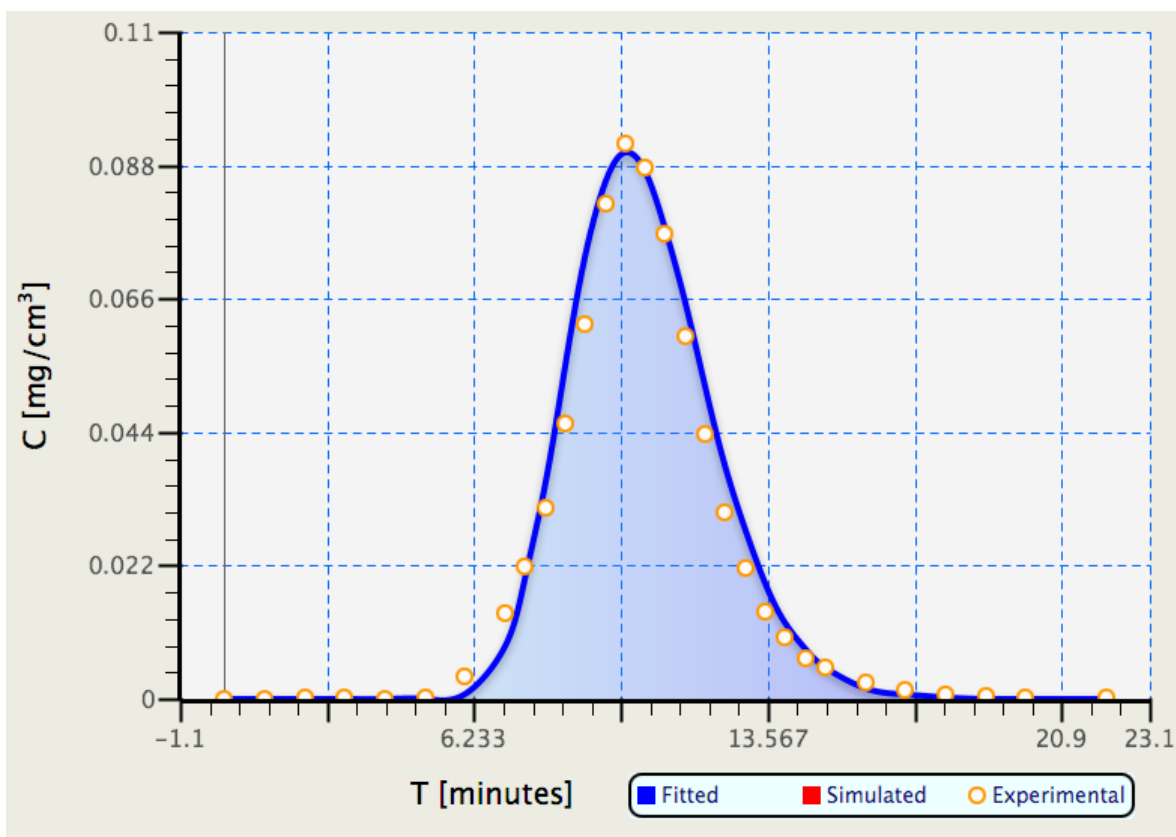


ColloidFit

A multipurpose fitting software for colloid fate and transport phenomena in porous media.

User Manual v.1.3.1



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1. How to install ColloidFit

The installation of ColloidFit is pretty straightforward because it is natively packaged with the necessary java runtime environment for both “Windows” and “Mac OS X” operating systems. Therefore, the user does not need to have java runtime environment already installed. All the necessary libraries required for ColloidFit++ to run are already included in the distributed installers. Just double click the respective installer, ColloidFit.msi for windows operating systems and ColloidFit++.dmg for Macintosh systems and execute the easy to follow installation steps (see Figure 1.1 and Figure 1.2, respectively). For any installation questions please visit the troubleshooting section of the current manual. The minimum requirements for an operating system to be compatible with ColloidFit++ can be found in Table 1.

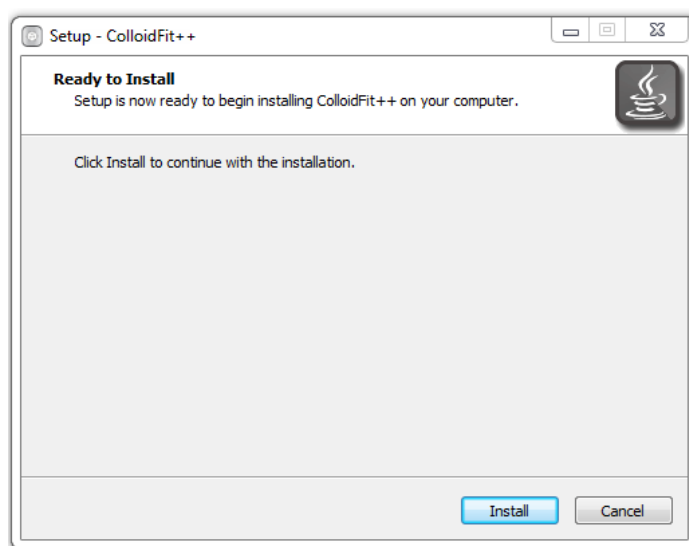


Figure 1.1. Installer in Windows



Figure 1.2. Installer in Macintosh

Table 1.1 System requirements

ColloidFit++ minimum OS requirements:

Processor	Minimum Intel Core i3 or similar Recommended Intel Core i7 or similar
RAM	More memory allows even larger graphs, but runs the risk of inducing larger Garbage Collection operations. Minimum 2GB Recommended 16—32GB or more
Available Hard Disk Space	Minimum 10GB SATA Recommended 100GB SSD w/ SATA
Operating System	<p>Windows</p> <ul style="list-style-type: none"> • Windows 10 • Windows 8.x (Desktop) • Windows 7 SP1 • Windows Vista SP2 • Windows Server 2008 R2 SP1 (64-bit) • Windows Server 2012 and 2012 R2 (64-bit) <p>Mac OS X</p> <ul style="list-style-type: none"> • Intel-based Mac running Mac OS X 10.8.3+, 10.9+ • Administrator privileges for installation • 64-bit browser <p>See supported Java 8 System Configurations for information about supported platforms, operating systems, desktop managers, and browsers.</p>
CD-ROM or DVD-ROM Drive	Optional
Video	1280 x 800, 256 colors (recommended: 1920x1080, true color 32bit)
Mouse	Microsoft Mouse or Compatible pointing component

2. About ColloidFit

The ColloidFit is an autonomous multipurpose fitting software for colloid fate and transport phenomena in porous media. The software is accompanied by an easy to use graphical user interface. ColloidFit can simulate the migration of colloid or biocolloid particles in one-dimensional water saturated, homogeneous porous media with uniform flow, accounting for non-equilibrium attachment onto the solid matrix. ColloidFit is using the state of the art fitting software, Pest. Therefore, ColloidFit is able to estimate unknown model parameters and to calculate the associated 95% confidence intervals.

Pest is a model-independent parameter estimation software, which can adjust model parameters or excitation data, so that the discrepancies between the pertinent model-generated numbers and the corresponding measurements are reduced to a minimum. More information related to the Pest software can be found at the official web page: <http://www.pesthomepage.org/>

Furthermore, given the advanced capabilities of ColloidFit, updated simulation results are provided graphically during the fitting process, so that the user can have a critical insight about how the various coefficient values affect the fitting process. Also, the model parameters, together with all necessary input and output information are displayed on the graphical interface. The fitting process may stop and resume at any point, upon user request. At the end of each parameter estimation-run, the best-fitted parameter values are displayed together with their 95% confidence intervals. Finally, extra attention is given to the way the raw data are manipulated by ColloidFit, so that data columns displayed on the user interface can be directly copied and pasted to Excel spreadsheets, by simple cut-copy-paste actions. It is worth mentioning here that in order to maximize the compatibility with the various operating systems, when pasting raw data to ColloidFit, the number format can use either “comma” or “dot” as decimal separators. There is no distinction between these two. However, when copying from ColloidFit the exported number format will use Operating Systems decimal separators.

2.1. Quick walk through

For a quick tour of how ColloidFit can be used, a relatively simple fitting example is presented next.

When ColloidFit is executed for the first time, Figure 2.1 should be visible to the user. This is the step-by-step “User Guide” that allows for an assisted interaction with ColloidFit. Given that this is the first execution, the “Create New Project” button should be clicked. This gives the user the opportunity to create a new ColloidFit project file, and customize its name and position within the system.



Figure 2.1. The User Guide, Step 1: welcome screen.

Creating a project file is a necessary step for any single simulation or fitting process. In order to protect the user, ColloidFit shows multiple warnings for most of its functions when no project file is available. A project file allows the user to save the current work, and reload it at a later time. All ColloidFit project files use the extension “.cfi”, for both Windows and Macintosh operating systems. Keep in mind that the project file name should not be longer than 20 characters. This restriction considerably reduces the possibility that there will not be enough space available in the user interface to display the complete file name.

After creating a new project file name, the user should click the “Next” button located at the bottom right corner (see Figure 2.1). This operation allows the user to select one of the four available simulation models. Here, for the needs of this simple example, the “Virus transport” model is selected (see Figure 2.2). Each of the available models will be described thoroughly in subsequent sections of this manual (see sections §4.1-4.8).

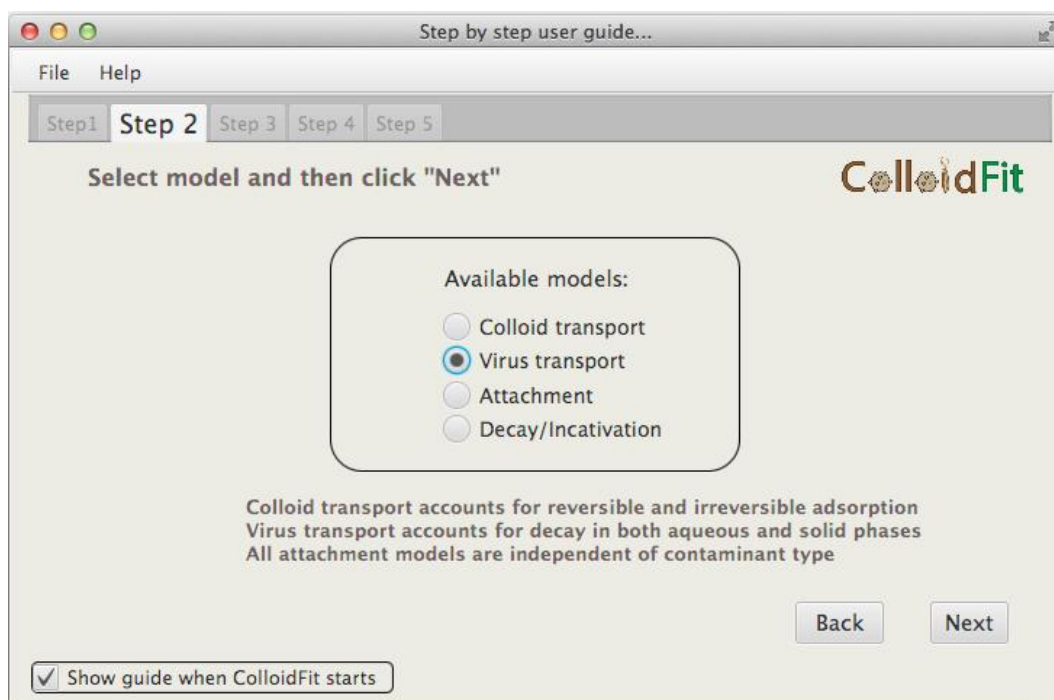


Figure 2.2. The User Guide, Step 2: Available models.

After selecting the desired model, here the “Virus transport” model, by clicking the “Next” button the display presented in Figure 2.3 is shown. ColloidFit supports two different colloid/biocolloid source configurations: (1) Instantaneous and (2) Broad pulse source (for detailed description of the sources see section §4). To continue with this tutorial, please select “Instantaneous source” and then click on the “Next” button, in order for Step 4 display to appear, as shown in Figure 2.4.

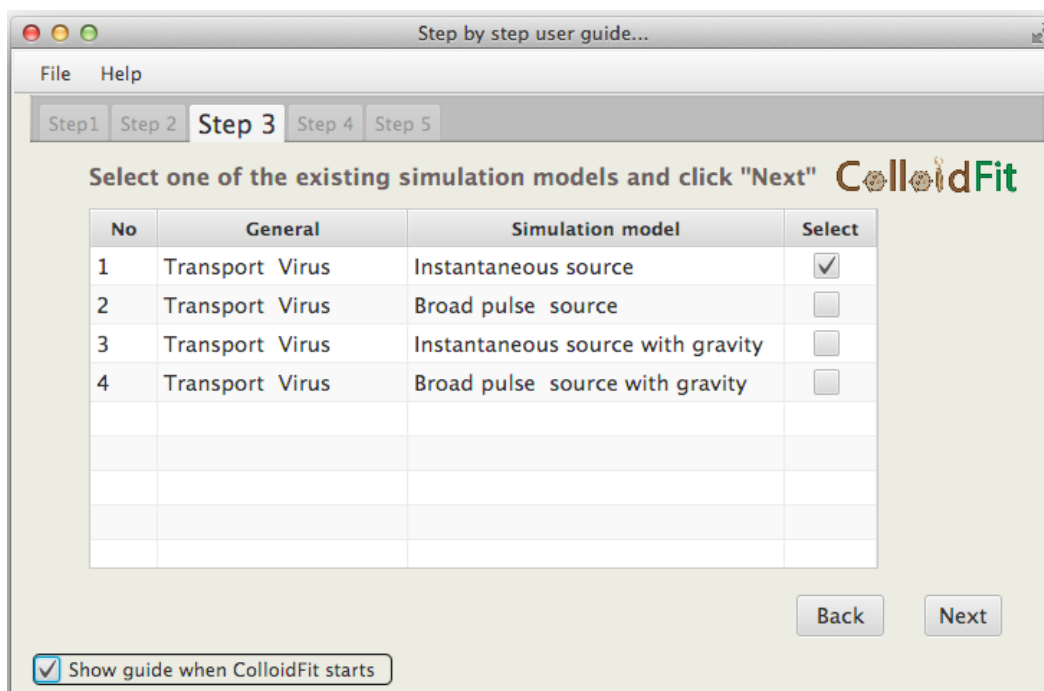


Figure 2.3. The User Guide, Step 3: Available source configurations.

Step by step user guide...

File Help

Step1 Step 2 Step 3 **Step 4** Step 5

Fill in the table with the experimental data and click "Next" **ColloidFit**

Num	Time (t)	Length (x)	Cexp (t,x)
1	0	0	0

"Time" column: Time of collected sample.
 "Length" column: Coordinate of collected sample.
 "Concentration" column: Measured concentration.

Row actions:

Graph choice: ☒ C (time) ☐ C (length) ☐ C* (time) ☐ C* (Conc)

T: X: C:

☒ Show guide when ColloidFit starts

Figure 2.4. The User Guide, Step 4: Time and Coordinate information.

The selected "Virus transport" model requires that the user enters three different data lists: (1) the sample collection times should be provided under the header "Time (t)"; (2) the sample collection x-coordinates should be provided under the header "Length (x)"; and (3) the collected sample concentrations should be provided under the header "Cexp (t,x)". An example of the three filled lists of data is shown in Figure 2.5.

Step by step user guide...

File Help

Step1 Step 2 Step 3 **Step 4** Step 5

Fill in the table with the experimental data and click "Next" **ColloidFit**

Num	Time (t)	Length (x)	Cexp (t,x)
1	0.005	30	4.592E-06
2	1	30	0
3	2	30	0.000280952
4	3	30	0.00024164
5	4	30	0
6	5	30	0.000240128
7	6	30	0.003612392
8	7	30	0.014069384
9	7.5	30	0.021791336
10	8	30	0.03150448

"Time" column: Time of collected sample.
 "Length" column: Coordinate of collected sample.
 "Concentration" column: Measured concentration.

Row actions:

Graph choice: ☒ C (time) ☐ C (length) ☐ C* (time) ☐ C* (Conc)

T: X: C:

☒ Show guide when ColloidFit starts

Figure 2.5. The User Guide, Step 4: Time and Coordinate information. Columns are now filled with required experimental data.

Note that, data can be inserted or edited in the table shown in the Step 4 display, either by double clicking onto individual shells, or by simply editing the “T:”, “X:” and “C:” textboxes located just below the table and then clicking the “Add” button to the right (see Figure 2.5). At this stage, by clicking the “Next” button the user reaches the final step, “Step 5”, which is displayed in Figure 2.6. Here, the initial parameter values should be inserted for all the parameters required by the selected model, which are already defined in Steps 2 and 3. The various parameter symbols displayed are defined in subsequent sections (§4.1-4.7). Furthermore, each parameter displayed in Figure 2.6 is followed by a check box, indicating whether this parameter should be fitted or not. In general, it is a good practice to fit two parameters at a time, and under no circumstances fit more than three (Katzourakis and Chrysikopoulos, 2014).

Step by step user guide...

File Help

Step 1 Step 2 Step 3 Step 4 **Step 5**

Provide initial parameter value and pick the ones to fit ColloidFit

Dispersion	Fit	Cross sectional area	Fit
D_x <input type="text"/>	<input type="checkbox"/>	A <input type="text"/>	<input type="checkbox"/>
Forward rate (sorption)		Porosity	
r_1 <input type="text" value="0"/>	<input type="checkbox"/>	θ <input type="text"/>	<input type="checkbox"/>
Reverse rate (desorption)		Mass injected	
r_2 <input type="text" value="0"/>	<input type="checkbox"/>	M_{in} <input type="text"/>	<input type="checkbox"/>
Virus inactivation		Decay rate of sorbed species	
λ <input type="text" value="0"/>	<input type="checkbox"/>	λ^* <input type="text" value="0"/>	<input type="checkbox"/>
Interstitial velocity			
U <input type="text"/>	<input type="checkbox"/>		

Back Finish

☒ Show guide when ColloidFit starts

Figure 2.6. The User Guide, Step 5: Initial parameter values and fitting status.

When all parameter textboxes are filled with valid numerical values (see Figure 2.7), by clicking the “Finish” button, the parameter values undergo a final quality check and subsequently they are transferred to the main ColloidFit user interface. At this point, many warnings may appear if something is wrong. For example, warnings may show if an invalid project name was inserted by the user, or if none of the model parameters were selected as fitted parameters, and so on...

Step by step user guide...

File Help

Step 1 Step 2 Step 3 Step 4 **Step 5**

Provide initial parameter value and pick the ones to fit

ColloidFit

Dispersion	Fit	Cross sectional area	Fit
D_x 0.2	<input checked="" type="checkbox"/>	A 4.900	<input type="checkbox"/>
Forward rate (sorption)		Porosity	
r_1 0.0020	<input type="checkbox"/>	θ 0.350	<input type="checkbox"/>
Reverse rate (desorption)		Mass injected	
r_2 0.100	<input type="checkbox"/>	M_{in} 2.000	<input type="checkbox"/>
Virus inactivation		Decay rate of sorbed species	
λ 0.0000e+	<input type="checkbox"/>	λ^* 0	<input type="checkbox"/>
Interstitial velocity			
U 2	<input checked="" type="checkbox"/>		

☒ Show guide when ColloidFit starts

Back Finish

Figure 2.7. The User Guide, Step 5: Initial parameter values and fitting status.

After the validation process is successfully completed, the main ColloidFit interface is displayed (see Figure 2.8). Initially, this interface consists of an empty plot area with a set of blank parameter text-boxes. In this “Graphing” tab the user gets updates about the fitting progress. Note that in the display presented in Figure 2.8 all text-boxes are empty because the fitting process has not been initiated yet.

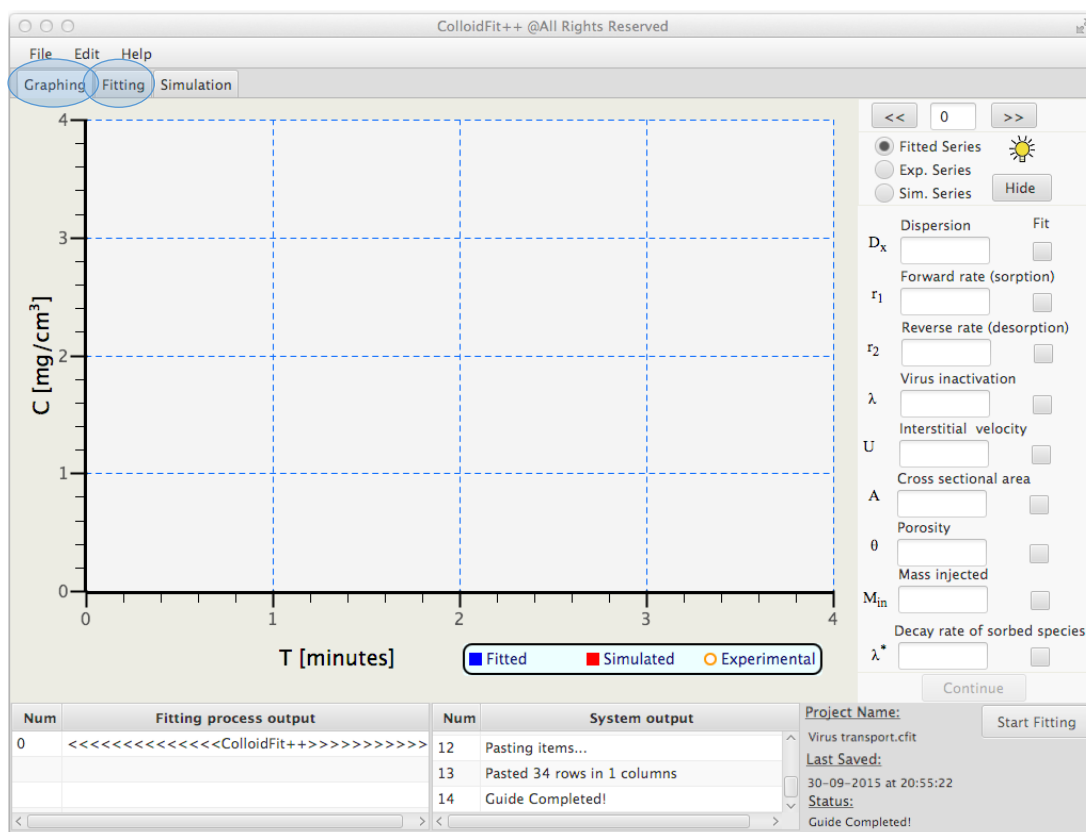


Figure 2.8. Main ColloidFit interface produced by the User Guide: Graphing tab.

Clicking on the “Fitting” tab, which is located at the top left corner (see Figure 2.8), a new page is displayed (see Figure 2.9), that holds all the experimental data provided to the User Guide up to this point. This is a compact and intuitive interface that allows the user to review, and edit if necessary, all the necessary information associated with the current fitting process. More about the fitting tab can be found in section §3.2.

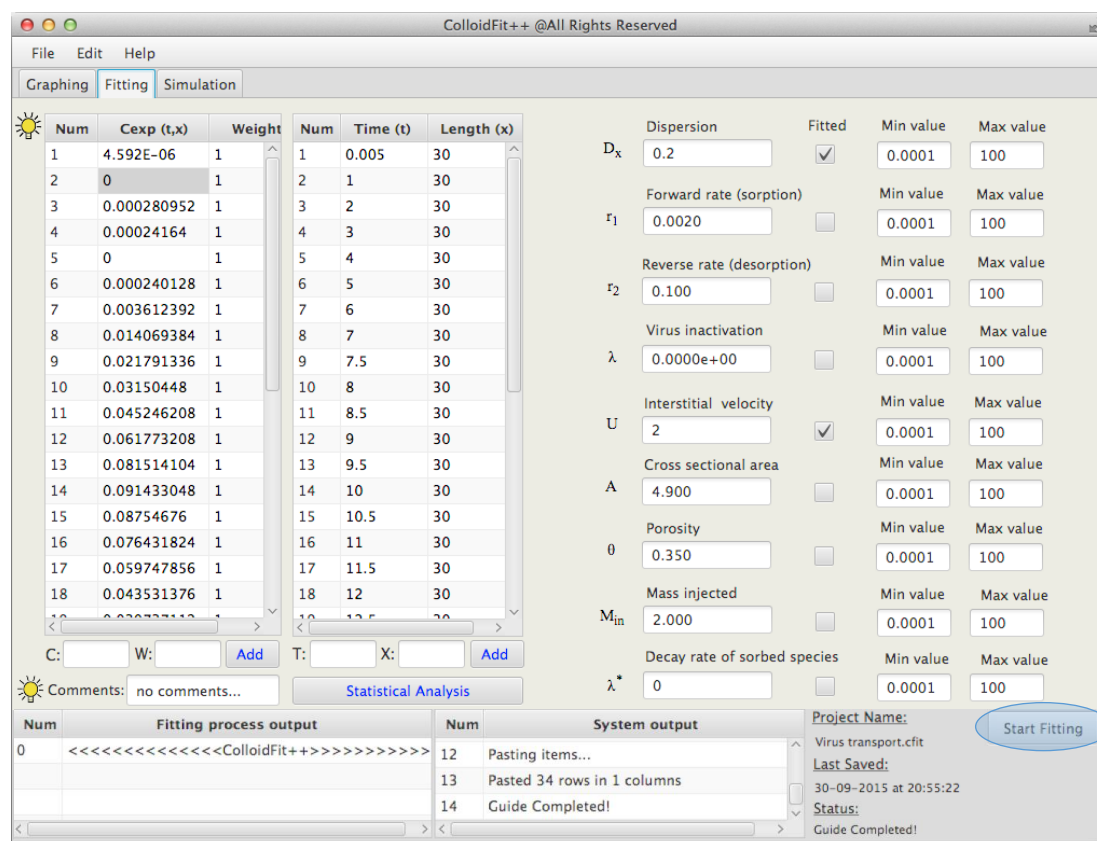


Figure 2.9. Main ColloidFit interface produced by the user Guide: Fitting tab.

Finally, the user now can press the “Start Fitting” button, which is located at the bottom right corner of the Fitting tab (see Figure 2.9). This action initiates a validation check, in order to make sure all data were properly inserted (i.e. no missing parameters, no unexpected zeroes, the number of experimental concentrations and time entries are equal, at least one of the model parameters is selected to be fitted, etc), and subsequently begins the fitting procedures. At this point, ColloidFit displays a new page (see Figure 2.10) with both the experimental data (orange circles), and splines of the current parameter simulations (blue curve). After a sufficient number of fitting iterations, the best-fitted parameters are found and displayed (see Figure 2.11). In this case, the fitting process is finished successfully. The total number of model simulations used is shown at the top right corner of the current display (see Figure 2.11). For the present illustrative example, the value 75 is shown, indicating that the complete fitting process required seventy-five model simulations.

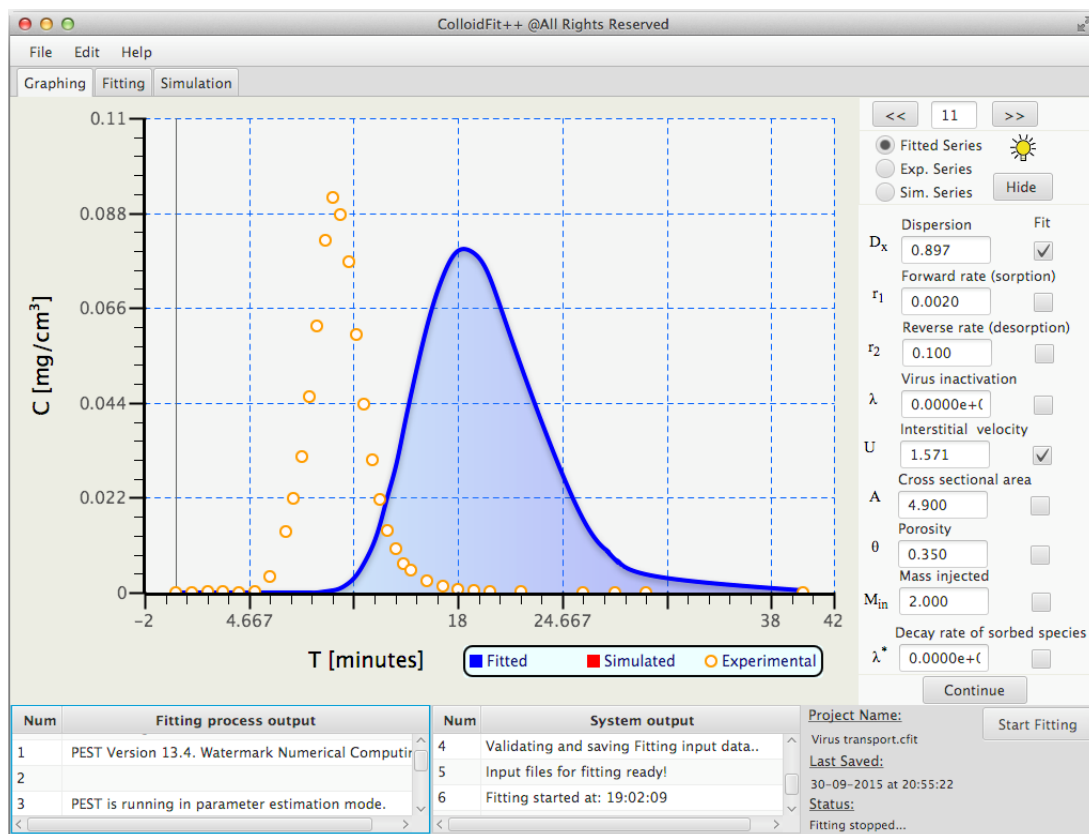


Figure 2.10. Main ColloidFit “Graphing” tab: Fitting procedure in progress.

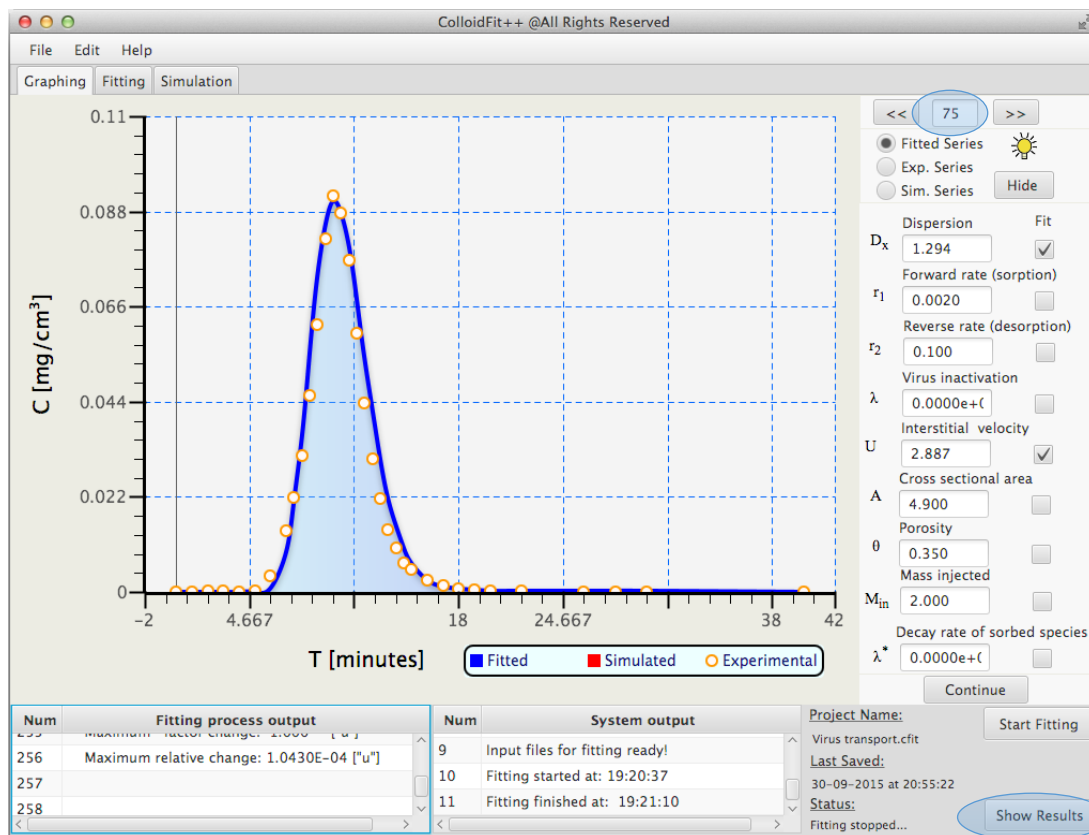


Figure 2.11. Main ColloidFit “Graphing” tab: Fitting procedure successfully ended.

By clicking the “Show Results” button, which is located at the bottom right corner of the current display (see Figure 2.11), the results of the finished fitting process are presented (see Figure 2.12). The fitted parameter values and their 95% confidence intervals are shown, together with the columns containing: (1) number of data point, (2) x-coordinate, (3) time, (4) concentration, and (5) simulated concentration.

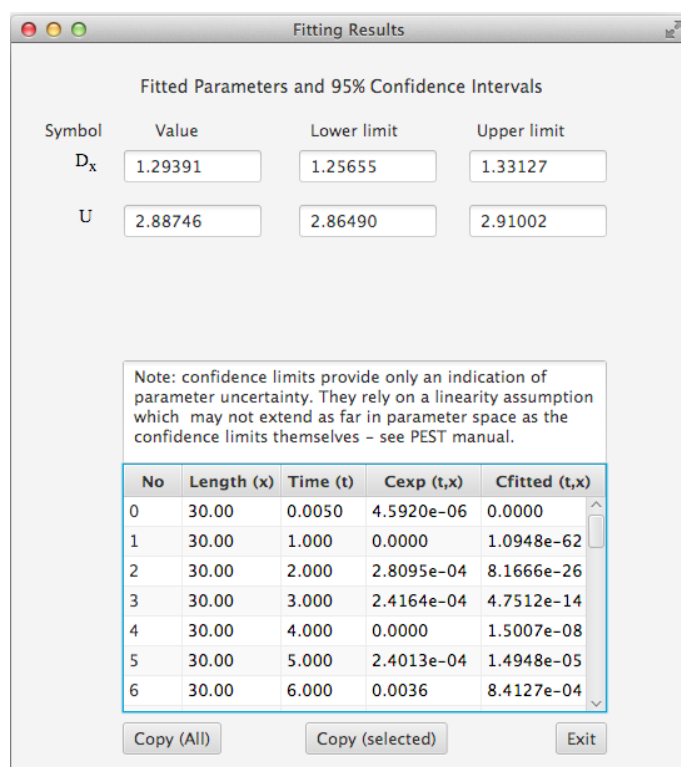


Figure 2.12. “Show results” pane.

3. ColloidFit in depth

The next sections present an in-depth overview of ColloidFit. Emphasis is given to detailed explanation of the three basic features of ColloidFit: (i) Graphing, (ii) Fitting, and (iii) Simulating.

3.1. The Graphing tab

The “Graphing” tab (see Figure 3.1) is dominated by the graph area {7} that contains up to three different kinds of information: (1) Experimental data, (2) Fitted curve, and (3) Simulated curve. The orange circles represent the experimental concentration data that need to be fitted, the blue curve represents the fitted concentration curve, and the red curve represents the simulated concentration curve (not shown in Figure 3.1) produced with model parameters defined by the user.

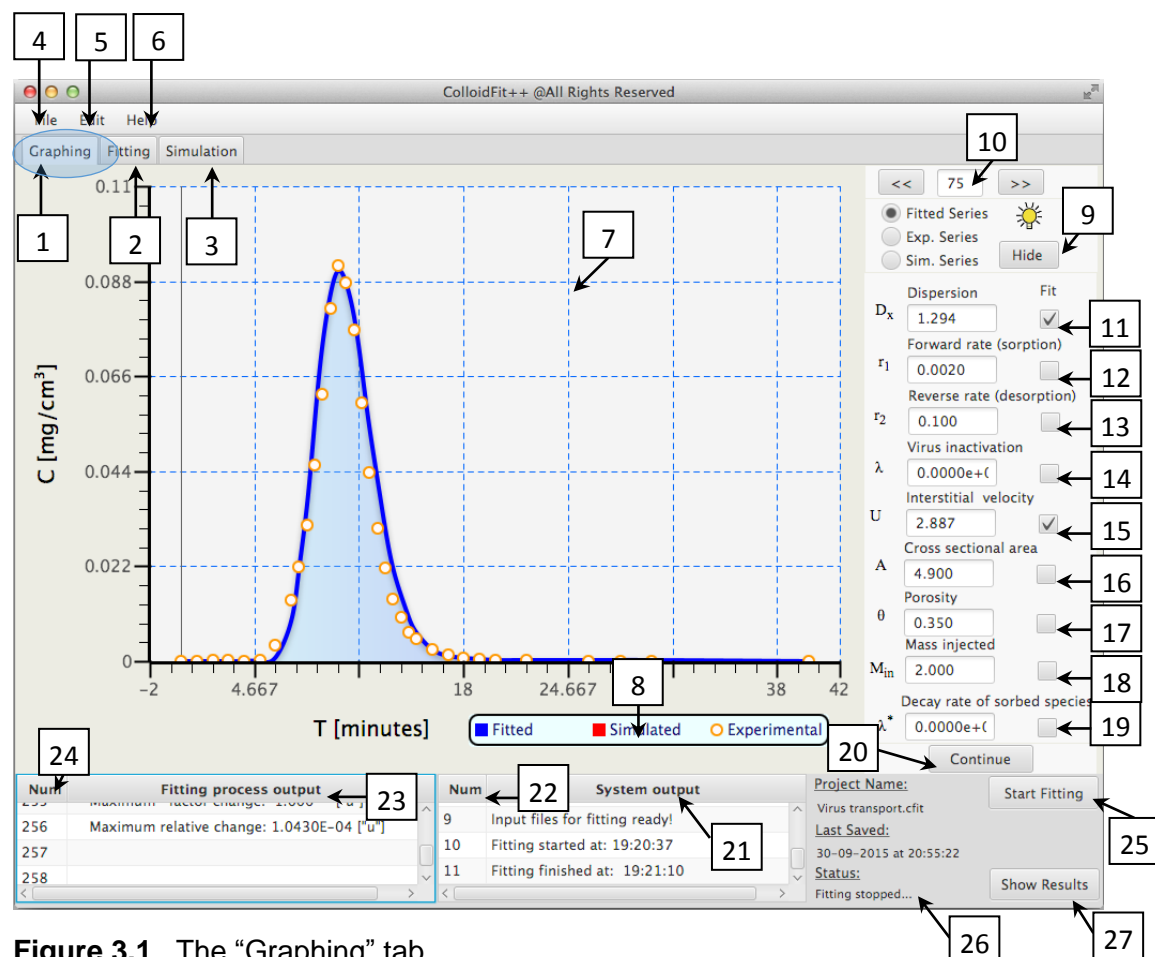


Figure 3.1. The “Graphing” tab.

The key elements of the “Graphing” tab (see Figure 3.1) are:

- {1} Graphing tab: The display shown in Figure 3.1 becomes visible when the Graphing tab is clicked.
- {2} Fitting Parameters tab: The fitting configuration tab becomes visible when the “Fitting” tab is clicked.
- {3} Simulation tab: The simulation tab becomes visible when the “Simulation” tab is clicked.

- {4} File menu: Saves the current experiment to the hard disk drive together with the produced graphs.
- {5} Options menu: Determines the constants for the simulations and the amount of cpus that the user dedicates to the fitting. ColloidFit allows up to eight cores to be used in parallel for the fitting process.
- {6} Help menu: Provides helpful information.
- {7} Main graph element.
- {8} Legend of the various data displayed on the graphing element {7}.
- {9} Clear button: Removes selected data from the graphing element {7}.
- {10} History element: By clicking the respective arrows after the completion of the fitting process, all of the model simulations that took place during the fitting can be viewed one after the other. Also, for each simulation the associated model parameters can be found in elements {11}-{19}
- {11} Hydrodynamic dispersion coefficient, $[L^2/t]$
- {12} Rate coefficient of virus attachment onto the solid matrix, $[1/t]$
- {13} Rate coefficient of virus detachment from the solid matrix, $[1/t]$
- {14} Virus inactivation rate coefficient, $[1/t]$
- {15} Interstitial velocity, $[L/t]$
- {16} Cross sectional area of the aquifer, $[L^2]$
- {17} Porosity of the solid matrix, $[-]$
- {18} Virus mass injected into the aquifer, $[M]$
- {19} Decay rate of viruses attached onto the solid matrix, $[1/t]$. Please set this parameter to **zero** if the virus inactivation rate coefficient (see element {14}) is set to zero.
- {20} The “Continue” button restarts the fitting process with initial parameter values the set of values resulted at the end of the previous fitting run. Note that, if necessary, the user can easily modify these initial parameter values.
- {21} This window displays messages related to current user actions. Messages may indicate system success or failure, depending on the quality of the input data provided by the user.
- {22} This window presents the incremental number of the message being displayed by element {21}.
- {23} This window displays messages generated by the “Pest” software. These messages describe the current status of fitting.
- {24} This window presents the incremental number of the messages being displayed by element {23}.
- {25} The “Start Fitting” button initiates the fitting process. When the “Start Fitting” button is clicked, the “Graphing” tab (see element {1}) becomes active.
- {26} This line of text presents crucial messages about the status of ColloidFit.
- {27} When the fitting process is finished successfully, the “Show Results” button becomes visible. By clicking the “Show Results” button the fitting results are displayed (see Figure 2.12).

As soon as the fitting button is pressed, the “Graphing” tab becomes active and the experimental data are graphically illustrated (see orange circles in Figure 3.1). Moreover, on the bottom left corner of the display shown in Figure 3.1, the “Pest” software describes the status of the fitting process. Whereas, at the bottom right corner of the display shown in Figure 3.1, the “Stop Fitting” button becomes active allowing the user to stop the fitting process at any time.

After the “Pest” software has completed the testing phase, the transport model simulations appear in the main graph area of the current display, indicating that the

fitting is in progress (see blue curve in Figure 3.1). As time passes, the consecutive model simulations improve and match better and better the experimental data. At the same time the parameters used to produce the current model simulations are listed on the right side of the current display (see Figure 3.1). When the fitting process is finished, the “Stop Fitting” button fades away and the “Show Results” button becomes visible on the bottom right corner of the current display (see Figure 3.2). By clicking the “Show Results” button, the results of the fitting process (final fitted parameter values and corresponding confidence intervals) are displayed.

Note that a useful functionality of ColloidFit is the ability to continue further the fitting process. By pressing the “Continue” button, which is located on the bottom right corner of the display presented in Figure 3.1, the fitting process restarts with initial parameter values the set of values produced by the last fitting iteration. This is a useful function for coping with unsuccessful initial value guesses that yield poor results, and thus necessitate the modification of one or more initial values prior to starting another fitting run.

3.2. The Fitting tab

When the “Fitting” tab is active, Figure 3.2 is displayed.

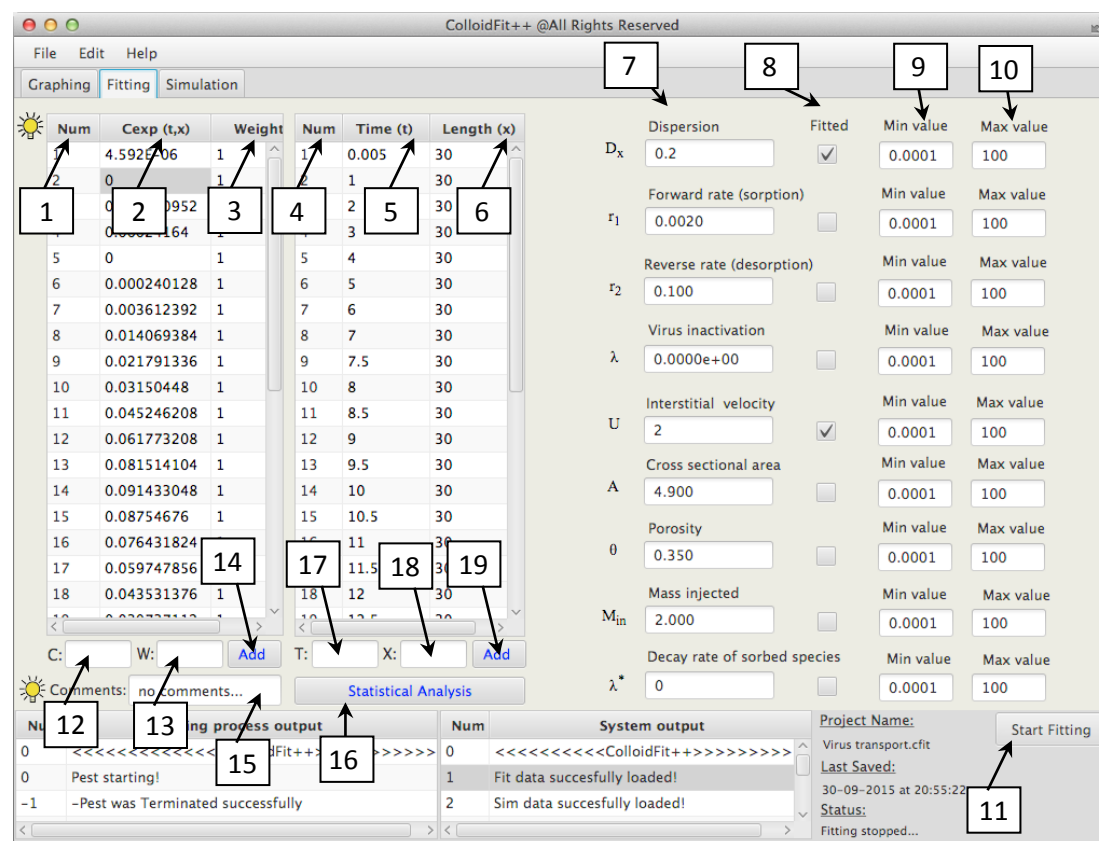


Figure 3.2. Details of the “Fitting” tab.

The key elements of the “Fitting” tab are:

- {1} Incremental number of data values listed in column {2}.
- {2} Experimental concentration values.

- {3} This is the column with the “Weights”, which reflect how important (accurate) are the corresponding concentration values. Some concentrations may incorporate experimental error (uncertainty). The user can reduce the impact of uncertain data to the fitting process by simply assigning to these uncertain data points a smaller relative weight (importance). If all weights are set to unity, then all concentrations are of equal importance to the fitting process. Note that the absolute value of the weights does not really affect the fitting process. The fitting results will be the same if all weights are set to “one” or “two”.
- {4} Incremental number of the data values listed in columns {5} and {6}.
- {5} Collection times of experimental concentration samples.
- {6} Longitudinal coordinates of sampling points.
- {7} Fixed or initial guess values of the model parameters.
- {8} Indicates whether the corresponding parameter is fixed or will be fitted. It is highly recommended that no more than three parameters are fitted simultaneously. Of course, ColloidFit can cope with more than three fitting parameters; however, the resulting fitted parameter values may not be unique (for additional discussion see §5.1).
- {9} Minimum values that the model parameters to be fitted are allowed to take.
- {10} Maximum values that the model parameters to be fitted are allowed to take.
- {11} “Start Fitting” is the button that initiates the fitting process.
- {12} This is a text box for manual insertion of concentration values.
- {13} This is a text box for manual insertion of weight values.
- {14} “Add” is the button that adds the manually inserted values into the text boxes {12} and {13} at the end of the “Cexp (t,x)” and “Weight” columns, respectively.
- {15} In this window, the user can type notes related to the current fitting project. However, the user should **avoid** using system-reserved symbols like “<” or “>”. If such symbols are used an error message will appear.
- {16} “Statistical Analysis” is the button that displays extensive statistical information and data (for additional discussion see §3.4.4).
- {17} This is a text box for manual insertion of time values.
- {18} This is a text box for manual insertion of x-coordinate values.
- {19} “Add” is the button that adds the manually inserted values into the boxes {17} and {18} at the end of the “Time (t)” and “Length (x)” columns, respectively.

The recommended actions that the user must follow for a successful fitting are:

- {1} Insert all experimental concentrations that need to be fitted in the column “Cexp”.
- {2} Fill the “Weights” column. Please note that the “Weights” inserted in the column reflect how important (accurate) are the corresponding concentration values. Some concentrations may incorporate experimental error (uncertainty). The user can reduce the impact of uncertain data to the fitting process by simply assigning to these data points a smaller relative weight (importance). If all values are of the same importance, then a value equal to “1” can be used to fill the entire column.
- {3} Insert the collection times of the experimental concentrations in the “Time (t)” column.
- {4} Insert the x-coordinate of each sampling point.

- {5} Provide the fixed or initial guess value of each model parameter.
- {6} Specify whether each parameter is fixed or will be fitted. It is highly recommended that no more than three parameters should be fitted at a time. Of course, ColloidFit can cope with more than three parameters, but the resulted parameters may be not unique.
- {7} Finally, press the “Start Fitting” button, located in the right lower corner of the current display (see Figure 3.2), to initiate the fitting process.

3.3. The Simulation tab

When the “Simulation” tab is active, Figure 3.3 is displayed.

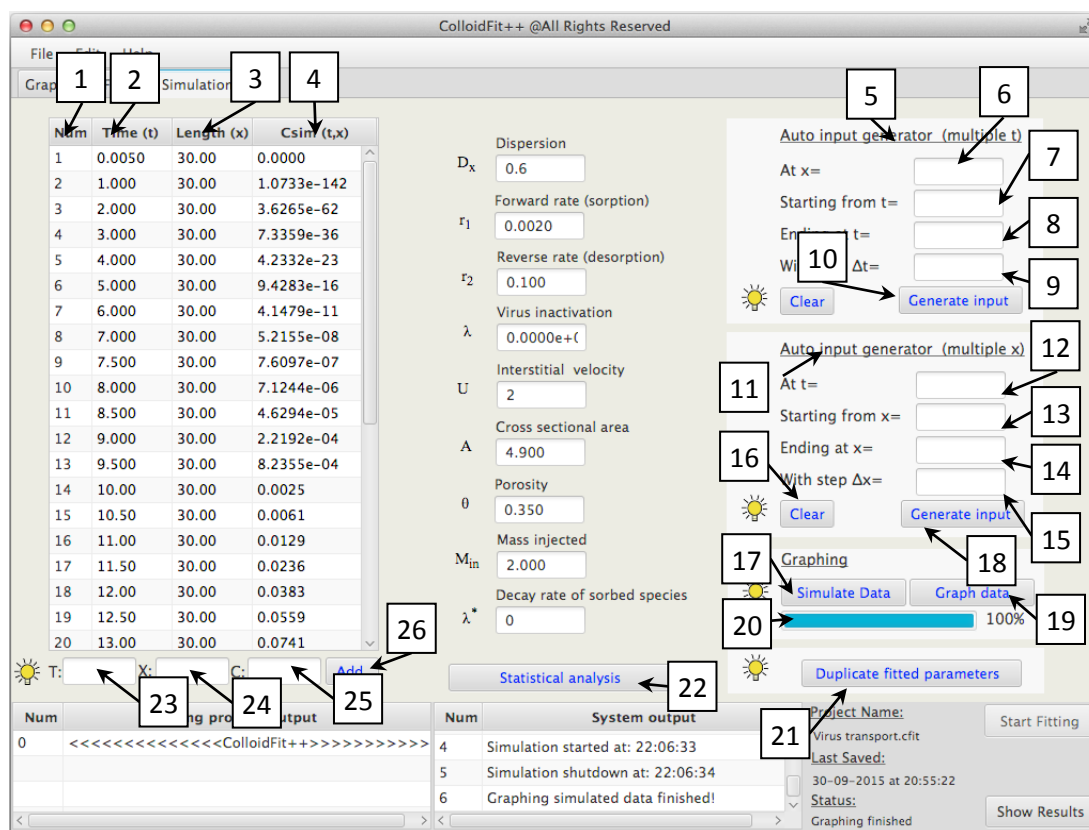


Figure 3.3. Details of the “Simulation” tab.

The “Simulation” tab allows the user to perform additional single transport simulations at preselected specific points in time and space, independently of any fitting process. The user may either fill manually the “Time (t)” (element {2}) and “Length (x)” (element {3}) columns by typing in the appropriate values, or generate automatically input data over the temporal and the spatial domains. For the second case the user may choose a constant x-coordinate value (element {6}) and then select an initial temporal value (element {7}) and a final temporal value (element {8}) along with a desired temporal step value (element {9}). Clicking the “Generate input” button creates new rows in elements {1}-{4} that hold the generated pairs of time and space coordinates. In this case, the space coordinates hold a constant value equal to the preselected initial selection, while the time values range from the preselected

initial temporal value to the preselected final temporal value, with an incremental step equal the preselected temporal step. Similarly, the user may iterate through space while holding a constant temporal value, by just using elements {12}-{15}. It is worthy to note here that in both cases, the generated temporal and spatial pairs do not substitute any already existing values found in columns {1}-{4}. Instead, they will be added at the end of these columns. Also, note that all simulation results are displayed graphically.

The key elements of the “Simulation” tab displayed in Figure 3.3 are:

- {1} Incremental number of data values listed in columns {2}-{4}.
- {2} Collection times of experimental concentration samples.
- {3} Longitudinal coordinates of sampling points.
- {4} Simulated concentration values.
- {5} This pane automatically generates input data over a user specified temporal space.
- {6} The spatial coordinate of sample collection location.
- {7} Starting value for automatic temporal input data generation.
- {8} Ending value for automatic temporal input data generation.
- {9} Time step for automatic temporal input data generation.
- {10} “Generate input” is the button that initiates the automatic generation of input data (consisting of temporal and spatial pairs). The columns {2} and {3} are filled with the temporal and spatial data, as specified by the elements {6}-{9}.
Note that the extra rows generated do not overwrite any existing rows, they are just added to the end of the corresponding columns.
- {11} This pane automatically generates input data over a user specified spatial space.
- {12} Collection times of experimental concentration samples.
- {13} Starting value for automatic spatial input data generation.
- {14} Ending value for automatic spatial input data generation.
- {15} Spatial step for automatic input data generation.
- {16} “Clear” is the button that clears any data found in elements {12}-{15}.
- {17} “Simulate Data” is the button that starts the transport simulation based on the parameter values given, as well as the spatial and temporal data defined in elements {2} and {3}. Moreover, elements {2} and {3} can be manually modified by typing in the time and x-coordinate data.
- {18} “Generate input” is the button that initiates the automatic generation of input time and spatial coordinates. The columns {2} and {3} will be filled with the temporal and spatial data, respectively, as specified by the elements {12}-{15}.
- {19} “Graph data” is the button that graphically illustrates the concentrations found in column {4}.
- {20} This horizontal bar represents the level of progress towards the complete determination of the requested concentrations.
- {21} “Duplicate fitted parameters” is the button that copies the model parameters from the “Graphing” tab (see elements {11}-{19} in Figure 3.1) to the respective parameter text boxes in Figure 3.3.
- {22} “Statistical analysis” is the button that displays statistical information for the concentrations listed in column {4}.
- {23} Text box for manual insertion of time values.
- {24} Text box for manual insertion of x-coordinate values.
- {25} Text box for manual insertion of concentration values.

{26} “Add” is the button that adds the manually inserted values into the text boxes {23}-{25} to the end of the “Time (t)”, “Length (x)” and “Cexp (t,x)” columns, respectively.

The recommended actions that the user should follow in order to effectively take advantage of the “Simulation” tab are the following:

- 1) Fill the time and x-coordinate data in the appropriate columns shown in Figure 3.3. The data can be inserted either manually by simply typing the numerical values, or automatically by using the temporal and spatial generators.
- 2) Provide the desired model parameter values by either manual typing in the appropriate text boxes shown in Figure 3.3, or by copying the existing parameter values from the “Graphing” tab shown in Figure 3.1. Note that this copying operation can be achieved easily by clicking the “Duplicate fitted parameters” button.
- 3) Click the “Simulate data” button to start the desired simulation, and then view the simulated data in the concentration column.
- 4) Note that any “Time (t)”, “Length (x)” and “Cexp (t,x)” column entry can be modified if needed.
- 5) Click the “Graph data” button to display the generated simulation data in the “Graphing” tab with a red curve, as shown in Figure 3.4.

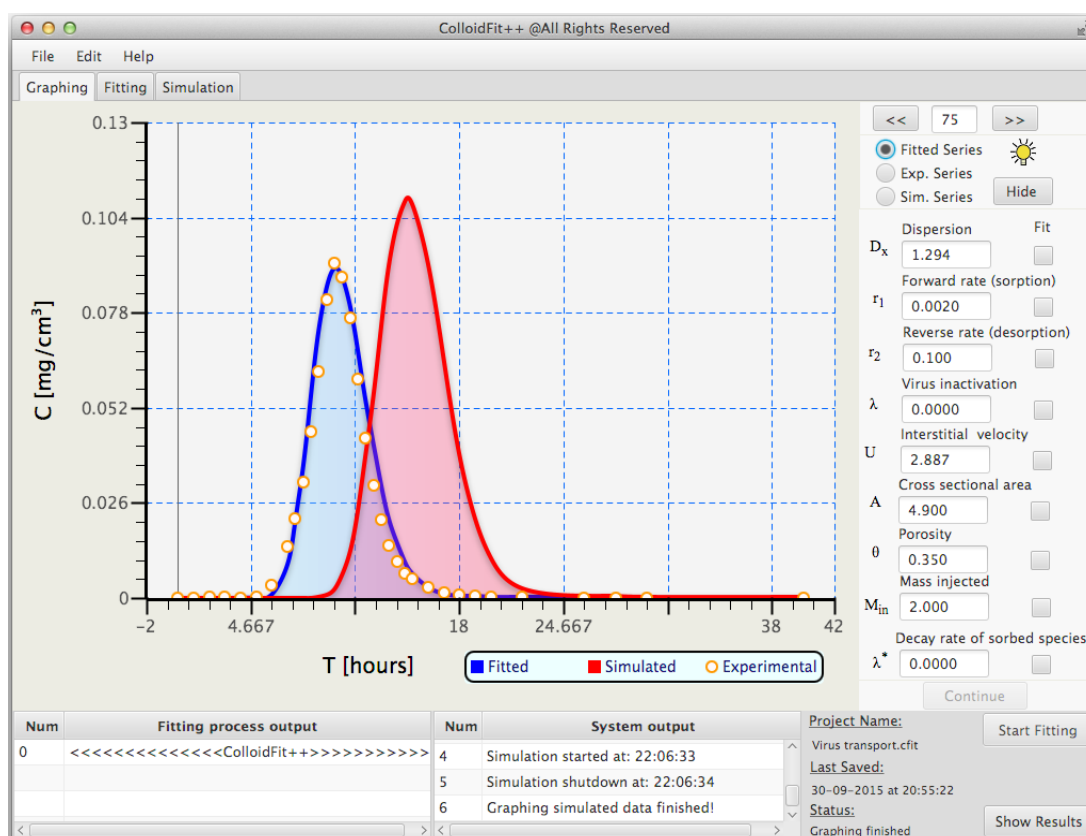


Figure 3.4. Display of fitted experimental concentration data together with user specified simulated data.

3.4. Additional menus

ColloidFit provides several additional user-friendly menus that allow for fast usage and comfortable interaction.

3.4.1. The “File” menu

By clicking the “File” menu, an interesting pane is presented, as shown in Figure 3.5.

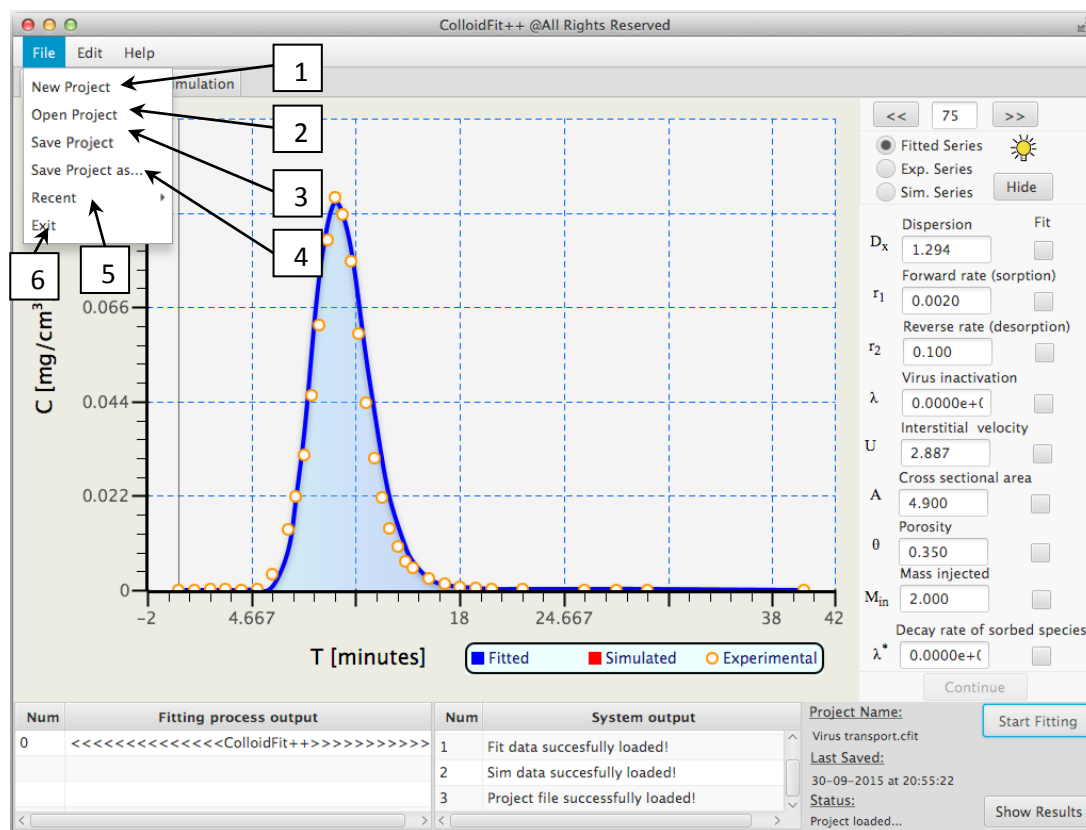


Figure 3.5. The “File” menu.

The key elements of the “File” menu, shown in Figure 3.5, are:

- (1) The item “New Project” creates a new ColloidFit project and clears all previously occupied text fields.
- (2) The item “Open Project” allows the user to search the hard drive and open an existing ColloidFit project.
- (3) The item “Save Project” saves the current ColloidFit project to the hard disk with the previously saved project name, or initiates a save dialog in order to choose a new project name and specify the folder that will be saved.
- (4) The item “Save Project as ...” displays a window with instructions on how to save the current project for the first time.
- (5) The item “Recent” shows any recently opened or closed ColloidFit projects.
- (6) The item “Exit” shuts down all processes and closes the ColloidFit program.

3.4.2. The Options menu

Clicking on “Edit” -> “Options”, the options menu is displayed.

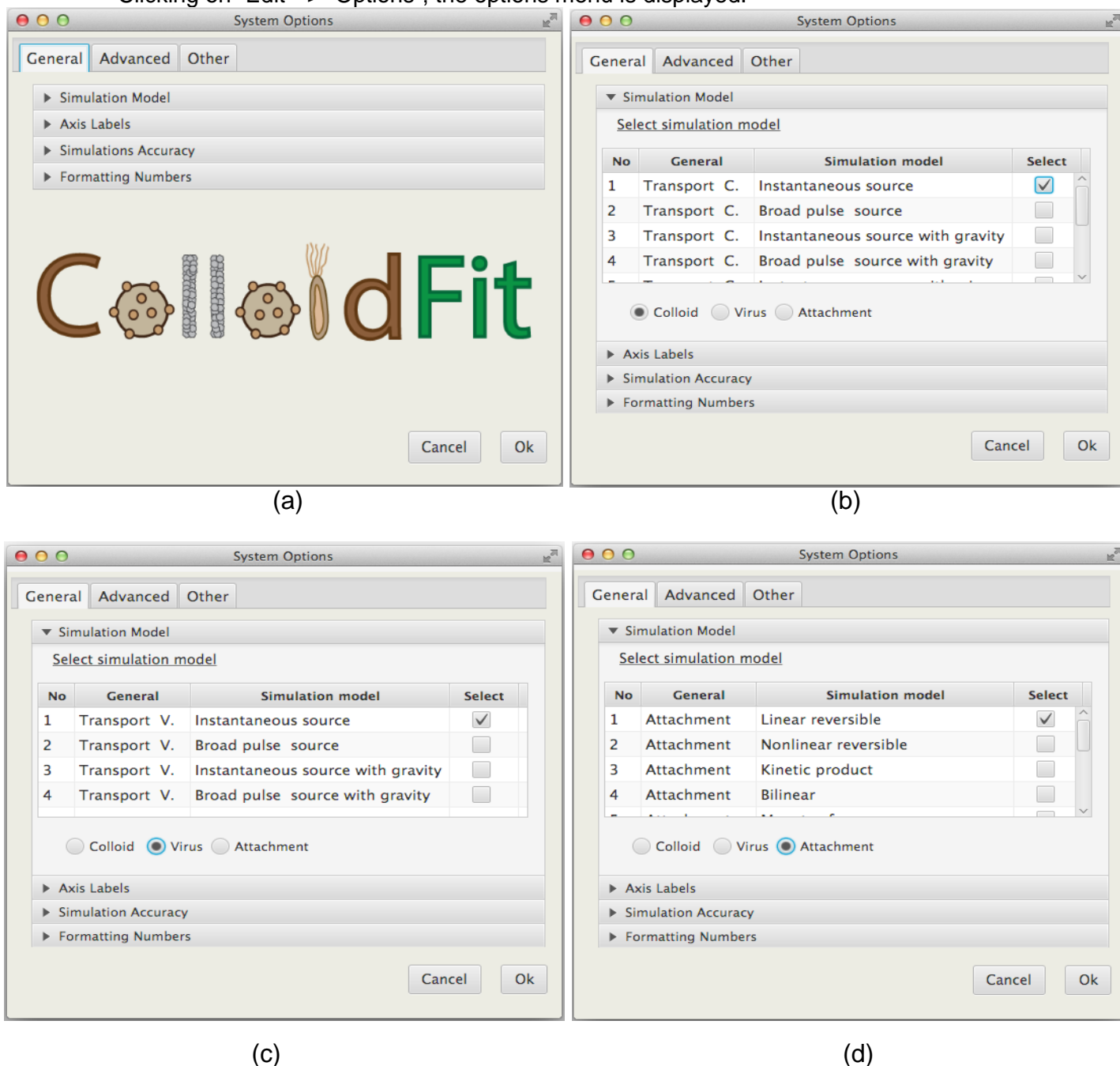


Figure 3.6. The “Options” menu: “Simulation Models” tab.

The “System Options” menu, as shown in Figure 3.6a, contains various system configurations and options that allow the user to optimize the fitting process as needed. The most important item of the menu is the “Simulation Model”, found under the “General” tab (see Figures 3.6a,b,c,d). The user is free to select any simulation model at any time. The only restriction is that no fitting should be active at the moment of selection. Upon the selection of the model, several necessary changes occur in the various user interface tabs (see Figures 3.1-3.3), so that the new model parameters may be properly accommodated. ColloidFit can handle the transport of

two different types of suspended particles: (i) Colloids, indicated as “Transport C.” (see Figure 3.6b), and (ii) Viruses, indicated as “Transport V.” (see Figure 3.6c). Also, ColloidFit can handle batch particle attachment experimental data by the use of various frequently employed equilibrium and kinetic particle attachment models (see Figure 3.6d). Furthermore, if any of the selected transport models accounts for gravity then the “Gravity effects” button become visible (see Figure 7a,b). When the “Gravity effects” button is clicked the “Set gravity parameters” menu appears (see Figure 3.14).

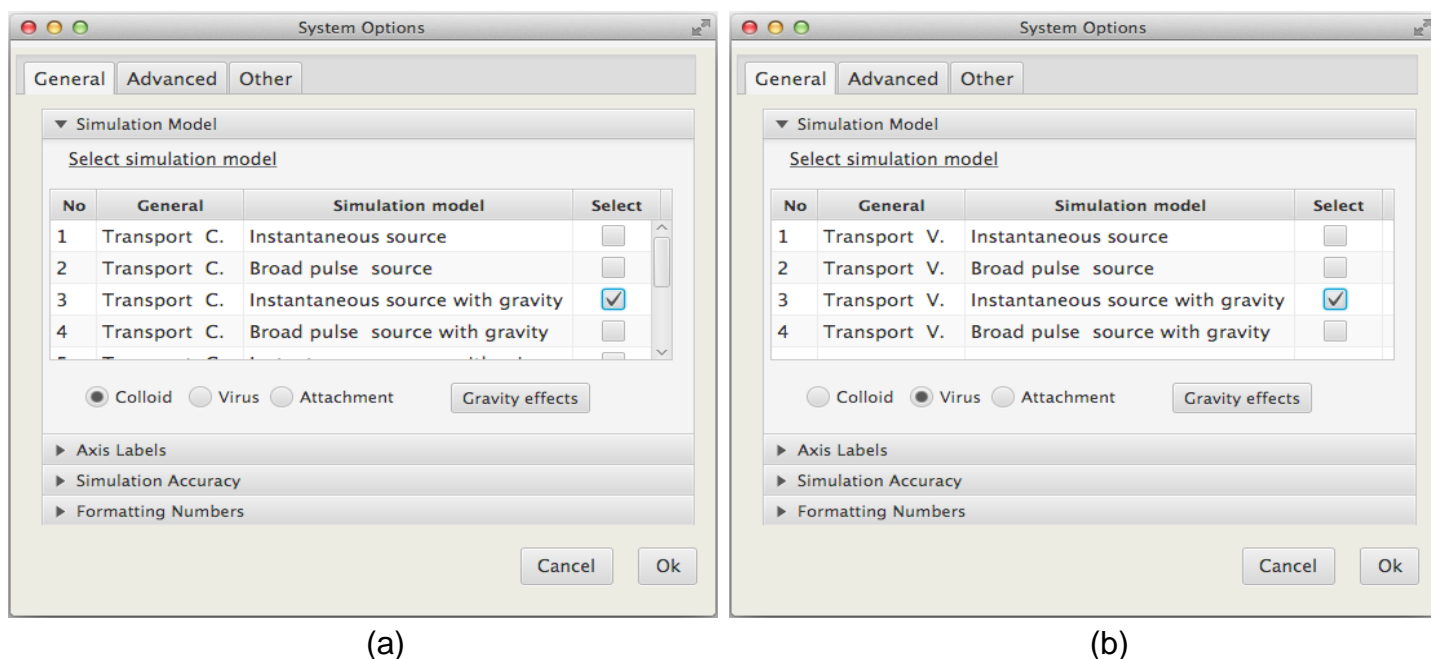


Figure 3.7. The “Options” menu: “Simulation Models” tab showing the available particle transport options with gravity effects.

Within the “General” tab (see Figure 3.6a) the user can find options of how to change the units displayed in graph (see Figure 3.5). Several combinations are available for the nominator and denominator part of y-axis (see Figure 3.9a,b). Also, the x-axis may have units of either time or x-coordinate length (see Figure 3.9c,d).

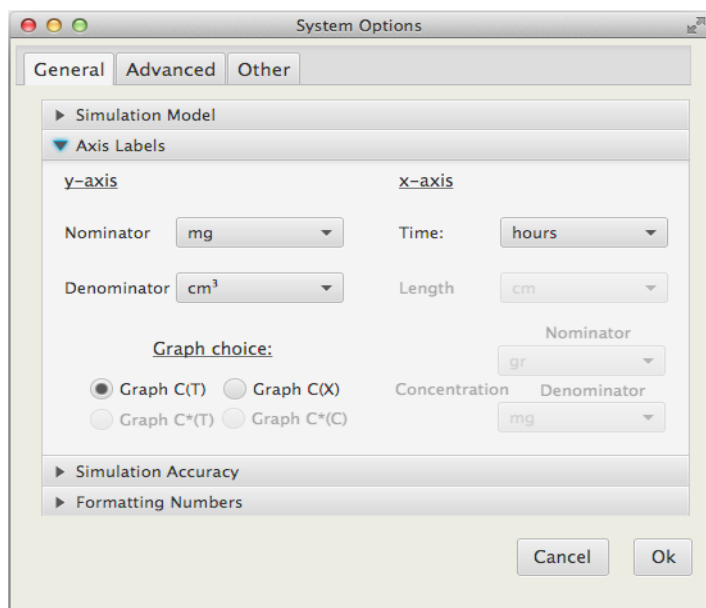
All necessary information related to the accuracy of the numerical procedures employed by ColloidFit can be found in Figure 3.8b. For additional numerical accuracy details see the section §4.10.

The available “Simulations Accuracy” options, as shown in Figure 3.8b, are:

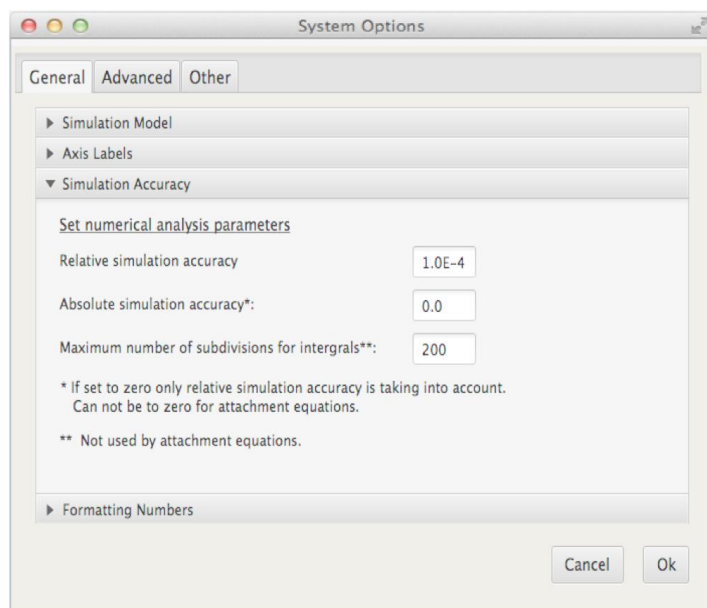
- (1) The “Relative simulation accuracy” value represents the relative error allowed between successive iterations of the integration solver.
- (2) The “Absolute simulation accuracy” value represents the maximum absolute error allowed between successive iterations of the integration solver. If this value is set to zero, then only the relative accuracy is considered.
- (3) The “Maximum number of subdivisions for integrals” value sets the maximum number of allowed subdivisions in a single integration step.

Finally, the “Formatting Numbers” tab (see Figure 3.8c), which contains the following formatting notation options for the numerical values: “Original”, “Decimal”, “Exponential” and “Auto”. The “Original” format keeps the numerical values exactly as

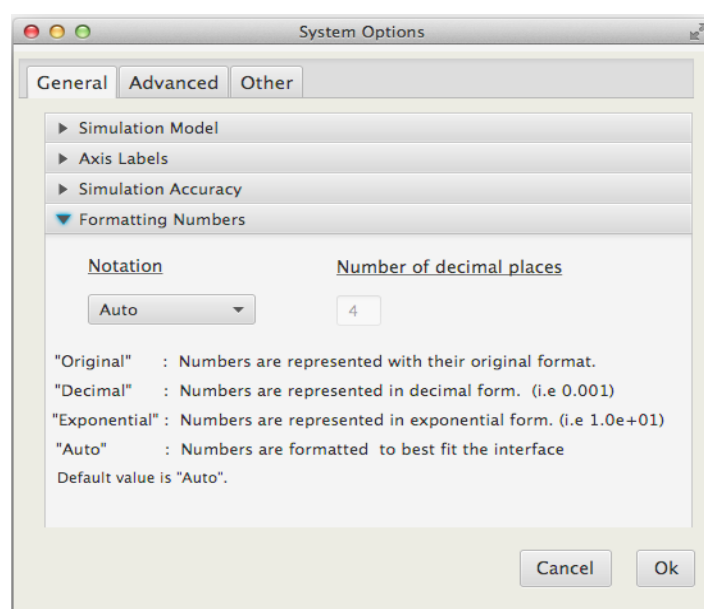
they were inserted originally in ColloidFit. The “Decimal” format displays the numerical values in decimal notation, and the “Exponential” format displays the numerical values in E notation. For both “Decimal” and “Exponential” formats, the number of decimal places can be customized. The “Auto” format displays the numbers in a mixed style by combining both the “Exponential” and “Decimal” format in order to create a visually appealing result. It is worthy to mention here that all formatting notation options keep the inserted numerical values to their original level of accuracy, and only the style of representation is changed.



(a)



(b)



(c)

Figure 3.8. The “Options” menu: “Axis Labels”, “Simulation Accuracy” and “Formatting Number” tabs.

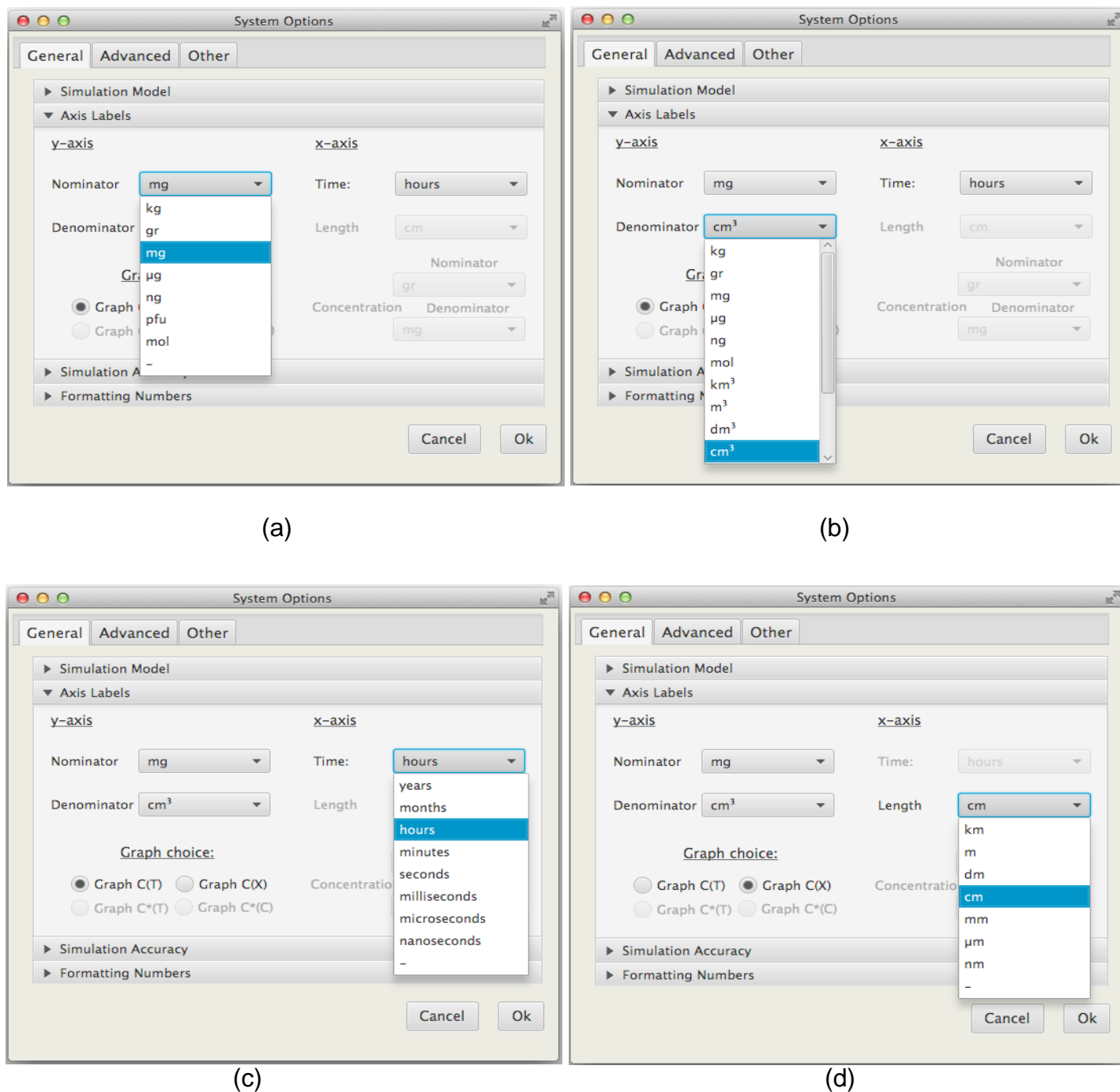
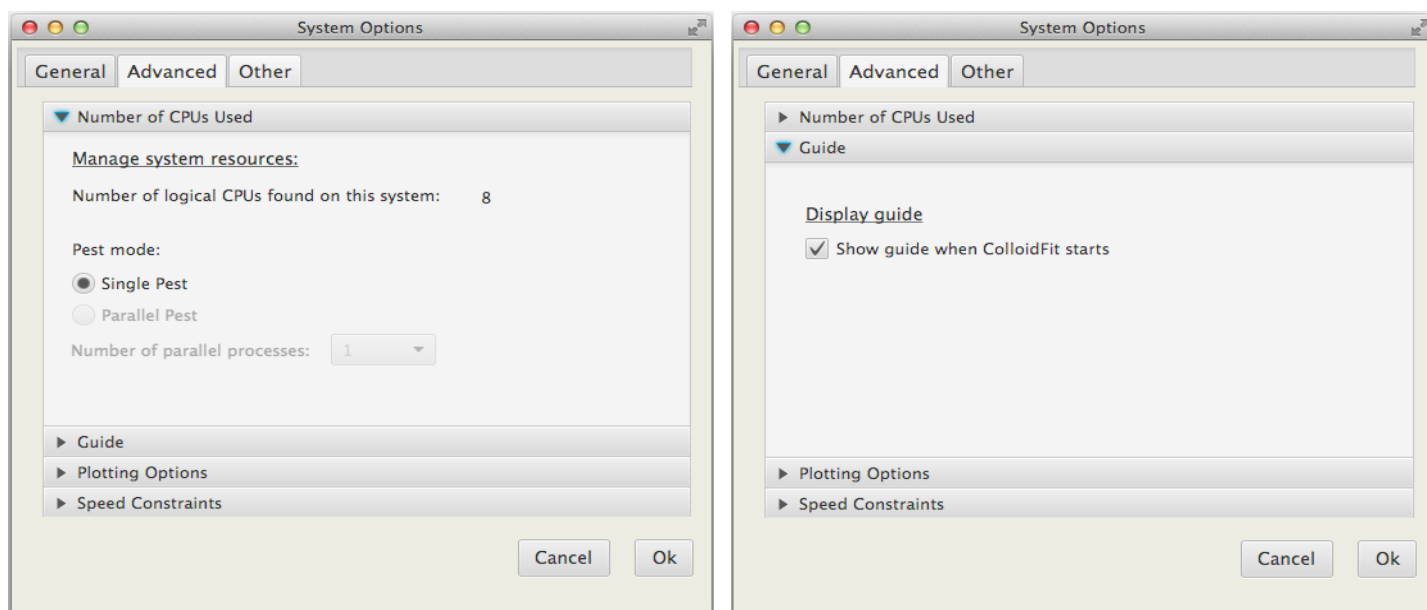


Figure 3.9. The “Options” menu showing all the available units for the x-axis and y-axis.

In order to use most of the processing resources of the latest PC systems, there are build in options available (see Figure 3.10a) that allow for parallel execution of fitting. This is an important and effective way to cut down the total time of execution. For parallel simulation to work properly, the system needs to have multi CPU processors without any load, at least at the beginning of the fitting process, and the time for each model execution exceeds 20 seconds. Otherwise, the

parallelization is not effective, and the total time for the fitting process is increased due to the extra time needed for the parallel reading and writing of internal system files that coordinate the fitting process. The current version of ColloidFit++ V1.1 beta allows up to 8 different parallel processes, a feature which most of the times is not needed. The user should gradually increase the parallel processes from two to three and so on, while keeping in check the total fitting time. As long as the total time is decreasing, then the number of parallel processes can be increased.

ColloidFit was introduced, in section §2.1, with the help of a simple step-by-step “Guide”. The advanced user may avoid the step-by-step “Guide” by disabling it from the “Display guide” option, which can be found in the “Advanced” options menu (see Figure 3.10b). Certainly, if needed, the step-by-step “Guide” can be re-enabled.



(a)

(b)

Figure 3.10. The “Options” menu: “Number of CPUs” and “Guide”.

Furthermore, both “Fitted” and “Simulated” curves shown in the “Graphing” tab (see Figure 3.4) can be constructed either by connecting the data points with simple lines or by the use of Bezier cubic splines. The second option (see Figure 3.11) yields smoother curves. Unfortunately, Bezier cubic splines are bound to overshoot and create artificial oscillations in some cases when the slope between sequential points is great. For most cases it is recommended to use the default “Bezier cubic spline” option. An overshooting example is illustrated in Figure 3.12.

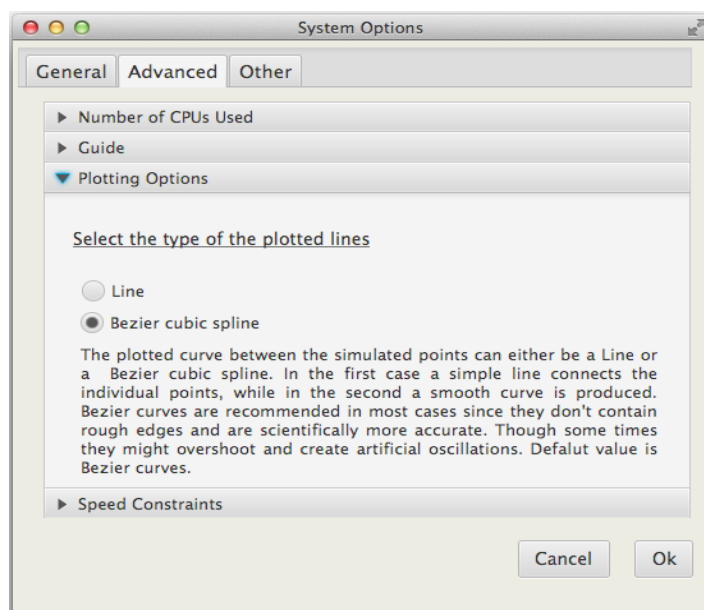


Figure 3.11. The “Options” menu: “Plotting Options” tab.

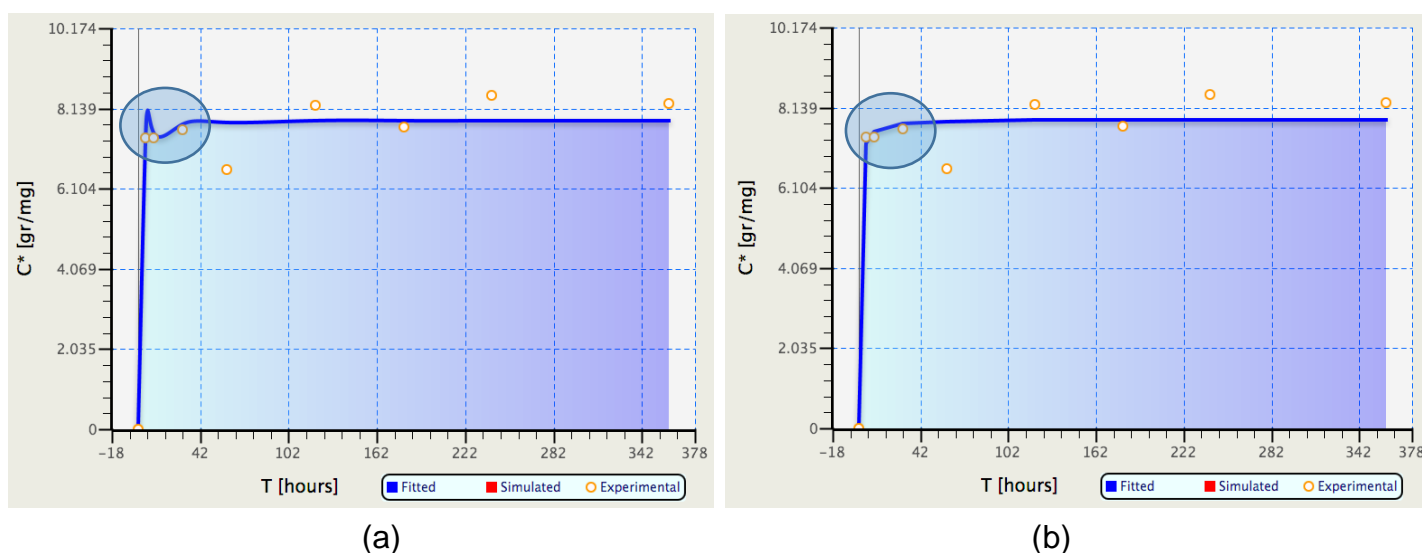


Figure 3.12. Curve construction by: (a) Bezier cubic splines (illustrating a case of overshooting), (b) linear approach.

The last option of the “System Options” menu is the “Speed Constraints” feature (see Figure 3.13). This option allows the user to change the predefined delay time that is automatically inserted between successive reads and writes of important fitting system files. The original value of 50% can be used for most of the existing PCs. For strong computer systems, this value can be reduced to 25% or less. The result will be faster fitting times. This is effective only when single simulations are extremely fast and need approximately 0.1 seconds to complete. This is the case for most of the adsorption models employed by ColloidFit. If execution time for a single simulation is not small enough (more than 10 seconds), then no acceleration in the total fitting time will be noticed. The “Delay time” should be decreased only with extreme caution. For older computer systems it could lead to system instability with unexpected behavior.

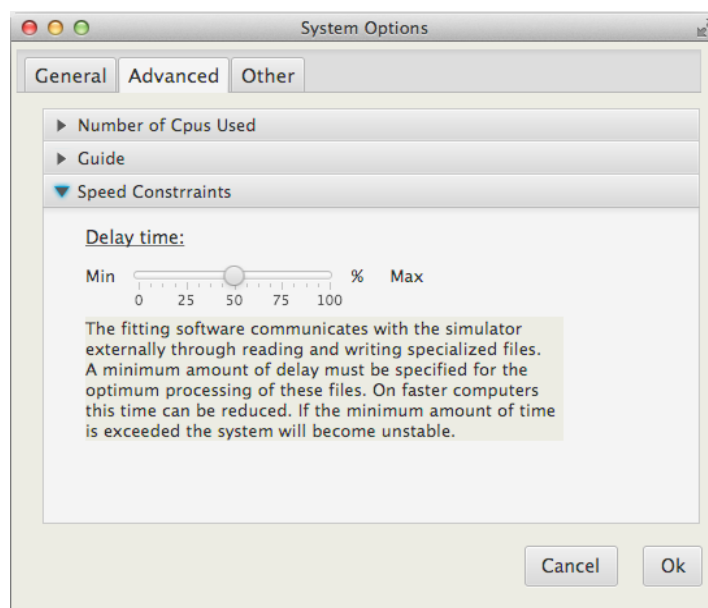


Figure 3.13. The “Options” menu: “Speed Constraints” tab.

3.4.3. The Gravitational forces menu

ColloidFit allows certain models to account for gravity effects. The corresponding menu appears (see Figure 3.14) when the “Gravity effects” button is pressed (see Figure 3.7a,b). The user can fill all the blank text boxes with the required parameters. Subsequently, by clicking the “Calculate effective U” button, the corresponding interstitial velocity that accounts for gravity effects is determined. This value can be copied directly into the “Fitting” tab (see Figure 3.2) and then initiate a fitting process that accounts for gravity effects.

There are two additional options displayed in Figure 3.14 that provide more flexibility for the determination of the effective velocity: (1) The parameter f_s [-] can be set equal to 0.9 ($f_s \approx 0.9$) if the grains of the porous medium do not provide additional frictional resistance, but only contribute to the tortuosity (Wan and Tsang, 1995). Otherwise, f_s [-] can be evaluated from equation (4.4) with the appropriate values for b [-] and ε [-]. (2) The interstitial water velocity can be either determined with the following equation $U = Q / (A \cdot \theta)$, or can be inserted directly in the proper window, assuming that its value is known.

Furthermore, in the “Determination of Gravitational Effects” display (see Figure 3.14), a table is provided with water dynamic viscosity and density values for various temperatures (http://www.thermexcel.com/english/tables/eau_atm.htm). This table is useful when the ρ_w and μ_w parameter values are needed. The user must fill in all parameters values with the specified units, otherwise mathematical errors will occur.

Figure 3.14. The “Set gravity parameters” menu.

3.4.4. The Statistical menu

When the “statistical analysis” button (introduced in sections §3.2-3.3) is clicked, the corresponding “Statistical Information” menu appears, as shown in Figure 3.13. This menu contains on the left side the statistical properties, and on the right side the parameter values used. The statistical information can be displayed even while the fitting process is in progress. If for an unfortunate reason one or more of the parameter values used are incorrect, the user can easily edit the parameter values and then by clicking the “refresh” button, all statistical values are recalculated with the freshly edited parameter values. Furthermore, the temporal moments are calculated based on the theoretical developments presented by Chrysikopoulos and Syngouna (2014), which are also described in section §4.8. Note that the statistical analysis option is available only for the transport models (see Table 4.1). Attachment models don’t support this feature.

Figure 3.15 The “Statistical Information” menu.

4. Mathematical modeling for particle transport

ColloidFit employs two different categories of models for: (i) particle transport in porous media, and (ii) particle attachment onto the solid matrix (batch systems). The transport models are applicable to two different types of particles (colloids and viruses) under two different source loadings (instantaneous and broad pulse). The colloid particles may be either suspended in the aqueous phase or attached reversibly and/or irreversibly onto the solid matrix. The virus particles may be either suspended in the aqueous phase or attached reversibly onto the solid matrix. Viruses suspended in the aqueous phase and attached onto the solid matrix are assumed to undergo inactivation with different rates. The transport of particles undergoing strictly reversible attachment is described by the models developed by Sim and Chrysikopoulos (1995), and Thomas and Chrysikopoulos (2007). Furthermore, the transport of particles undergoing a combination of reversible as well as irreversible attachment (mixed) is handled by the methods developed by Katzourakis and Chrysikopoulos (2014). All of the transport models employed by ColloidFit can be modified to handle dense particles by accounting for gravity forces as described by Chrysikopoulos and Syngouna (2014) and Katzourakis and Chrysikopoulos (2015). The various transport models employed by ColloidFit are listed in Table 4.1.

Table 4.1 Available ColloidFit transport models

No	Particle type	Source type	Gravity effects*	Attachment**
1	Virus	Instantaneous	w/o gravity	Reversible
2	Virus	Broad pulse	w/o gravity	Reversible
3	Virus	Instantaneous	w/ gravity	Reversible
4	Virus	Broad pulse	w/ gravity	Reversible
5	Colloid	Instantaneous	w/o gravity	Reversible
6	Colloid	Broad pulse	w/o gravity	Reversible
7	Colloid	Instantaneous	w/ gravity	Reversible
8	Colloid	Broad pulse	w/ gravity	Reversible
9	Colloid	Instantaneous	w/o gravity	Mixed
10	Colloid	Broad pulse	w/o gravity	Mixed
11	Colloid	Instantaneous	w/ gravity	Mixed
12	Colloid	Broad pulse	w/ gravity	Mixed

* “w/o” indicates without and “w/” with.

** Mixed attachment refers to the combined reversible and/or irreversible attachment.

4.1 Virus transport modeling

The transport of suspended virus particles in one-dimensional, saturated, homogeneous porous media with uniform flow, accounting for nonequilibrium reversible attachment onto the solid matrix, inactivation with different rates, and gravity effects, is governed by the following partial differential equation (Sim and Chrysikopoulos, 1995):

$$\begin{aligned} \frac{\partial C_v(t,x)}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial C_{v^*}(t,x)}{\partial t} = \\ -U \frac{\partial C_v(t,x)}{\partial x} - U_{s(\pm i)} \frac{\partial C_v(t,x)}{\partial x} + D_v \frac{\partial^2 C_v(t,x)}{\partial x^2} - \lambda_v C_v(t,x) - \lambda_{v^*} \frac{\rho_b}{\theta} C_{v^*}(t,x) \end{aligned} \quad (4.1)$$

where C_v [M_v/L^3] is the concentration of virus; D_v [L^2/t] is the longitudinal hydrodynamic dispersion coefficients of the suspended virus particles; λ_v [$1/t$] is the decay rate of the viruses suspended in aqueous phase; and λ_{v^*} [$1/t$] is the decay rate of the viruses attached onto the solid matrix. U [L/t] is the average interstitial velocity along the x-direction; and $U_{s(\pm i)}$ [L/t] is the $\pm x$ -directional component of the “restricted particle” settling velocity, which is just a modification of the “free particle” settling velocity, commonly used in static water columns (Russel et al., 1989), applicable to granular porous media (Chrysikopoulos and Syngouna, 2014):

$$U_{s(\pm i)} = f_s \frac{(\rho_p - \rho_w) d_p^2}{18\mu_w} g_{(\pm i)} \quad (4.2)$$

where f_s [–] is the correction factor accounting for particle settling in the presence of the solid matrix of granular porous media; ρ_w [M/L^3] is the density of the suspending fluid (water); ρ_p [M/L^3] is the density of the colloid particle; μ_w [$M/(L \cdot t)$] is the dynamic viscosity of water; d_p [L] is the colloid particle diameter; and $g_{(\pm i)}$ [L/t^2] is the x-directional component of the gravity vector defined as:

$$g_{(\pm i)} = g \cos \beta \quad (4.3)$$

where g [L/t^2] is the acceleration due to gravity; β [$^\circ$] is the angle of the main flow direction (x-direction) with respect to the direction of gravity ($0^\circ \leq \beta \leq 180^\circ$); $\pm i$ is the unit vector parallel ($\pm x$ -direction) to the flow, respectively (see Figure 4.1). The correction factor, f_s , is expressed as follows (Wan and Tsang, 1995):

$$f_s = \frac{b + 0.67}{b + 0.93 / \varepsilon} \quad (4.4)$$

where $b \approx 1$ is the average free settling segment length to the grain radius ratio, and ε [–] ($0 \leq \varepsilon \leq 1$) is an empirical correction factor that takes into account the effect of the grain surface. Note that $f_s \approx 0.9$ when the grains of the granular porous media do not provide additional frictional resistance, but only contribute to the tortuosity (Wan and Tsang, 1995).

The second accumulation term on the left hand side of equation (4.1) is given by (Sim and Chrysikopoulos, 1995):

$$\frac{\rho_b}{\theta} \frac{\partial C_{v^*}(t,x)}{\partial t} = r_{v-v^*} C_v(t,x) - r_{v^*-v} \frac{\rho_b}{\theta} C_{v^*}(t,x) \quad (4.5)$$

where r_{v-v^*} [1/t] is the rate coefficient of virus attachment onto the solid matrix; and r_{v^*-v} [1/t] is the rate coefficient of virus detachment from the solid matrix.

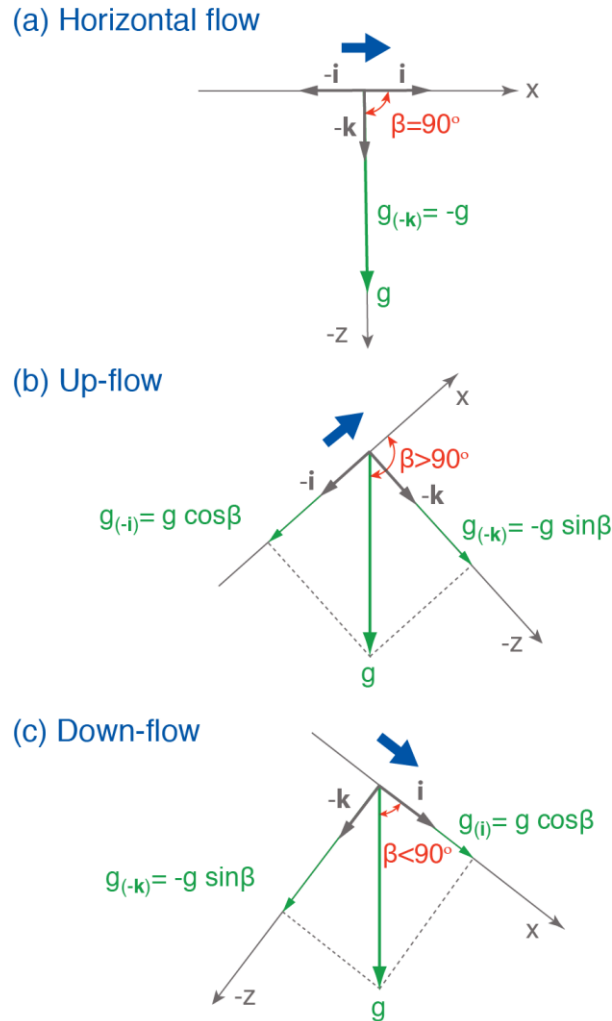


Figure 4.1. Schematic illustration of the gravity vector components for: (a) horizontal flow, (b) up-flow, and (c) down-flow conditions. The angle β ($0^\circ \leq \beta \leq 180^\circ$) is between the main flow direction (x-direction) and the direction of gravity (Katzourakis and Chrysikopoulos, 2014).

4.2 Virus source loading

The initial condition and the appropriate boundary conditions for a one-dimensional semi-infinite aquifer are as follows (Sim and Chrysikopoulos, 1995; Thomas and Chrysikopoulos, 2007):

$$C_v(0,x) = 0 \quad (4.6)$$

$$\frac{dC_v(t,\infty)}{dx} = 0 \quad (4.7)$$

$$-D_v \frac{\partial C_v(t,0)}{\partial x} + U C_v(t,0) = \begin{cases} UC_{v_0}, & t \leq t_p \\ 0, & t > t_p \end{cases} \quad (4.8)$$

$$-D_v \frac{\partial C_v(t,0)}{\partial x} + U C_v(t,0) = M_\delta \delta(t) \quad (4.9)$$

where $M_\delta = M_{in}/A_c \theta$ [M_v/L^2] is the mass injected “instantaneously” over the cross-sectional area of the column (where M_{in} [M_v] is the colloid injected mass, A_c [L^2] is the cross sectional area of the porous medium); C_{v_0} [M_v/L^3] is the injected constant concentration of virus; D_v [L^2/t] is hydrodynamic dispersion of the virus; U [L/T] is the interstitial velocity; M_{in} [M] is the injected mass, and $\delta(t)$ is the modified Dirac delta function. Condition (4.6) establishes that there is no initial concentration of virus within the porous medium. While downstream condition (4.7) preserves concentration continuity (Sim and Chrysikopoulos, 1995). Upstream equations (4.8) and (4.9) define the way the viruses are introduced into the aquifer. Condition (4.8) refers to a continuous source that provides constant concentration of virus over a predefined time period t_p (Sim and Chrysikopoulos, 1995). Whereas, equation (4.9) refers to an instant injection of the virus with total injected mass equal to M_{in} .

4.2.1 Analytical solution for instantaneous source

The analytical solution to the model for virus transport in porous media described in §4.1 (see Table 4.2) with instantaneous source has been derived by Thomas and Chrysikopoulos (2007):

$$\begin{aligned} C_v(t,x) = & \frac{M_\delta}{D_v^{1/2}} \exp\left[\frac{U_{tot}x}{2D_v} - Ht\right] \left\{ \frac{1}{(\pi t)^{1/2}} \exp\left[\frac{-x^2}{4D_v t} + \left(H - A - \frac{U_{tot}^2}{4D_v}\right)t\right] \right. \\ & - \frac{U_{tot}}{2D_v^{1/2}} \exp\left[\frac{U_{tot}x}{2D_v} + (H-A)t\right] \operatorname{erfc}\left[\frac{x}{2(D_v t)^{1/2}} + \frac{U_{tot}}{2}\left(\frac{t}{D_v}\right)^{1/2}\right] \\ & - \int_0^t \frac{B\zeta}{\{B\zeta(t-\zeta)\}^{1/2}} J_1\left[2(B\zeta(t-\zeta))^{1/2}\right] \left\{ \frac{1}{(\pi\zeta)^{1/2}} \exp\left[\frac{-x^2}{4D_v \zeta} + \left(H - A - \frac{U_{tot}^2}{4D_v}\right)\zeta\right] \right. \\ & \left. \left. - \frac{U_{tot}}{2D_v^{1/2}} \exp\left[\frac{U_{tot}x}{2D_v} + (H-A)\zeta\right] \operatorname{erfc}\left[\frac{x}{2(D_v \zeta)^{1/2}} + \frac{U_{tot}}{2}\left(\frac{\zeta}{D_v}\right)^{1/2}\right] \right\} d\zeta \right\} \end{aligned} \quad (4.10)$$

where J_1 is the Bessel function of the first kind of order one; “exp” is the exponential function; “erfc” is the complementary error function, ζ is a dummy integration variable; $A = r_{v-v^*} + \lambda_v$; $B = r_{v-v^*}(\lambda_{v^*} - H)$; and $H = r_{v^*-v}$. In order to evaluate the above analytical solution for $B < 0$, the following relationship is employed (Abramowitz and Stegun, 1964):

$$J_1(ix) = i \cdot I_1(x) \quad (4.11)$$

where I_1 is the modified Bessel function of the first kind of order one. Therefore, the term $J_1 \left[2 \{B\zeta(t-\zeta)\}^{1/2} \right] / \{B\zeta(t-\zeta)\}^{1/2}$ is replaced by $-I_1 \left[2 \{|B\zeta(t-\zeta)|\}^{1/2} \right] / \{|B\zeta(t-\zeta)|\}^{1/2}$.

Furthermore, in order to account for gravity effects, the velocity term in the analytical solution (4.10) was replaced with U_{tot} , which is the sum of the average interstitial velocity U and the settling vector component $U_{s(\pm i)}$, as follows:

$$U_{tot} = U + U_{s(\pm i)} \quad (4.12)$$

4.2.2 Analytical solution for broad pulse source

The analytical solution to the model for virus transport in porous media described in §4.1 (see Table 4.2) with a broad pulse injection source is obtained by a slight modification of the analytical solution presented by Sim and Chrysikopoulos (1995) as follows:

$$C_v(t, x) = \begin{cases} \Omega(t, x) & 0 < t \leq t_p \\ \Omega(t, x) - \Omega(t - t_p, x) & t > t_p \end{cases} \quad (4.13)$$

where

$$\begin{aligned} \Omega(t, x) = & \frac{C_{v_0} U_{\text{tot}}}{D_v^{1/2}} \exp\left[\frac{U_{\text{tot}} x}{2D_v}\right] \left\{ \int_0^t \int_0^\tau \text{He}^{-H\tau} J_0 \left[2(B\xi(\tau - \xi))^{1/2} \right] \right. \\ & \cdot \left[\frac{1}{(\pi\xi)^{1/2}} \exp\left[\frac{-x^2}{4D_v\xi} + \left(H - A - \frac{U_{\text{tot}}^2}{4D_v}\right)\xi\right] \right. \\ & - \frac{U_{\text{tot}}}{2D_v^{1/2}} \exp\left[\frac{U_{\text{tot}} x}{2D_v} + (H - A)\xi\right] \\ & \cdot \text{erfc}\left[\frac{x}{2(D_v\xi)^{1/2}} + \frac{U_{\text{tot}}}{2} \left(\frac{\xi}{D_v}\right)^{1/2}\right] \left. \right] d\xi d\tau \\ & + e^{-Ht} \int_0^t J_0 \left[2(B\xi(t - \xi))^{1/2} \right] \\ & \cdot \left[\frac{1}{(\pi\xi)^{1/2}} \exp\left[\frac{-x^2}{4D_v\xi} + \left(H - A - \frac{U_{\text{tot}}^2}{4D_v}\right)\xi\right] \right. \\ & - \frac{U_{\text{tot}}}{2D_v^{1/2}} \exp\left[\frac{U_{\text{tot}} x}{2D_v} + (H - A)\xi\right] \\ & \cdot \text{erfc}\left[\frac{x}{2(D_v\xi)^{1/2}} + \frac{U_{\text{tot}}}{2} \left(\frac{\xi}{D_v}\right)^{1/2}\right] \left. \right] d\xi \left. \right\} \end{aligned} \quad (4.14)$$

where J_0 is the Bessel function of the first kind of zeroth order, “exp” is the exponential function; “erfc” is the complementary error function; ξ and τ are dummy integration variables; $A = r_{v-v^*} + \lambda_v$; $B = r_{v-v^*}(\lambda_{v^*} - H)$; and $H = r_{v^*-v}$. In the analytical solution (4.14), to account for gravity effects, the velocity term was replaced with U_{tot} , which is defined by equation (4.12).

4.3 Colloid transport in porous media with reversible attachment

The transport of suspended colloid particles in one-dimensional, saturated, homogeneous porous media with uniform flow, accounting for nonequilibrium reversible attachment onto the solid matrix along with gravity effects, is governed by the following partial differential equation (Sim and Chrysikopoulos, 1995; Chrysikopoulos and Syngouna, 2014; Katzourakis and Chrysikopoulos, 2014):

$$\frac{\partial C_c(t,x)}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial C_{c^*}(t,x)}{\partial t} = -U \frac{\partial C_c(t,x)}{\partial x} - U_{s(\pm i)} \frac{\partial C_c(t,x)}{\partial x} + D_c \frac{\partial^2 C_c(t,x)}{\partial x^2} \quad (4.15)$$

where C_c [M_o/L^3] is the concentration of colloids; t [t] is time; x [L] is the Cartesian coordinate in the longitudinal direction; ρ_b [M_s/L^3] is the bulk density of the solid matrix; θ [–] is the porosity of the porous medium; D_c [L^2/t] is the longitudinal hydrodynamic dispersion coefficient of the suspended colloids; and U [L/t] is the average interstitial velocity along the x -direction.

Given that the colloids attached onto the solid matrix, C_{c^*} , are assumed to be reversibly attached, $C_{c^*}^{(r)}$ [M_o/M_s], then $C_{c^*} = C_{c^*}^{(r)}$ and the accumulation term in equation (4.15) can be expressed by (Sim and Chrysikopoulos, 1995):

$$\frac{\rho_b}{\theta} \frac{\partial C_{c^*}^{(r)}(t,x)}{\partial t} = r_{c-c^*(r)} C_c(t,x) - r_{c^*(r)-c} \frac{\rho_b}{\theta} C_{c^*}^{(r)}(t,x) \quad (4.16)$$

where $r_{c-c^*(r)}$ [$1/t$] is the forward rate coefficient of colloid attachment onto the solid matrix, and $r_{c^*(r)-c}$ [$1/t$] is the reverse rate coefficient of colloid detachment from the solid matrix.

4.4 Colloids source loading

The initial condition and the appropriate boundary conditions for a one-dimensional semi-infinite aquifer are as follows (Sim and Chrysikopoulos, 1995; Thomas and Chrysikopoulos, 2007):

$$C_c(0,x) = 0 \quad (4.17)$$

$$\frac{dC_c(t,\infty)}{dx} = 0 \quad (4.18)$$

$$-D_c \frac{\partial C_c(t,0)}{\partial x} + U C_c(t,0) = \begin{cases} U C_{c_0}, & t \leq t_p \\ 0, & t > t_p \end{cases} \quad (4.19)$$

$$-D_c \frac{\partial C_c(t,0)}{\partial x} + U C_c(t,0) = M_\delta \delta(t) \quad (4.20)$$

where $M_\delta = M_{in}/A_c \theta$ [M_o/L^2] is the mass injected “instantaneously” over the cross-sectional area of the column (where M_{in} [M_c] is the colloid injected mass, A_c [L^2] is the cross sectional area of the porous medium); C_{c_0} [M_o/L^3] is the injected constant concentration of colloids; D_c [L^2/t] is hydrodynamic dispersion of the colloids; U [L/t]

is the interstitial velocity; M_{in} [M] is the injected mass, and $\delta(t)$ is the modified Dirac delta function. Condition (4.17) establishes that there is no initial concentration of colloids within the porous medium. While downstream condition (4.18) preserves concentration continuity (Sim and Chrysikopoulos, 1995). Upstream equations (4.19) and (4.20) define the way the colloids are introduced into the aquifer. Condition (4.19) refers to a continuous source that provides constant concentration of the colloids over a predefined time period t_p (Sim and Chrysikopoulos, 1995). Whereas, equation (4.20) refers to an instant injection of the colloids with total injected mass equal to M_{in} .

4.4.1 Analytical solution for instantaneous source

The analytical solution for the colloid transport model for instantaneous source with reversible attachment, described in §4.4 (see Table 4.2), is given by (Thomas and Chrysikopoulos, 2007):

$$\begin{aligned}
 C_c(t, x) = & \frac{M_{\delta}}{D_c^{1/2}} \exp\left[\frac{U_{tot}x}{2D_c} - Ht\right] \left\{ \frac{1}{(\pi t)^{1/2}} \exp\left[\frac{-x^2}{4D_c t} + \left(H - A - \frac{U_{tot}^2}{4D_c}\right)t\right] \right. \\
 & - \frac{U_{tot}}{2D_c^{1/2}} \exp\left[\frac{U_{tot}x}{2D_c} + (H - A)t\right] \operatorname{erfc}\left[\frac{x}{2(D_c t)^{1/2}} + \frac{U_{tot}}{2}\left(\frac{t}{D_c}\right)^{1/2}\right] \\
 & - \int_0^t \frac{B\zeta}{\{B\zeta(t-\zeta)\}^{1/2}} J_1\left[2(B\zeta(t-\zeta))^{1/2}\right] \left\{ \frac{1}{(\pi\zeta)^{1/2}} \exp\left[\frac{-x^2}{4D_c\zeta} + \left(H - A - \frac{U_{tot}^2}{4D_c}\right)\zeta\right] \right. \\
 & \left. \left. - \frac{U_{tot}}{2D_c^{1/2}} \exp\left[\frac{U_{tot}x}{2D_c} + (H - A)\zeta\right] \operatorname{erfc}\left[\frac{x}{2(D_c\zeta)^{1/2}} + \frac{U_{tot}}{2}\left(\frac{\zeta}{D_c}\right)^{1/2}\right] \right\} d\zeta \right\} \quad (4.21)
 \end{aligned}$$

where J_1 is the Bessel function of the first kind of order one; “exp” is the exponential function; “erfc” is the complementary error function, ζ is a dummy integration variable; $A = r_{c-c^*(t)}$; $B = -r_{c-c^*(t)} r_{c^*(t)-c}$; and $H = r_{c^*(t)-c}$. In order to evaluate the above analytical solution for $B < 0$, the following relationship is employed (Abramowitz and Stegun, 1964):

$$J_1(ix) = i \cdot I_1(x) \quad (4.22)$$

where I_1 is the modified Bessel function of the first kind of order one. Therefore, the term $J_1\left[2\{B\zeta(t-\zeta)\}^{1/2}\right] / \{B\zeta(t-\zeta)\}^{1/2}$ is replaced by $-I_1\left[2\{B\zeta(t-\zeta)\}^{1/2}\right] / \{B\zeta(t-\zeta)\}^{1/2}$.

Furthermore, in order to account for gravity effects, the velocity term in the analytical solution (4.21) was replaced with U_{tot} , which is defined by equation (4.12).

4.4.2 Analytical solution for broad pulse source

The analytical solution for the colloid transport model with broad pulse injection source and reversible attachment, described in §4.4 (see Table 4.2) can be obtained by slight modification of the solution reported by Sim and Chrysikopoulos (1995) as follows:

$$C_c(t, x) = \begin{cases} \Omega(t, x) & 0 < t \leq t_p \\ \Omega(t, x) - \Omega(t - t_p, x) & t > t_p \end{cases} \quad (4.23)$$

where

$$\begin{aligned} \Omega(t, x) = & \frac{C_{c0} U_{tot}}{D_c^{1/2}} \exp\left[\frac{U_{tot} x}{2D_c}\right] \left\{ \int_0^t \int_0^\tau \text{He}^{-H\tau} J_0 \left[2(B\xi(\tau - \xi))^{1/2} \right] \right. \\ & \cdot \left\{ \frac{1}{(\pi\xi)^{1/2}} \exp\left[\frac{-x^2}{4D_c\xi} + \left(H - A - \frac{U_{tot}^2}{4D_c}\right)\xi\right] \right. \\ & - \frac{U_{tot}}{2D_c^{1/2}} \exp\left[\frac{U_{tot} x}{2D_c} + (H - A)\xi\right] \\ & \cdot \text{erfc}\left[\frac{x}{2(D_c\xi)^{1/2}} + \frac{U_{tot}}{2} \left(\frac{\xi}{D_c}\right)^{1/2}\right] \left. \right\} d\xi d\tau \\ & + e^{-Ht} \int_0^t J_0 \left[2(B\xi(t - \xi))^{1/2} \right] \\ & \cdot \left\{ \frac{1}{(\pi\xi)^{1/2}} \exp\left[\frac{-x^2}{4D_c\xi} + \left(H - A - \frac{U_{tot}^2}{4D_c}\right)\xi\right] \right. \\ & - \frac{U_{tot}}{2D_c^{1/2}} \exp\left[\frac{U_{tot} x}{2D_c} + (H - A)\xi\right] \\ & \cdot \text{erfc}\left[\frac{x}{2(D_c\xi)^{1/2}} + \frac{U_{tot}}{2} \left(\frac{\xi}{D_c}\right)^{1/2}\right] \left. \right\} d\xi \left. \right\}. \end{aligned} \quad (4.24)$$

where J_0 is the Bessel function of the first kind of zeroth order, “exp” is the exponential function; “erfc” is the complementary error function; ξ and τ are dummy integration variables; $A = r_{c-c^*(r)}$; $B = -r_{c-c^*(r)} r_{c^*(r)-c}$; and $H = r_{c^*(r)-c}$. In the analytical solution (4.24), to account for gravity effects, the velocity term was replaced with U_{tot} , which is defined by equation (4.12).

4.5 Colloid transport in porous media with combined reversible and irreversible (mixed) attachment

For colloids undergoing reversible as well as irreversible (mixed) attachment, the total attached colloids concentration, C_{c^*} [M_c/M_s], in the governing colloid transport partial differential equation (4.1) is represented as (Katzourakis and Chrysikopoulos, 2014):

$$C_{c^*} = C_{c^*}^{(r)} + C_{c^*}^{(i)} \quad (4.25)$$

where $C_{c^*}^{(i)}$ [M_c/M_s] is the colloid concentration irreversibly attached onto the solid matrix; $C_{c^*}^{(r)}$ [M_c/M_s] is the colloid concentration reversibly attached onto the solid matrix. Consequently, the colloid accumulation term in equation (4.15) is expressed as (Compere et al., 2001; Katzourakis and Chrysikopoulos, 2014):

$$\frac{\rho_b}{\theta} \frac{\partial C_{c^*}(t,x)}{\partial t} = \frac{\rho_b}{\theta} \left[\frac{\partial C_{c^*}^{(r)}(t,x)}{\partial t} + \frac{\partial C_{c^*}^{(i)}(t,x)}{\partial t} \right] \quad (4.26)$$

where the reversible accumulation terms is given by (Sim and Chrysikopoulos, 1995):

$$\frac{\rho_b}{\theta} \frac{\partial C_{c^*}^{(r)}(t,x)}{\partial t} = r_{c-c^*(r)} C_c(t,x) - r_{c^*(r)-c} \frac{\rho_b}{\theta} C_{c^*}^{(r)}(t,x) \quad (4.27)$$

and the irreversible accumulation term is given by:

$$\frac{\rho_b}{\theta} \frac{\partial C_{c^*}^{(i)}(t,x)}{\partial t} = r_{c-c^*(i)} C_c(t,x) \quad (4.28)$$

where $r_{c-c^*(i)}$ [$1/t$] is the forward rate coefficient of irreversible colloid attachment onto the solid matrix. Substituting equations (4.26) and (4.28) in the colloid transport equation (4.15) yields the following relationship:

$$\begin{aligned} \frac{\partial C_c(t,x)}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial C_{c^*}^{(r)}(t,x)}{\partial t} = & -U \frac{\partial C_c(t,x)}{\partial x} - U_{s(\pm i)} \frac{\partial C_c(t,x)}{\partial x} \\ & + D_c \frac{\partial^2 C_c(t,x)}{\partial x^2} - r_{c-c^*(i)} C_c(t,x) \end{aligned} \quad (4.29)$$

which is the governing colloid transport equation in porous media with combined reversible and irreversible attachment. Note that the reversible term found on the left hand side of (4.29) is described by equation (4.27).

4.5.1 Analytical solution for instantaneous source

The analytical solution to the model for colloid transport in porous media with combined reversible and irreversible (mixed) attachment described in §4.5 (see Table 4.2), for an instantaneous source can be obtained by direct comparison of the governing virus transport equation (4.1) and colloid transport equation (4.29). Clearly, it is evident that the forward irreversible attachment rate ($r_{c-c^*(i)}$) corresponds to the inactivation or decay rate of the viruses suspended in aqueous phase (λ_v), while the decay rate of the viruses attached onto the solid matrix (λ_{v^*}) is equal to zero for the case of colloids. Therefore, the analytical solution to the model for colloid transport

with mixed attachment and instantaneous source is essentially the virus analytical solution (4.10) with λ_v replaced by $r_{c-c^{*(i)}}$ and λ_{v^*} set to zero. Naturally, r_{v-v^*} and r_{v^*-v} correspond to $r_{c-c^{*(i)}}$ and $r_{c^*(i)-c}$, respectively. The resulting analytical solution is:

$$\begin{aligned}
 C_c(t, x) = & \frac{M_\delta}{D_c^{1/2}} \exp\left[\frac{U_{\text{tot}} x}{2D_c} - Ht\right] \left\{ \frac{1}{(\pi t)^{1/2}} \exp\left[\frac{-x^2}{4D_c t} + \left(H - A - \frac{U_{\text{tot}}^2}{4D_c}\right)t\right] \right. \\
 & - \frac{U_{\text{tot}}}{2D_c^{1/2}} \exp\left[\frac{U_{\text{tot}} x}{2D_c} + (H - A)t\right] \text{erfc}\left[\frac{x}{2(D_c t)^{1/2}} + \frac{U_{\text{tot}}}{2} \left(\frac{t}{D_c}\right)^{1/2}\right] \\
 & - \int_0^t \frac{B \zeta}{\{B \zeta(t - \zeta)\}^{1/2}} J_1\left[2(B \zeta(t - \zeta))^{1/2}\right] \left\{ \frac{1}{(\pi \zeta)^{1/2}} \exp\left[\frac{-x^2}{4D_c \zeta} + \left(H - A - \frac{U_{\text{tot}}^2}{4D_c}\right)\zeta\right] \right. \\
 & \left. \left. - \frac{U_{\text{tot}}}{2D_c^{1/2}} \exp\left[\frac{U_{\text{tot}} x}{2D_c} + (H - A)\zeta\right] \text{erfc}\left[\frac{x}{2(D_c \zeta)^{1/2}} + \frac{U_{\text{tot}}}{2} \left(\frac{\zeta}{D_c}\right)^{1/2}\right] \right\} d\zeta \right\} \quad (4.30)
 \end{aligned}$$

where J_1 is the Bessel function of the first kind of order one; “exp” is the exponential function; “erfc” is the complementary error function, ζ is a dummy integration variable; $A = r_{c-c^{*(i)}} + r_{c-c^{*(i)}}$; $B = -r_{c-c^{*(i)}} r_{c^*(i)-c}$; and $H = r_{c^*(i)-c}$. In order to evaluate the above analytical solution for $B < 0$, the following relationship is employed (Abramowitz and Stegun, 1964):

$$J_1(ix) = i \cdot I_1(x) \quad (4.31)$$

where I_1 is the modified Bessel function of the first kind of order one. Therefore, the term $J_1\left[2\{B\zeta(t-\zeta)\}^{1/2}\right] / \{B\zeta(t-\zeta)\}^{1/2}$ is replaced by $-I_1\left[2\{|B\zeta(t-\zeta)|\}^{1/2}\right] / \{|B\zeta(t-\zeta)|\}^{1/2}$. Furthermore, in the analytical solution (4.30), to account for gravity effects, the velocity term was replaced with U_{tot} , which is defined by equation (4.12).

4.5.2 Analytical solution for broad pulse source

The analytical solution to the model for colloid transport in porous media with combined reversible and irreversible (mixed) attachment described in §4.5 (see Table 4.2), for a broad pulse source can be obtained by direct comparison of the governing virus transport equation (4.1) and colloid transport equation (4.29). Clearly, it is evident that the forward irreversible attachment rate ($r_{c-c^*(t)}$) corresponds to the inactivation or decay rate of the viruses suspended in aqueous phase (λ_v), while the decay rate of the viruses attached onto the solid matrix (λ_{v^*}) is equal to zero for the case of colloids. Therefore, the analytical solution to the model for colloid transport with mixed attachment and broad pulse source is essentially the virus analytical solution (4.13) and (4.14) with λ_v replaced by $r_{c-c^*(t)}$ and λ_{v^*} set to zero. Naturally, r_{v-v^*} and r_{v^*-v} correspond to $r_{c-c^*(t)}$ and $r_{c^*(t)-c}$, respectively. The resulting analytical solution is:

$$C_c(t, x) = \begin{cases} \Omega(t, x) & 0 < t \leq t_p \\ \Omega(t, x) - \Omega(t - t_p, x) & t > t_p \end{cases} \quad (4.32)$$

where

$$\begin{aligned} \Omega(t, x) = & \frac{C_{c_0} U_{tot}}{D_c^{1/2}} \exp\left[\frac{U_{tot} x}{2D_c}\right] \left\{ \int_0^t \int_0^\tau \text{He}^{-H\tau} J_0\left[2(B\xi(\tau - \xi))^{1/2}\right] \right. \\ & \cdot \left\{ \frac{1}{(\pi\xi)^{1/2}} \exp\left[\frac{-x^2}{4D_c\xi} + \left(H - A - \frac{U_{tot}^2}{4D_c}\right)\xi\right] \right. \\ & - \frac{U_{tot}}{2D_c^{1/2}} \exp\left[\frac{U_{tot} x}{2D_c} + (H - A)\xi\right] \\ & \cdot \text{erfc}\left[\frac{x}{2(D_c\xi)^{1/2}} + \frac{U_{tot}}{2}\left(\frac{\xi}{D_c}\right)^{1/2}\right] \left. \right\} d\xi d\tau \\ & + e^{-Ht} \int_0^t J_0\left[2(B\xi(t - \xi))^{1/2}\right] \\ & \cdot \left\{ \frac{1}{(\pi\xi)^{1/2}} \exp\left[\frac{-x^2}{4D_c\xi} + \left(H - A - \frac{U_{tot}^2}{4D_c}\right)\xi\right] \right. \\ & - \frac{U_{tot}}{2D_c^{1/2}} \exp\left[\frac{U_{tot} x}{2D_c} + (H - A)\xi\right] \\ & \cdot \text{erfc}\left[\frac{x}{2(D_c\xi)^{1/2}} + \frac{U_{tot}}{2}\left(\frac{\xi}{D_c}\right)^{1/2}\right] \left. \right\} d\xi \left. \right\} \end{aligned} \quad (4.33)$$

where J_0 is the Bessel function of the first kind of zeroth order, “exp” is the exponential function; “erfc” is the complementary error function; ξ and τ are dummy integration variables; $A = r_{c-c^*(r)} + r_{c-c^*(\tau)}$; $B = -r_{c-c^*(r)} r_{c^*(r)-c}$; and $H = r_{c^*(r)-c}$. In the analytical solution (4.33), to account for gravity effects, the velocity term was replaced with U_{tot} , which is defined by equation (4.12).

4.6 List of the transport models employed in ColloidFit

The particle (colloid and virus) transport models described in sections §4.1-4.5 are summarized as follows in Table 4.2.

Table 4.2 Available ColloidFit transport models

No	Particle type - Source type	Attachment*	Equations
1	Virus Instantaneous	Reversible	(4.1), (4.5)-(4.7), (4.9)
2	Virus Broad pulse	Reversible	(4.1), (4.5)-(4.8)
3	Virus Instantaneous with gravity	Reversible	(4.1)-(4.7), (4.9)
4	Virus Broad pulse with gravity	Reversible	(4.1)-(4.8)
5	Colloid Instantaneous	Reversible	(4.15)-(4.18), (4.20)
6	Colloid Broad pulse	Reversible	(4.15)-(4.19)
7	Colloid Instantaneous with gravity	Reversible	(4.2)-(4.4), (4.15)-(4.18), (4.20)
8	Colloid Broad pulse with gravity	Reversible	(4.2)-(4.4), (4.15)-(4.19)
9	Colloid Instantaneous	Mixed	(4.15), (4.17), (4.18), (4.20), (4.25)-(4.28)
10	Colloid Broad pulse	Mixed	(4.15), (4.17)-(4.19), (4.25)-(4.28)
11	Colloid Instantaneous with gravity	Mixed	(4.2)-(4.4), (4.15), (4.17), (4.18), (4.20), (4.25)-(4.28)
12	Colloid Broad pulse with gravity	Mixed	(4.2)-(4.4), (4.15), (4.17)-(4.19), (4.25)-(4.28)

*Mixed attachment refers to the combined reversible and/or irreversible attachment.

4.7 Attachment equations

In section §3.4.2 and more specifically in Figure 3.6d the user had the chance to view a number of the available attachment equations. All the attachment model equations used by ColloidFit are listed in Tables 4.3 and 4.4:

Table 4.3 Available ColloidFit non-equilibrium adsorption models

Num	Model	Mathematical Description	Equation #
1	Linear reversible	$\frac{\partial C^*}{\partial t} = \frac{k_1 \theta}{\rho_b} C - k_2 C^*$	(4.34)
2	Non linear reversible	$\frac{\partial C^*}{\partial t} = \frac{k_1 \theta}{\rho_b} C^n - k_2 C^*$	(4.35)
3	Kinetic product	$\frac{\partial C^*}{\partial t} = a C^{a_1} C^{*a_2}$	(4.36)
4	Bilinear	$\frac{\partial C^*}{\partial t} = k_1 C(Q^0 - C^*) - k_2 C^*$	(4.37)
5	Mass transfer	$\frac{\partial C^*}{\partial t} = k(c - C_g)$	(4.38)
6	Elovich model	$\frac{\partial C^*}{\partial t} = a_1 e^{-a_2 C^*}$	(4.39)
7	Pseudo second-order	$\frac{\partial C^*}{\partial t} = k_{p2} (C_{eq}^* - C^*)^2$	(4.40)

Table 4.4 Available ColloidFit equilibrium attachment models

Num	Model	Mathematical Description	Equation #
1	Linear	$C^* = K_d C_{eq}$	(4.41)
2	Freundlich	$C^* = K_f C_{eq}^m$	(4.42)
3	Langmuir	$C^* = \frac{Q^0 C_{eq}}{1 + a_1 C_{eq}}$	(4.43)

Note that for all adsorption/attachment models (4.34)–(4.43) it is assumed that initially the attached concentration C^* [M_c/M_s] is zero:

$$C^*[0] = 0 \quad (4.44)$$

4.8 Decay/inactivation models

The decay/inactivation model equations used by ColloidFit are listed in Tables 4.5:

Table 4.5 Available ColloidFit decay/inactivation models

Num	Model	Mathematical Description	Equation #
1	Two-parameters	$\ln(C / C_0) = -\lambda t$	(4.45)
2	Three-parameters	$\ln(C / C_0) = \frac{\lambda}{\alpha} \{e^{-\alpha t} - 1\}$	(4.46)

where in equations (4.45)-(4.46) C_0 [M_v/L^3] is the initial virus concentration.

4.8 Temporal moments

The particle (virus or colloid) concentrations collected at the column exit can be analyzed by the absolute temporal moments:

$$m_n(L) = \int_0^\infty t^n C(L,t) dt \quad (4.47)$$

where the subscript $n=0, 1, 2, \dots$ indicates the order of the moment, and L [L] is the porous medium (column) length. The zeroth absolute temporal moment, m_0 [tM/L^3], quantifies the total mass in the concentration distribution curve; the first absolute moment, m_1 [t^2M/L^3], describes the mean residence time; and the second absolute temporal moment, m_2 [t^3M/L^3], describes the degree of spreading of the concentration distribution curve. Also, the normalized temporal moments are defined as (James and Chrysikopoulos, 2011):

$$M_n(L) = \frac{m_n(L)}{m_0(L)} = \frac{\int_0^\infty t^n C(L,t) dt}{\int_0^\infty C(L,t) dt} \quad (4.48)$$

The first normalized temporal moment, M_1 [t], characterizes the center of mass of the concentration distribution curve and defines the average velocity. The second normalized temporal moment, M_2 [t^2], characterizes the spreading of the concentration distribution curve. Worthy of note is that the mass recovery, M_r [-], of the suspended particles is quantified for the instantaneous loading by the following expression (Chrysikopoulos and Katzourakis, 2014):

$$M_r(L) = \frac{m_0(L)}{M_\delta / U_{tot}} \quad (4.49)$$

where $M_\delta = M_{in}/A\theta$ [M/L^2] is the mass injected “instantaneously” over the cross-sectional area of the column (where M_{in} [M] is the injected mass; A [L^2] is the cross

sectional area of the porous medium); U_{tot} [L/T] is the total velocity given from equation (4.12). Furthermore, for broad-pulse source loading the mass recovered is given from (Chrysikopoulos and Syngouna, 2014):

$$M_r(L) = \frac{m_0(L)}{C_0 t_p} \quad (4.50)$$

Where C_0 [M/L³] is the constant injected concentration of suspended particles, over a predefined time period t_p .

4.9 Simplified parameter notation

In order to simplify the ColloidFit user interface parameter notation, the symbols described and used in sections §4.1-4.6 were changed as shown in Table 4.5. The “Equations Symbols” column refers to the symbols used in equations found in section §4. The “Colloid Symbols” column refers to the symbols plotted in ColloidFit user interface when the colloid simulation model is selected. The “Virus Symbols” column refers to the symbols plotted in ColloidFit user interface when the virus simulation model is selected (see Figures 3.1 and 3.7).

Table 4.5 Available ColloidFit equilibrium adsorption models

Equation Symbols	Colloid Symbols	Virus Symbols
D_x	D_x	D_x
$r_{c-c^{*(t)}}$	r_1	-
$r_{c^{*(t)}-c}$	r_2	-
$r_{c-c^{*(0)}}$	k_{irr}	-
r_{v-v^*}	-	r_1
r_{v^*-v}	-	r_2
λ_v	-	λ
λ_{v^*}	-	λ^*
U_{tot}	U_{eff}	U_{eff}

4.10 Numerical procedures

The transport model equations were solved analytically by using already existing 1-D solutions found in literature (Sim and Chrysikopoulos, 1995; Thomas and Chrysikopoulos, 2007). The resulting integrals were approximated numerically using open source libraries Quadpack QAGS integrator. QAGS is a simple globally adaptive integrator using the strategy of Amdt (Piessens, 1973). It is possible to choose between 6 pairs of Gauss-Kronrod quadrature formula for the rule evaluation component. The pairs of high degree of precision are suitable for handling integration difficulties due to a strongly oscillating integrand. All mathematical handling was implemented in Fortran using the highest possible accuracy settings.

Adsorption equations were solved again with the open source software ODEPACK (Hindmarsh et al., 1983; Petzold et al., 1983) using DLSODA subroutines that implement an automatic stiff or not stiff differential equation solver.

5. Fitting process

5.1 Introduction to fitting

The fitting process should not be considered as an easy task to perform. Certainly, starting with any set of preselected initial parameter values may not always yield the absolute best-fitted parameter values. Therefore, it is important to carefully select initial parameter values as close as possible to the best-fitted values. Also, by providing, in the “Fitting” tab, the lower and upper limits for each parameter to be fitted, ColloidFit is restricted from giving best-fitted parameter values with no physical meaning.

Another important parameter when performing a fitting is the number of parameters to be fitted. An absolute number of three parameters fitted at a time (for the transport models) is a rule of thumb that protects the fitted results from having no physical meaning. ColloidFit allows a max number of four parameters to be fitted at a time but that’s to be on the safe side. Even if someone tried to fit four or more parameters the local minimums and maximum are so many that prevent any fitting progress. To that end there is special case for the virus transport problems, where the λ^* parameter is tied to the λ parameter. Consequently, the ratio λ/λ^* is kept constant and only the coefficient λ is fitted.

5.2 Theory of fitting

ColloidFit utilizes the state of the art fitting software package Pest (Doherty, 2005). Pest provides the smallest possible sum of squared deviations between experimental and model-generated data. This sum is known as the “objective function” and the smaller is this value the greater is the consistency between experimental and model observations and the greater is our confidence that the parameters determined are correct. From a mathematical point of view, we want to minimize Φ , where Φ is given by the following equation:

$$\Phi = (c - Xb)^t(c - Xb) \quad (5.1)$$

where c now holds the set of experimental data; the X is a matrix containing the response of any physical system to any outside excitation; the superscript “ t ” indicates the matrix transpose operation. Note that the vector b , that minimizes Φ in equation (5.1), is given by:

$$b = (X^tX)^{-1}X^tc \quad (5.2)$$

which provides a unique solution to the parameter estimation problem, as long as that the number of observations m equals or exceeds the number of parameters n . Assuming that the matrix (X^tX) is positive definite under these conditions, the solution can easily be obtained numerically.

Despite the fact that equation (5.2) is enough to perform the parameter estimation, equation (5.2) is not applicable to all kind of problems because it inherently assumes that all observations are of equal importance and have the same uncertainty.

The aforementioned problem can be resolved if a weight is supplied with each observation. The larger the weight associated with a particular observation the greater the impact that the observation has in the objective function. If the observation weights are housed in a square, m -dimensional, diagonal matrix Q

whose i^{th} diagonal element is the square of the weight w_i attached to the i^{th} observation, then equation (5.2) can be written as:

$$\Phi = (c - Xb)^t Q (c - Xb) \quad (5.3)$$

or, equivalently as,

$$\Phi = \sum_{i=1}^m (w_i r_i)^2 \quad (5.4)$$

where r_i (the i^{th} residual) is the difference between the actual field or laboratory measurement and the model outcome for the i^{th} observation. If observation weights are properly assigned (i.e. if they are assigned such that each weight is inversely proportional to the standard deviation of the observation with which it is associated), then equation (5.3) can be written as follows:

$$\Phi = (c - Xb)^t P^{-1} (c - Xb) \quad (5.5)$$

where

$$P(= Q^{-1}) = \frac{C(c)}{\sigma^2} \quad (5.6)$$

And σ^2 (variance of each of the elements of c) is obtained from:

$$\sigma^2 = \frac{\Phi}{(m - n)} \quad (5.7)$$

where n is the dimension of vector b ; $m-n$ is the dimension of vector c ; $C(c)$ represents the covariance matrix of the m -dimensional observation random vector c of which our measurement vector is a particular realization. Given that Q is a diagonal matrix, so is P , its elements being the reciprocals of the corresponding elements of Q . The assumption of independence of the observations is maintained through insisting that Q (and hence P) have diagonal elements only. Where the elements of Q are the squares of the observation weights. It is worthy to note here that the weights as defined in equations (5.3) and (5.4) are actually the square roots of the weights defined by some other investigators. This alternative style was adopted because users find it easier to think in terms of standard deviations than variances, when assigning weights to observations.

Finally, with the inclusion of observation weights equation (5.2), by which the system parameter vector is estimated, can be written as.

$$b = (X^t Q X)^{-1} X^t Q c \quad (5.8)$$

For additional information about the fitting procedures employed by the Pest software (Doherty, 2005), the users are encouraged to consult: “[The new PEST manual part I](#)” & “[The new PEST manual part II](#)”, which can be found at the download section of Pest homepage <http://www.pesthomepage.org/Downloads.php>.

6. Troubleshooting

There are cases for which even if the user presses the start fitting button nothing happens, despite having properly inputted all the parameters required. This is because some antiviruses like Avira treat FORTRAN executable as false positive viruses, and as such they guarantee them. Please note the official release of ColloidFit, downloaded from <http://tuceel.tuc.gr/downloads>, is absolutely clean of viruses. Download only from official servers.

7. Known issues

Current version 1.3 beta:

1. Depending on operating system's default font there is a chance some explanatory texts, contained in textboxes in the system options menu, not to be displayed properly (seen as a whole).
2. In some cases, the ColloidFit log file that holds the Pest output, may resist the delete commands, which are issued after the initiation of a fitting cycle. Consequently, previous useless output information may be displayed every time a fitting process is initiated. This problematic issue yields long Pest output that exceeds 1000 lines. This issue can be fixed only by a complete Operating System restart.
3. The ColloidFit project icon in the Mac version may not always be displayed properly.

8. Changelog

Changes of version 1.3.1 from version 1.2.1

1. Minor manual changes.
2. The “Gravity” pane functionality was improved: typing on temperature text box causes the table with the μ_w parameters to scroll to the respective value.
3. Fixed a bug that under certain circumstances caused the μ_w parameter not to be properly read from the “Gravity” user interface.

Changes of version 1.2.1 from version 1.1.2

1. Minor manual corrections.
2. A misspelled item in the ColloidFit interface was corrected.
3. The automatic input generating: Auto input generator (multiple X), found in the “Simulating tab” was improved in order to produce consistent results.
4. The problem with projects that could not be reopened because the simulations included non-number values (“Infinity” or “NaN”), which cannot be displayed was fixed. Such results are now substituted by zero “0”, along with a warning message in the “System output” table.
5. Small changes were made in the “Pest configuration” file. It is now possible for parameters to obtain negative values during the fitting processes, assuming that the imposed boundaries allow it.
6. The manual was revised to include an explanation that the “Absolute simulation accuracy” cannot be set to zero for attachment equations. An appropriate warning was added in the interface.
7. The inability to change the number of decimal places of a particular mathematical format (i.e. “Exponential” format), without changing the mathematical format, was fixed.
8. Numerical errors that may occur during simulation time will now be reported to the user.
9. Fixed occurrences where the y-axis is pushed away from the respective border due to an internal java glitch that rounds up numerical values after it has rendered them on screen

Changes of version 1.1.2 from version 1.1.1

1. Minor manual changes
2. Added extended explanations on virus and colloidal transport models
3. The initial condition assumed by the attachment models solver is now documented in manual.

Changes of version 1.1.1 from version 1.0.1

1. Additional system checking was added to make sure that boundaries and the initial main parameter values are in agreement.
2. New colloid simulation models were added. The new models support strictly reversible attachment.
3. The error output system is now reporting more accurately which parameters were found to be incorrectly initialized (i.e. empty, negative, non numerical...).
4. Several minor visual changes in the system options menu.

9. Notation

A	cross-sectional area of the porous medium (column), L^2
A_c	cross-sectional area of the porous medium (column), L^2
b	ratio of average free settling segment length to the grain radius, (–)
C_c	concentration of suspended colloids, M_c/L^3 .
C_{c_0}	constant injected concentration of suspended colloid particles, M/L^3
C_{v_0}	constant injected concentration of suspended virus particles, M/L^3
C_{c^*}	concentration of colloids attached onto the solid matrix, M_c/M_s .
C_v	concentration of suspended viruses, M_v/L^3 .
C_{v^*}	concentration of viruses attached onto the solid matrix, M_v/M_s .
$C_{c^{(i)}}$	concentration of colloids irreversibly attached onto the solid matrix, M_c/M_s .
$C_{c^{(r)}}$	concentration of colloids reversibly attached onto the solid matrix, M_c/M_s .
d_p	colloid particle diameter, L
D_c	hydrodynamic dispersion coefficient of colloids, L^2/t .
D_v	hydrodynamic dispersion coefficient of viruses, L^2/t .
D_x	hydrodynamic dispersion coefficient of colloids or viruses, L^2/t .
f_s	settling velocity correction factor, (–)
g	gravitational acceleration, L/t^2 .
$g^{(i)}$	vector component of gravitational acceleration in the positive x-direction, L/t^2 .
$g^{(-i)}$	vector component of gravitational acceleration in the negative x-direction, L/t^2 .
$g^{(-k)}$	vector component of gravitational acceleration in the negative z-direction, L/t^2 .
i	species c=colloid, v=virus.
k_{irr}	rate coefficient of irreversible colloid attachment onto the solid matrix, $1/t$.
M_{in}	injected mass, M.
M_r	mass recovery ratio, (–)
M_δ	mass injected “instantaneously” over the porous medium cross-sectional area, M/L^2
m_n	n-th absolute temporal moment, $T^n M/L^3$
M_n	n-th normalized temporal moment, T^n
M_c	mass of colloids, M_c .
M_s	mass of the solid matrix, M_s .
M_v	mass of viruses, M_v .
r_1	rate coefficient of colloid or virus attachment onto the solid matrix (see table 4.5), $1/t$.
r_2	rate coefficient of colloid or virus detachment from the solid matrix (see table 4.5), $1/t$.
$r_{c-c^{*(i)}}$	rate coefficient of irreversible colloid attachment onto the solid matrix, $1/t$.
$r_{c-c^{*(r)}}$	rate coefficient of reversible colloid attachment onto the solid matrix, $1/t$.
$r_{c^{*(r)}-c}$	rate coefficient of reversible colloid detachment from the solid matrix, $1/t$.
r_{v-v^*}	rate coefficient of virus attachment onto the solid matrix, $1/t$.
r_{v^*-v}	rate coefficient of virus detachment from the solid matrix, $1/t$.
t	time, t.
t_p	time period during of which the source has a constant concentration, t.
U	interstitial velocity n, L/t .
U_{tot}	total velocity (sum of average interstitial velocity with settling velocity), L/t .
U_{eff}	total velocity (sum of average interstitial velocity with settling velocity) (see table 4.5), L/t .
$U_{s(\pm i)}$	x-directional component of the restricted settling velocity of species i, L/t .
x	Cartesian coordinate in the longitudinal direction, L.

Greek Letters

β	angle of the main flow direction (x-direction) with respect to the direction of gravity.
ε	empirical correction factor, (–)
δ	modified Dirac delta function, 1/L.
θ	porosity of the column material, (L ³ voids)/(L ³ solid matrix).
μ_w	dynamic viscosity of water, M/(L·t)
λ_v	decay rate of viruses suspended in the liquid phase, 1/t.
λ_{v*}	decay rate of viruses sorbed or attached onto the solid matrix, 1/t.
λ	decay rate of particles suspended in the liquid phase (see table 4.5), 1/t.
λ^*	decay rate of particles sorbed or attached onto the solid matrix (see table 4.5), 1/t.
ρ_b	bulk density of the solid matrix, M _s /L ³ .
ρ_p	particle density, M/L ³
ρ_w	fluid density, M/L ³

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11. Web links

ColloidFit official homepage: <http://tuceel.tuc.gr/>

Pest homepage: <http://www.pesthomepage.org/>

Java homepage: <https://www.oracle.com/java/index.html>

JavaFx license: <http://www.oracle.com/technetwork/java/javase/terms/license/index.html>

GNU Fortran compiler, gFortran homepage: <https://gcc.gnu.org/wiki/GFortran>

GNU General Public License: <https://gcc.gnu.org/onlinedocs/gfortran/Copying.html#Copying>