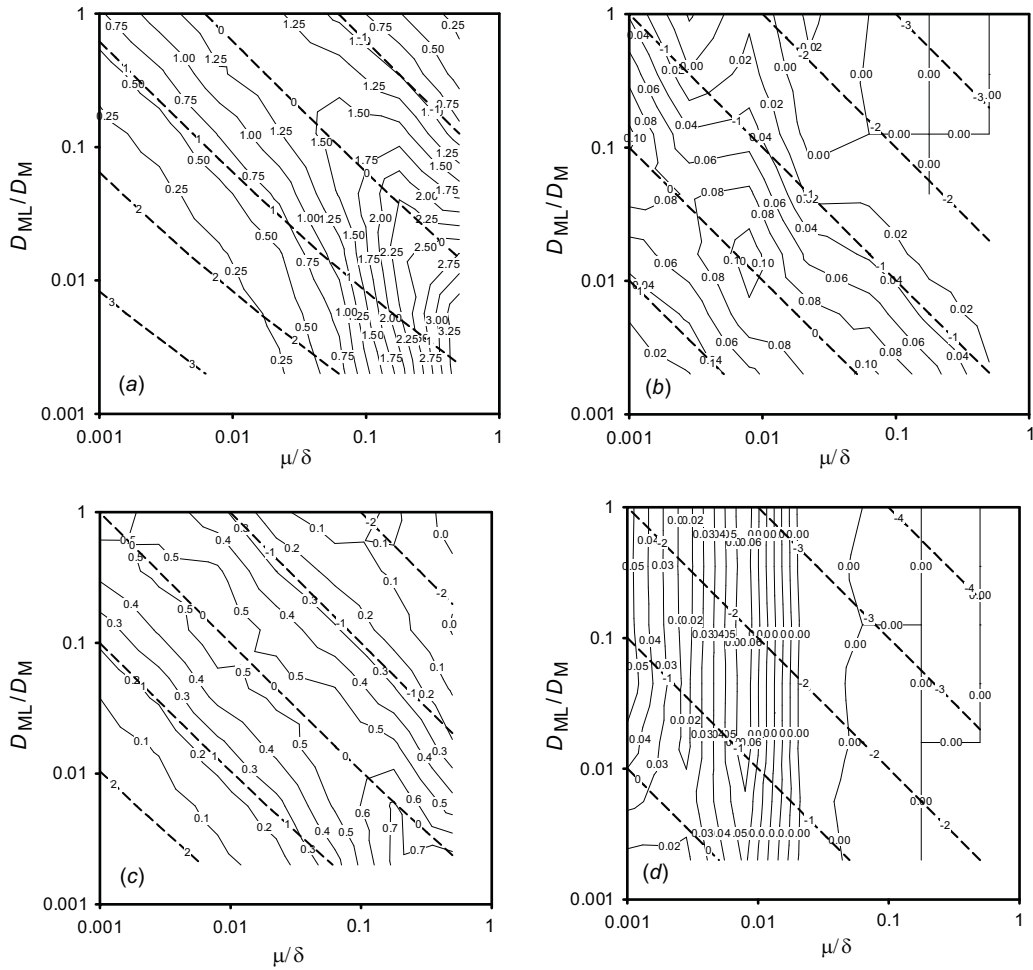


Fig. A1. Contour plots of the relative errors (fraction of 1) on the degree of lability, ξ , given by *FLUXY-RS*, due to the assumption of ligand excess. (a) $[ML]^*/[L]^* = 61.5$; (b) $[ML]^*/[L]^* = 9.89$; (c) $[ML]^*/[L]^* = 1.00$; (d) $[ML]^*/[L]^* = 0.10$, $K = 10^7 \text{ M}^{-1}$, $D_M = 7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $D_L = D_{ML}$.

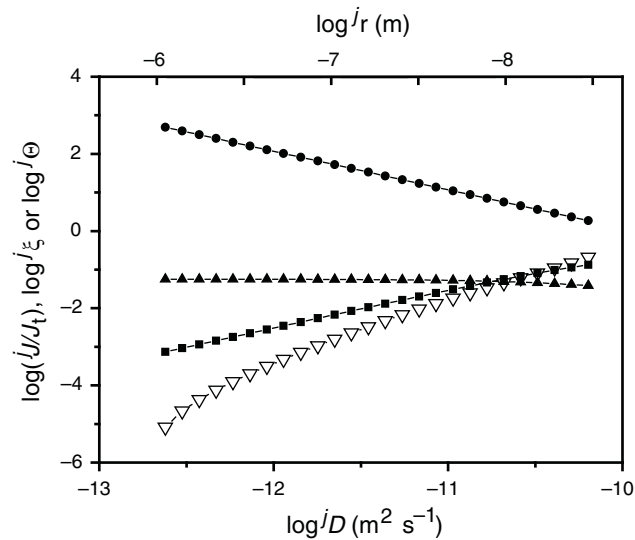


Fig. A2. Comparison of individual fluxes of Cu complexes with aggregates, computed with *MHDYN* and *FLUXY-RLA*. \blacktriangle , $^j\xi$; \bullet , $^j\theta$; \blacksquare , $^jJ/J_1$ *MHDYN*; ∇ , $^jJ/J_1$ *FLUXY*. Free Cu, 0.00127%; Cu-aggregates, 99.9%; conditions, see Table 6.

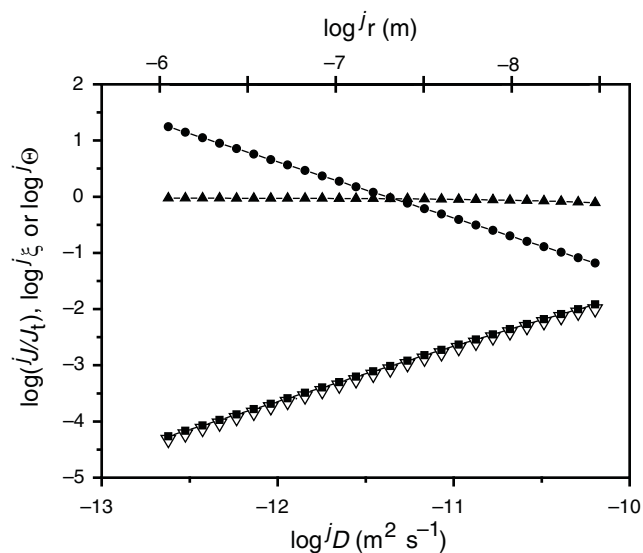


Fig. A3. Comparison of individual fluxes of Zn complexes with aggregates, computed with *MHEDYN* and *FLUXY-RLA*. ▲, $^j\xi$; ●, $^j\theta$; ■, $^jJ/J_t$ *MHEDYN*; ▽, $^jJ/J_t$ *FLUXY*. Free Zn, 17.7%; Zn–aggregates, 79.5%; conditions, see Table 6.

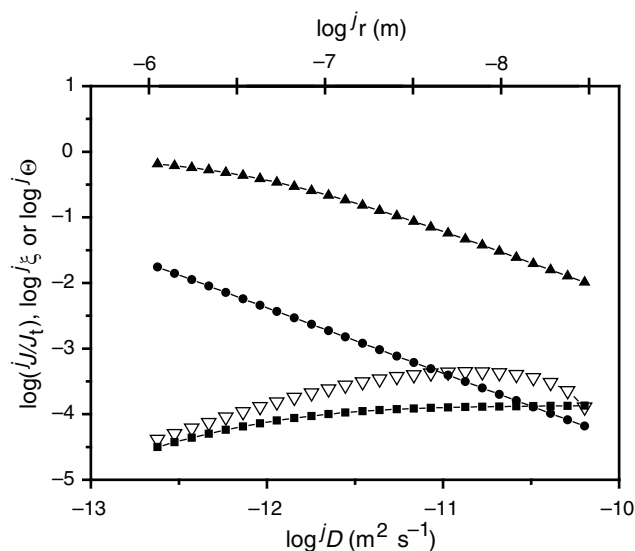


Fig. A4. Comparison of individual fluxes of Ni complexes with aggregates, computed with *MHEDYN* and *FLUXY-RLA*. ▲, $^j\xi$; ●, $^j\theta$; ■, $^jJ/J_t$ *MHEDYN*; ▽, $^jJ/J_t$ *FLUXY*. Free Ni, 21% ; Ni–aggregates, 79%; conditions, see Table 6.