FLUXY MANUAL . ADDENDUM FOR FLUXY VERSION 3.11

1. The main changes compared to FLUXY version 2.01

In the version 3.11 of FLUXY, FLUXY-RLA has been improved, compared to the algorithm described in [1] and used in version 2.01. A first improvement had been made in [2], to include a more general expression of the reaction layer thicknesses, based however on a semi-empirical approach. The present version of FLUXY-RLA is based on rigorous mathematical derivation [3] of the reaction layer thicknesses in mixtures of ligands, taking also into account the possible presence of successive complexes for each ligand. When using FLUXY-RLA, FLUXY version 3.11 is thus recommended. FLUXY-RS is not changed at all in version 3.11 compared to version 2.01.

The general expression for the reaction layer thickness, r.l.t, is given by [4]:

$$r.l.t = \sqrt{(D_M.\tau)} \qquad (1)$$

where D_M is the diffusion coefficient of free M, and τ the life-time of free M. The reaction layer thickness is thus the maximum distance which can be covered by M to reach the consuming interface before recombining to L, to form the complex ML. Conventionally, it is expressed as μ (eq. 2 [4,5]), under conditions of most laboratory experiments, i.e. i) for sufficiently strong complexes ($K[L] = [ML]/[M] >> 1$ which also corresponds to $k_a[L] >> k_d$), ii) for $D_{ML} \sim D_M$ and iii) for $\mu << \delta$.

$$\mu = \sqrt{\frac{D_M}{k_a[L]}} \qquad (2)$$

where k_a , k_d= association and dissociation rate constants of ML, $K = k_a/k_d$, and [L] = concentration of free L. This expression is used in the algorithm discussed in [1], and in FLUXY-RLA version 2.01, where each complex is characterized by a specific value of μ, corresponding to its specific value of $k_a[L]$.

It has been shown however [6], 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 in a solution containing only one ligand, L, is given by the more general expression, λ:

$$\lambda = \sqrt{\frac{D_M}{k_a[L] + k_d/\varepsilon}} \tag{3}$$

where $\varepsilon = D_{ML}/D_M$. In addition, it has also been shown [6] that when the reaction layer is not much smaller than the diffusion layer, δ, λ should be corrected by the term $\tanh(\delta/\lambda)$ so that the effective (=corrected) reaction layer thickness, ${}^c\lambda$, becomes:

$${}^c\lambda = \lambda.\tanh(\delta/\lambda)$$

For conditions of semi-infinite diffusion (where $\delta/\lambda \to \infty$), $\tanh(\delta/\lambda) \to 1$ and ${}^c\lambda \sim \lambda$. At the other extreme, when λ is much larger than δ, $(\delta/\lambda << 1)$, $\tanh(\delta/\lambda) \to \delta/\lambda$, and ${}^c\lambda = \delta$. This reflects the fact that the effective reaction layer thickness cannot be larger than δ.
By comparing eqs 1 and 3, one gets:

$$\tau = \frac{1}{k_a[L] + k_d/\varepsilon} \tag{4}$$

In a mixture of n_l ligands, ${}^jL$, each ligand react with M to form a fully-, semi- or non-labile complex, M^jL, with possible successive complexes, M^jL_i ($j = 1 \ldots n_l$; $i = 1..{}^jm$), where n_l is the total number of ligands and ${}^jm$ is the maximum number of ligand ${}^jL$ bound to M. It has been shown in [3] that, under the following conditions:

a) each ligand ${}^jL$ is in excess with respect to the metal (i.e. $[{}^jL]_t >> [M]_t$; where $[X]_t$ is the total concentration of X), and
b) all the successive complexes with the ligand ${}^jL$ are always in fast equilibrium (i.e. the slow chemical kinetics occur only for the reactions between M and M^jL)

then, each set of complexes M^jL_i ($i = 1 \ldots {}^jm$) has a so-called composite reaction layer thickness, $\overline{\lambda}_j$, given by:

$$\overline{\lambda}_j = \sqrt{\frac{D_M}{\sum_{i=j}^{n_l} {}^ik_{a1}[{}^iL]/\alpha'_{j-1} + {}^jk_{d1}/q_j}} \tag{5}$$

where

$$\alpha'_j = 1 + \sum_{i=1}^{j} \sum_{k=1}^{{}^jm} {}^i\varepsilon_k \, {}^i\beta_k [{}^iL]^k \tag{6}$$

with $\alpha'_0 = 1$, ${}^i\varepsilon_k = D_{M^jL_k}/D_M$ and

$$q_j = \frac{1}{{}^j\beta_1} \sum_{k=1}^{{}^j m} {}^j\varepsilon_k \, {}^j\beta_k \, [{}^jL]^{k-1} \qquad (7)$$

The computation of the effective reaction layer thickness, ${}^c\overline{\lambda}_j$ (see above), in a mixture of ligands ${}^jL$, is then computed as follows:

i - The parameters ${}^j\kappa = {}^jk_{d1}/ q_j$ are computed for all ligands ${}^jL$ and sorted out in their decreasing order, from 1 to n_l. As shown in [7], the composite reaction layer thicknesses increase according to the decreasing order of ${}^j\kappa$.

ii- the α'_j's and q_j's are computed, with this new order of ligands, ${}^jL$.

iii- the values of $\overline{\lambda}_j$ are then computed from eq. 5 and the effective (corrected) values ${}^c\overline{\lambda}_j$ are obtained iteratively by starting with ${}^c\overline{\lambda}_{n_l}$

$${}^c\overline{\lambda}_{n_l} = \overline{\lambda}_{n_l} . \tanh\left(\frac{\delta}{\overline{\lambda}_{n_l}}\right) \qquad (8)$$

$${}^c\overline{\lambda}_j = \overline{\lambda}_j \tanh\left(\frac{{}^c\overline{\lambda}_{j+1}}{\overline{\lambda}_j}\right) \qquad (9)$$

The values of ${}^c\overline{\lambda}_j$ then replace the μ_j values (eqs (2)), in the algorithm of FLUXY-RLA [1].

2. A few results

FLUXY-RLA, in FLUXY version 3.11, is significantly more performant than in version 2.01, or even in the improved version described in [2], in particular when the medium includes a large number of complexes with similar values of rate constants. For FLUXY-RLA, version 3.11 is thus recommended compared to version 2.01. In particular FLUXY RLA version 3.11 is applicable with fulvics, even though caution should be used. In FLUXY-RLA version 2.01, the expressions used for the reaction layer thicknesses (eq.2) impies that all complexes behave independently from each other. Comparing the results of versions 3.11 and 2.01 may thus be useful to evaluate the degree of kinetic interplay between the complexes in the mixture.

In absence of successive complexes, FLUXY-RS remains the best option since it is a rigorous mathematical solution [7]. In presence of successive complexes however it is not usable and FLUXY-RLA version 3.11 provides good results in most cases.

2.1. Flux of Pb(II) in a modified Aquil medium, at a planar consuming interface working as a parfect sink,

This case is discussed in details in [3].

Table 1. Composition of the modified Aquil culture medium. T= 25°C, I=0.576 M, pH=8. (Note: the original Aquil medium includes 5 10^{-6} M EDTA, and no NTA or IDA)

Component	Concentration (M)	Component	Concentration (M)
Na	0.4801	Cl	0.556
Mg	0.0546	SO_4	0.0288
Ca	0.0105	CO_3	0.00283
K	0.01023	Br	$8.40\ 10^{-4}$
Sr	$6.38\ 10^{-5}$	H_3BO_3	$4.85\ 10^{-4}$
Fe	$4.51\ 10^{-7}$	NO_3	$1.00\ 10^{-4}$
Mn	$2.3\ 10^{-8}$	F	$7.14\ 10^{-5}$
NH_4	$9\ 10^{-9}$	Citrate	$5.00\ 10^{-6}$
Zn	$4.00\ 10^{-9}$	SiO_3	$1.25\ 10^{-5}$
Co	$2.50\ 10^{-9}$	PO_4	$1.00\ 10^{-5}$
Pb	$2\ 10^{-9}$	MoO_4	$1.05\ 10^{-8}$
Cu	$9.97\ 10^{-10}$	IDA	$5.00\ 10^{-5}$
Cd	$5\ 10^{-10}$	NTA	$3.00\ 10^{-5}$

Table 2. Dynamic parameters of Pb species for the simulation of the Pb(II) flux in the modified Aquil culture medium system. pH=8.00, I=0.576 M. T =25°C. Fluxes are computed with $\delta = 21.7\mu m$.
Protonation constants of NTA: $\log\beta_1^H$=9.329, $\log\beta_2^H$=11.632, $\log\beta_3^H$=13.311, $\log\beta_2^H$=14.311.
Protonation constants of IDA: $\log\beta_1^H$=9.147, $\log\beta_2^H$=11.665.

Species X	D_x ($m^2.s^{-1}$)	k_a ($m^3.mol^{-1}.s^{-1}$)	logβ (M^{-1})
Pb	$9.45\ 10^{-10}$		
PbCl	$1.13\ 10^{-9}$	$5.22\ 10^6$	0.897
$PbCl_2$	$1.13\ 10^{-9}$	$2.62\ 10^6$	0955
$PbCl_3$	$1.13\ 10^{-9}$	$1.19\ 10^6$	0.835
$PbCl_4$	$1.13\ 10^{-9}$	$4.97\ 10^5$	0.737
$PbCO_3$	$9.45\ 10^{-10}$	$1.10\ 10^7$	5.714
PbIDA	$9.45\ 10^{-10}$	$1.12\ 10^7$	6.970
PbNTA	$7.30\ 10^{-10}$	$1.94\ 10^7$	9.691

Table 3. Comparison of the total flux and of individual fluxes and degrees of lability of Pb(II) species, in the modified Aquil medium (Table 1 for full composition and Table 2 for parameters used for computation), computed by FLUXY-RLA (version 3.11) and a rigorous numerical method (MHEDYN)[8]. Note: degree of lability is 1 for fully labile complexes and 0 for fully inert complexes.

Species X	Individual flux ($mol.m^{-2}.s^{-1}$)		Degree of lability	
	RLA	Rigorous method	RLA	Rigorous method
Pb	1.48e-12	1.48e-12	1	1
PbCl	6.78e-12	6.78e-12	0.999	0.998
$PbCl_2$	3.79e-12	3.79e-12	0.999	0.998
$PbCl_3$	1.40e-12	1.40e-12	0.999	0.998
$PbCl_4$	5.46e-13	5.45e-13	0.999	0.998
$PbCO_3$	2.31e-11	2.32e-11	0.971	0.972
PbIDA	1.91e-11	1.91e-11	0.924	0.927
PbNTA	9.00e-12	8.86e-12	0.387	0.380
Total	6.52e-11	6.52e-11		

2.2. Computation of Cu(II) flux in solution containing fulvic substances

Here we present the individual fluxes, ${}^{j}J$, and degrees of lability, ${}^{j}\xi$, of Cu(II)-fulvic complexes, as a function of the stability constant, ${}^{j}K$, of each complex. $[Cu]_t = 10^{-8}$M, pH = 8, Fulvic substances = 5 mg C/L. For other conditions, see [2]. Results of fig 1 [2] are obtained for solution conditions under which the version of FLUXY-RLA of [2] fails to provide good results.

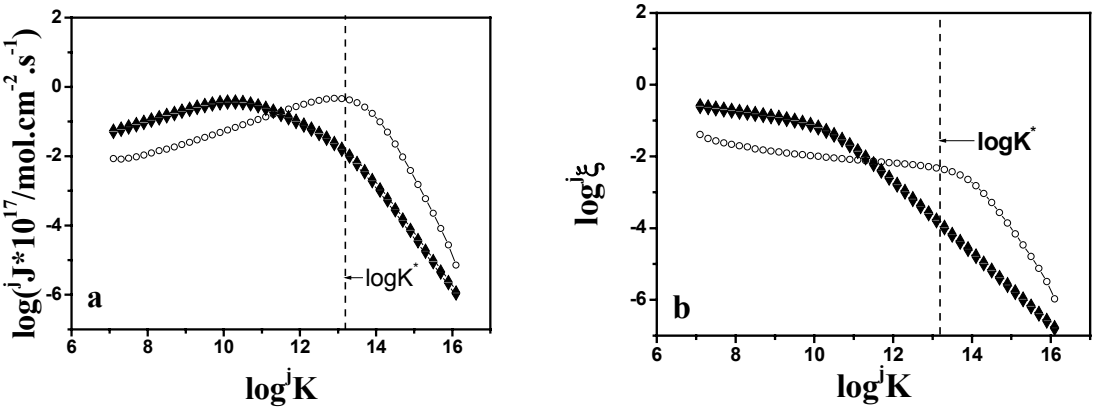

Figure 1, Individual contributions to the flux (a), and degrees of lability (b) of each $Cu^{j}L$ complexes, in a solution of fulvics, computed by a rigorous numerical method, MHEDYN[8] (J_{MHEDYN}), FLUXY-RLA version given in [2](J_{RLA}) and FLUXY-RS (J_{RS}).

a: ○: ${}^{j}J_{RLA}$; ▲: ${}^{j}J_{RS}$; ▼: ${}^{j}J_{MHEDYN}$; **b:** ○: ${}^{j}\xi_{RLA}$; ▲: ${}^{j}\xi_{RS}$; ▼: ${}^{j}\xi_{MHEDYN}$.

All curves are reproduced from [2] and computed with the corresponding version of FLUXY, less advanced than 3.11 for FLUXY-RLA.

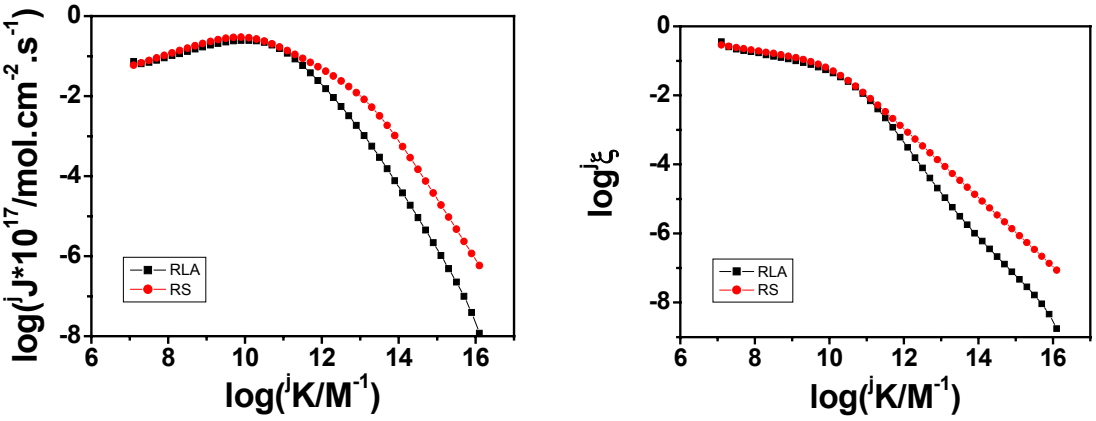

Figure 2 ab. Computations made under the same conditions as for Figure 1a,b. The curves are the results obtained with version 3.11 of FLUXY.

FLUXY-RS provides rigorous results (compare FLUXY-RS and MHEDYN in Fig. 1). So the difference between FLUXY-RS and FLUXY-RLA in Fig 2 represents the error of the latter, in version 3.11. Note that version 3.11 provides significantly much better results than the previous version. In particular, in Fig. 2a, the total flux (the sum of all individual fluxes) is very close to that provided by rigorous computations, since errors occur only on the less labile complexes, whose contribution to the total flux is very small.
When these latter complexes are of main interest, then one should be aware that significant differences may occur with rigorous calculations. In general, application of FLUXY-RLA is thus probably limited in presence of numerous non-labile complexes ($\xi < 0.01$) whose rate constants are close to each others. The same observation is made for flux calculations of metal complexed by aggregates with a broad size distribution [2]. In that case the version 3.11 of FLUXY-RLA does not improve significantly the results compared to those published in [2].

It must be emphasized however that metal flux computations in presence of fulvics or aggregates are very demanding. Due to the very large number of species interacting with each other, with widely varying values of stability constants, rate constants and/or diffusion coefficients. Under such conditions, FLUXY-RLA should be used with caution. On the other hand, there are many cases (as exemplified in section 2.1 and in refs [2,9]) where FLUXY-RLA provides very good results.

3. References

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