

Fluxy - User Manual

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1. Program Overview and Basic Definitions

Fluxy is a program for the calculation of equilibrium concentrations and dynamic fluxes of metal at consuming interfaces (e.g. sensors or microorganisms) in dilute aqueous complexing solutions. Equilibrium concentrations are calculated by solving numerically the non-linear set of equations describing the chemical equilibrium system. Two approaches are used for flux computation – the rigorous solution RS [1, 2] and the Reaction Layer Approximation (RLA) [2], which are somewhat complimentary. The RLA approach is not very good when the behaviour of complexes is close to inert, while, RS is presently not applicable to successive complexes (such theory is in principle feasible). Both RLA and RS approached can be used with simple ligands, fulvic/humic complexants and particulate/aggregate complexants (see 3, for definitions and 3,4 for detailed compilations of parameters or related models to compute them).

The chemical equilibrium reactions are built on the basis of the so-called “components and species” as defined in [5]. The components are the basic blocks for building of equilibrium complexation reactions (for example free cations, H^+ , H_2O and some anions), while species are the products of those reactions. Components and species are useful entities for equilibrium calculations. However additional information is required for complexation reactions with fulvics/humics and particles/aggregates (3,4) and for flux calculations.

Fluxy is written in Microsoft visual C++ version 6.0 and contains about 40000 lines (see also: www.unige.ch/cabe/dynamic). It is linked to a database, containing the dynamic and thermodynamic parameters required for the computations, as discussed in (3,4). The database contains in particular the thermodynamic stability constants of complexes with simple ligands, the parameters required to compute the chemical rate constants, and the diffusion coefficients of free metal ions, simple ligands, fulvics and some complexes. It also contains suggested parameters to compute equilibrium distribution of metal complexes with fulvics/humics and particles/aggregates, as well as the corresponding dynamic parameters (rate constants and diffusion coefficients) as explained in (3,4). Fulvic/humic complexes are assumed to be an ensemble of complexes with varying equilibrium constants, following a Sips distribution (Freundlich isotherm), from which the dissociation rate constant is deduced in each class of complexation strength. Particles/aggregates are assumed to follow a Pareto size distribution from which the diffusion coefficient and chemical rate constant in each size

class is deduced. Below, fulvics/humics are denoted as “FA” and particle/aggregates as “particles”.

The visualisation part of the code run under MS Windows environment. The screen is split into two parts. On the left part the components and species are stored in a tree view. This is called the “model” view. The “model” represents all components in the solution for which the calculation will be done as well as all required parameters for this calculation. On the right part the results on the current calculation are plotted (result view).

2. Getting started with Fluxy

Working with Fluxy is as easily as preparing a solution. When preparing a solution the components should be taken from those available on the shelf and added to the solution. With Fluxy you should click on the Data/AddCation (or Data/AddLigand Data/AddParticleComponent Data/AddFA) menu and then select cations, ligands or other type of components from the available list and add them to the model. The dynamic and thermodynamic parameters required for the computations will be add to the model (from the data base) at this moment, as well as the default concentrations. All parameters can be later redefined by Data/InputModelParameters and Data/InputComponentParameters, or by double click on the component in the model view.

To run the calculations you should click on Calculations/Run or use the Ctrl+R keys. The results appear on the result view. The results can also be exported to a text file by click on File/ExportResults.

You can save the model by click on File/Save and then open and used the model again by File/Open command. When open a previously saved model exactly the same parameters as saved to the model will be used not these from the data base.

Example: Calculation of Cu^{2+} fluxes in presence of CO_3^{2-}

Start Fluxy and go to Data/Input Model parameters. The dialog shown below appears on the screen. Change the pH from 7 to 8, then confirm with OK (all parameters on the dialog are explanted in paragraph 5.1). Then go to Data/Add Cation.

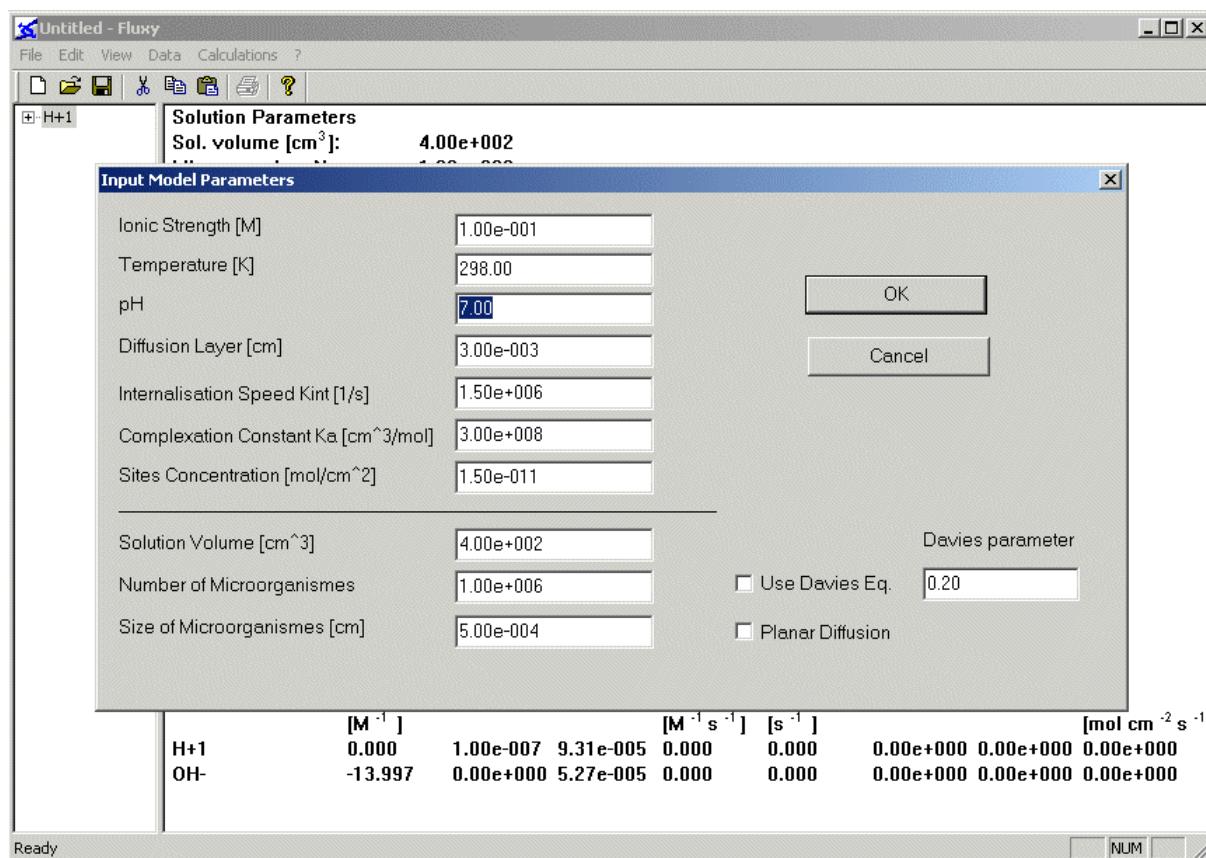


Fig.1. Dialog “Input Model Parameters”.

Chose Cu²⁺ from the list and click OK. On the “model” view Cu²⁺ appear after H⁺. On the “result” view all species of Cu²⁺ with H⁺ are plotted, however the fluxes are still 0, since no calculation is performed. Then open Data/Add Ligand dialog and chose CO₃²⁻ from the list. Confirm with OK. CO₃²⁻ component is now listed on the “model” view and CO₃²⁻ complexes add to the “result” view. Then start the calculation by click on Calculation/Run (or Ctrl+R keys). The results from the calculations appear on the result view. The cations are listed one after one. Scroll the screen to see the results from Cu²⁺. The results are shown on Fig.2. RLA flux is 4.4e-14 [mol cm⁻¹ s⁻¹], while RS flux is 2.57e-14 [mol cm⁻¹ s⁻¹]. However as mentioned on the screen RS flux included only contributions from ML complexes and free cation – in this case Cu²⁺, CuOH⁺ and CuCO₃. The rest of the information on the screen is explained in chapter 6. Save the model by click on File/Save As... then enter a name for the model (for example test_CuCO₃) then confirm with OK. You can reuse this set of components and parameters later by open the model with File/Open command.

Species	Log(K) [M ⁻¹]	Conc. [M]	D [cm ² s ⁻¹]	Log(ka) [M ⁻¹ s ⁻¹]	Log(kd) [s ⁻¹]	Lab.Deg.	μ [cm]	Ji [mol cm ⁻² s ⁻¹]
H+1	0.000	1.00e-008	9.31e-005	0.000	0.000	0.00e+000	0.00e+000	0.00e+000
OH-	-13.997	1.01e-006	5.27e-005	0.000	0.000	0.00e+000	0.00e+000	0.00e+000
HCO3-	10.329	9.74e-005	1.19e-005	0.000	0.000	0.00e+000	0.00e+000	0.00e+000
H2CO3* (aq)	16.681	2.19e-006	9.31e-005	0.000	0.000	0.00e+000	0.00e+000	0.00e+000
CuOH+	-7.600	8.66e-010	7.14e-006	9.297	2.897	2.27e-001	5.98e-005	3.30e-015
Cu2OH+3	-6.710	2.32e-018	7.14e-006	0.000	0.000	0.00e+000	0.00e+000	0.00e+000
Cu(OH)4-2	-39.730	6.42e-018	5.70e-006	0.000	0.000	2.22e-001	0.00e+000	2.44e-023
Cu(OH)3-	-26.640	7.90e-013	7.14e-006	0.000	0.000	2.24e-001	0.00e+000	3.01e-018
Cu(OH)2 (aq)	-14.640	7.90e-009	7.14e-006	0.000	0.000	2.25e-001	0.00e+000	3.01e-014
Cu2(OH)2+2	-10.494	3.81e-014	7.14e-006	0.000	0.000	0.00e+000	0.00e+000	0.00e+000
Cu3(OH)4+2	-20.788	6.68e-018	7.14e-006	0.000	0.000	0.00e+000	0.00e+000	0.00e+000
CuHCO3+	12.130	2.12e-012	7.14e-006	0.000	0.000	0.00e+000	0.00e+000	0.00e+000

Species	Log(K) [M ⁻¹]	Conc. [M]	D [cm ² s ⁻¹]	Log(ka) [M ⁻¹ s ⁻¹]	Log(kd) [s ⁻¹]	Lab.Deg.	μ [cm]	Ji [mol cm ⁻² s ⁻¹]
Cu+2	0.000	3.45e-010	7.14e-006	0.000	0.000	1.00e+000	0.00e+000	5.75e-015
CuOH+	-7.600	8.66e-010	7.14e-006	9.297	2.897	2.27e-001	5.98e-005	3.30e-015
Cu2OH+3	-6.710	2.32e-018	7.14e-006	0.000	0.000	0.00e+000	0.00e+000	0.00e+000
Cu(OH)4-2	-39.730	6.42e-018	5.70e-006	0.000	0.000	2.22e-001	0.00e+000	2.44e-023
Cu(OH)3-	-26.640	7.90e-013	7.14e-006	0.000	0.000	2.24e-001	0.00e+000	3.01e-018
Cu(OH)2 (aq)	-14.640	7.90e-009	7.14e-006	0.000	0.000	2.25e-001	0.00e+000	3.01e-014
Cu2(OH)2+2	-10.494	3.81e-014	7.14e-006	0.000	0.000	0.00e+000	0.00e+000	0.00e+000
Cu3(OH)4+2	-20.788	6.68e-018	7.14e-006	0.000	0.000	0.00e+000	0.00e+000	0.00e+000
CuCO3 (aq)	6.750	8.85e-010	7.14e-006	9.935	3.185	2.99e-001	4.26e-005	4.41e-015
CuHCO3+	12.130	2.12e-012	7.14e-006	0.000	0.000	0.00e+000	0.00e+000	0.00e+000
Cu[CO3]2-2	10.100	9.04e-013	7.14e-006	0.000	0.000	2.99e-001	0.00e+000	4.51e-018

Fig.2. Calculation on the Cu²⁺ fluxes

Changing the component parameters.

The concentrations Diffusion coefficients and other component parameters could be changed directly by double click on the component in the “model” view. For example double click on Cu+2 give the next dialog (Fig. 3):

Fig.3. Cation parameters dialog.

Change the concentration of Cu^{2+} to $1\text{e-}9$ then confirm with OK. Note please that the calculation with the new concentration is not performed until run the calculation by Calculation/Run again. When changing the component parameters of H^+ the concentration could not be changed, because fixed by the value of pH.

3. The “File” commands of the Menu

The File commands of the menu contains the file handling commands.

3.1. File/New

Set a new model, reinitialised all parameters. The water and H^+ components are automatically added to the model since computations are performed in aqueous environment. $[\text{OH}^-]$ is automatically introduced through the relationship: $[\text{H}^+][\text{OH}^-] = K_w$. In the “result” part of the screen the default model parameters are shown.

3.2. File/Open

Open a previously saved model. The current data and model will be lost if not saved previously. The file name and path should be set in the box. After loading the file the model parameters are printed on the result view of the screen.

3.3. File/Save.

The file name and path should be set in file box. The extension of these files is .flx. These files contained all current dynamic and thermodynamic parameters, as well as the total concentrations of the components, which will be used for the calculations. When reading such a file those parameters, but not the parameters from the database will be loaded and used for the calculations.

3.4. File/Save As.

Save the current model with new name. The file name and path should be given in file dialog.

3.5. File/Export Results.

Export current calculation (shown in the results view) to a text file. The file name and path should be set in file dialog. The results are exported to a text file, which contained also all

input dynamic and thermodynamic parameters used, the concentrations of species and some intermediate parameters.

3.6. File/Print.

Print the “result” part of the screen. All computational parameters and calculated results will be print. You should click in the “result” part of the screen to activate the print function.

3.7. File/Print Preview.

Print preview. You should click in the “result” part of the screen to activate the print preview function.

3.8. File/Print Configuration.

Printer configuration

3.9. File/Exit

Exit Fluxy.

4. The "Edit" commands of the Menu

Copy, *Paste* and *Cut* functions. These functions allow copying a component from the model to the clipboard, past the clipboard to the model, or cutting a component from the model. Copy/Past of the results view is not available. Click on the component in the “model” view, then on one of these functions or use the corresponding functional keys, for executing *Copy*, *Paste* or *Cut* functions. When cutting a component it is copied to the clipboard. Undo is not available.

5. The "Data" commands of the Menu.

This menu allows the user to manipulate the data. Two main types of data are used in Fluxy:

- 1) Data which are permanently stored in the database like the equilibrium thermodynamic constants, diffusion coefficients, dehydration rate constants, k_w , of metal ions, electronic charge. Thermodynamic constants for simple complexes are given at temperature 25°C and zero ionic strength. The correction for different ionic strengths can be done by using

Davies equation, but no correction is done for the temperature. The constants for the FA and particles are valid for the indicated pH, 25°C and ionic strength 0.1M. They are not corrected for ionic strength, by the Davies equation.

- 2) data which should be entered for each model like ionic strength, total concentrations, temperature.

On a new model default values of the second type are automatically assigned as well as default values on the database parameters if not found. For instance, only few values of diffusion coefficients of metal complexes are available in the literature (and thus in the database). When the value for the test complex is not found, the value of diffusion coefficient of the free metal ion is set as default value for a complex formed with a simple ligand, while those for FA or particles is set for the complexes with these complexants (see 3,4 for discussion). When a component and its parameters are added to the model, all possible reactions and complex species formed with the other components of the model are searched for in the database, and the complete set of equations of the model is rebuild. The equilibrium thermodynamic constants and other database parameters are also reloaded from the database, therefore if these parameters have been changed previously, then they will be replaced.

5.1. Data/Input Model Parameters.

In this menu a dialog appears where the parameters common for all components in the model can be entered or corrected (the default parameters or those read from a file are already set in the box). The parameters are the following:

General parameters for flux computation:

Ionic Strength [M]	ionic strength of the solution in M.
Temperature [K]	temperature of the system in °K
pH	pH of the solution. This pH determines the concentration of H ⁺ which is constant during equilibrium calculations.
Diffusion layer [micron]	Solution layer at the consuming surface, in which fluxes are computed. At distances larger than the diffusion layer, δ , all concentrations are

those of the bulk solution and all species are in equilibrium with each other.

Internalisation speed k_{int} [1/s]

internalisation rate constant, in s^{-1} , which regulates the kinetic of transport through the interface according to Michaelis-Menten mechanism (e.g. membrane of microorganism).

Complexation Constant K_a [1/M]

K_a is the surface complexation constant of the metal with the complexing sites at the consuming interface which leads to interfacial transport (assuming Michaelis-Menten mechanism).

Site Concentration [mol/cm²]

surface concentration of the complexing sites active for metal transport at the consuming interface

Parameters for long term metal depletion in solution

Solution Volume [cm³]

volume of the model solution in ml

Number microorganisms

number of microorganisms in the total volume

Radius of the microorganism [micron]

radius of the spherical consuming interface (microorganism, sensor,...). When planar diffusion checkbox is checked the calculation is performed for planar surface and therefore this parameter is not used.

The dialog contained also 2 check boxes:

Planar Diffusion

When this box is validated the code will use equations for planar Diffusion in RLA. For RS, a value of r_0 such that $r_0/\delta > 1000$ provides results valid for planar diffusion.

Use Davies Eq.

When this box is validated, the code will correct for ionic strength, all equilibrium constants introduced in the model, except those for complexes with FA and particles. This correction is performed by applying Davies equation (see below). When the check box is not validated, no correction is performed. This allows the user to introduce his own constants, already corrected by a different equation.

Finally an edit box is present close to the **Use Davies Eq.** check box, asking:

Davies Parameter.

This is the parameter B of the last term in Davies Equation (see below). Thermodynamic equilibrium constants, K , are corrected to K' by:

$$\log(K') = \log(K) + \sum n \log(\gamma_i) \quad (1)$$

where the summation is performed on all species and components taking part in the reaction. n is the stoichiometric coefficient of the corresponding component, with a negative sign for products of reaction and a positive sign for the reactive components. γ_i is the activity coefficient of component i , given by the Davies equation:

$$\log(\gamma) = -Az^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - BI \right) \quad (2)$$

where B is a parameter with default value = 0.2, z is the charge of the ion, I is the ionic strength, and A is given by $A = 1.82 \times 10^6 (\epsilon T)^{-3/2}$ where ϵ is the dielectric constant and T is the temperature.

When the dialog box is closed by OK the model will be updated as well as the result view on the screen. The equilibrium thermodynamic constants and other database parameters are also

reloaded from the database, therefore if these parameters have been changed previously, then they will be replaced.

5.2. Data/Input Component Parameters.

Open a dialog box with all parameters (see below) of a selected component.

5.3. Data/Add Cation.

In this step, one can add metal cations to the model. A list dialog appears, where the available cations in the database are listed. The user can click and select one or more cations then confirm by clicking on OK. Several cations can be used simultaneously. Fluxes are calculated for each cation separately, by assuming that there is no interaction between a complex and a ligand not incorporated in that complex. For accurate results, all ligands should be in excess with respect to all cations (equilibrium calculations do not require a condition of ligand excess compared to metal ion), even though good results may be obtained without this condition, depending on the lability and mobility of the complex.

Use Ctrl and Shft keys for selecting several cations simultaneously. The cation(s) will appear in the left (model) part of the screen. The value of the charge, k_w and the diffusion coefficient of cations will be loaded from the database.

Every cation parameter could be changed before running the calculations, by double click on the cation component in the “model” view or by Data/InputComponentParameters. Those parameters are:

Total Concentration [M] – total concentration

Diffusion coefficient [cm²/s] – diffusion coefficient of the cation

kw [1/s] - k_w rate constants for dehydration of metals.

The total concentration of H⁺ or OH⁻ cannot be imposed. The concentrations of H⁺ and OH⁻ are computed by the code from the value of pH introduced in Data/InputModelParameters, after correction of K_w for ionic strength, depending on the option used for Davies equation.

5.4. Data/Add Simple Ligand.

Add a simple ligand to the model to a similar way as a cation.

Every ligand parameter could be changed before running the calculations, by double click on the ligand component in the “model” view or by Data/InputComponentParameters. Those parameters are:

Total Concentration [M] – total concentration

Diffusion coefficient [cm²/s] – diffusion coefficient of the ligand

5.5. Data/Add Major Particle Component.

In the present version of FLUXY, only fractal aggregates (not compact particles) can be introduced as colloidal complexants. Nevertheless, the word “particle” is often used below and in Fluxy for both aggregates and compact particles. There can be only one type of particle/aggregate in a given model. However particle/aggregates can be composed of several components: they always include one major particle or aggregate component (major in proportion, e.g. aluminosilicate) on which one or a few minor components may be adsorbed (e.g. FeOOH or organic matter). The major component may be complexant or not. It always determines the aggregate structure.

In the present step, a major particle/aggregate component is introduced from the list, with its structural parameters (only one major particle could be introduced in the model). All aggregate parameters can be changed before running the calculations, by double clicking on the particle in the “model” view or by Data/InputComponentParameters. Those parameters are:

Fractal Dimension	fractal dimension of aggregates
Pareto Beta	exponent in the Pareto size distribution assumed for the particle/aggregates
Particle radius b [nm]	radius of elementary particle of the aggregates
Density [g/cm³]	density of major component forming elementary particles
Total concentration [g/L]	the total concentration of the major component
Sites Density [1/cm²]	Number of complexing sites per unit of surface area of the major component.

Psi Potential [V]

Ψ potential between the surface of the major component and the bulk solution.

The total molar concentration of complexing sites of the major particle component is calculated as follows:

$$[S]_t^P = \frac{3 n_s^P \{P\}_t}{b \rho_P N_A} - \frac{n_s^P}{N_A} \sum \frac{\{X\}_t}{h_X \rho_X} \quad (3)$$

where:

n_s^P is the number of complexing sites per unit surface area of the major component

b is the radius of elementary particle (major particle component) of the aggregates

ρ_p is the density of the major particle component

$\{X\}_t, \{P\}_t$ are the mass concentrations of minor and major component X and P respectively

h_X is the thickness of the active layer of minor particles component X

ρ_X is the density of the active layer of minor particles component X

5.6. Data/Add Minor Particle Component.

In this step, a minor particle/aggregate component is added from the list. Many minor components can be added to the model. After adding each minor component the total concentration of complexing sites of the major component P is recalculated according eq. (3). When this value is negative a message box appears, warning for an error. The user should change the properties of the minor or major components (in particular the mass concentrations of X and P) until this calculation give correct value.

List of parameters to introduce:

Fractal Dimension	fractal dimension of aggregates
Pareto Beta	exponent in the Pareto law
h layer [cm]	thickness of the layer of the minor component
Density [g/cm³]	density of the minor component
Total concentration [g/L]	total mass concentration of the minor component
Sites Density [1/cm²]	Number of complexing sites per unit surface area of minor component
Psi Potential [V]	Ψ potential between the surface of the minor component and the bulk solution.

The total concentration of Minor particle component is calculated according:

$$[S]_t^x = \frac{n_s^x \{X\}_t}{N_A h_x \rho_x} \quad (4)$$

Note: The minor components are not related to the structure but only to the complexing properties. However structural properties (fractal dimension and Pareto Beta) could be also changed from the minor particles dialog. These changes are automatically assigned to the major particle parameters.

5.7. Data/Add FA.

In this step, fulvic/humic complexants are added to the model. Note that when fulvics/humics are present, FLUXY can compute the flux of only one cation associated with a FA. The FA examples in the database could be scanned by < > buttons in the menu. Input parameters related to FA could be changed from here or later by double click on the FA in the “model” view or by Data/InputComponentParameters. Those parameters are:

Assoc. Cation

Nature of the cation, which forms complexes with FA and for which the flux is computed.

pH validity for data

pH for which the parameters below are valid. This pH is only informative and is not used for calculations. It cannot be changed.

Gama

Parameter Γ reflecting the chemical heterogeneity of the whole of fulvic/humic complexants and the broadness of the complexing site distribution (see below; $0 < \Gamma < 1$)

Log(K0)

Logarithm of K^*_o , in M^{-1} i.e. the value of equilibrium constant when $\log([M]_b/\{S\}_t) = 0$; $[M]_b$ = bound metal concentration (M); $\{S\}_t$ = fulvic/humic mass concentration (kg/L). Note that the value of K^*_o depends on the units used for $[M]_b/\{S\}_t$ [3]

Psi potential [V]

ψ is the average electrical potential between the bulk solution and the inside of the

	fulvics/humics, at the given pH and ionic strength.
D[cm²/s]	diffusion coefficient of fulvics/humics and their metal complexes.
Sigma [mol/kg]	total density of complexing sites in fulvics/humics
Log(Kmin)	minimum of the range of log(K), in M ⁻¹ . This is the lower boundary of the tested log(K) domain of the fulvic/humic complexes.
Log(Kmax)	maximum of the range of log(K), in M ⁻¹ . This is the upper boundary of the tested log(K) domain of the fulvic/humic complexes.
Delta Log(K)	step of log(K), in M ⁻¹ , in the discretized site distribution of fulvics/humics.
DOC [g/L]	Mass concentration of fulvics/humics, expressed as dissolved organic carbon, in g/L – this value can be changed by double click on the FA in the “model” view or by Data/Input Component Parameters.

The parameters for fulvics/humic will be used to compute a discretized distribution of complexing fulvic/humic molecules, with molar fraction and equilibrium constant following a Sips distribution, based on the parameters Γ and K_o^* . The total number of complexing sites (or molecules) depends on $\log(K_{\min})$ and $\log(K_{\max})$. The values of $\log({}^iK)$ of two successive site are separated by $\Delta\log K$ (see eqs 28-31 in ref. 3).

The total concentration of complexing site is:

$$[L]_t = \Delta_i \chi \sigma DOC \quad (5)$$

Where $\Delta_i \chi$ is obtained by subtraction of two consecutive values of $\log^i \chi$ (corresponding to $\log^i K$) and $\log^{i+1} \chi$ (corresponding to $\log^{i+1} K + \Delta\log K$).

$$\log({}^i \chi) = \Gamma \log(K_o^*) - \Gamma \log({}^i K^*) - \log(\sigma) + \log \left\{ \left(\frac{\Gamma}{1-\Gamma} \right)^\Gamma \frac{\sin((1-\Gamma)\pi)}{\Gamma \pi} \right\} \quad (6)$$

6. The "Calculations" commands of the Menu.

In this menu the user runs the calculations.

6.1 Calculations/Run

This will run the flux calculation with the current parameters. The results are shown on the screen after the model parameters. The results are composed of 3 parts.

6.1.1. Results on total flux of given cation

The values of the parameters shown on the screen are in bold characters below:

k_w [s^{-1}]

dehydration rate constant k_w of hydrated free metal ion, in [1/s]. It depends on the cation and is read in the database.

Diff. Coef. [cm^2s^{-1}]

Diffusion coefficients of the metal in [cm^2s^{-1}] read in the data base.

Initial Met. Conc. [M]

Input total concentration of the cation in [M]

τ_1 [$s\ cm^{-1}$]

calculated term τ_1 . This term corresponds to the resistance to the flux due to the internalisation process through the consuming surface:

$$\tau_1 = \frac{1}{k_{int} K_a [R]} \quad (7)$$

where k_{int} – is the internalisation rate constant

K_a is the complexation constant of the cation at the consuming interface.

$[R]$ is the surface site concentration at the consuming interface.

τ_2 [$s\ cm^{-1}$]

calculated term τ_2 . This term correspond to the resistance to transport to the solution by diffusion without limitation of chemical kinetics.

For spherical diffusion:

$$\tau_2 = \frac{r_0}{D_m \alpha_m} \left(\frac{\delta}{r_0 + \delta} \right) \quad (8)$$

where r_0 is the radius of the spherical consuming surface (e.g. microorganism). For computation at planar surfaces, the condition $r_0 \gg \delta$ is used.

δ is the diffusion layer thickness

$\overline{D_m}$ is an average diffusion coefficient of complexes. The term $\overline{D_m} \alpha_m$ is:

$$\overline{D_m} \alpha_m = D_M + \sum_{j=1}^m \sum_{k=1}^n D_{M^j L_k} \beta_k |L|^k \quad (9)$$

For more details see [2].

τ_3 [s cm⁻¹]

τ_3 can be seen as a term, which corrects τ_2 for the fact that chemical reactions may slow down the process. For more details see [2].

The overall resistance to the flux τ is therefore:

$$\tau = \tau_1 + \tau_2 + \tau_3$$

J_{RLA} [mol*cm⁻²*s⁻¹]

Total flux calculated according to RLA in [mol cm⁻²s⁻¹]

$$J_{RLA} = \frac{[M]^*}{\tau} \quad (10)$$

where M^* is the equilibrium free metal concentration in the bulk.

J_{RS} [mol*cm⁻²*s⁻¹]

Total flux calculated according to RS in [mol cm⁻²s⁻¹], as described in the literature [1,2].

6.1.2. Flux contributions of individual species

The following part of the screen contains a table with parameters and results for each individual species as follow:

Species

species name

Log(K)

logarithm of thermodynamic equilibrium constant, in M⁻¹, read from the data base. When

the Davies equation checkbox is validated, the values of K given here are those corrected for ionic strength (see § 5.1).

Conc. [M]

Equilibrium calculated concentration of the species [M]. It is calculated by solving numerically the non-linear set of equations describing the chemical equilibrium system

D [cm²s⁻¹]

Diffusion coefficients of the species in [cm²s⁻¹].

Log(k_a) [M⁻¹s⁻¹]

Association rate constant, in M⁻¹s⁻¹, of the complex mentioned in the first column. It is computed as discussed in [3] (eqs 11,14,16, for simple ligands; eqs 11, 15,16 with $U(a) = z_M F \psi$ for fulvics/humics) and [4] (eqs 6, 7 or 7', 11 or 11', 36) for particles.

log(k_d) [s⁻¹]

dissociation rate constant (in s⁻¹), calculated from $k_d = k_a/K$ (11)

Lab.Deg.

lability degree which is defined as:

$${}^i \xi = \frac{J_{M^i L_k}^{\text{complex}}}{J_{M^i L_k}^{\text{dif}}} = \frac{\left(1 - \frac{[M^i L_k]_0}{[M^i L_k]^*}\right)}{\left(1 - \frac{[M]_0}{[M]^*}\right)} \quad (12)$$

where the subscripts ₀ and the superscript * indicate the concentration at the consuming surface and in the bulk solution respectively.

The flux for fully labile complexes is:

$$J_{M^i L_k}^{\text{dif}} = D_{M^i L_k} \left([M^i L_k]^* - {}^i \beta_k [L]^k [M]_0 \right) \left(\frac{1}{r_0} + \frac{1}{\delta} \right) \quad (13)$$

μ_i [cm]

is the reaction layer thickness of cation i given by eq:

$$\mu_i = \sqrt{\frac{D_M}{k_a \cdot [i] L}} \quad (14)$$

J_i [mol*cm⁻²*s⁻¹]

Individual fluxes due to the species i computed as discussed in [2]. Complexes of type M^iL_n are taken into account only in RLA calculations. In this case all M^iL_n ($n>1$) are assumed to be at equilibrium with M^iL and J_i is the sum of all contributions due to M^iL_n ($n>0$). In RS, only the flux of M^iL is computed.

6.1.3. Long-term metal depletion in solution.

The last part of the screen is a graph, where the free and total concentrations of non-inert complexes are plotted as function of time.

For the free metal the concentration is described by eq:

$$[M]^* = [M]_0^* \exp(-\kappa t) \quad (15)$$

where t is the time, $[M]_0^*$ and $[M]^*$ are the initial free metal concentration and the free metal concentration at time t in the bulk solution and κ is given by:

$$\kappa = \frac{4.0n\pi r_0^2}{V\tau\alpha_m} \quad (16)$$

where V is the solution volume, n is the number of microorganisms in V and τ is given in section 6.1.1. The bulk concentrations, $[ML]^*$ of each non inert complex, is calculated by:

$$[ML]^* = [ML]_0^* \exp(-\kappa t) \quad (17)$$

The total concentration of all non inert complexes, at time t , is the sum of all the above values of $[ML]^*$ at that time.

The time evolution of each inert complex in the bulk solution is given by:

$$\boxed{[ML_{in}] = \frac{[ML_{in}]_0}{1 - \kappa/k_d^{in}} \left[\exp(-\kappa t) - \frac{\kappa}{k_d^{in}} \exp(-k_d^{in} t) \right]} \quad (18)$$

Where ML_{in} is an inert complex, k_d^{in} its dissociation rate constant, and $[ML_{in}]_0$ its initial concentration. Values of $[ML_{in}]$ as function of time, for each inert complex of the model, as well as those of $[ML]^*$ (eq. 17) for non-inert complexes are not plotted on the screen, but tabulated in the export file.

6.2 Calculations/Add to buffer

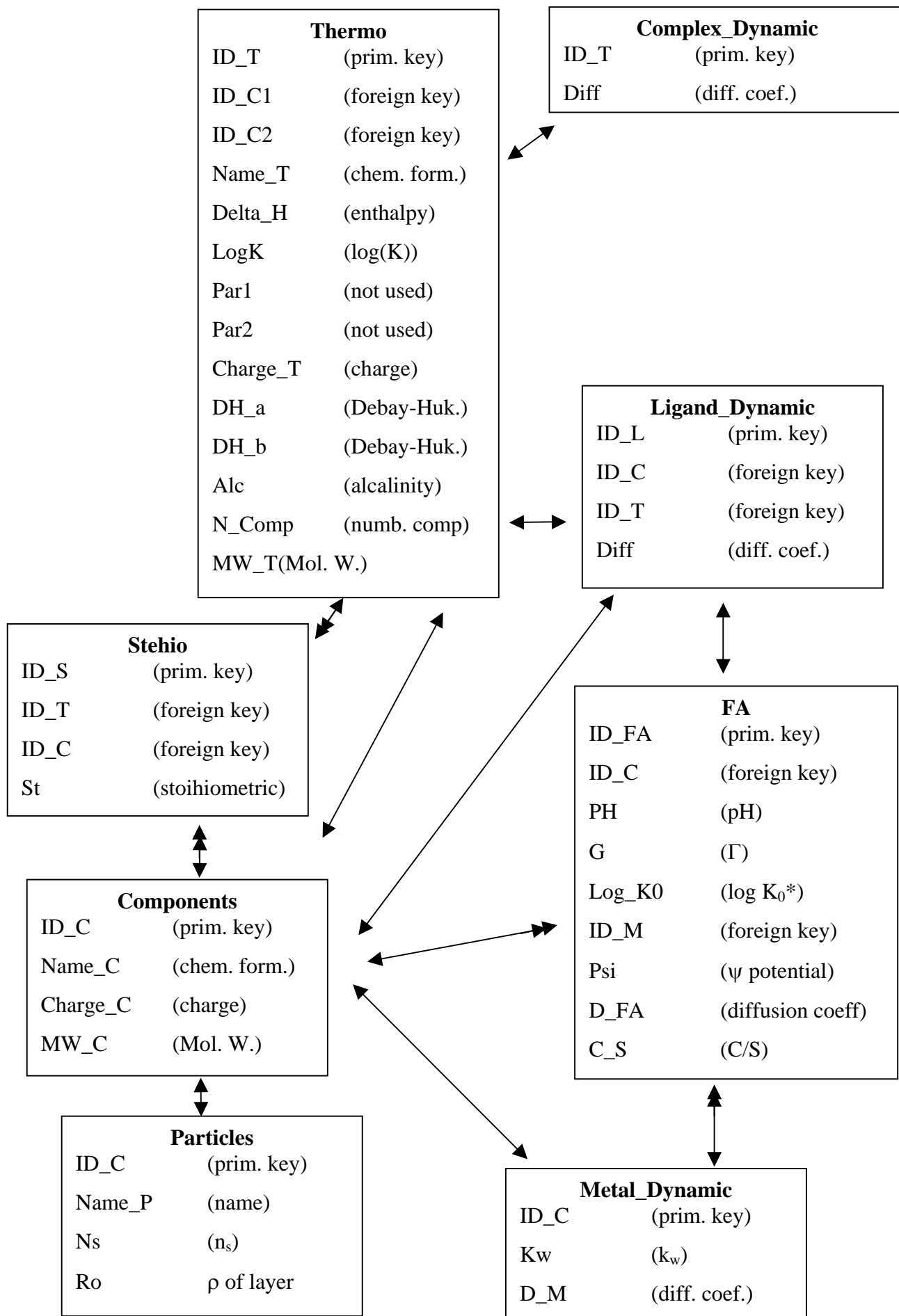
Not available in the present version of Fluxy.

6.3 Calculations/Graph Scaling

Changing the axes scaling from logarithmic to linear for the long-term metal depletion graph.

7. Database

Fluxy use a MS Access data base which contains 8 tables. The logical schema of the database is given below. Components are listed in table “**Components**”. Table “**Thermo**”, describe the chemical equilibrium with stoichiometric coefficients in table “**Stehio**”. Dynamic parameters are given in tables “**Complex_Dynamic**”, “**Ligand_Dynamic**”, “**Metal_Dynamic**”, “**FA**”, and “**Particles**”. More detailed description of the fields of the tables will be given in following document. Relational schema of the database is given below.



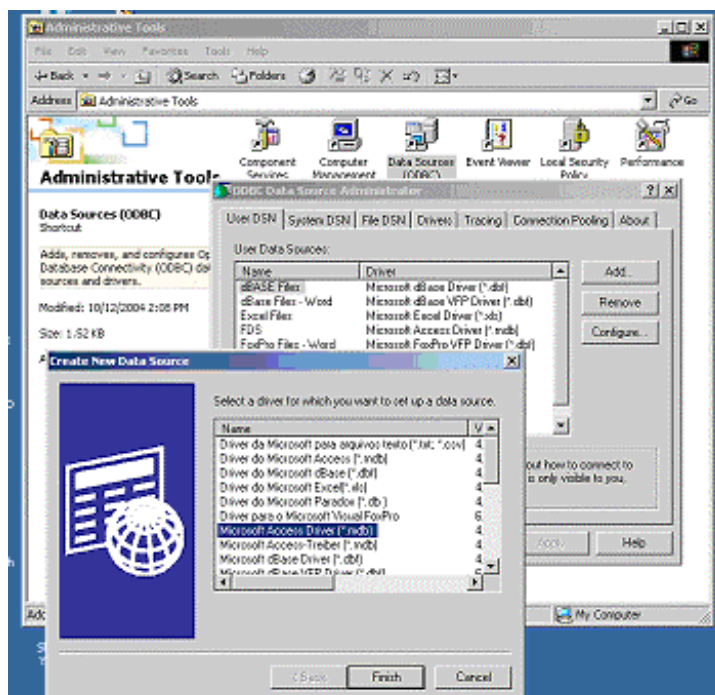
8. Installation

The files which are supplied are:

Fluxy.exe	executable
FluxyManual_v201.doc	this user manual
fl.mdb	data base file

For installation of Fluxy copy the exe file on a directory for example fluxy and copy the database files in the subdirectory called data.

For the installation of the data base go to Start/Settings/Control Panel in Windows menu, then in the Control Panel window click on Administrative Tools and then to Data Sources (ODBC). Click on “User DSN”, then on Add and select then select “Microsoft Access Driver *.mdb” from the list and click on “Finish”. A menu called “ODBC Microsoft Access Setup appear. Set the Data Source Name to be “FDS”. Below click on “Select” button and select the data path and name of the file fl.mdb. Confirm by OK and the data base is installed.



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- 2 J. Buffle, K. Starchev, J. Galceran, Computing steady-state metal flux at microorganism and bioanalytical sensor interfaces in multiligand systems. A reaction layer approximation and its comparison with the rigorous solution, *Phys.Chem.Chem.Phys* (2007), 9,
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