Quick User Guide for MHEDYN INTERFACE

WELCOME

This guide is intended for people who already are familiar with environmental chemistry and associated subjects.
Welcome to the MHEDYN INTERFACE quick user guide. This is a user manual to quickly get familiar with the possibilities offered you by the MHEDYN INTERFACE. You will be able to use the interface to prepare and run experiment to compute metal ion flux at planar interface by considering aqueous solution containing simple ligands and/or fulvic substances and/or aggregate of particles (for physicochemical discussions and dynamic parameters related to these complexes, see [1] and [2]; for examples of flux computations, see [3] and [4])

This is just a quick reference guide. A more complete user guide will come soon.
Any suggestion to improve the interface is welcome.

REQUIREMENTS

Please, verify that the following components are installed on your computer
- Windows XP (or any able to run access2003)
- Java installed

GETTING STARTED

The following procedure will help you in download and install the MHEDYN user interface from the page website http://www.unige.ch/cabe/dynamic/ :

1. Download the ZIP file : **CHIAM.ZIP**

2. Decompress the file on the **C:** drive
   ➔ A directory called **C:\CHIAM** will be created

3.1 If **ACCESS 2003** is installed on your computer
   ➔ Go on **C:\CHIAM** Double click on the access file

3.2 If **ACCESS 2003** is **NOT** installed on your computer
   ➔ Go on **C:\CHIAM\INSTALL\MHEDYN_VXXX**
   ➔ Double click on the **SETUP.EXE**
   ➔ Follow the instructions
   ➔ This will install the MHEDYN Interface and the Access 2003 runtime

4 Double click on the icon, the main menu of the MHEDYN interface will display

MhedynInterface.MDB

MHEDYN INTERFACE

When you run the interface, the screen shown in figure 1 will appear.

Figure 1: Initial screen when you first run the interface.

By clicking on the button "General Parameters" you will be redirected to the General Parameters screen, as shown in figure 2.
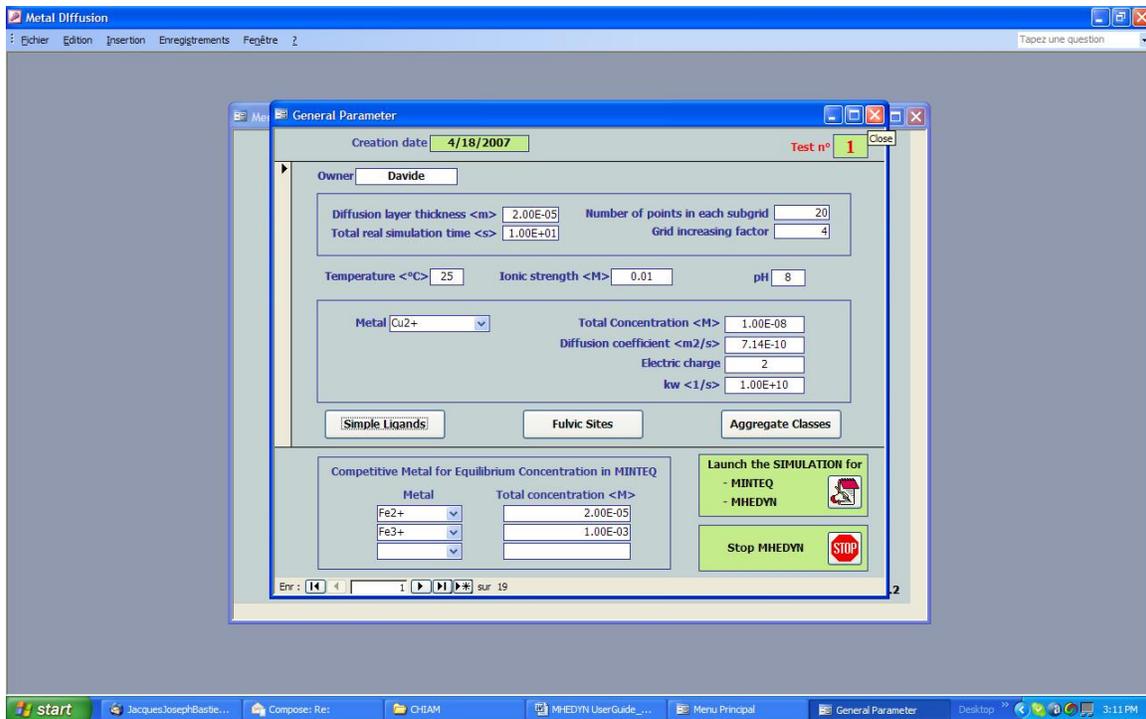
Figure 2: General Parameter screen. This is the starting point to create your experiment.

General Parameters

Let's have a look at each section in the General Parameter screen.
Section 1. There are two fields, the "Creation date" field and the "Test n°" field. Both are automatically updated by the system.

Section 2. This is the core section of the screen. The user must fill all the fields. It contains the following fields.
Owner = The user must put a reference name which will appear as the owner of the experiment.
Diffusion layer thickness = The user must put the diffusion layer thickness in meters. This is the physical domain where concentration gradients will occur and where the computation will be done. The flux is computed at the left hand side of the domain (corresponding physically with the origin, $x=0$, and with the position of the consuming interface). The boundary conditions on the domain are already implemented in the code and are the following:

- Perfect sink condition for the metal ion at $x=0$.
- At the right hand side of the domain ($x=\delta$) the concentration of each species is fixed to the initial concentration values (as shown in the file "initialconc.txt", corresponding to the bulk values).
- Nil flux condition are ensured for each ligand and each complex at $x=0$.
- The initial concentrations of each species are set everywhere in the domain equal to the bulk values.

Total real simulation time = The user must put an estimation of the total real simulation time in seconds. Simulation will be stopped after that time.

Number of points in each subgrid = This is a spatial discretization parameter. The user must put the number of points within each sub domain. Usually, the larger this value is, the more accurate the simulation is. Best values are between 15 and 30. However, too large value could compromise stability and/or increase the computational time.

Grid increasing factor = This is another spatial discretization parameter. It defines the increasing factor from the subdomain with the smallest grid (close to $x=0$) to the subdomain with the largest grid (close to $x=\delta$). It must be given by the user. Best values are between 2 and 5.

Temperature = The user must put the temperature in centigrade (Celsius) degrees at which the experiment is performed.

Ionic strength = The user must put the ionic strength value in mol/dm^3. If the user leaves the field empty, the default value of 0 (zero) is taken.

pH = The user must put the pH value.

Metal = The user must select one metal from the list for the computation of the flux.

Total Concentration = The user must give a total concentration value (in mol/dm^3) for the chosen metal.

Diffusion Coefficient = The user must give the diffusion coefficient (in m^2/s) of the chosen metal. A value is proposed from the database.

Electric charge = The user must give the electric charge of the metal. A value is proposed from the database.

Kw = The user must give a value of k$_w$ (in 1/s) for the chosen metal. A value is proposed from the database.

Once the user has filled in the above mentioned fields, he must confirm the values by clicking on the vertical gray strip on the left as shown in the picture below.

This is the bar where to click to confirm the added values

The three buttons "Simple Ligands", "Fulvic Sites" and "Aggregate Classes" allows the user to make simulations with simple ligands, fulvic sites and aggregate classes respectively.

Section 3. The last section is optional. It allows the user to add up to 3 metals in the simulation, called competitive metals because they may be important in the computation of the equilibrium concentration with MINTEQ. They are not involved in the flux computations.

Simple Ligands

By clicking on the button "Simple Ligands", a new window appears, as shown in figure 3.
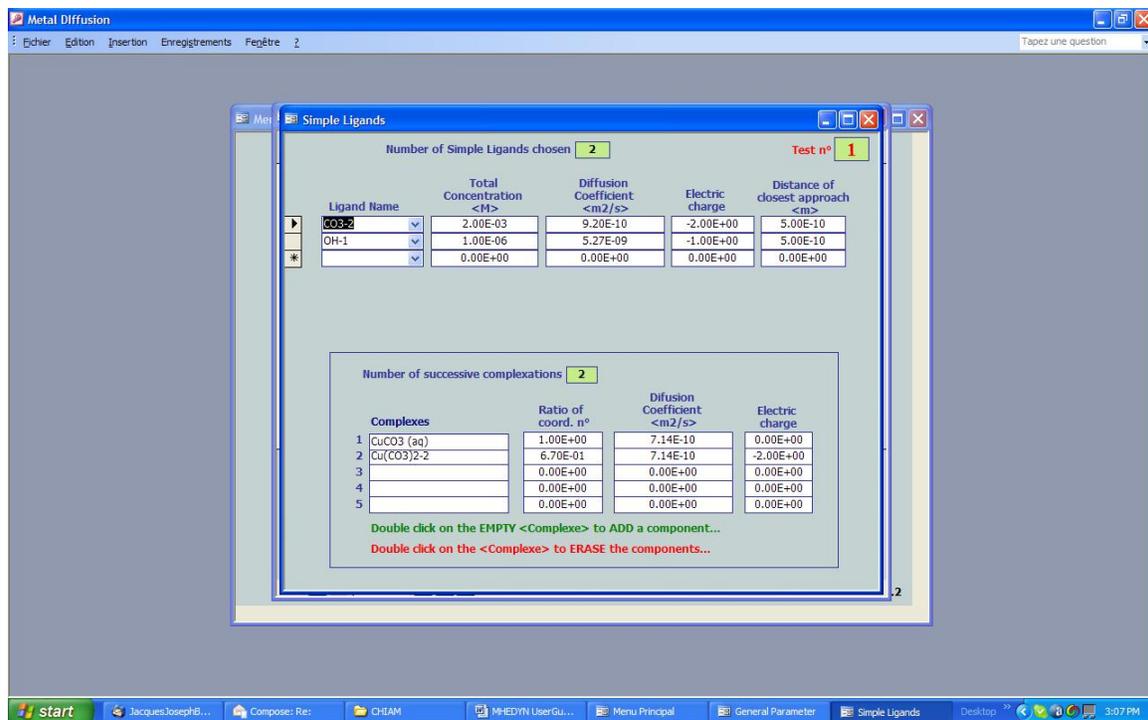

Figure 3: The window of the Simple Ligands.

In this window the user can introduce the simple ligands. It is made of 2 sections. In the first section the user can choose the ligands he wants to add by giving the
Ligand Name = The user can introduce a ligand by picking up from a scroll list
Total Concentration = The user must give the total concentration (in mol/dm^3) of the chosen ligand.
Diffusion Coefficient = The user must give the diffusion coefficient (in m^2/s) of the chosen ligand. A value is proposed from the database when available.
Electric charge = The user must give the electric charge of the chosen ligand. A default value is proposed from the database.
**Distance of closest approach** = The user must give the distance of closest approach (in m) of the selected ligand. A default value is proposed.

When the user has chosen a ligand, he must confirm its addition, by clicking on the grey bar located just at the left of its name, as shown in the picture below

	Ligand Name		Total Concentration <M>	Diffusion Coefficient <m2/s>	Electric charge	Distance of closest approach <m>
►	CO3	∨	2.00E-03	9.20E-10	-2.00E+00	5.00E-10
	OH	∨	1.00E-06	5.27E-09	-1.00E+00	1.00E-10
*		∨	0.00E+00	0.00E+00	0.00E+00	0.00E+00

Click here to confirm the values for the simple ligand (CO3)

The user can at anytime remove one or more of the ligands he has introduced, simply by selecting the ligand/s he want to remove and clicking on the removal button, as shown in the picture below:
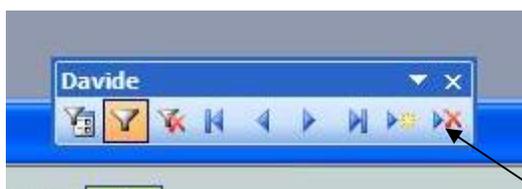
Click here to remove the selected ligand/s.

Once the user has introduced a ligand, he must add at least one complex resulting from the reaction between the metal and the selected ligand. In order to do that, the user must use the second section (starting with the label "number of successive complexations") by giving the

Complexes = By double clicking on the first line, the first complex will appear. By clicking on the following line, the following complexes will appear until no more component has been found in the database. To remove a complex, double click from the last added complex. It is possible to introduce up to 5 complexes per ligand.

Ratio of Coord. N° = To each selected complex the ratio of coordination number is required. This is the ratio of the metal free coordination number in the complex to the total metal coordination number.

Diffusion coefficient = The user must give the diffusion coefficient (in m^2/s) of the complex. A value is proposed from the database, when available. Otherwise the value of diffusion coefficient of the free metal ion can be used as a first approximation.

Electric charge = The user must give the electric charge of the complex.

Once the user has finished to add simpe ligands, he can come back to the General parameters screen by closing the window.

Fulvic Sites

If the user wants to add fulvic sites, he must press the button "Fulvic Sites" in the "General Parameter" screen, and the fulvic sites screen will appear, as shown in figure 4.
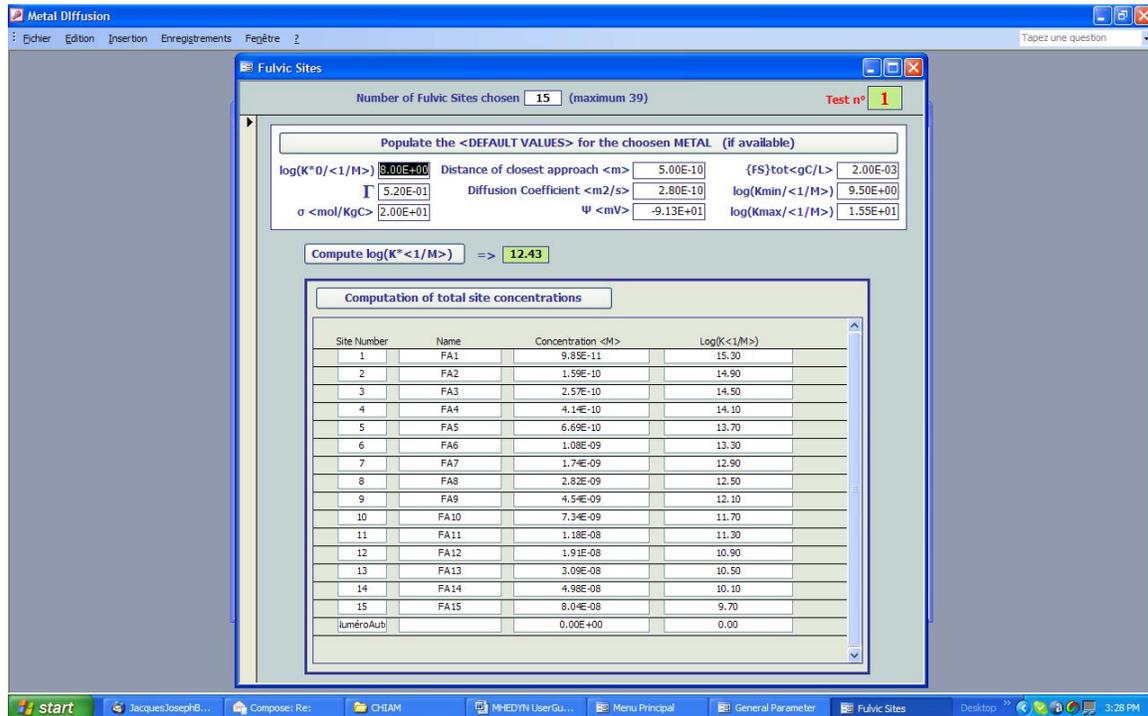
Figure 4: The fulvic sites screen.

The user must give the number of fulvic sites in the field at the top of the screen (39 sites is the maximum value permitted). Then the user must populate the fulvic site parameter either by accepting the default value from the database, by pressing the corresponding button, or choosing values by himself. The parameters to be introduced are the following (for definitions, discussion and values of these parameters, see ref [1]:

Log(K*0) = Characteristic stability constant of the metal-fulvic complexes, provided by their Freundlich isotherm, at given pH, ionic strength and temperature.

Γ = Characteristic parameter of the metal-fulvic complexes, provided by the slope of their Freundlich isotherm, at given pH, ionic strength and temperature. Γ is representative of the chemical heterogeneity of the fulvics ($0<\Gamma<1$).

Σ = Total density of sites (in mol/KgC; with fulvic mass expressed in Kg of carbon).

Distance of closest approach = Minimum distance between metal and site, to be given in meters.

**Diffusion Coefficient** = To be given in m^2/s.

Ψ = electric potential difference between the inside of fulvics and the bulk solution (in mV).

{FS} = Total concentration of fulvic sites (in gC/L).

Log(Kmin) = Minimun value of the equilibrium constant of fulvic sites, used for the computation.

Log(Kmax) =   Maximum value of the equilibrium constant of fulvic sires, used for the computation.

Then the user can compute the weighted average stability constant of the whole of fulvic complexes considered, log K* (see [1]), by clicking on the button "Compute Log(K*)". If the user is happy with his choice, he must confirm the values introduced by clicking on the grey strip on the left side of the screen, as shown below:
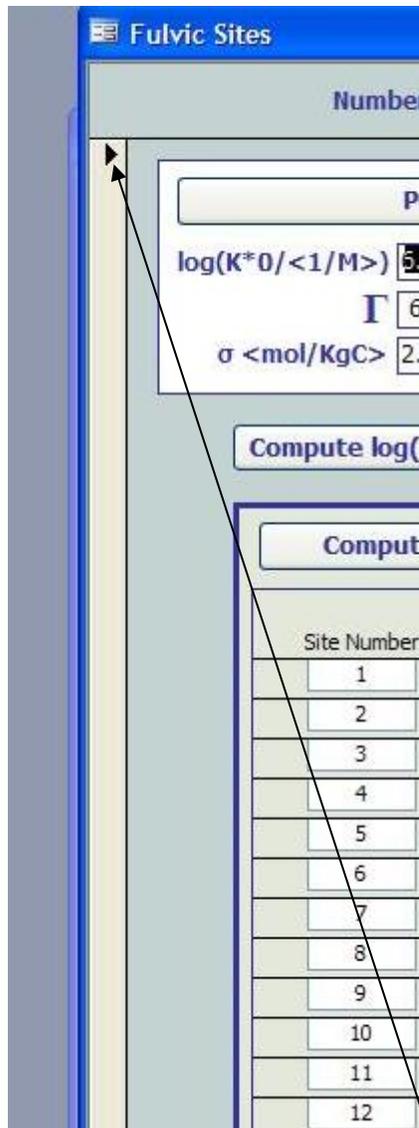
Click here to confirm the values introduced for the fulvics

Now the user must click on the button "Computation of total site concentrations" to compute the total site concentrations of fulvics.

Aggregate Classes

If the user wants to add classes of aggregate complexes, he must click on the button "Aggregate Classes" in the General Parameters screen. The Aggregate classes screen will

appear as shown in figure 5. Complexes with aggregates, as well as the corresponding dynamic parameters, are discussed in [2].
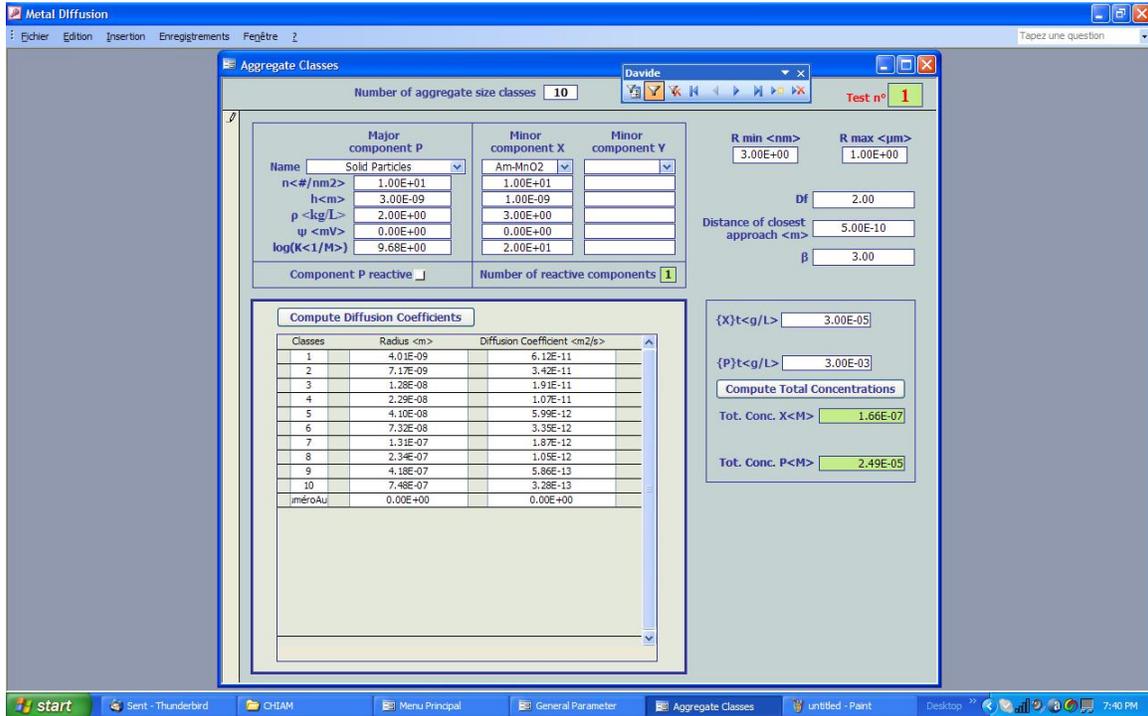

Figure 5: Aggregate classes screen

First of all the user must enter the "number of the aggregate size chosen" at the top of the screen. Then, the user must choose a Major Component P from the list and at least one of the two minor component X or/and Y. P is the component related to the structure and the size distribution of aggregates. It may also be complexing. X and Y are complexing components, adsorbed on P in minor proportions, inside the aggregate. *For the moment the major component P is considered as not reactive with the metal, therefore the user MUST add a minor component to see a complexation effect of the aggregate classes.* For each component a list of values of complexation parameters is proposed from the database, but the user can change as he wishes any of the parameter.

On the right side of the screen, the characteristic parameters for aggregate classes must be given. In particular the user must give the minimum and the maximum aggregate radius (in nm and in μm respectively) for the computation of the diffusion coefficient of the aggregate classes, the fractal dimension, D_f, of the aggregates (usually $1 < D_f < 3$), and the exponent, β, (usually $2 < β < 4$) of the Pareto size distribution of aggregates.

The mass concentration of the minor components, {X}, {Y}, and of the major component, {P}, must also be given in g/L. The user must click on the button "Compute Total Concentrations" to compute the total molar concentration of sites of X, Y and P.

Before to compute the diffusion coefficient by clicking the button "Compute Diffusion Coefficients", the user must confirm the values introduced by clicking on the grey strip on the left side of the screen (as for fulvics).

Then the button "Compute Diffusion Coefficients" must be pressed to compute the diffusion coefficients of each size class.

RUN OF A SIMULATION

When all the values have been introduced by the user, it is possible to run a simulation by clicking on the button "Launch the SIMULATION for –MINTEQ –MHEDYN" in the General Parameters screen. Note that the computation of the initial bulk equilibrium species distribution, by MINTEQ, is usually much faster than the following flux computation performed by MHEDYN. The latter may take minutes to days or even more, for steady-state flux computations, in particular when quickly reacting metals and large size (slowly diffusing) aggregates are considered. For that reason, the user can stop MHEDYN with the appropriate button, at the right bottom of the "General Parameter" screen. This may allow him/her to check (see results below) that the species distribution computed by MINTEQ is the appropriate one, before running an experiment requiring a long computer time with MHEDYN. In particular, the user can check the file C:\CHIAM\MINTEQA2\data.out which is the output of MINTEQ.
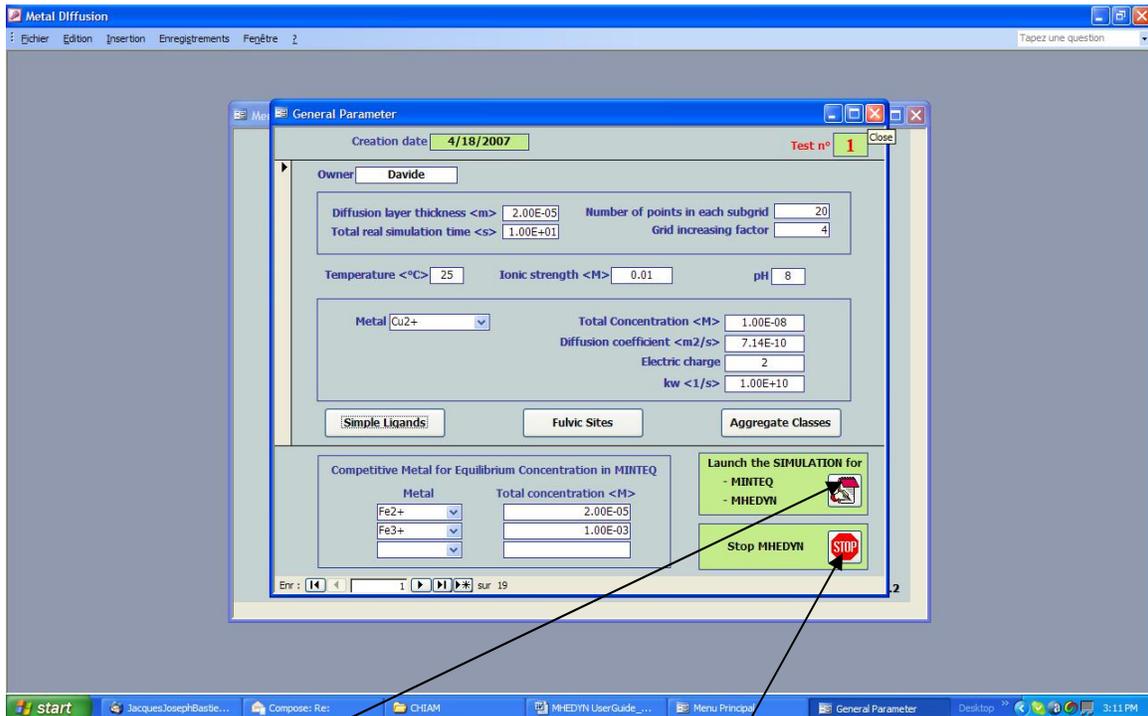
Click here to RUN a simulation   **Click here to STOP a simulation**

CHECK OF THE RESULTS

Once the simulation is running, the user can check the results by opening the file:
C:\CHIAM\Mhedyn\output\site_flux.txt
The "*site_flux.txt*" is a text file that summarizes the most relevant results of the
simulation during the evolution time. In particular, it gives information on:

- The total flux and the real time of computation
- The flux of the free metal ion and its proportion with respect to the total flux and
  the ratio between the free metal ion concentrations at $x=0$ and at $x=\delta$.
- The flux of each complex and its proportion with respect to the total flux and the
  ratio between its concentrations at $x=0$ and at $x=\delta$.
- The ratio between the concentrations at $x=0$ and at $x=\delta$ for each ligand, fulvic site
  and aggregate classes.
- The equilibrium constant (as reminder of input data) and the lability degree of
  each complex generated by the metal with ligands, fulvic sites and aggregates.
  NOTE: The lability degree is computed under the steady-state conditions.

When the simulation has stopped, the general output results are available at
C:\CHIAM\work\chiam_xx, where xx is the test number of the experiment. In particular
this file says whether or not the simulation has reached the steady state.

The file *C:\CHIAM\Mhedyn\output\summary.txt* gives a summary of the main parameters
of the simulation. It can be opened at any time, after the simulation has started.

USING THE TOOLBAR

When opening the application a toolbar is displayed on the top of each screen. Depending of the context, the buttons of the toolbar are available or not.

1) Applying a filter in searching records

Press the first button and put the screen in « search » mode
➔ Enter any "filter" on any field (i.e. search for owner beginning with: **A***)

Press the second button and display the records

On the bottom of the screen you can see the number of records returned and that you used a filter

To cancel the filter and display ALL the records, click on the third button

2) Navigation between records

Press this button to display the FIRST record

Press this button to display the LAST record

Press this button to display the PREVIOUS record

Press this button to display the NEXT record

3) Create or Delete records

Press this button to display the CREATED record

Press this button to display the DELETED record

SPECIAL RULES FOR DELETING RECORDS

- You cannot delete a « **MASTER RECORD** » without having deleted all the « **SLAVE RECORDS** ».
- Each record has to be deleted one by one and a confirmation is asked.
- To delete a record you have to place the cursor on any field of it and then press the delete button

Example:

➔ For instance, in the screen below, you have a "master record" of aggregate class and 10 "slave records" of Diffusion coefficients. If you press the

 DELETE button,

in the **AGGREGATE CLASSES** the system will remind you to delete first the 10 records as shown in the next picture.

DIFFERENCE BETWEEN "displayed" FIELDS AND FIELDS AVAILABLE FOR "Input"

- When fields are available for INPUT, the background colour is **WHITE**.
- When fields are NOT available for INPUT, the background colour is **GREEN** as shown in the next screen picture.
- When possible, the fields are filled in with default values, but the user can always modify them.
- IMPORTANT TO KNOW: When you quit a screen, if no errors are detected, the modifications will automatically be validated (as if you press the vertical toolbar).

Fulvic Sites

Number of Fulvic Sites choosen   10   (maximum 39)   Test n° 26

Populate the <DEFAULT VALUES> for the choosen METAL   (if available)

log(K*0/<1/M>) 6.40E+00	Distance of closest approach <m> 5.00E-10	{FS}tot<gC/L> 1.00E-05
Γ 6.00E-01	Diffusion Coefficient <m2/s> 2.8E-10	log(Kmin/<1/M>) 3.20E+00
σ <mol/KgC> 2.00E+01	Ψ <mV> -9.13E+01	log(Kmax/<1/M>) 7.10E+00

Compute log(K*<1/M>)   =>   4.73

Computation of total site concentrations

Site Number	Name	Concentration <M>	Log(K<1/M>)
1	FA1	1.75E-09	6.91
2	FA2	2.99E-09	6.52
3	FA3	5.13E-09	6.13
4	FA4	8.79E-09	5.74
5	FA5	1.51E-08	5.35
6	FA6	2.58E-08	4.96
7	FA7	4.43E-08	4.57
8	FA8	7.59E-08	4.18
9	FA9	1.30E-07	3.79
10	FA10	2.23E-07	3.40
NuméroAuto		0.00E+00	0.00

Press the VERTICAL TOOLBAR to add or modify values in the database, once pressed, the PENCIL will change in an ARROW

REFERENCES

[1] Buffle J., Zhang Z. and Startchev K. Metal flux and dynamic speciation at
     (bio)interfaces. Part I: critical evaluation and compilation of physicochemical
     parameters for complexes with simple ligands and fulvic/humic substances.
     Environ. Sci. Technol. **41**, 7609-7620 (2007).

[2] Zhang Z., Buffle J. and Alemani D. Metal flux and dynamic speciation at
    (bio)interfaces. Part II: evaluation and compilation of physicochemical parameters for
    complexes with particles and aggregates.
    Environ. Sci. Technol. **41**, 7621-7631 (2007).

[3] Alemani D., Buffle J., Zhang Z., Galceran J. and Chopard B. Metal flux and
    dynamic speciation at (bio)interfaces . Part III: MHEDYN, a general code for metal
    flux computation; application to simple and fulvic complexants.
    Env. Sci. Technol. **42**, 2021 (2008).

[4] Alemani D., Buffle J., Zhang Z., Galceran J. and Chopard B. Metal flux and dynamic
    speciation at (bio)interfaces . Part IV: MHEDYN, a general code for metal flux
    computation; application to particulate complexants and their mixtures with the other
    natural ligands.
     Env. Sci. Technol. **42**, 2028 (2008).