Software Models for

Chemical Kinetic Retention and Transport in Soils and Geological Media

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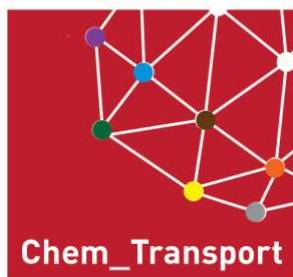
User's Manual

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Chem_Transport

LIST OF MODELS

BATCH KINETIC

Simulations Models:

Nonlinear Kinetic (NKM)
Langmuir Kinetic (LKM)
Multireaction Model (MRM)
Second Order Two-Site (SOTS)
Stir-Flow with MRM (STIRFLOW-MRM)
Thin-Disk Flow with MRM (THINDISK-MRM)
Competitive-MRM

Fitting Models:

Multireaction Model (MRM-FIT)
Second Order Two-Site (SO-FIT)
Competitive MRM (CMRM-FIT)

TRANSPORT

Simulations Models:

Multireaction and Transport Model (MRTML)
Second Order Two-Site (SOTSL)
SOTS Mobile-Immobile (SOMIM)
Competitive-MRTM (CMRM)
MRTM Mobile Immobile (MRTM_MIM)
Ion-Exchange Transport Model (ION-EXCH)
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Fitting Models:

Multireaction Model (MRTM-FIT)
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Second Order Mobile-Immobile (SOMIM-FIT)
Multireaction-Immobile Model (MRTM-MIM-FIT)
Competitive-Multireaction (CMRTM-FIT)
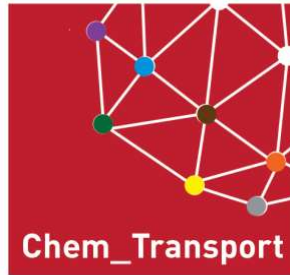
Overview

Chem_Transport is a software package of several models that describe the transport and sorption of chemicals in soils and other porous media. These models are characterized by two main features; they are nonlinear and kinetic in nature. The models represent our recent advances made in the understanding of transport characteristics of chemicals in soils and geological media. The models are broad in nature and address various physical and chemical processes that influence the behavior of solutes in porous media.

Chem_Transport models are applicable for variety of chemicals in field settings as well as controlled laboratory and greenhouse environments. The models represent transport conditions and batch type reactors under no-flow conditions where transport is ignored. For each class of models, first simulation type models where the user provides all physical and chemical parameters. This class of models are most suitable for classroom teaching and risk assessment. The second class of models is that where the user provides an experimentally measured data set and a selected model will provide best-fit (based on non-linear least-squares) description of measured results.

Chem_Transport models are based on solutions of the advective-dispersive equation for the transport of chemicals in one-dimensional soils and geological media. The solutions are based on numerical approximations using finite –difference (Crank-Nickolson) techniques.

Physical Nonequilibrium Models
- Uniform and stratified soils
- Multiple Regions
- Multiple Porosities
- Fractured Media, mobile-immobile

Kinetic Sorption Models
- Nonlinear and Langmuir Kinetics
- Desorption-Hysteresis
- Second-Order
- Kinetic Ion Exchange
- Multi-Site and Multireaction

Applications of Chem_Transport

The models presented are applicable for chemicals including organics and inorganics, e.g., insecticides, herbicides, industrial chemicals, military explosives, and radionuclides. Other include macro nutrients; nitrogen, phosphorus and potassium, as well as micronutrients, e.g., boron, zinc, and copper. Others also include heavy metals such as arsenic, lead, cobalt, cadmium, trace elements and tracer.

Users

Teaching - Can be incorporated in classroom teaching for undergraduate and graduate students in chemical and civil engineering, hydrology, geology, soil physics and chemistry, environmental sciences and environmental engineering. Simulations based on various scenarios provide information on system parameters (sensitivity analysis) and risk assessment.

Research -   This software should be also useful to environmental scientists, engineers, and geologists whose desire is to describe laboratory or field observations under various constraints such as batch reactors, miscible displacements, and transport in saturated and unsaturated soils. This software should also be useful for federal and state agencies, researchers, consulting engineers, and decision makers in the management and restoration of contaminated sites.

System Requirements

The software runs on Windows platform and a recent version of Java is required to install and execute this software on personal computers.

Input and Output Data Files

An input file must be provided by the user. The input file specifies initial and boundary conditions associated with each model and can be provided in two ways:

   i. Manual entry by filling out the template provided.
   ii. As an external ASII file (,dat or txt).

Samples of input data files in ASCII format for all models are give in INPUTFILES folder to be downloaded by the user. Samples of input files in a template format are included in this package. Model output is given in txt format and must be named and saved by the user. Graphics of simulations and experimental measurements are also generated which can be saved by the user. Graphics include breakthrough curves, time-dependent sorption-desorption and sorption isotherms
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Message to Users

User's feedback on this software package is important to help improve the structure and provide a user friendly environment.

Types of Models

In this software package, two classes of models are presented.

- **Transport Models**

- **Sorption or Kinetic Batch Models**

Transport models are a set of models which account for the simultaneous transport and retention of chemicals in soils.   Sorption or Kinetic batch models are a set of models which deal with the kinetic retention (adsorption-desorption) of chemicals in soils when water (mass) flow of water is negligible. This is often the case for sorption and release experiments where laboratory batch methods are used.

Select
Model Type

Batch or Kinetic Models
A set of models which deal with kinetic retention (adsorption-desorption) of chemicals in soils.

Transport Models
A set of models which deal with the simultaneous transport and retention of chemicals in soils.

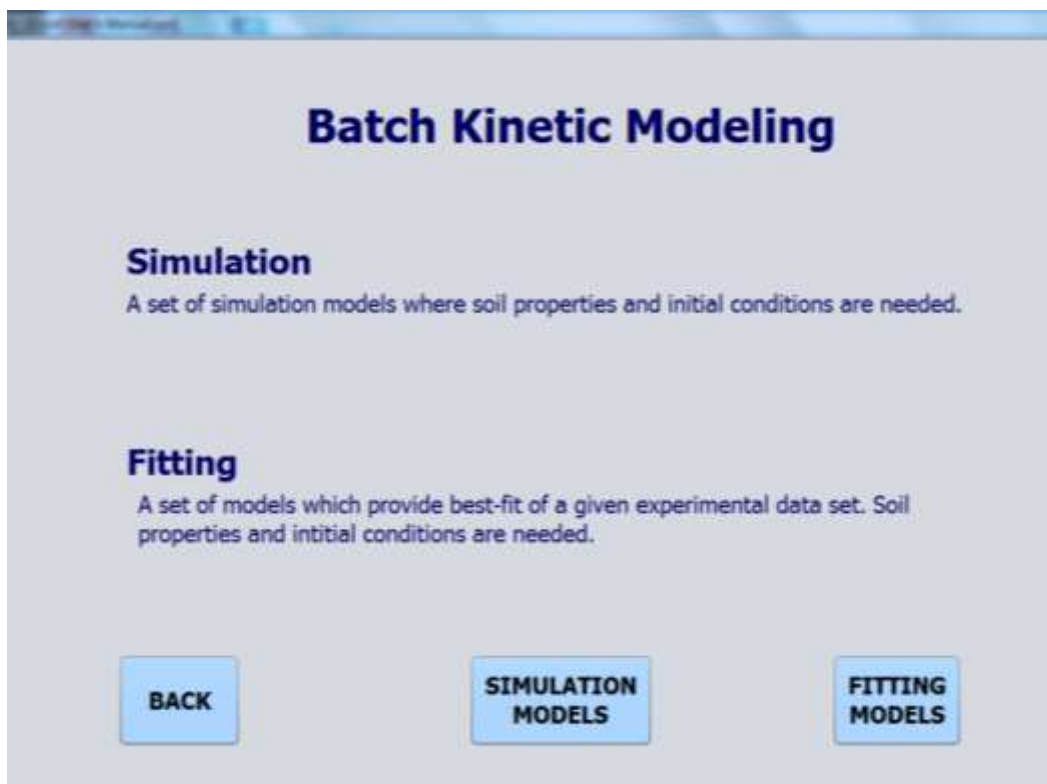| BACK	BATCH KINETIC	TRANSPORT
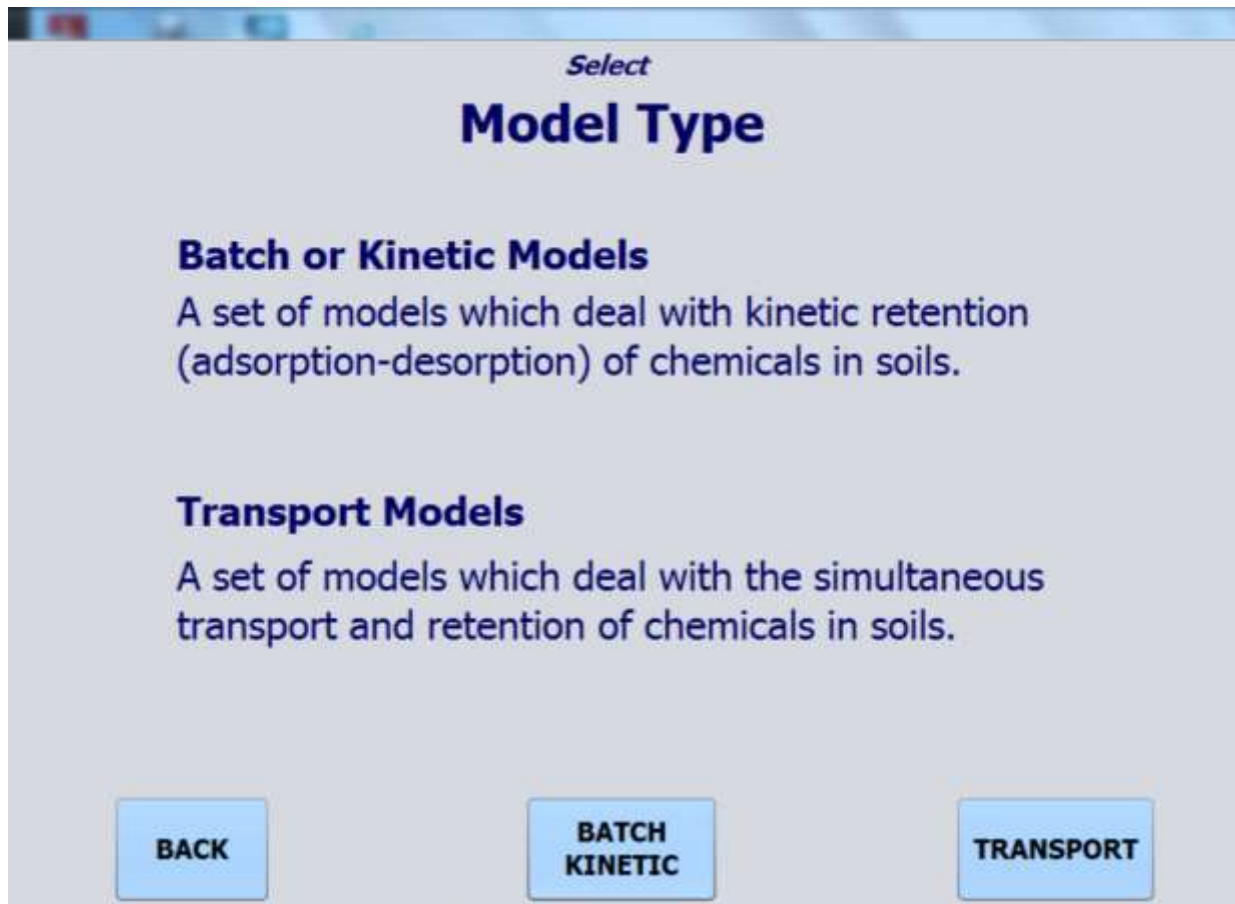
Kinetic and transport models are further classified into two types

- **Simulation Models**
- **Fitting Models**

Simulation models are those models; subject to the appropriate initial and boundary conditions that provide calculations of chemical retention and transport, for a given set of model parameters; flux, equilibrium rate coefficient, forward and backward rates of reactions, etc. As such, these generic models can provide information on the role of each or combination of model parameters on the chemical behavior in soils. In this mode, it is recommended for teaching for senior undergraduate and graduate students in various disciplines.

Fitting models are more complex than the simulation or generic models. Each model utilizes nonlinear least-square approximation procedure to find best estimates of model parameters that describe a set of experimental observations. As such, the user must identify a set of model parameter for which estimates are sought (inverse-modeling). For a given model, different model processes best describe the experimental data. To achieve this, several attempts of combination of model parameters are often sought.

Batch Kinetic Modeling

Simulation
A set of simulation models where soil properties and initial conditions are needed.

Fitting
A set of models which provide best-fit of a given experimental data set. Soil properties and intitial conditions are needed.

| BACK | SIMULATION MODELS | FITTING MODELS |

Sorption or Kinetic Batch Models

Soils and other geochemical systems are quite complex, and various sorption reactions are likely to occur. In general, chemical retention processes with matrix surfaces have been quantified by scientists using a number of empirically-based approaches. One approach represents equilibrium-type reactions and the other of the kinetic type.

In this software, emphasis is on kinetic type retention models. Kinetic models represent slow reactions where the amount of solute sorption or transformation is a function of contact time. Most commonly encountered is the first-order kinetic reversible reaction for describing time-dependent adsorption/desorption in soils. Others include linear irreversible and nonlinear reversible kinetic models. Recently, combination of equilibrium and kinetic type (two-site) models, and consecutive and concurrent multireaction type models has been proposed.

SIMULATION MODELS

1. *Nonlinear Kinetic Model (NKM)*

Kinetic sorption which exhibit nonlinear or curve linear retention behavior is commonly observed between the amount sorbed S (mg/g soil) and solution concentration C (mg/ml) for several reactive chemicals such as trace elements and heavy metals. To describe such nonlinear behavior, the following fully reversible nonlinear kinetic reaction is used,

$$\frac{\partial S}{\partial t} = k_f \left(\frac{\theta}{\rho}\right) C^b - k_b S \tag{1}$$

where the parameters k_f and k_b represent the forward and backward rates of reactions (h^{-1}) for the retention mechanism, respectively and b is a dimensionless parameter commonly less than unity. The magnitudes of the rate coefficients dictate the extent of kinetic behavior of retention of the solute from the soil solution. For small values of k_f and k_b, the rate of retention is slow and strong kinetic dependence is anticipated. The parameter b is a measure of the extent of the heterogeneity of sorption sites of the soil matrix where sorption sites have different affinities for heavy metal retention by matrix surfaces, where sorption by the highest energy sites takes place preferentially at the lowest solution concentrations. Moreover, for $b=1$, equation 1 reduced to a first order (linear) kinetic equation..

At large times (i.e, as t $\rightarrow \infty$), the rate of retention approaches zero, equation (1) yields,

$$S = K_f C^b \quad where \quad K_f = \left(\frac{\theta k_f}{\rho k_b}\right) \tag{2}$$

which is analogous from to the Freundlich equilibrium equation where K_f is the solute partitioning coefficient (cm^3/g). Therefore, one may regard the parameter K_f as the ratio of the rate coefficients for sorption (forward reaction) to that for desorption or release (backward reaction).

This model also accounts for irreversible sorption or a sink of the linear type,

$$\rho \frac{\partial S_s}{\partial t} = k_s \theta C \tag{3}$$

where S_s is the amount irreversible sorbed (mg/g soil) and k_s is the rate of irreversible retention.

Input and Output Data Files

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

a. Manual entry by filling out the template provided below.

b. As an external ASII file (,dat or txt).

A sample of the input data file referred as NKM-IPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. For a given initial concentration (Ci) and input concentration (Cs) at time t > 0, the model provides results of concentration, the amount sorbed versus time, and sorption isotherms. Model output is given in txt format and must be named and saved by the user. Graphics of simulations are also generated which can be saved by the user. Graphics include time-dependent sorption-desorption and sorption isotherms.

Template for the NKM model

Model selected is NKM

Tittle	NONLINEAR KINETIC MODEL (NKM) SENSITIVITY ANALYSIS			
NUMBER OF ISOTHERMS DESIRED	5		NUMBER OF CASES	
Input parameters	Case 1	Case 2	Case 3	
MOISTURE CONTENT,CM3/CM3 (TH)	25.000E00	25.000E00	25.000E00	
BULK DENSITY,G/CM3 (ROU)	5.000E00	5.000E00	5.000E00	
APPLIED CONCENTRATION,MG/L (CS)	5.000E00	10.000E00	20.000E00	
DISTRIBUTION COEFFICIENT, Kd CM3/G (KF)	0.000E00	0.000E00	0.000E00	
NONLINEAR FREUNDLICH PARAMETER(N) (NEQ)	1.0E00	1.0E00	1.0E00	
FORWARD RATE REACTION, K1,Hr-1 (K1)	0.050E00	0.050E00	0.050E00	
BACKWARD RATE REACTION, K2,Hr-1 (K2)	0.0050E00	0.0050E00	0.0050E00	
NONLINEAR KINETIC PARAMETER , W, (W)	0.50E00	0.50E00	0.50E00	
TOTAL SIMULATION TIME,HOURS (TTOTAL)	720.0E00	720.0E00	720.0E00	
PRINTOUT TIME DESIRED,HOURS (TPRINT)	4.000E00	4.000E00	4.000E00	

OK

NKM Concentration versus Time

NKM Sorbed versus Time

10
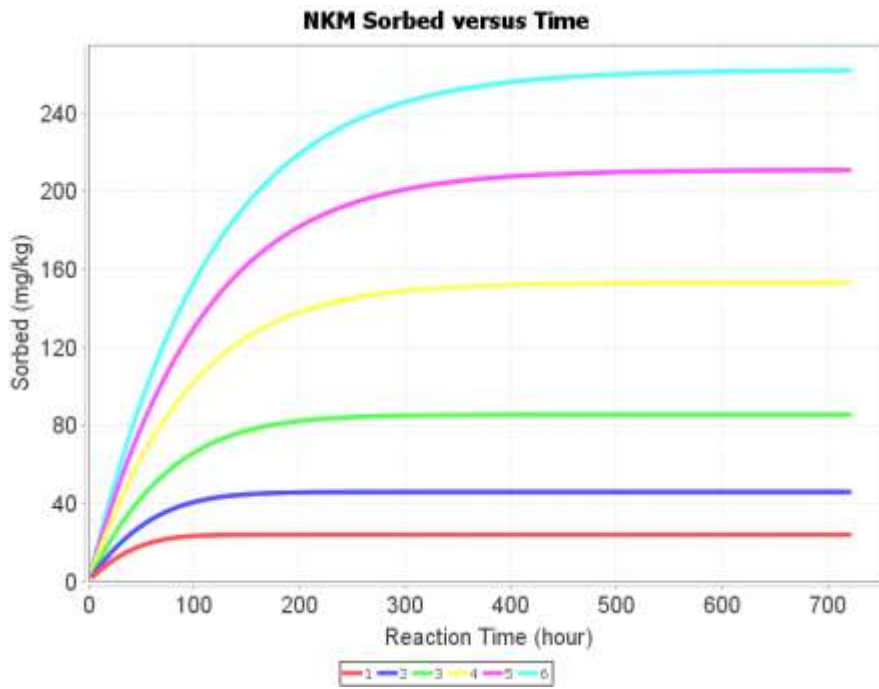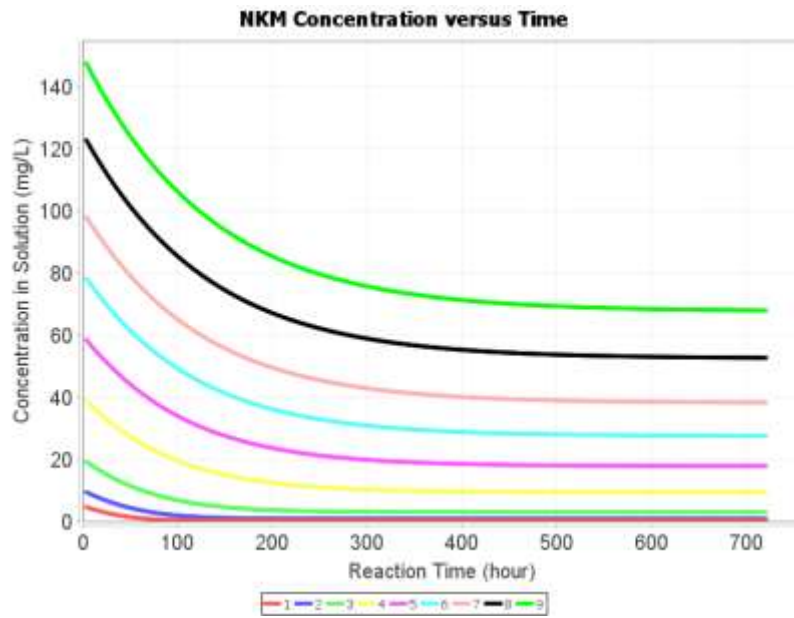
NKM Sorbed versus Concentration
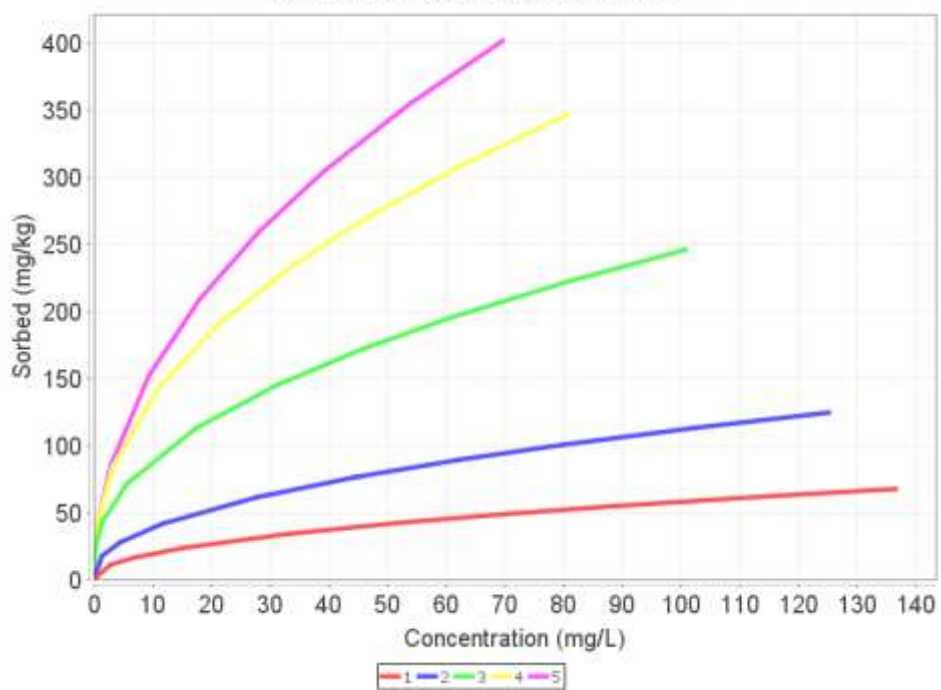
2. *Langmuir Kinetic Model (LKM)*

Here we follow second-order formulation, where one assumed that the retention mechanisms are site-specific where the rate of reaction is a function of the solute concentration present in the soil solution phase (C) and the amount of available or unoccupied sites ϕ (µg/g soil), such that

$$C + \phi \underset{k_b}{\overset{k_f}{\rightleftharpoons}} S \qquad (4)$$

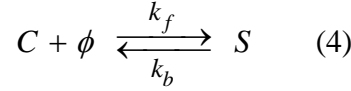where k_f and k_b are the associated rate coefficients (hr) and S the total amount of solute retained by the soil matrix. As a result, the rate of solute retention may be expressed as,

$$\rho \frac{\partial S}{\partial t} = k_f \theta \phi \; C - k_b \rho S$$

$$or \qquad\qquad\qquad (5)$$

$$\rho \frac{\partial S}{\partial t} = k_f \theta (S_T - S) C - k_b \rho S$$

where S_T (µg/g soil) represents the total amount of total sorption sites or sorption capacity (ug/ml). This model also accounts for irreversible sorption or a sink of the linear type,

$$\rho \frac{\partial S_s}{\partial t} = k_s \theta C \qquad (6)$$

where S_s is the amount irreversible sorbed (mg/g soil) and k_s is the rate of irreversible retention.

As the sites become occupied by the retained solute, the amount of vacant sites approaches zero ($\phi \rightarrow 0$) and the amount of solute retained by the soil approaches that of the total capacity of sites, i.e., $S \rightarrow S_T$. Vacant specific sites are not strictly vacant. They are assumed occupied by hydrogen, hydroxyl or by other specifically sorbed species. As $t \rightarrow \infty$, i.e. when the reaction achieves local equilibrium, the rate of retention becomes,

$$k_f \theta \phi C - k_b \rho S = 0, \qquad or \qquad \frac{S}{\phi C} = \left(\frac{\theta}{\rho}\right) \frac{k_f}{k_b} = \omega \qquad (7)$$

Upon further rearrangement, the second order formulation, at equilibrium, obeys the widely recognized Langmuir isotherm equation,

$$\frac{S}{S_T} = \frac{KC}{1+KC} \qquad (8)$$

where the parameter K ($= \theta k_f / k_b \rho$) is now equivalent to ω of Eq. (7) and represents Langmuir equilibrium constant. Sorption/desorption studies showed that highly specific sorption mechanisms are responsible for solute retention at low concentrations. The general view was that metal ions have a high affinity for sorption sites of oxide minerals surfaces in soils. In addition, these specific sites react slowly with reactive chemicals such as heavy metals and are weakly reversible.

Input and Output Data Files

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

a. Manual entry by filling out the template provided below.

b. As an external ASII file (,dat or txt).

A sample of the input data file referred as LKM-IPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. For a given initial concentration (Ci) and input concentration (Cs) at time t > 0, the model provides results of concentration, the amount sorbed versus time, and sorption isotherms. Model output is given in txt format and must be named and saved by the user. Graphics of simulations are also generated which can be saved by the user. Graphics include time-dependent sorption-desorption and sorption isotherms.

Template for the LKM model

Model selected is LKM

Tittle LANGMUIR BATCH KINETCS - TEST CASE

NUMBER OF ISOTHERMS DESIRED	5		NUMBER OF CASES	
Input parameters	Case 1	Case 2	Case 3	ADD CASE
MOISTURE CONTENT,CM3/CM3 (TH)	25.00E00	25.00E00	25.00E00	
BULK DENSITY,G/CM3 (ROU)	5.000E00	5.000E00	5.000E00	
APPLIED CONCENTRATION,PPM (CS)	20.000E00	50.000E00	75.000E00	
TOTAL AMOUNT OF AVAIALBLE SITES,ST (ST)	200.000E00	200.000E00	200.000E00	
FORWARD RATE REACTION, K1,Hr-1 (K1)	0.00010E0	0.00010E0	0.00010E0	
BACKWARD RATE REACTION, K2,Hr-1 (K2)	0.0005E00	0.0005E00	0.0005E00	
IRREVERSIBLE REACTION RATE,KS,Hr-1 (KS)	0.000E00	0.000E00	0.000E00	
PRINTOUT TIME DESIRED,HOURS (TPRINT)	0.50E00	0.50E00	0.50E00	
TOTAL SIMULATION TIME,HOURS (TTOTAL)	240.0000E00	240.0000E00	240.0000E00	

OK

LKM Concentration versus Time

LKM Sorbed versus Time

LKM Sorbed versus Concentration
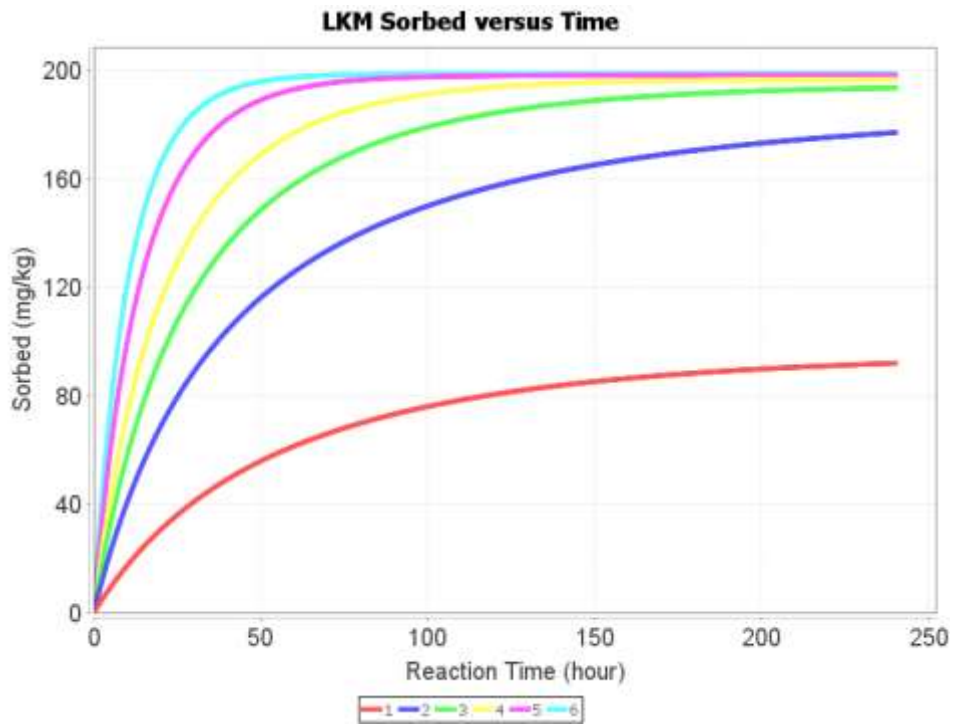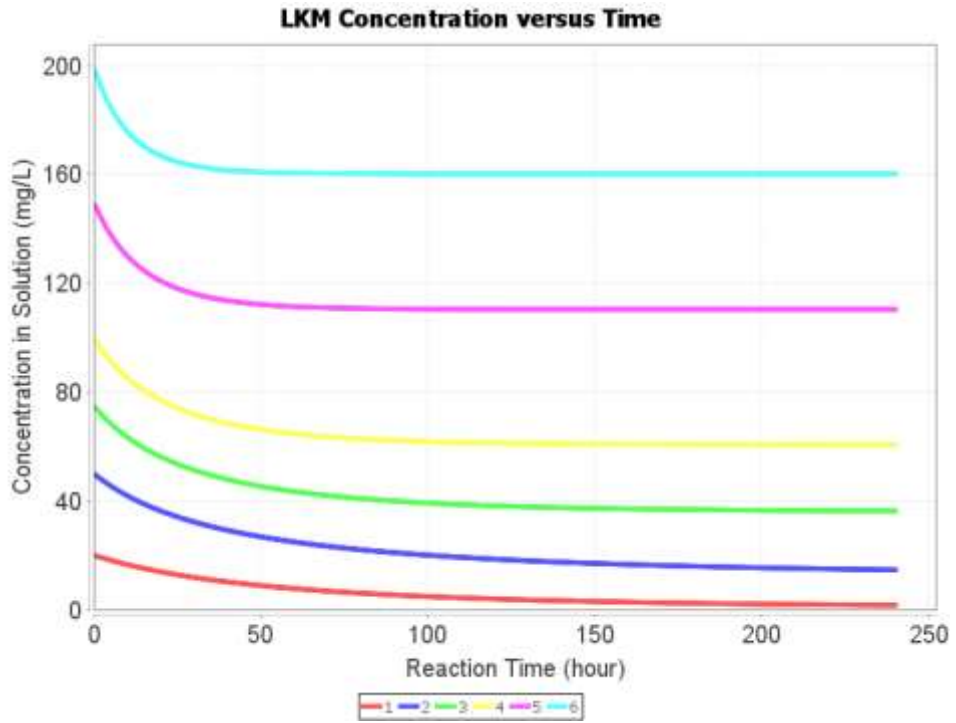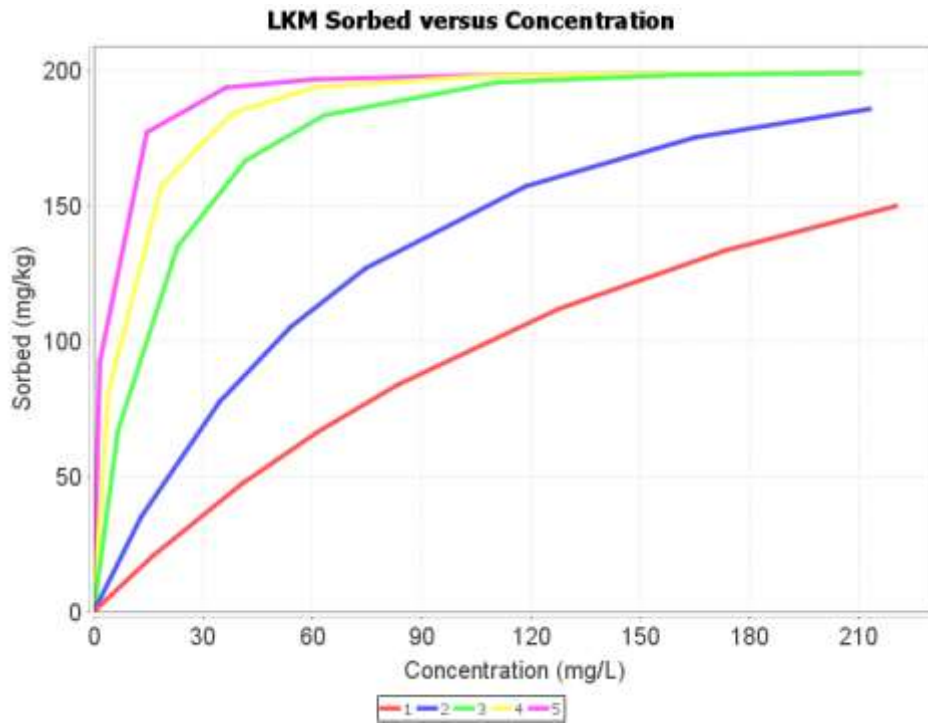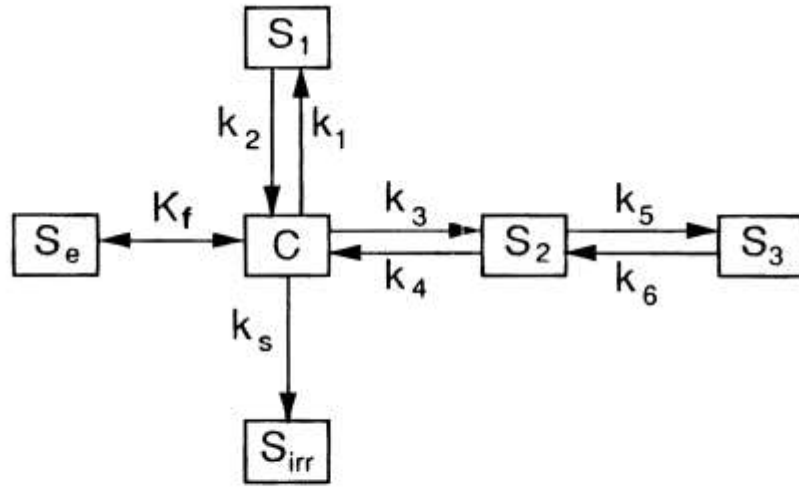
A schematic representation of the multireaction model (MRM).

Multireaction Model (MRM-BATCH)

A schematic representation of the multireaction model is shown in Fig. 3. In this model we consider the solute to be present in the soil solution phase (C) and in five phases representing solute retained by the soil matrix as S_e, S_1, S_2, S_3 and S_{irr}. We further assume that S_e, S_1 and S_2 are in direct contact with the solution phase and are governed by concurrent type reactions. Here we assume S_e is the amount of solute that is sorbed reversibly and is in equilibrium with C at all times. Specifically, the multireaction assumes that the total amount sorbed S_T *or simply S* as the total amount retained reversibly or reversibly by soil matrix surfaces,

$$S = S_e + S_1 + S_2 + S_3 + S_{irr}$$

The governing equilibrium retention/release mechanism is the nonlinear Freundlich type as

$$S_e = K_f C^b$$

where K_f is the associated distribution coefficient ($cm^3 kg^{-1}$) and b is a dimensionless Freundlich parameter ($b < 1$). Other equilibrium type retention mechanisms are given in Chapter 3. This includes linear (b=1), Langmuir, two-site Langmuir, and others.

The retention/release reactions associated with S_1, S_2, and S_3 are concurrent or consecutive type kinetic reactions. Specifically, the S_1 and S_2 phases were considered to be in direct contact with C and reversible rate coefficients of the (nonlinear) kinetic type govern their reactions,

$$\frac{\partial S_1}{\partial t} = k_1 \frac{\Theta}{\rho} C^n - k_2 S_1$$

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\Theta}{\rho} C^m - (k_4 + k_5) S_2 + k_6 S_3$$

$$\frac{\partial S_3}{\partial t} = k_5 S_2 - k_6 S_3$$

where k_1 and k_2 are the forward and backward rates coefficients (h^{-1}), respectively and n is the reaction order associated with S_1. Similarly, k_3 and k_4 are the rate coefficients and m is the reaction order associated with S_2, and k_5 and k_6 are the reaction parameters associated with S_3. In the absence of the consecutive reaction between S_2 and S_3, that is if $S_3 = 0$ at all times ($k_5 = k_6 = 0$), eq (44) reduces to,

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\Theta}{\rho} C^m - k_4 S_2$$

Thus eq. (7) for S_2 resembles that for S_1 except for the magnitude of the associated parameters k_3, k_4 and m.

The sorbed phases (S_e, S_1, S_2, S_3) may be regarded as the amounts sorbed on surfaces of soil particles and chemically bound to Al and Fe oxide surfaces or other types of surfaces, although it is not necessary to have a priori knowledge of the exact retention mechanisms for these reactions to be applicable. These phases may be characterized by their kinetic sorption and release behavior to the soil solution and thus are susceptible to leaching in the soil. In addition, the primary difference between these two phases not only lie in the difference in their kinetic behavior but also on the degree of nonlinearity as indicated by the parameters n and m. The sink/source term Q is commonly used to account for irreversible reactions such as precipitation/dissolution, mineralization, and immobilization, among others. We expressed the sink term as a first-order kinetic process;

$$Q = \rho \frac{\partial S_3}{\partial t} = k_s \Theta C$$

where k_s is the associated rate coefficient (h^{-1}). The sink term Q was expressed in terms of a first-order irreversible reaction for reductive sorption or precipitation or internal diffusion. Equation (13) is similar to that for diffusion-controlled precipitation reaction if one assumes that the equilibrium concentration for precipitation is negligible.

Input and Output Data Files

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

      a. Manual entry by filling out the template provided below.

      b. As an external ASII file (,dat or txt).

A sample of the input data file referred as MRM-IPUT.DAT and is given in the INPUTFILES

folder to be downloaded by the user. For a given initial concentration (Ci) and input concentration

(Cs) at time t > 0, the model provides results of concentration, the amount sorbed versus time, and

sorption isotherms. Model output is given in txt format and must be named and saved by the

user. Graphics of simulations are also generated which can be saved by the user. Graphics

include time-dependent sorption-desorption and sorption isotherms.

Template for the MRM model

Model selected is MRM

Tittle MULTIREACTION MODEL (MRM) TEST CASE - SENSITIVITY ANALYSIS

NUMBER OF ISOTHERMS DESIRED	4	NUMBER OF CASES	5
Input parameters	Case 1	Case 2	Case 3 ADD CASE
MOISTURE CONTENT,CM3/CM3 (TH)	10.000E00	10.000E00	10.000E00
BULK DENSITY,G/CM3 (ROU)	1.000E00	1.000E00	1.000E00
APPLIED CONCENTRATION,MG/L (CS)	5.000E00	10.000E00	20.000E00
DISTRIBUTION COEFFICIENT, KD CM3/G (KD)	0.000E00	0.000E00	0.000E00
NONLINEAR FREUNDLICH PARAMETER(N) (NEQ)	0.000E00	0.000E00	0.000E00
FORWARD RATE REACTION, K1,HR-1 (K1)	1.131	1.131	1.131
FORWARD RATE REACTION, K2,HR-1 (K2)	0.323	0.323	0.323
NONLINEAR KINETIC PARAMETER , U, (U)	0.629E00	0.629E00	0.629E00
FORWARD RATE REACTION, K3,HR-1 (K3)	0.00E00	0.00E00	0.00E00
BACKWARD RATE REACTION, K4,HR-1 (K4)	0.0E00	0.0E00	0.0E00
NONLINEAR KINETIC PARAMETER , W, (W)	0.6290E00	0.6290E00	0.6290E00
FORWARD RATE REACTION, K5,HR-1 (K5)	0.0000	0.0000	0.0000
BACKWARD RATE REACTION, K6,HR-1 (K6)	0.000E00	0.000E00	0.000E00
IRREVERSIBLE REACTION RATE,KIRR,HR-1 (KIRR)	0.0020E00	0.0020E00	0.0020E00
TOTAL SIMULATION TIME,HOURS (TTOTAL)	200.0E00	200.0E00	200.0E00
PRINTOUT TIME DESIRED,HOURS (TPRINT)	2.000E00	2.000E00	2.000E00

OK

MRM Sorbed versus Concentration

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MRM Sorbed versus Time

MRM Sorbed versus Concentration

Inflow Solution

k_1 S_1 k_2 **Chemical in the soil solution** k_3 k_4 S_2

Outflow Solution

Schematic diagram of a two-site model for kinetic adsorption-desorption of chemicals in soils.
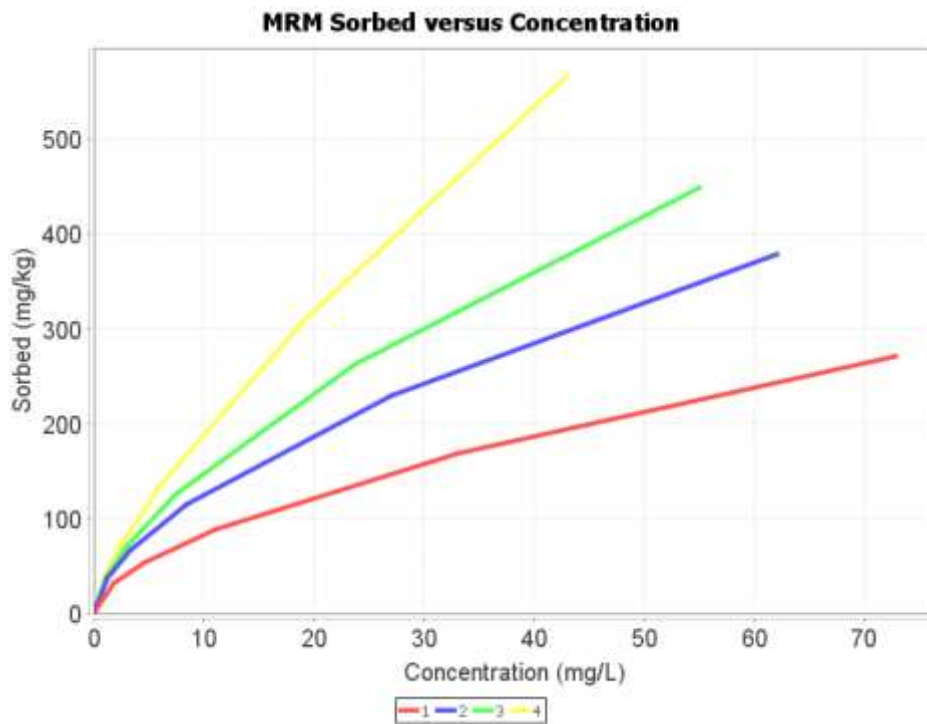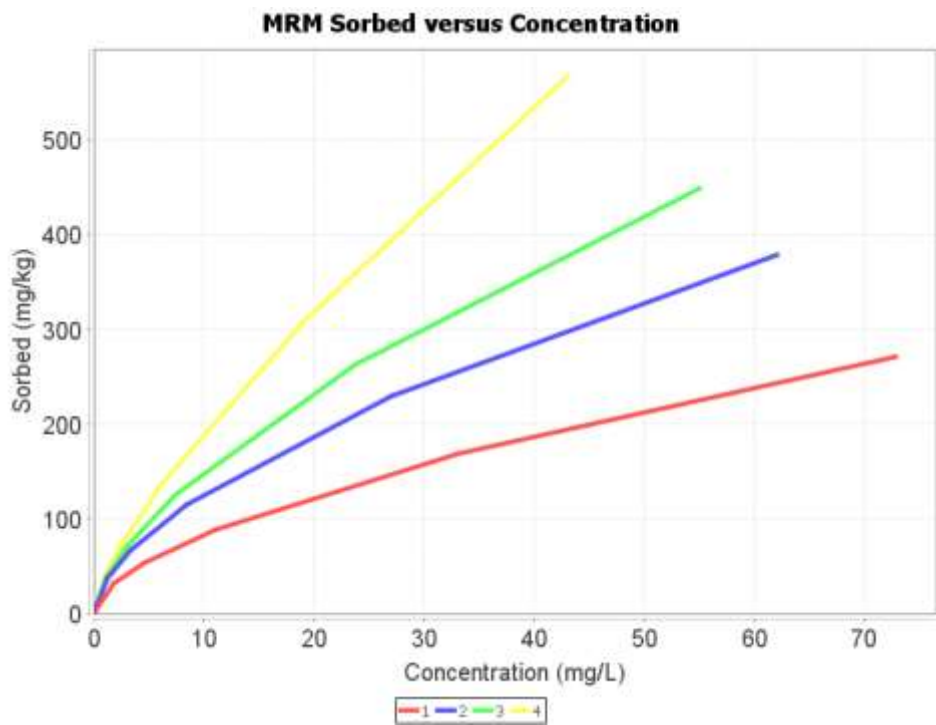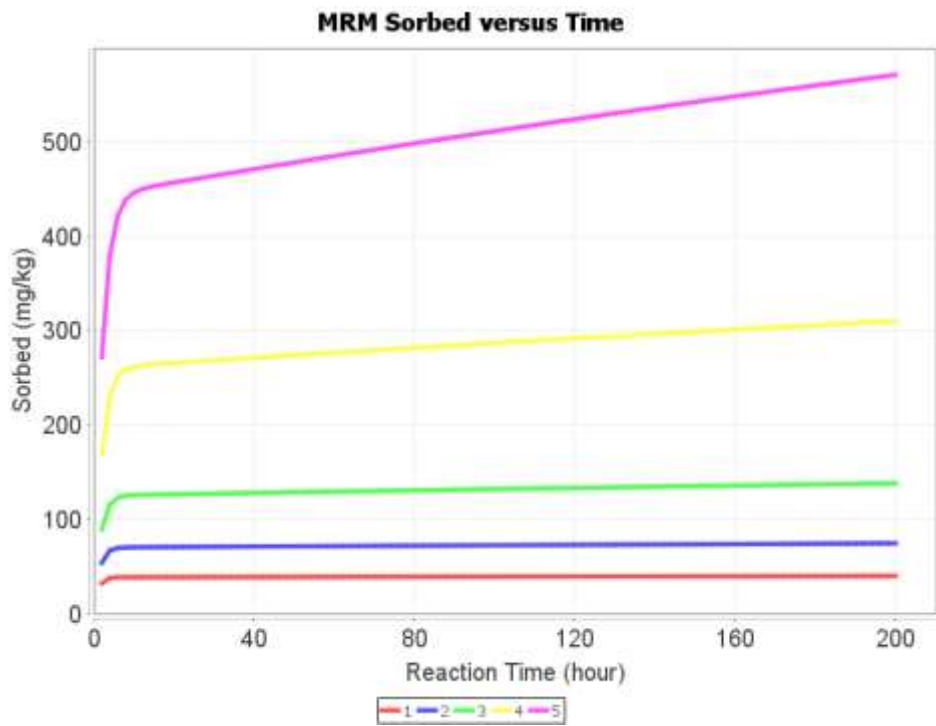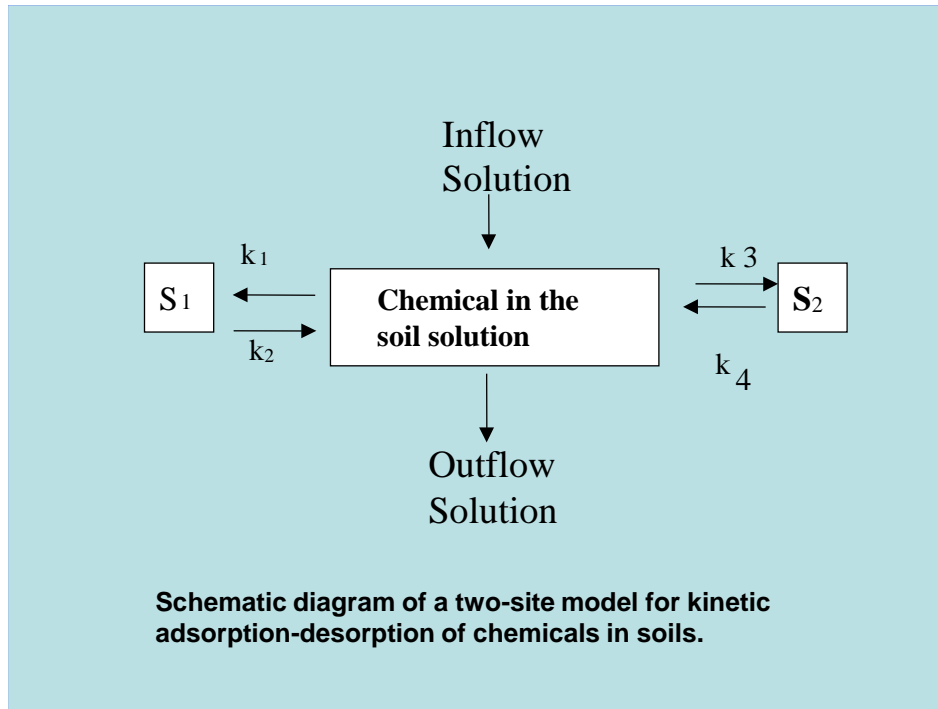
4. **Second-Order Two-Site Model (SOTS)**

In this model, it is assumed that a soil contains a maximum adsorption or total retention capacity or sites (S_{max}). Furthermore, the total sites can be partitioned into two types such that,

$$S_{max} = (S_{max})_1 + (S_{max})_2$$

where $(S_{max})_1$ and $(S_{max})_2$ are the total amount of type 1 sites and type 2 sites, respectively. If F represents the fraction of type 1 sites to the total amount of sites or the adsorption capacity for an individual soil, we thus have

Based on second order formulation, the retention reaction of each site is governed by

$$(S_{max})_1 = F\ S_{max} \qquad and \qquad (S_{max})_2 = (1 - F\ )\ S_{max}$$

$$\rho \frac{\partial S_1}{\partial t} = k_1 \Theta\ (S_{max1} - (S_1)\ C - k_2\ \rho\ S_1 \qquad for\ type\ 1\ sites$$

and

$$\rho \frac{\partial S_2}{\partial t} = k_3 \Theta (S_{max\,2} - S_2) C - 4 \rho S_2 \qquad \textit{for type 2 sites}$$

where k_1 and k_2 (h^{-1}) are forward and backward rate coefficients for type 1 sites, whereas k_3 and k_4 are rate coefficients for type 2 reaction sites, respectively. In addition, Θ is the soil water content ($cm^3\ cm^{-3}$), ρ is the soil bulk density ($g\ cm^{-3}$), and t is time (h). As $t \to \infty$, i.e., when both sites achieve local equilibrium, eq. (7) and (8) yield the following expressions.

$$k_1 \Theta \varphi_1 C - k_2 \rho S_1 = 0, \qquad or \qquad \frac{S_1}{\varphi_1 C} = \frac{\Theta}{\rho} \frac{k_1}{k_2} = \omega_1 \qquad \textit{for type 1 sites}$$

and

$$k_3 \Theta \varphi_2 C - k_4 \rho S_2 = 0, \qquad or \qquad \frac{S_2}{\varphi_2 C} = \frac{\Theta}{\rho} \frac{k_3}{k_4} = \omega_2 \qquad \textit{for type 2 sites}$$

Here ω_1 and ω_2 represent equilibrium constants for the retention reactions associated with type 1 and type 2 sites, respectively. The formulation of eq. (9) and (10) are analogous to expressions for homovalent ion-exchange equilibrium reactions. Further rearrangement yields the following expressions for the amounts retained by type 1 and 2 sites at t 6 4,

$$\frac{S_1}{(S_{max})_1} = \left[\frac{\omega_1 C}{1 + \omega_1 C} \right], \qquad and \qquad \frac{S_2}{(S_{max})_2} = \left[\frac{\omega_1 C}{1 + \omega_2 C} \right]$$

Therefore, the total amount sorbed in the soil S ($=S_1+S_2$), is

$$\frac{S}{S_{max}} = \left[\frac{\omega_1 C}{1 + \omega_1 C} \right] F + \left[\frac{\omega_2 C}{1 + \omega_2 C} \right] (1 - F)$$

Equation (12) is analogous to the two-site Langmuir formulation where the amount sorbed in each region is clearly expressed. Such Langmuir formulations are commonly used to obtain independent parameter estimates for S_{max} and the affinity constants ω_1 and ω_2.

Input and Output Data Files

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

a. Manual entry by filling out the template provided below.

b. As an external ASII file (,dat or txt).

A sample of the input data file referred as SOTS-IPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. For a given initial concentration (Ci) and input concentration (Cs) at time t > 0, the model provides results of concentration, the amount sorbed versus time, and sorption isotherms. Model output is given in txt format and must be named and saved by the user. Graphics of simulations are also generated which can be saved by the user. Graphics include time-dependent sorption-desorption and sorption isotherms.

Template for the SOTS model

Model selected is SOTS

Tittle TWO-SITE BATCH KINETICS - TEST CASE

Input parameters	Case 1	Case 2	Case 3
NUMBER OF ISOTHERMS DESIRED	5	NUMBER OF CASES	
MOISTURE CONTENT,CM3/CM3 (TH)	25.00E00	25.00E00	25.00E00
BULK DENSITY,G/CM3 (ROU)	5.00E00	5.00E00	5.00E00
APPLIED CONCENTRATION,PPM (CS)	10.000E00	20.000E00	50.000E00
TOTAL AMOUNT OF AVAIALBLE SITES,ST (ST)	200.000E00	200.000E00	200.000E00
FRACTION OF TYPE 1 SITES, F (F)	0.250E00	0.250E00	0.250E00
FORWARD RATE REACTION, K1,Hr-1 (K1)	0.0100e00	0.0100e00	0.0100e00
BACKWARD RATE REACTION, K2,Hr-1 (K2)	0.00100E00	0.00100E00	0.00100E00
FORWARD RATE REACTION, K3,Hr-1 (K3)	0.0001E00	0.0001E00	0.0001E00
BACKWARD RATE REACTION, K4,Hr-1 (K4)	0.0005E00	0.0005E00	0.0005E00
IRREVERSIBLE REACTION RATE,KS,Hr-1 (KS)	0.000E00	0.000E00	0.000E00
PRINTOUT TIME DESIRED,HOURS (TPRINT)	0.2000E00	0.2000E00	0.2000E00
TOTAL SIMULATION TIME,HOURS (TTOTAL)	240.0E00	240.0E00	240.0E00

OK

SOTS Concentration versus Time

SOTS Sorbed versus Time
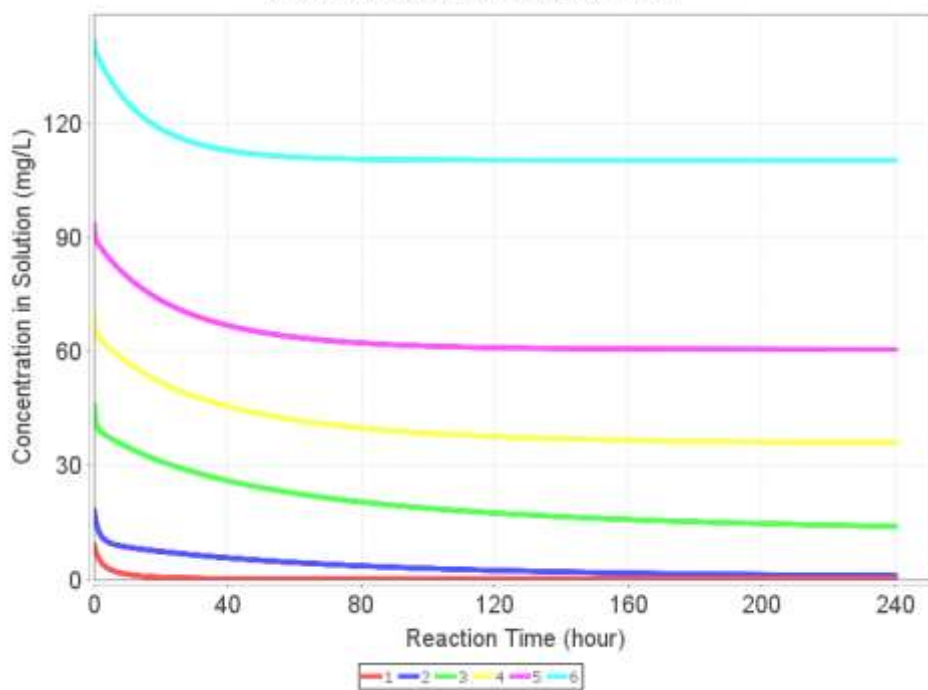
SOTS Sorbed versus Concentration
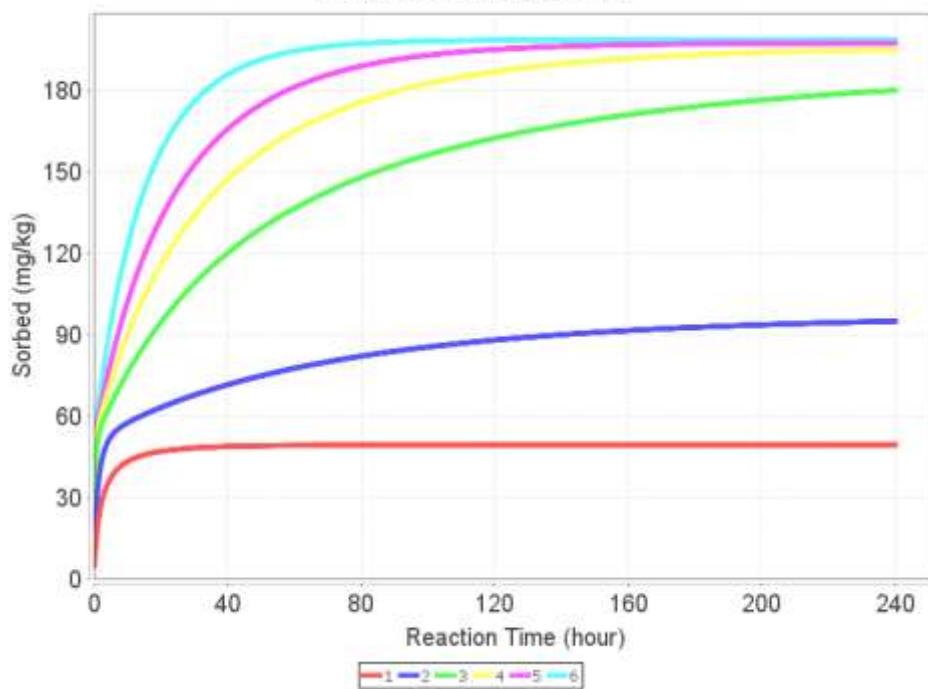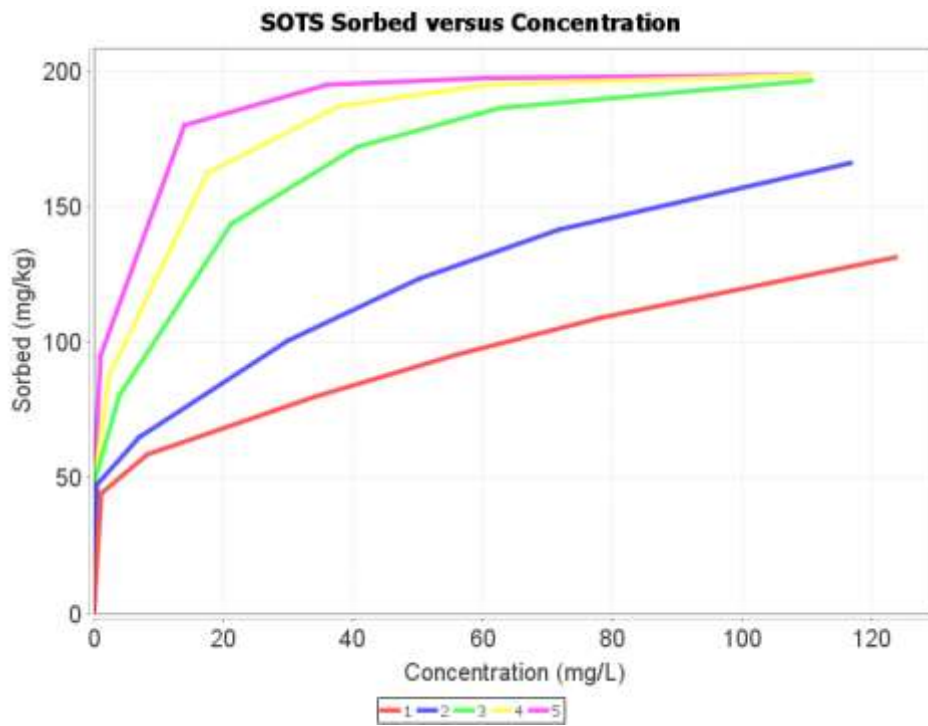
Stir-Flow Model (STIRFLOW-MRM)

The reactivity and transport of a solute species inn the soil system under stir-flow conditions can be represented by,

$$\Theta \frac{\partial C}{\partial t} + \rho \frac{\partial S}{\partial t} = \frac{q}{V_T}(C_{in} - C_{out})$$

Where C is the solution concentration (mg/L), q is the rate of flow (ml/h), ρ soil bulk density (g/cm^3), θ volumetric water content (cm^3/cm^3) and V_T is the volume of the vessel (ml). Moreover, C_{in} and C_{out} are concentration and in the input and effluent, respectively.

In this formulation, it is assumed that C is similar to the effluent concentration C_{out} and that solute sorption is based on multi-reaction model formulation. As such we consider the solute to be present in the soil solution phase (C) and in five phases representing solute retained by the soil matrix as S_e, S_1, S_2, S_3 and S_{irr}. We further assume that S_e, S_1 and S_2 are in direct contact with the solution phase and are governed by concurrent type reactions. Here we assume S_e is the amount of solute that is sorbed reversibly and is in equilibrium with C at all times. Specifically, the multireaction assumes that the total amount sorbed S_T or simply S as the total amount retained reversibly or reversibly by soil matrix surfaces,

$$S = S_e + S_1 + S_2 + S_3$$

The governing equilibrium retention/release mechanism is the nonlinear Freundlich type as

$$S_e = K_f C^b$$

where K_f is the associated distribution coefficient $(cm^3 kg^{-1})$ and b is a dimensionless Freundlich parameter (b < 1). Other equilibrium type retention mechanisms are given in Chapter 3. This includes linear (b=1), Langmuir, two-site Langmuir, and others.

The retention/release reactions associated with S_1, S_2, and S_3 are concurrent or consecutive type kinetic reactions. Specifically, the S_1 and S_2 phases were considered to be in direct contact with C and reversible rate coefficients of the (nonlinear) kinetic type govern their reactions,

Stirred-Flow Reactor Method

Stirred-flow reactor connected to a reservoir of a solute solution through a pump and the effluent is being collected by a fraction collector.

$$\frac{\partial S_1}{\partial t} = k_1 \frac{\Theta}{\rho} C^n - k_2 S_1$$

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\Theta}{\rho} C^m - (k_4 + k_5) S_2 + k_6 S_3$$

$$\frac{\partial S_3}{\partial t} = k_5 S_2 - k_6 S_3$$

where k_1 and k_2 are the forward and backward rates coefficients (h^{-1}), respectively and n is the reaction order associated with S_1. Similarly, k_3 and k_4 are the rate coefficients and m is the reaction order associated with S_2, and k_5 and k_6 are the reaction parameters associated with S_3. In the

absence of the consecutive reaction between S_2 and S_3, that is if $S_3 = 0$ at all times ($k_5=k_6=0$), eq (44) reduces to,

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\Theta}{\rho} C^m - k_4 S_2$$

Thus eq. (7) for S_2 resembles that for S_1 except for the magnitude of the associated parameters k_3, k_4 and m.

The sorbed phases (S_e, S_1, S_2, S_3) may be regarded as the amounts sorbed on surfaces of soil particles and chemically bound to Al and Fe oxide surfaces or other types of surfaces, although it is not necessary to have a priori knowledge of the exact retention mechanisms for these reactions to be applicable. These phases may be characterized by their kinetic sorption and release behavior to the soil solution and thus are susceptible to leaching in the soil. In addition, the primary difference between these two phases not only lie in the difference in their kinetic behavior but also on the degree of nonlinearity as indicated by the parameters n and m. The sink/source term Q is commonly used to account for irreversible reactions such as precipitation/dissolution, mineralization, and immobilization, among others. We expressed the sink term as a first-order kinetic process;

$$Q = \rho \frac{\partial S_3}{\partial t} = k_s \Theta C$$

where k_s is the associated rate coefficient (h^{-1}). In this presentation, the notations k_s and k_{irr} are used interchangeably through this manual. The sink term Q was expressed in terms of a first-order irreversible reaction for reductive sorption or precipitation or internal diffusion. This equation is similar to that for diffusion-controlled precipitation reaction if one assumes that the equilibrium concentration for precipitation is negligible.

Flow interruption is accounted for in this model where the flow rate q is set equal to zero. As a result, reactions between the soil matrix and solution continue and accounted for by the model where no flow is taking place.

Input and Output Data Files

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

a. Manual entry by filling out the template provided below.

b. As an external ASII file (,dat or txt).

A sample of the input data file referred as STIRFLOW-MRM -IPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. For a given initial concentration (Ci) and input concentration (Cs) at time t > 0, the model provides results of concentration, the amount sorbed versus time, and sorption isotherms. Model output is given in txt format and must be named and saved by the user. Graphics of simulations are also generated which can be saved by the user. Graphics include time-dependent sorption-desorption.

Template for the STIRFLOW-MRM model

Model selected is STIRFLOW-MRM

Tittle | STIR FLOW USING MRM - TEST CASE - SENSITIVITY ANALYSES

NUMBER OF ISOTHERMS DESIRED	4	NUMBER OF CASES	
Input parameters	Case 1	Case 2	Case 3
MOISTURE CONTENT,CM3/CM3 (TH)	20.000E00	20.000E00	20.000E00
BULK DENSITY,G/CM3 (ROU)	1.000E00	1.000E00	1.000E00
VOLUME OF VESSEL (ML) (VOLUME)	30	30	30
FLOW RATE (ML/HR) (QFLOW)	1	1	1
INITIAL CONCENTRATION,MG/L (C0)	0.000E0	0.000E0	0.000E0
APPLIED CONCENTRATION,MG/L (CS)	10.000E00	20.000E00	40.000E00
DISTRIBUTION COEFFICIENT, KD CM3/G (KD)	20.000E00	20.000E00	20.000E00
NONLINEAR FREUNDLICH PARAMETER(N) (NEQ)	0.7500E00	0.7500E00	0.7500E00
FORWARD RATE REACTION, K1,min-1 (K1)	0.1	0.1	0.1
FORWARD RATE REACTION, K2,min-1 (K2)	0.1	0.1	0.1
NONLINEAR KINETIC PARAMETER , U, (U)	0.500E00	0.500E00	0.500E00
FORWARD RATE REACTION, K3,min-1 (K3)	0.010E00	0.010E00	0.010E00
BACKWARD RATE REACTION, K4,min-1 (K4)	0.01E00	0.01E00	0.01E00
NONLINEAR KINETIC PARAMETER , U, (U)	0.5000E00	0.5000E00	0.5000E00
FORWARD RATE REACTION, K5,min-1 (K5)	0.0	0	0
BACKWARD RATE REACTION, K6,min-1 (K6)	0.000E00	0.000E00	0.000E00
IRREVERSIBLE REACTION RATE,KS,min-1 (KS)	0.0010E00	0.0010E00	0.0010E00
DURATION OF INPUT PULSE APPLIACTION (TP)	100	100	100
CONCENT OF LEACHING SOLITION,MG/L (CSL)	0.0	0.0	0.0
TOTAL SIMULATION TIME,minutes (TTOTAL)	200.0E00	200.0E00	200.0E00
PRINTOUT TIME DESIRED,minutes (TPRINT)	1.00E00	1.00E00	1.00E00
NUMBER OF STOP FLOW OR INTERRUPTIONS (NSF)	2	2	2
STARTING TIME FOR STOP FLOW # 1 (MIN)	50	50	50
DURATION OF STOP FLOW # 1 (MIN)	10	10	10
STARTING TIME FOR STOP FLOW # 2 (MIN)	125	125	125
DURATION OF STOP FLOW # 2 (MIN)	10	10	10

OK

STIR Concentration versus Flow Volume
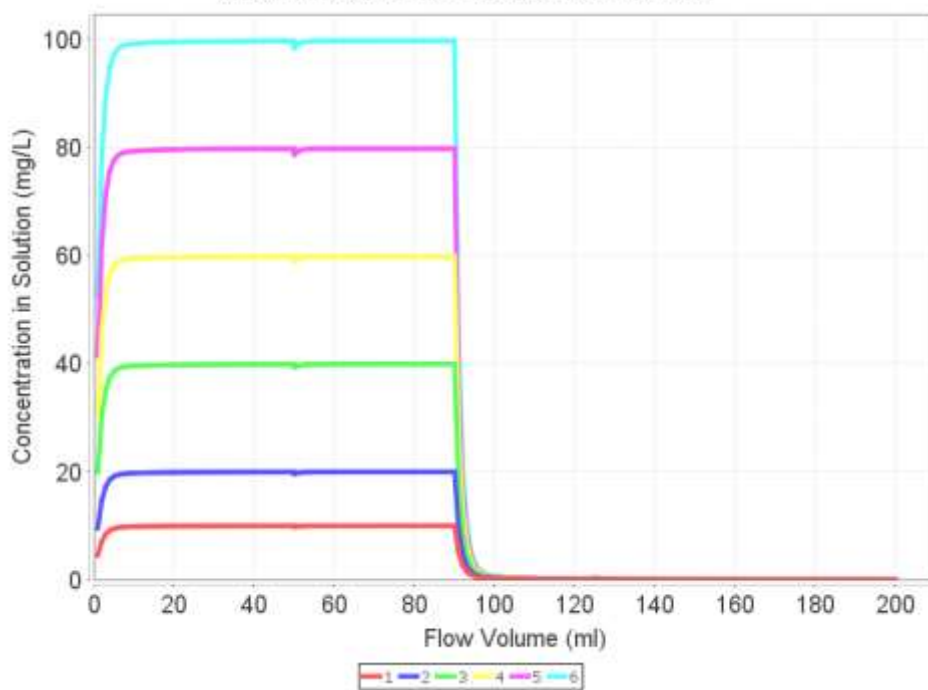
STIR Sorbed versus Flow Volume
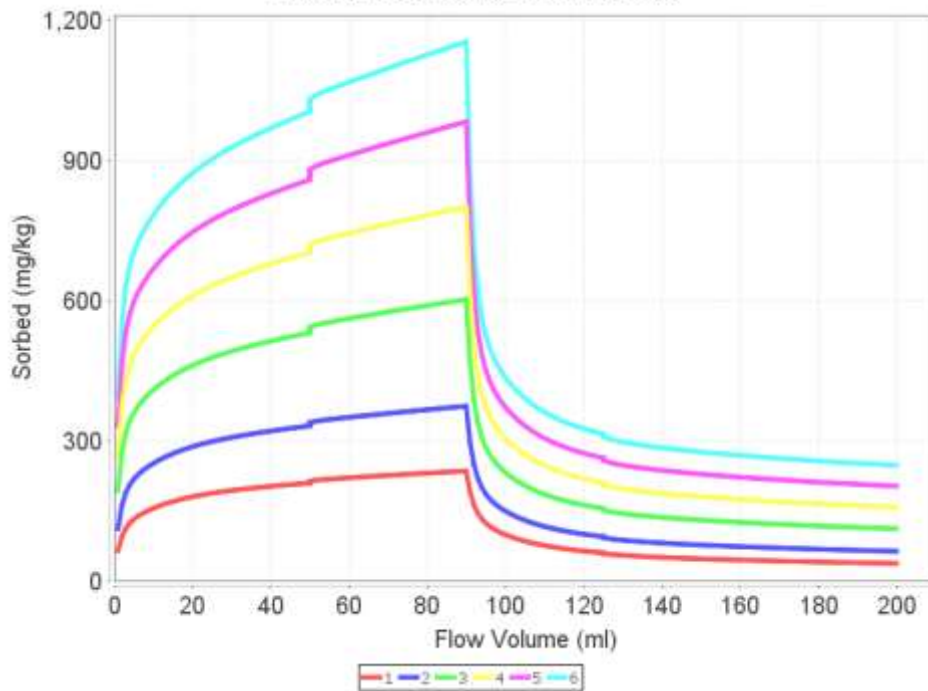
Thin-Disk Flow Model (THINDISK-MRM)

      The reactivity and transport of a solute species in the soil system under thin-disk flow conditions can be represented by,

$$\Theta \frac{\partial C}{\partial t} + \rho \frac{\partial S}{\partial t} = \frac{q}{d\,A}\,(C_{in} - C_{out})$$

Where C is the solution concentration (mg/L), q is the rate of flow (ml/h), ρ soil bulk density (g/cm^3), θ volumetric water content (cm^3/cm^3), and d and A are the thickness and cross-sectional area of the thin-disk, respectively. Moreover, C_{in} and C_{out} are concentration and in the input and effluent, respectively.

In this formulation, it is assumed that C is similar to the effluent concentration C_{out} and that solute sorption is based on multi-reaction model formulation. As such we consider the solute to be present in the soil solution phase (C) and in five phases representing solute retained by the soil matrix as S_e, S_1, S_2, S_3 and S_{irr}. We further assume that S_e, S_1 and S_2 are in direct contact with the solution phase and are governed by concurrent type reactions. Here we assume S_e is the amount of solute that is sorbed reversibly and is in equilibrium with C at all times. Specifically, the multireaction assumes that the total amount sorbed S_T *or simply S* as the total amount retained reversibly or reversibly by soil matrix surfaces,

Thin-disk flow method experimental setup. Background solute solution is pumped from the reservoir into the thin disk and the effluent is being collected by a fraction collector.

$$S = S_e + S_1 + S_2 + S_3$$

The governing equilibrium retention/release mechanism is the nonlinear Freundlich type as

$$S_e = K_f \, C^b$$

where K_f is the associated distribution coefficient ($cm^3 \, kg^{-1}$) and b is a dimensionless Freundlich parameter ($b < 1$). Other equilibrium type retention mechanisms are given in Chapter 3. This includes linear ($b=1$), Langmuir, two-site Langmuir, and others.

The retention/release reactions associated with S_1, S_2, and S_3 are concurrent or consecutive type kinetic reactions. Specifically, the S_1 and S_2 phases were considered to be in direct contact with C and reversible rate coefficients of the (nonlinear) kinetic type govern their reactions,

$$\frac{\partial S_1}{\partial t} = k_1 \frac{\Theta}{\rho} C^n - k_2 \, S_1$$

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\Theta}{\rho} C^m - (k_4 + k_5) \, S_2 + k_6 \, S_3$$

$$\frac{\partial S_3}{\partial t} = k_5 \, S_2 - k_6 \, S_3$$

where k_1 and k_2 are the forward and backward rates coefficients (h^{-1}), respectively and n is the reaction order associated with S_1. Similarly, k_3 and k_4 are the rate coefficients and m is the reaction order associated with S_2, and k_5 and k_6 are the reaction parameters associated with S_3. In the absence of the consecutive reaction between S_2 and S_3, that is if $S_3 = 0$ at all times ($k_5=k_6=0$), eq (44) reduces to,

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\Theta}{\rho} C^m - k_4 \, S_2$$

Thus eq. (7) for S_2 resembles that for S_1 except for the magnitude of the associated parameters k_3, k_4 and m.

The sorbed phases (S_e, S_1, S_2, S_3) may be regarded as the amounts sorbed on surfaces of soil particles and chemically bound to Al and Fe oxide surfaces or other types of surfaces, although it is not necessary to have a priori knowledge of the exact retention mechanisms for these reactions to be applicable. These phases may be characterized by their kinetic sorption and release behavior to the soil solution and thus are susceptible to leaching in the soil. In addition, the primary difference between these two phases not only lie in the difference in their kinetic behavior but also on the degree of nonlinearity as indicated by the parameters n and m. The sink/source term Q is commonly used to account for irreversible reactions such as precipitation/dissolution, mineralization, and immobilization, among others. We expressed the sink term as a first-order kinetic process;

$$Q = \rho \frac{\partial S_3}{\partial t} = k_s \, \Theta \, C$$

where k_s is the associated rate coefficient (h^{-1}). In this presentation, the notations k_s and k_{irr} are used interchangeably through this manual. The sink term Q was expressed in terms of a first-order irreversible reaction for reductive sorption or precipitation or internal diffusion. This equation is similar to that for diffusion-controlled precipitation reaction if one assumes that the equilibrium concentration for precipitation is negligible.

Input and Output Data Files

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

a. Manual entry by filling out the template provided below.

b. As an external ASII file (,dat or txt).

A sample of the input data file referred as THINDISK-MRM -IPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. For a given initial concentration (Ci) and input concentration (Cs) at time t > 0, the model provides results of concentration, the amount sorbed

versus time, and sorption isotherms. Model output is given in txt format and must be named and

saved by the user. Graphics of simulations are also generated which can be saved by the user.

Graphics include time-dependent sorption-desorption.

Template for the THINDISK-MRM model

Model selected is THINDISK-MRM

**Tittle** | THIN DISK FLOW WITH MRM - TEST CASE - SENSITIVITY ANALYSIS

NUMBER OF ISOTHERMS DESIRED	4		NUMBER OF CASES	
Input parameters	Case 1	Case 2	Case 3 ADD CASE	
MOISTURE CONTENT,CM3/CM3 (TH)	10.000E00	10.000E00	10.000E00	
BULK DENSITY,G/CM3 (ROU)	0.500	0.500	0.500	
THICNESS OF DISK (CM) (D)	0.2	0.2	0.2	
CROSS-SECTIONAL REA (CM2) (A)	5	5	5	
FLUX (CM/MIN) (J)	0.1	0.1	0.1	
INITIAL CONCENTRATION,MG/L (C0)	0.000E0	0.000E0	0.000E0	
APPLIED CONCENTRATION,MG/L (CS)	10.000E00	20.000E00	40.000E00	
DISTRIBUTION COEFFICIENT, KD CM3/G (KD)	2.000E00	2.000E00	2.000E00	
NONLINEAR FREUNDLICH PARAMETER(N) (NEQ)	0.7500E00	0.7500E00	0.7500E00	
FORWARD RATE REACTION, K1,min-1 (K1)	0.1	0.1	0.1	
FORWARD RATE REACTION, K2,min-1 (K2)	0.01	0.01	0.01	
NONLINEAR KINETIC PARAMETER , U, (U)	0.500E00	0.500E00	0.500E00	
FORWARD RATE REACTION, K3,min-1 (K3)	0.0100E00	0.0100E00	0.0100E00	
BACKWARD RATE REACTION, K4,min-1 (K4)	0.0001E00	0.0001E00	0.0001E00	
NONLINEAR KINETIC PARAMETER , W, (U)	0.5000E00	0.5000E00	0.5000E00	
FORWARD RATE REACTION, K5,min-1 (K5)	0.001	0.001	0.001	
BACKWARD RATE REACTION, K6,min-1 (K6)	0.000E00	0.000E00	0.000E00	
IRREVERSIBLE REACTION RATE,KS,min-1 (KS)	0.000E00	0.000E00	0.000E00	
DURATION OF INPUT PULSE APPLIACTION (TP)	100	100	100	
CONCENT OF LEACHING SOLITION,MG/L (CSL)	0.0	0.0	0.0	
TOTAL SIMULATION TIME,minutes (TTOTAL)	200.0E00	200.0E00	200.0E00	
PRINTOUT TIME DESIRED,minutes (TPRINT)	1.00E00	1.00E00	1.00E00	

OK

THIN-DISK-MRM Concentration versus Flow Volume
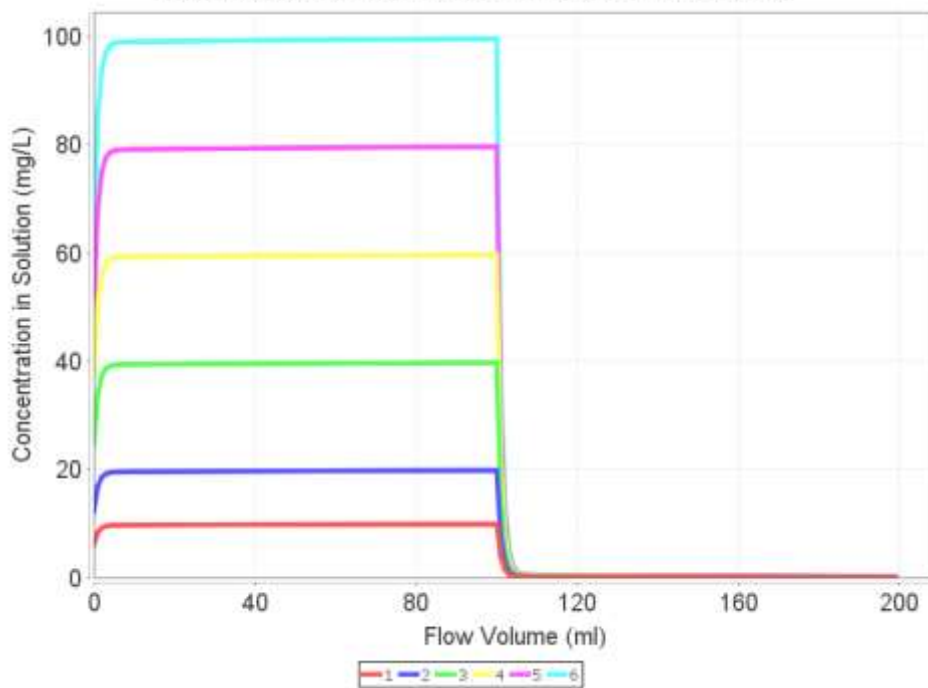
THIN-DISK-MRM Sorbed versus Flow Volume
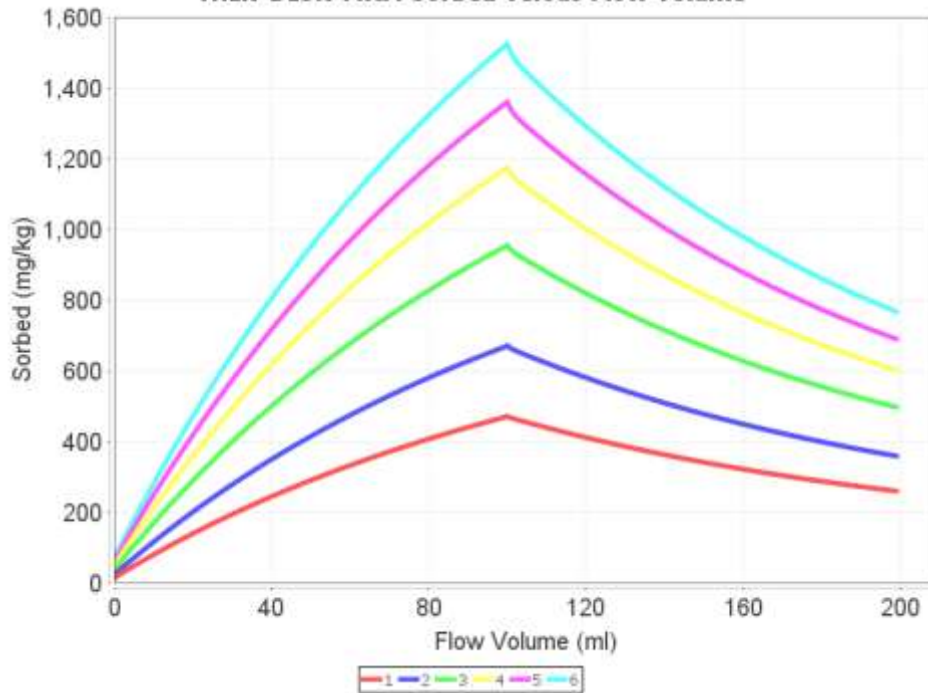
Competitive MRM Model (C_MRM)

       The competitive model was developed to describe competitive equilibrium sorption for multicomponent systems where the sorption isotherms of single component follow the Freundlich equation. A general form of the competitive equation can be written as

$$S_i = K_i C_i \left(\sum_{j=1}^{l} \alpha_{i,j} \, C_j \right)^{n_i - 1}$$

where the subscripts i and j denote metal component i and j, l is the total number of components, and $\alpha_{i,j}$ is a dimensionless competition coefficient for the adsorption of component i in the presence of component j. The parameters K_i and n_i are the Freundlich parameters representing a single component system i as described in eq. (14) above. By definition, $\alpha_{i,j}$ equals 1 when $i = j$. If there is no competition, i.e., $\alpha_{i,j} = 0$ for all $j \neq i$, eq. (15) yields a single species Freundlich equation for component i identical to eq. (14). The Competitive MRM model presented here accounts for competitive Freundlich type retention along with MRM formulation discussed earlier such that,

$$(S_e)_i = K_{e,i} C_i \left(\sum_{j=1}^{l} \alpha_{i,j} C_j \right)^{n_i - 1}$$

$$\frac{\partial (S_1)_i}{\partial t} = k_{1,i} \frac{\theta}{\rho} C_i \left(\sum_{j=1}^{l} \alpha_{i,j} C_j \right)^{n_i - 1} - k_{2,i} (S_1)_i$$

$$\frac{\partial (S_2)_i}{\partial t} = k_{3,i} \frac{\theta}{\rho} C_i \left(\sum_{j=1}^{l} \alpha_{i,j} C_j \right)^{n_i - 1} - (k_{4,i} + k_{s,i}) (S_2)_i$$

$$\frac{\partial (S_s)_i}{\partial t} = k_{s,i} (S_s)_i$$

$$\frac{\partial (S_{irr})_i}{\partial t} = k_{irr,i} \frac{\theta}{\rho} C_i$$

When competition is ignored, i.e., $\alpha_{i,j}$ for all $j \neq i$, eq. (21) to a single species nth- order kinetic sorption.

Input and Output Data Files

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

 a. Manual entry by filling out the template provided below.

 b. As an external ASII file (,dat or txt).

A sample of the input data file referred as CMRM-IPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. For a given initial concentration (Ci) and input concentration (Cs) at time t > 0, the model provides results of concentration, the amount sorbed versus time, and sorption isotherms. Model output is given in txt format and must be named and saved by the user. Graphics of simulations are also generated which can be saved by the user. Graphics include time-dependent sorption-desorption.

Template for the C-MRM model

Model selected is C-MRM

Tittle SIMULATION OF CEMPETITIVE ADSORPTION-DESORPTION WITH SRS EQUITION

Input parameters

NONLINEAR COEFFICIENT FOR COMPONENT 1 (N_1)	0.31
COMPETITIVE COEFFICIENTS OF C1 FOR C2 (A12)	1.04
DISTRIBUTION COEFFICIENT OF COMPONENT 1 (KE_1)	1.40
FORWARD REACTION RATE OF COMPONENT 1 (K1_1)	0.0806
BACKWARD REACTION RATE OF COMPONENT 1 (K2_1)	0.027
CONECUTIVE REACTION RATE OF COMPONENT 1 (K3_1)	0.0019
IRREVERSIBLE REACTION RATE OF COMPONENT 1 (KI_1)	0.00
NONLINEAR COEFFICIENT FOR COMPONENT 2 (N_2)	0.46
COMPETITIVE COEFFICIENTS OF C2 FOR C1 (A21)	0.28
DISTRIBUTION COEFFICIENT OF COMPONENT 2 (KE_2)	2.52
FORWARD REACTION RATE OF COMPONENT 2 (K1_2)	0.0902
BACKWARD REACTION RATE OF COMPONENT 2 (K2_2)	0.0390
CONECUTIVE REACTION RATE OF COMPONENT 2 (K3_2)	0.0011
IRREVERSIBLE REACTION RATE OF COMPONENT 2 (KI_2)	0.00
SIMULATION SETTING	
MOISTURE CONTENT,CM3/CM3 (TH)	10.0
BULK DENSITY,G/CM3 (ROU)	1.0
APPLIED CONCENTRATION OF COMPONENT 1,MG/L (CS1)	10.0
APPLIED CONCENTRATION OF COMPONENT 2,MG/L (CS2)	10.0
TOTAL SIMULATION TIME,HOURS (TTOTAL)	500
PRINTOUT TIME DESIRED,HOURS (TPRINT)	4.0

OK

CMRM Concentration versus Time

CMRM Sorbed versus Time
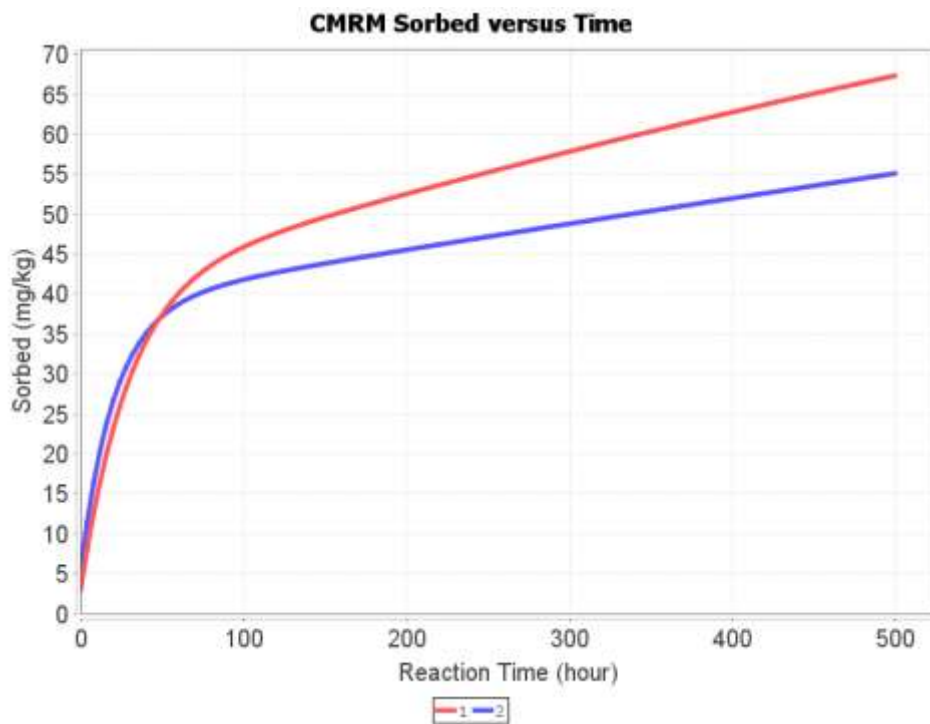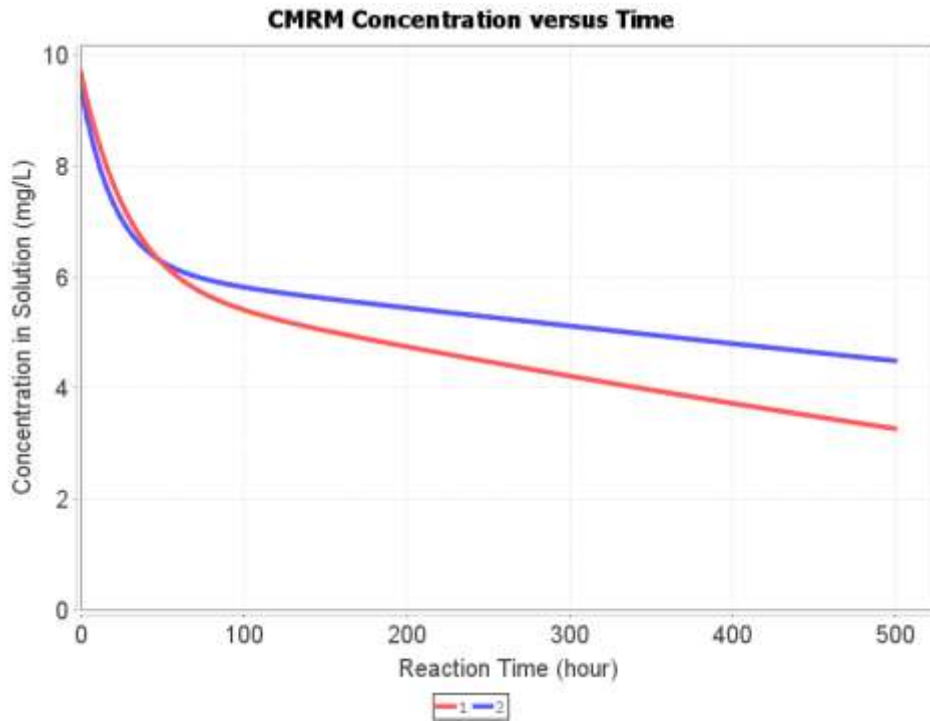
Fitting Models for Batch Sorption

Multireaction Fitting Model (MRM-FIT)

This model is that of the multireaction model described earlier. However, the model is capable of inverse action; that is to describe a data set or a set of observations based on best estimates of model parameters. Specifically, experimental results are fitted to the multireaction model described above using Levenberg-Marquardt nonlinear least square optimization method (Press et al., 1992). Statistical criteria used for estimating the goodness-of-fit of the models to the data were the coefficients of determination r^2 and the root mean square error (RMSE). This fitting model is tailored to the adsorption-desorption kinetic batch method.

Model Fitting - Batch Kinetic

Select One:

○ Multireaction Model (MRM-FIT)

This model is similair to previously discussed MRM except that the purpose here is to describe a set of experimental data based on MRM. The model provides parameter estimates that best describe the data.

○ Second-Order Two-Site (SO-FIT)

This model describes solute retention based on second order retention and provides parameter model estimates that best describe experimental data.

○ Competitive MRM (CMRM-FIT)

This model describes solute retention based on competitive solute reaction with the MRTM model. The model provides parameter estimates that best describe experimental data.

BACK   RUN

Batch reactors are normally used describe the kinetics of chemical reaction in a suspension (some 1-2 liters in volume). The soil to solution ratio is much larger (5:100 or less) than that using the one step reactor. As shown the suspension is mixed with an overhead stirrer or from below with a magnetic stirrer. A pH electrode connected to maintain a constant pH during the duration of the reaction. To maintain conditions of oxidation and reduction, gas dispersion tubes of CO_2 and O_2 out of the suspension are maintained.

A schematic showing a typical adsorption-desorption experiment of chemicals in soils using centrifuge tubes is shown here. In this method, solute adsorption as well desorption kinetics studies with soils and other matrices are carried out in centrifuge tubes. The volume of the centrifuge tubes vary from 40-50 mL where a soil to solution of 3 g to 40 ml solution (or 4 g to 40 ml solution) is used. The solution contains the solute at the desired concentration dissolved in a background solution. For other matrices, such as plant material, 1 gm or less of matrix material to 30 or 40 mL solutions is used. The range of initial concentrations to be used varies dependent on the objectives of each study.
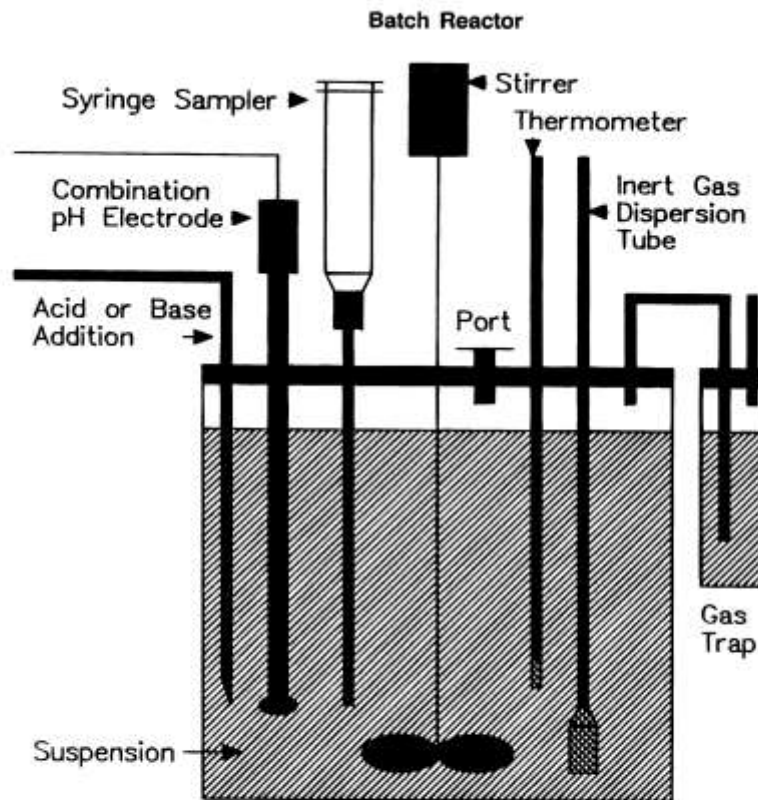
Typical batch reactor configuration where a syringe sampler allows for removal of subsample of suspension over time.

The mixtures or slurries in the centrifuge tubes are then shaken continuously, and after each reaction time, the tubes are centrifuged. An aliquot (3-4 mL) is then sampled from the supernatant at the specified reaction time. The volume to be decanted can be as little as 0.2 mL if radionuclide's are used. These steps are repeated for each adsorption time. Generally, initial reaction times may vary from 2 to 4 hrs followed by daily sampling for 1-7 days, and weekly for 4 -6 weeks or longer. To avoid excessive changes in the soil to solution ration, the number of samples should be limited to 3-4 if large aliquots are needed. In contrast as many as 12 or more, reaction times may be carried out if radionuclide's are used.

Kinetic Batch Method
for Adsorption & Desoprtion
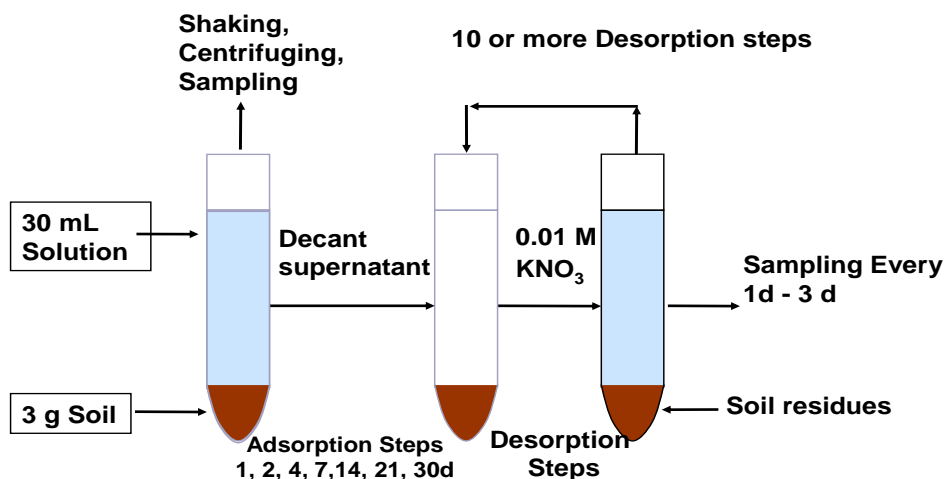
A *schematic of batch adsorption-desorption studies in centrifuge tubes.*

Desorption is carried out based on the method of successive dilutions and commences immediately after the last adsorption time step. Each desorption step is carried out by replacing as much of the supernatant with the background solution. The amount of decanted solution and that of the background solution added must be recorded for mass balance calculations. A desorption step often consists of few hour, days, or weekd of shaking for each step. Desorption is repeated for several steps as desired. The total desorption or release time depends on is number and time intervals between each desorption step. The decanted solution from each

adsorption and desorption step are analyzed for the solute and the amount retained by the soil matrix is calculated.

Input and Output Data Files

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

a. Manual entry by filling out the template provided below.

b. As an external ASII file (,dat or txt).

A sample of the input data file referred as MRM –FIT-INPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. For a given initial concentration (C_i) and input concentration (C_s) at time t > 0, the model provides results of concentration, and the amount sorbed versus time. Measured data are indicated by various symbols and continuous curves are model calculations. Model output is given in txt format and must be named and saved by the user. Graphics of simulations are also generated which can be saved by the user. Graphics include time-dependent sorption-desorption.

The model carries out all mass calculations for a batch experiment and thus requires a complete accounting of the weights of the soil and solution (added as well as decanted) at each time step. For each input concentration (C_o), the model requires the weight of the soil and the solution, the weight of decanted solution, and experimental measured final concentration (C_f) for each time step. Moreover, the number of time steps and the time of sorption and desorption must be given. The user must provide values for all model parameters. If a process is not to be considered, the associated rate coefficient(s) must be set equals to zero. Parameters that estimates are being sought must be identified (by choosing 1) and their initial estimates must be given. The model will carry out nonlinear-least approximation for the entire data set, that is all initial concentrations versus time and are thus represent overall parameter fit. A user may wish to test the capability of the model for only one input concentration versus time and thus compare individual versus overall fitting.

The example given here is for atrazine adsorption by sugarcane mulch residue over a wide range of concentrations (Selim and Zhu, 2005). Measured and predicted results are shown for atrazine concentration and the amount sorbed versus time during sorption and desorption.

Selim, H. M. and H. Zhu. 2005. Atrazine sorption–desorption hysteresis by sugarcane mulch residue. Journal of Environmental Quality 34: 325-335.

Template for the MRM-FIT model

Model selected is MRM-FIT

Tittle DATA FROM ATRAZINE-SUGARCEN RESIDUE-ADSOR-DESOR,JEQ (2005) 34.325-335,Figs 5&6

Input parameters

|		Ne Bi = 0
INITIAL CONCENTRATION,MG/L (CI)	0.0000E00	0
INCREMENTAL TIME STEP,HOUR (DT)	0.1000E00	0
PRINTOUT TIME INTERVAL (FRQOUT)	2.0000E00	0
MAXIMUM NUMBER OF ITERATIONS (MIT)	40	0
DISTRIB. COEFF. FOR EQL. SORP,CM3/G (KF)	0.8000E00	1
NONLINEAR PARAM.FOR EQUL. MECH. (NF)	0.9477E00	0
IRREVERSIBLE REACTION RATE,KS,HR-1 (KIRR)	0.0000E00	0
FORWARD RATE REACTION, K1,HR-1 (K1)	0.0000E00	0
BACKWARD RATE REACTION, K2,HR-1 (K2)	0.0000E00	0
NONLINEAR KINETIC PARAMETER , W, (NS1)	0.0000E00	0
FORWARD RATE REACTION, K3,HR-1 (K3)	0.3500E00	1
BACKWARD RATE REACTION, K4,HR-1 (K4)	0.1100E00	1
NONLINEAR KINETIC PARAMETER , U, (NS2)	0.9477E00	0
FORWARD RATE REACTION, K5,HR-1 (K5)	0.00022E00	1
BACKWARD RATE REACTION, K6,HR-1 (K6)	0.000E00	0
NUMBER OF FITTED PARAMETERS (NP)	4	

NEXT

Screen 2

MEASURED DATA

BACK   OK

NUMBER OF DATA SET: 6   NUMBER OF OBSERVATIONS IN EACH SET: 14

Time (hr)	Soil weight (g)	Total water (g)	Decanted water (g)	Input C (ppm)	Final C (ppm)
	1.079	29.591	0.500	3.370	2.391
8.00	1.079	29.391	0.500	3.370	2.180
24.00	1.079	29.591	0.500	3.370	2.057
40.00	1.079	28.991	0.500	3.370	2.012
96.00	1.079	27.591	0.500	3.370	1.984
192.00	1.079	27.091	0.500	3.370	1.884
288.00	1.079	26.591	0.500	3.370	1.848
504.00	1.079	26.091	17.183	3.370	1.632
528.00	1.079	38.127	28.525	3.370	0.695
552.00	1.079	39.467	31.032	3.370	0.332
576.00	1.079	38.421	29.550	3.370	0.149
600.00	1.079	38.697	30.583	3.370	0.084
624.00	1.079	37.907	30.048	3.370	0.052
648.00	1.079	37.734	30.453	3.370	0.037
2.00	1.079	29.617	0.500	6.360	4.475
8.00	1.079	29.117	0.500	6.360	4.111
24.00	1.079	29.617	0.500	6.360	3.859
48.00	1.079	28.117	0.500	6.360	3.788
96.00	1.079	27.617	0.500	6.360	3.751
192.00	1.079	27.117	0.500	6.360	3.591
288.00	1.079	26.617	0.500	6.360	3.536
504.00	1.079	26.117	16.978	6.360	3.236
528.00	1.079	38.356	29.545	6.360	1.463
552.00	1.079	38.636	30.127	6.360	0.653

MRMFIT Concentration versus Time
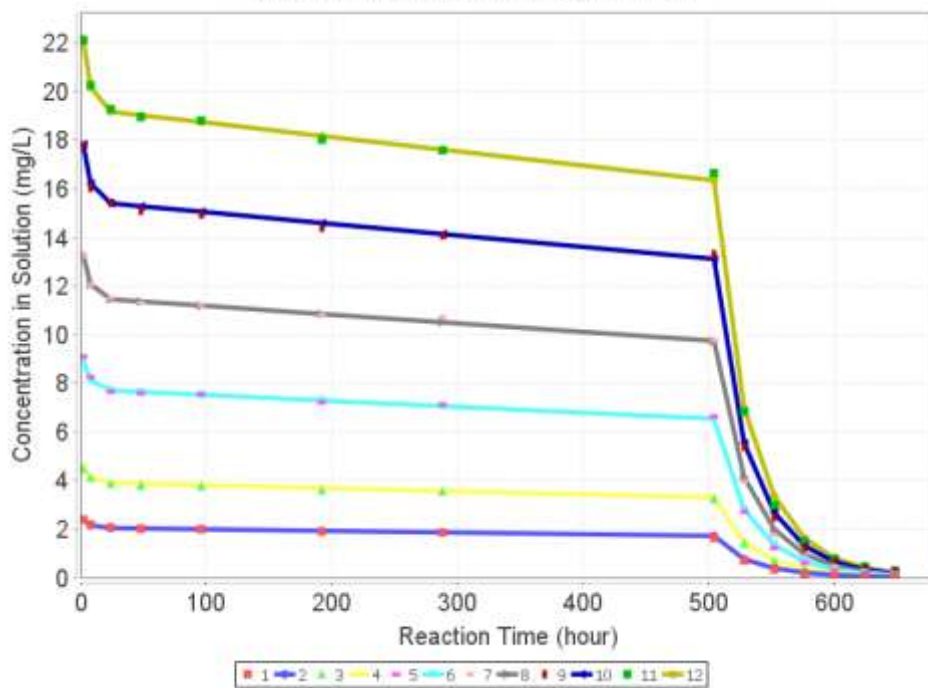
MRMFIT Sorbed versus Time
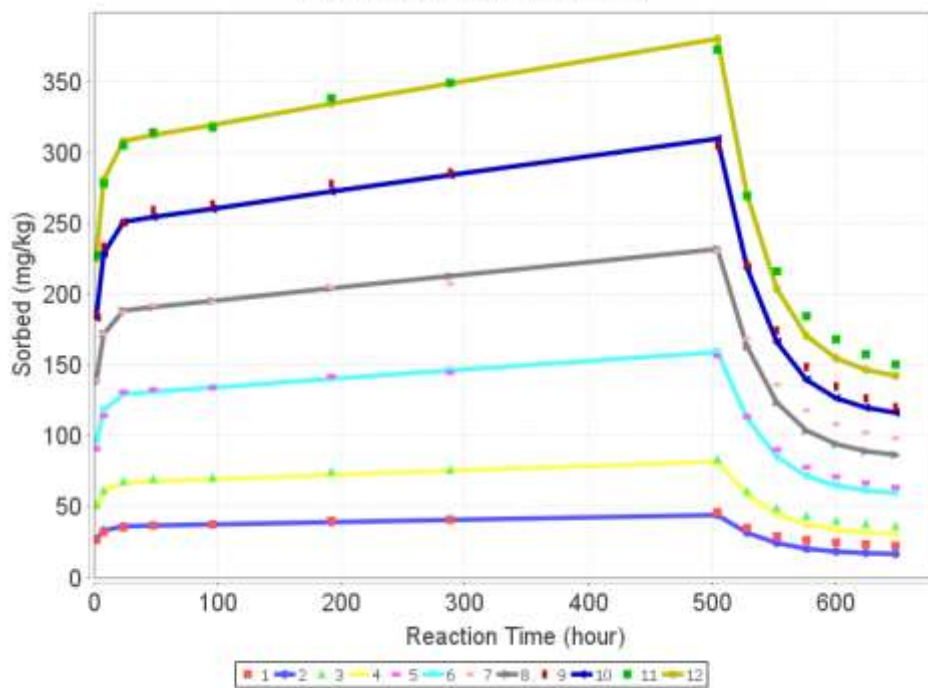
SECOND-Order (SOFIT) Model

      This model is that of the multireaction transport (MRTML) model described earlier. However, the model is capable of inverse action; that is to describe a data set or a set of observations based on best estimates of model parameters. Specifically, experimental results are fitted to the multireaction model described above using Levenberg-Marquardt nonlinear least square optimization method (Press et al., 1992). Statistical criteria used for estimating the goodness-of-fit of the models to the data were the coefficients of determination r^2 and the root mean square error (RMSE). This fitting model is tailored to the adsorption-desorption kinetic batch method. The model carries out all mass calculations for soil column experiments and thus requires a complete accounting of the weights of the soil and solution (input and output or effluent) with time. Other necessary constrains include the length of the soil column, soil bulk density and the flux density. A constant or variable flux density can be specified.   If a retention process in the model to be ignored , the associated rate coefficient(s) must be set equals to zero. Parameters that estimates are being sought must be identified (by choosing 1) and their initial estimates must be given. The model will carry out nonlinear-least approximation for the entire data set, that is all initial concentrations versus time and are thus represent overall parameter fit. A user may wish to test the capability of the model for only one input concentration versus time and thus compare individual versus overall fitting.

Input and Output Data Files

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

      a. Manual entry by filling out the template provided below.

      b. As an external ASII file (,dat or txt).

A sample of the input data file referred as SO–FIT-INPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. For a given initial concentration (Ci) and input concentration (Cs) at time t > 0, the model provides results of concentration, and the amount sorbed versus time. Measured data are indicated by various symbols and continuous curves are model calculations. Model output is given in txt format and must be named and saved by the user. Graphics of simulations are also generated which can be saved by the user.

      The model carries out all mass calculations for a batch experiment and thus requires a complete accounting of the weights of the soil and solution (added as well as decanted) at each

time step. For each input concentration (Co), the model requires the weight of the soil and the solution, the weight of decanted solution, and experimental measured final concentration (C_f) for each time step. Moreover, the number of time steps and the time of sorption and desorption must be given. The user must provide values for all model parameters. If a process is not to be considered, the associated rate coefficient(s) must be set equals to zero. Parameters that estimates are being sought must be identified (by choosing 1) and their initial estimates must be given. The model will carry out nonlinear-least approximation for the entire data set, that is all initial concentrations versus time and are thus represent overall parameter fit. A user may wish to test the capability of the model for only one input concentration versus time and thus compare individual versus overall fitting. The example shown is Copper (Cu) results from miscible displacement experiments for a McLaren soil (Selim and Ma 2001) The results are shown by the effluent results of concentration and the amount sorbed versus time shown in the plot below.

Selim, H. M. and L. Ma. 2001. Modeling nonlinear kinetic behavior of copper adsorption-desorption in soil. Soil Sci. Soc. Am. Spec. Publ. 56:189-212.

Model selected is SO-FIT

Tittle: CU MCLAREN SOIL ADSORPTION SOTS MODEL (k1,k2,KIRR and CAP)

Input parameters

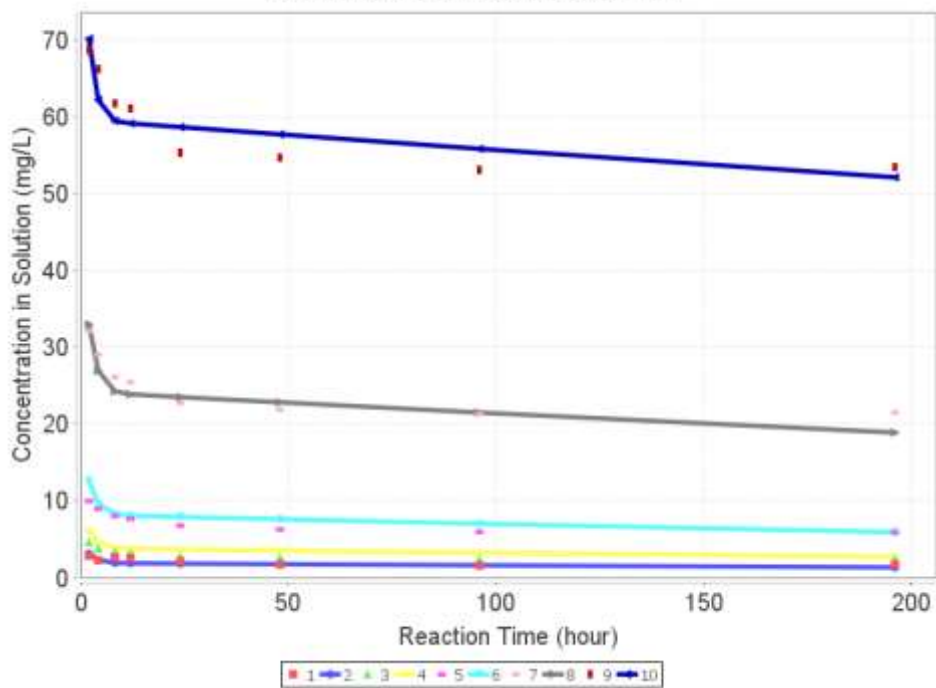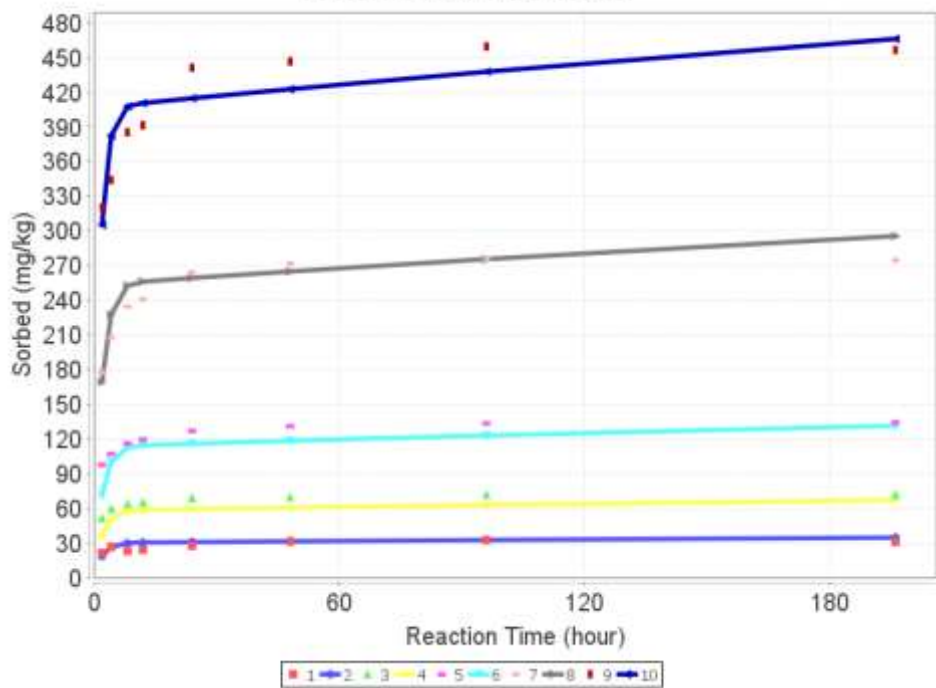|		Fit = 1 No fit = 0
INITIAL CONCENTRATION,MG/L (CI)	0.0000E00	0
INCREMENTAL TIME STEP,HOUR (DT)	0.5000E00	0
PRINTOUT TIME INTERVAL (FRQOUT)	2.0000E00	0
MAXIMUM NUMBER OF ITERATIONS (MIT)	40	0
SORPTION CAPACITY, SMAX (MG/KG) (CAP)	690.00E00	1
DISTRIB. COEFF. FOR EQL. SORP,CM3/G (KF)	0.0000E00	0
IRREVERSIBLE REACTION RATE,KS,HR-1 (KIRR)	0.0001E00	1
FORWARD RATE REACTION, K1,HR-1 (K1)	0.0010E00	1
BACKWARD RATE REACTION, K2,HR-1 (K2)	0.1000E00	1
FORWARD RATE REACTION, K3,HR-1 (K3)	0.0000E00	0
BACKWARD RATE REACTION, K4,HR-1 (K4)	0.0000E00	0
FORWARD RATE REACTION, K5,HR-1 (K5)	0.0000E00	0
BACKWARD RATE REACTION, K6,HR-1 (K6)	0.0000E00	0
NUMBER OF FITTED PARAMETERS (NP)	4	

NEXT

Screen 4

MEASURED DATA   BACK   OK

NUMBER OF DATA SET: 1   NUMBER OF OBSERVATIONS IN EACH SET: 4

SOFIT Concentration versus Time

SOFIT Sorbed versus Time

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Competitive MRM Fitting Model (CMRM-FIT)

The competitive model described earlier is used here. Specifically, the model deals only two competing ions based on the kinetic approach as outlined. The model is capable of inverse action; that is to describe a data set or a set of observations based on best estimates of model parameters. Specifically, experimental results are fitted to the multireaction model described above using Levenberg-Marquardt nonlinear least square optimization method (Press et al., 1992). Statistical criteria used for estimating the goodness-of-fit of the models to the data were the coefficients of determination r^2 and the root mean square error (RMSE). This fitting model is tailored to the adsorption-desorption kinetic batch method.

Input and Output Data Files

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

      a. Manual entry by filling out the template provided below.

      b. As an external ASII file (,dat or txt).

A sample of the input data file referred as CMRM –FIT-INPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. For a given initial concentration (Ci) and input concentration (Cs) at time t > 0, the model provides results of concentration, and the amount sorbed versus time. Measured data are indicated by various symbols and continuous curves are model calculations. Model output is given in txt format and must be named and saved by the user. Graphics of simulations are also generated which can be saved by the user. Graphics include time-dependent sorption-desorption.

      The model carries out all mass calculations for a batch experiment and thus requires a complete accounting of the weights of the soil and solution (added as well as decanted) at each time step. For each input concentration (Co), the model requires the weight of the soil and the solution, the weight of decanted solution, and experimental measured final concentration (C_f) for each time step. Moreover, the number of time steps and the time of sorption and desorption must be given. The user must provide values for all model parameters. If a process is not to be considered, the associated rate coefficient(s) must be set equals to zero. Parameters that estimates are being sought must be identified (by choosing 1) and their initial estimates must be given. The model will carry out nonlinear-least approximation for the entire data set, that is all initial concentrations versus time and are thus represent overall parameter fit. A user may wish

to test the capability of the model for only one input concentration versus time and thus compare individual versus overall fitting.

The model deals with only two competitive ions simultaneously and carries out all mass calculations for a batch experiment and thus requires a complete accounting of the weights of the soil and solution (added as well as decanted) at each time step. For each input concentration (Co) for each ion, the model requires the weight of the soil and the solution, the weight of decanted solution, and experimental measured final concentration (C_f) for each time step. Moreover, the number of time steps and the time of sorption and desorption must be given. The user must provide values for all model parameters. If a process is not to be considered, the associated rate coefficient(s) must be set equals to zero. Parameters that estimates are being sought must be identified (by choosing 1) and their initial estimates must be given. The model will carry out nonlinear-least approximation for the entire data set, that is all initial concentrations versus time and are thus represent overall parameter fit. A user may wish to test the capability of the model for only one input concentration versus time and thus compare individual versus overall fitting. The example shown is for Arsenic sorption at different levels of phosphate from Zhang and Selim (2008)

Zhang, H. and H. M. Selim. 2008. Competitive sorption-desorption kinetics of arsenate and phosphate in soils. Soil Sci. 173:3-12.

Template for the CMRM-FIT model

Model selected is CMRM-FIT

Tittle [SIMULATION OF CEMPETITIVE ADSORPTION-DESORPTION WITH RRS EQUITION]

Input parameters   Fit = 1 / No fit = 0

NONLINEAR COEFFICIENT FOR COMPONENT 1 (N_1)	0.31	0
COMPETITIVE COEFFICIENTS OF C1 FOR C2 (A12)	1.04	1
FREUNDLICH COEFFICIENT OF COMPONENT 1 (KE_1)	0.40	0
FORWARD REACTION RATE OF COMPONENT 1 (K1_1)	0.0106	0
BACKWARD REACTION RATE OF COMPONENT 1 (K2_1)	0.027	0
CONECUTIVE REACTION RATE OF COMPONENT 1 (K3_1)	0.0019	0
IRREVERSIBLE REACTION RATE OF COMPONENT 1 (KI_1)	0.00	0
NONLINEAR COEFFICIENT FOR COMPONENT 2 (N_2)	0.46	0
COMPETITIVE COEFFICIENTS OF C2 FOR C1 (A21)	0.28	1
FREUNDLICH COEFFICIENT OF COMPONENT 2 (KE_2)	1.52	0
FORWARD REACTION RATE OF COMPONENT 2 (K1_2)	0.0202	0
BACKWARD REACTION RATE OF COMPONENT 2 (K2_2)	0.0390	0
CONECUTIVE REACTION RATE OF COMPONENT 2 (K3_2)	0.0011	0
IRREVERSIBLE REACTION RATE OF COMPONENT 2 (KI_2)	0.00	0
PRINTOUT TIME DESIRED,HOURS (TPRINT)	4.0	
NUMER OF FITTING ITERATIONS (IT)	20	

NEXT

MEASURED DATA   BACK   OK

NUMBER OF DATA SET 1   NUMBER OF OBSERVATIONS IN EACH SET 6

CMRMFIT ION1 Concentration versus Time

Concentration in Solution (mg/L) vs Reaction Time (hour)

■ 1 ■ 2 ▲ 3 — 4 ■ 5 — 6 · 7 ■ 8 ■ 9 — 10
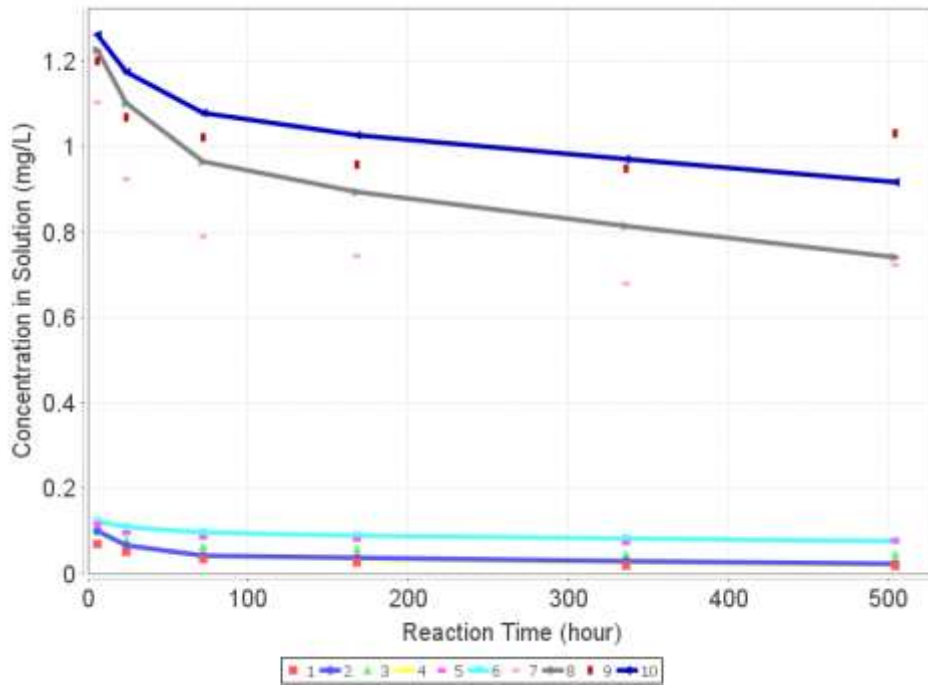
CMRMFIT ION2 Concentration versus Time

Concentration in Solution (mg/L) vs Reaction Time (hour)

■ 1 ■ 2 ▲ 3 — 4 ■ 5 — 6 · 7 ■ 8 ■ 9 — 10

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Transport Models
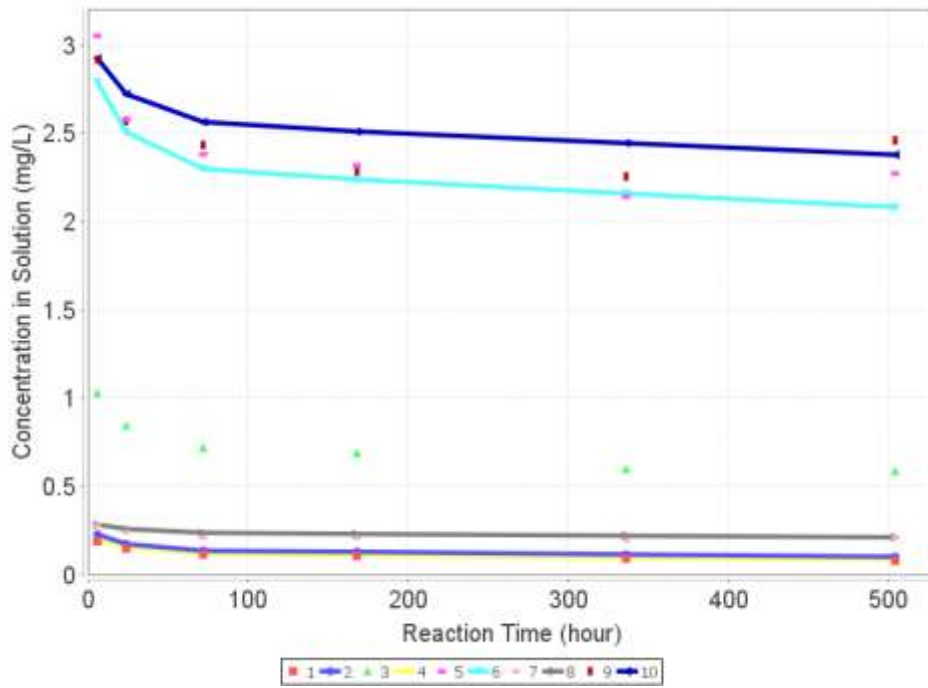
Conceptualization of transport and reactivity of chemicals in soils.
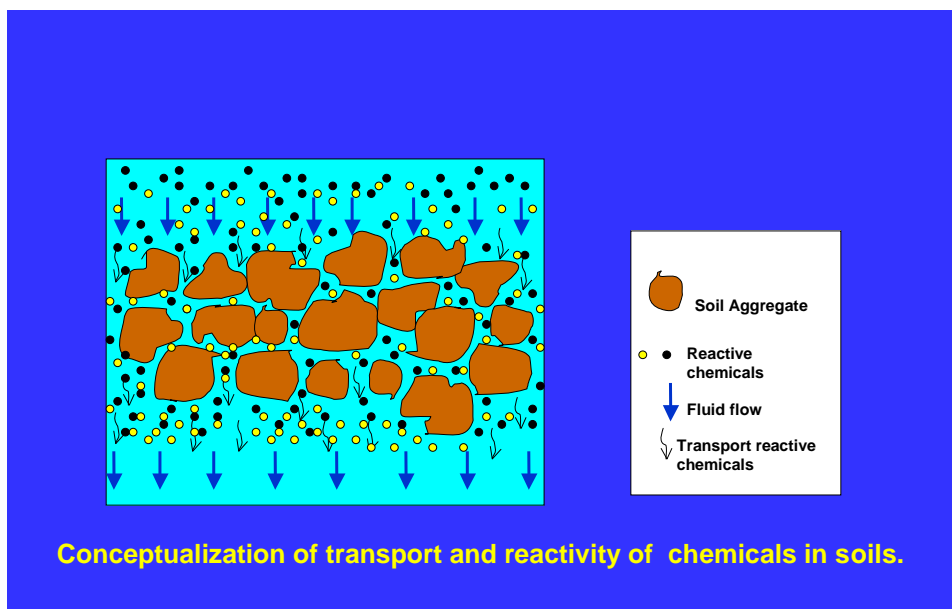
It is commonly accepted that there are two types of mechanisms which govern the transport of dissolved chemicals in soils or geological media. The first type is molecular diffusion (D_o) which is an active type and occurs regardless whether there water flow in the soil system. The second is mechanical dispersion which is passive one and is applicable only when there is water flow. Dispersion is a highly significant transport mechanism which is unique to porous media. A linear relationship between unique between longitudinal dispersion D_L and the pore pore-water velocity v,

$$D_L = D_o + \lambda\, v$$

where D_o is the molecular diffusion coefficient in water. The term λ is a characteristic property of the porous media known as the *dispersivity* (cm). Dispersivity values λ vary from a few centimeters for uniformly packed (disturbed) laboratory soil columns to several meters for field-scale experiments. Large values of λ are also reported for well-aggregated oils. In practice, an empirical parameter D rather than D_L is often introduced to simplify the flux equation. The above yields the following simplified solute flux expression in the z-direction as

$$J_z = -\,\Theta\, D\, \frac{\partial C}{\partial z} + q_z\, C$$

which incorporates the effects of mass flow or convection as well as diffusion and mechanical dispersion. Here J_z is the solute flux (mg/mL.cm^2) and q_z is darcy flux (cm/hr) the z-direction. Incorporation of flux eq. (19) into the conservation of mass or continuity equation yields the following generalized form for solute transport in soils in one-dimension,

$$\frac{\partial \theta C}{\partial t} + \rho \frac{\partial S}{\partial t} = \frac{\partial}{\partial z}\left[\theta D \frac{\partial C}{\partial z}\right] - \frac{\partial q_z C}{\partial z}$$

The above equation is commonly known as the convection-dispersion equation (CDE) for solute transport in porous media, and is applicable for fully-saturated and partially saturated water contents and under transient and steady flow. For conditions where steady water flow is dominant, q and θ are constants over space and time, i.e, for uniform θ in the soil, we have the simplified form of the convection-dispersion equation for reactive chemicals as,

$$\frac{\partial C}{\partial t} + \rho \frac{\partial S}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z}$$

where v is the pore-water velocity (q_z/θ).

Model Simulation -Transport

Select One:

○ Multireaction and Transport Model (MRTML)

This model considers one-dimensional solute transport in uniform or multilayered soil where a constant flux is maintained. Sorption reactions considered here by several simultaneous processes of the equilibrium and kinetic type.

○ Second Order Two-Site (SOTSL)

This model considers solute transport in uniform or multilayered where a constant flux is maintained. Sorption reactions are based on second order formulation. Reaction is the governing mechanisms. A prerequisite of this approach is that a sorption maximum or sorption capacity must be known.

○ SOTS Mobile-Immobile (SOMIM)

The model is similar to SOTSL except that one fraction of the soil water is assumed mobile and the other stagnant and the soil matrix is divided into two regions; a dynamic and a stagnant region with mass transfer or diffusion as dominant between the mobile- and immobile-waters.

BACK

Page: 1/2 NEXT>>

RUN

Model Simulation - Transport (cont.)

Select One:

○ MRTM Mobile Immobile (MRTM_MIM)
This model is similar to MRTM where the Mobile Immobile approach is implemented.

○ Ion-Exchange Transform Model (ION-EXCH)
The model considers ion exchange as the dominant sorption mechanism for ions during transport in layered soils. Vanselow selectivies for binary homovalent ion rxchange are the principal parameters.

○ Model for Mixed Media (MRTM-MIXED)
The model is similar to MRTM except that solute transport is taking place in mixed soil systems; consisting of two or more media. The model accounts for flow interruption where diffusion becomes dominant.

○ Tracer Transport (TRACER)
This model is a special case for tracer solutes such as tritium, bromide, etc. Here a retardation factor is the only reaction mechanism. The tansport model is based on is the mobile-immobile approach.

[<<PREVIOUS]   Page: 2/2   [RUN]

Mulireaction Transport Model for Layered Soils (MRTML)

In this model solute sorption reactions as expressed by the term $(\partial S / \partial t)$ in the above convection-dispersion equation was represented here by the mutlireaction model described earlier. Here, the total amount sorbed S_T *or simply S* as the total amount retained reversibly or reversibly by soil matrix surfaces,

$$S = S_e + S_1 + S_2 + S_{irr}$$

The governing equilibrium retention/release mechanism is the nonlinear Freundlich type as

$$S_e = K_f \, C^b$$

where K_f is the associated distribution coefficient ($cm^3 \, kg^{-1}$) and b is a dimensionless Freundlich parameter ($b < 1$). Other equilibrium type retention mechanisms are given in Chapter 3. This includes linear (b=1), Langmuir, two-site Langmuir, and others.

The retention/release reactions associated with S_1, S_2, and S_3 are concurrent or consecutive type kinetic reactions. Specifically, the S_1 and S_2 phases were considered to be in direct contact with C and reversible rate coefficients of the (nonlinear) kinetic type govern their reactions,

$$\frac{\partial S_1}{\partial t} = k_1 \frac{\Theta}{\rho} C^n - k_2 S_1$$

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\Theta}{\rho} C^m - (k_4 + k_5) S_2 + k_6 S_3$$

$$\frac{\partial S_3}{\partial t} = k_5 S_2 - k_6 S_3$$

where k_1 and k_2 are the forward and backward rates coefficients (h^{-1}), respectively and n is the reaction order associated with S_1. Similarly, k_3 and k_4 are the rate coefficients and m is the reaction order associated with S_2, and k_5 and k_6 are the reaction parameters associated with S_3. In the absence of the consecutive reaction between S_2 and S_3, that is if $S_3 = 0$ at all times ($k_5 = k_6 = 0$), reduces to,

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\Theta}{\rho} C^m - k_4 S_2$$

Thus the eq. for S_2 resembles that for S_1 except for the magnitude of the associated parameters k_3, k_4 and m.
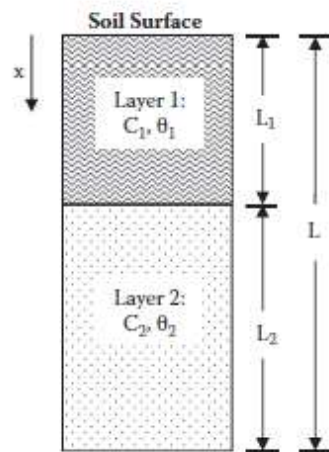
A schematic diagram of a two-layered soil.

The initial and boundary conditions used here is for a finite soil column length L (cm) are

$$C(x) = C_{init} \qquad t = 0$$

$$S(x) = S_{init} \qquad t = 0$$

$$\left(-D\frac{\partial C}{\partial x} + vC\right)\bigg|_{x=0} = \begin{cases} vC_o & t \in T_p \\ 0 & t \notin T_p \end{cases}$$

$$\frac{\partial C}{\partial x}\bigg|_{x=L} = 0 \qquad t > 0$$

where C_{init} is the initial solution concentration (mg L^{-1}), S_{init} is the initial amount of sorption (mg kg^{-1}), C_o is the input solute concentration (mg L^{-1}), T_p is the duration of applied solute pulses, L is the length of column (cm).

In this model, we extend the solution to that for the general case of solute transport in multilayered systems. For the simplest case of a two-layered soil of length L is shown in the schematic Figure. The length of each layer is denoted by L$_1$ and L$_2$, respectively. To show heterogeneity, each soil layer has specific, but not necessarily the same water content, bulk density, and solute retention properties. Only vertical direction steady state water flow perpendicular to the soil layers is considered here. The convective-dispersive equation (CDE) governing solute transport in the ith layer is given by

$$\rho_i\frac{\partial S_i}{\partial t} + \theta_i\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x}\theta_i D_i\frac{\partial C_i}{\partial x} - q\frac{\partial C_i}{\partial x} \qquad where \qquad (0 \le x \le L_i, i = 1,2) \qquad (1)$$

where (omitting the i):

C = resident concentration of solute in soil solution (μg cm^{-3}),

S = amount of solute adsorbed by the soil matrix (μg g^{-1}),

ρ = soil bulk density (g cm^{-3}),

θ = volumetric soil water content (cm^3 cm^{-3}),

D = solute dispersion coefficient (cm^2 d^{-1}),

q = Darcy soil-water flow velocity (cm d^{-1}),

Q = a sink or source for irreversible solute interaction (μg cm^{-3} d^{-1}),

x = distance from the soil surface (cm), and

t = time (d).

An important boundary condition needed in the analysis of multilayered soils is that at the interface between layers. It should be noted that both first-type and third-type boundary conditions are applicable at the interface. It has been shown that although the principle of solute mass conservation is satisfied, a discontinuity in concentration develops when a third-type interface condition is used. On the other hand, a first-type interface condition will result in a continuous concentration profile across the boundary interface at the expense of solute mass balance. To overcome the limitations of both first- and third-type conditions, a combination of first- and third-type condition was implemented. The first-type condition can be written as:

$$C_I\big|_{x\to L_1^-} = C_{II}\big|_{x\to L_1^+}, \qquad t > 0$$

where $x \to L_1^-$ and $x \to L_1^+$ denote that $x = L_1$ is approached from upper and lower layer respectively. Similarly, the third-type condition can be written as:

$$\left(qC_I - \theta_I D_I \frac{\partial C_I}{\partial x} \right)\Bigg|_{x\to L_1^-} = \left(qC_{II} - \theta_{II} D_{II} \frac{\partial C_{II}}{\partial x} \right)\Bigg|_{x\to L_1^+}, \quad t > 0$$

Incorporation of Equation (6) into Equation (7) yields

$$\theta_I D_I \frac{\partial C_I}{\partial x}\Bigg|_{x\to L_1^-} = \theta_{II} D_{II} \frac{\partial C_{II}}{\partial x}\Bigg|_{x\to L_1^+}, \quad t > 0$$

This above BC of Equation (4) was successfully tested.

Input and Output Data Files

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

 a. Manual entry by filling out the template provided below.

 b. As an external ASII file (,dat or txt).

A sample of the input data file referred as MRMTL –FIT-INPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. Model output is given in txt format and must be named and saved by the user. Graphics of simulations are also generated which can be saved by the user. Graphics include time-dependent sorption-desorption.

The model carries out all mass calculations for a batch experiment and thus requires a complete accounting of the weights of the soil and solution (added as well as decanted) at each time step. For each input concentration (Co), the model requires the weight of the soil and the solution, the weight of decanted solution, and experimental measured final concentration (C_f) for each time step. Moreover, the number of time steps and the time of sorption and desorption must be given. The user must provide values for all model parameters. If a process is not to be considered, the associated rate coefficient(s) must be set equals to zero. Parameters that estimates are being sought must be identified (by choosing 1) and their initial estimates must be given. The model will carry out nonlinear-least approximation for the entire data set, that is all initial concentrations versus time and are thus represent overall parameter fit. A user may wish to test the capability of the model for only one input concentration versus time and thus compare individual versus overall fitting.

The example shown demonstrates the influence of the nonlinearity of the Freundlich parameter on the shape of the breakthrough (BTC) curve. Transport results are shown by the effluent results of concentration versus pore volume (time) shown in the plot below. Six values (cases) were selected for this sensitivity analysis namely; 0.5, 0.75, 1.0, 1.25, 1.5 and 2.

Template for the MRTML model

Model selected is MRTML

| Title | MULTIREACTION TRANSPORT MODEL - SENSITIVITY ANALYSIS | | NUMBER OF CASES | 6 |

Input parameters	Case 1	Case 2	Case 3	ADD CASE
WATER FLUX, CM/DAY (WFLX)	1.0000	1.0000	1.0000	
INITIAL CONCENTRATION,MG/ML (CI)	0.0	0.0	0.0	
SOLUTE CONCE. IN INPUTPULSE, MG/ML (CS)	10.0	10.0	10.0	
DURATION OF INPUT PULSE, DAYS (TPULSE)	12.0000	12.0000	12.0000	
TOTAL SIMULATION TIME, DAYS (TTOTAL)	40.0000	48.0000	80.0000	
PRINTOUT TIME DESIRED, DAYS (TPRINT)	0.5000	0.5000	1.0000	
INITIAL TIME STEP, DT, DAYS (DT)	0.2000	0.2000	0.2000	
INITIAL INCREM. DISTANCE,DX,CM (DX)	1.0000	1.0000	1.0000	
NUMBER OF SOIL LAYER IN PROFILE (NX)	001	001	001	
NUMBER OF ITERATIONS DESIRED (IT)	1	1	1	
INPUT DATA FOR LAYER 1				
THICKNESS (CM) OF LAYER 1, (COL)	10	10	10	
SOIL MOISTURE CONTENT OF LAYER 1, (TH)	0.4000	0.4000	0.4000	
SOIL BULK DENSITY OF LAYER 1, (ROU)	1.2500	1.2500	1.2500	
DISPERSION COEFF. OF LAYER 1, CM2/DAY (D)	1.000	1.000	1.000	
DISTRIBUTION COEFF. FOR EQ., CM3/G, (KD)	1.00	1.00	1.00	
NOLINEAR EQ. PARAM., N, LAYER 1 (NEQ)	0.5000	0.75000	1.0000	
FORWARD REACTION RATE, K1, DAY-1, L-1 (K1)	0.0000	0.0000	0.0000	
BACKWARD REACTION RATE, K2, DAY-1, L-1 (K2)	0.000	0.000	0.000	
NONLINEAR KINETIC PARA, W, LAYER 1 (W)	0.000	0.000	0.000	
FORWARD REACTION RATE, K3, DAY-1, L-1 (K3)	0.000	0.000	0.000	
BACKWARD REACTION RATE, K4, DAY-1, L-1(K4)	0.0000	0.0000	0.0000	
NONLINEAR KINETIC PARA, U, LAYER 1 (U)	0.000	0.000	0.000	
IRREVERSIBLE RATE COEFFICIENT, DAY-1, 1(KS)	0.000	0.000	0.000	
FORWARD REACTION RATE, K5, DAY-1, L-1 (K5)	0.0000	0.0000	0.0000	
BACKWARD REACTION RATE, K6, DAY-1, L-1(K6)	0.000	0.000	0.000	

OK

MRTML Simulation
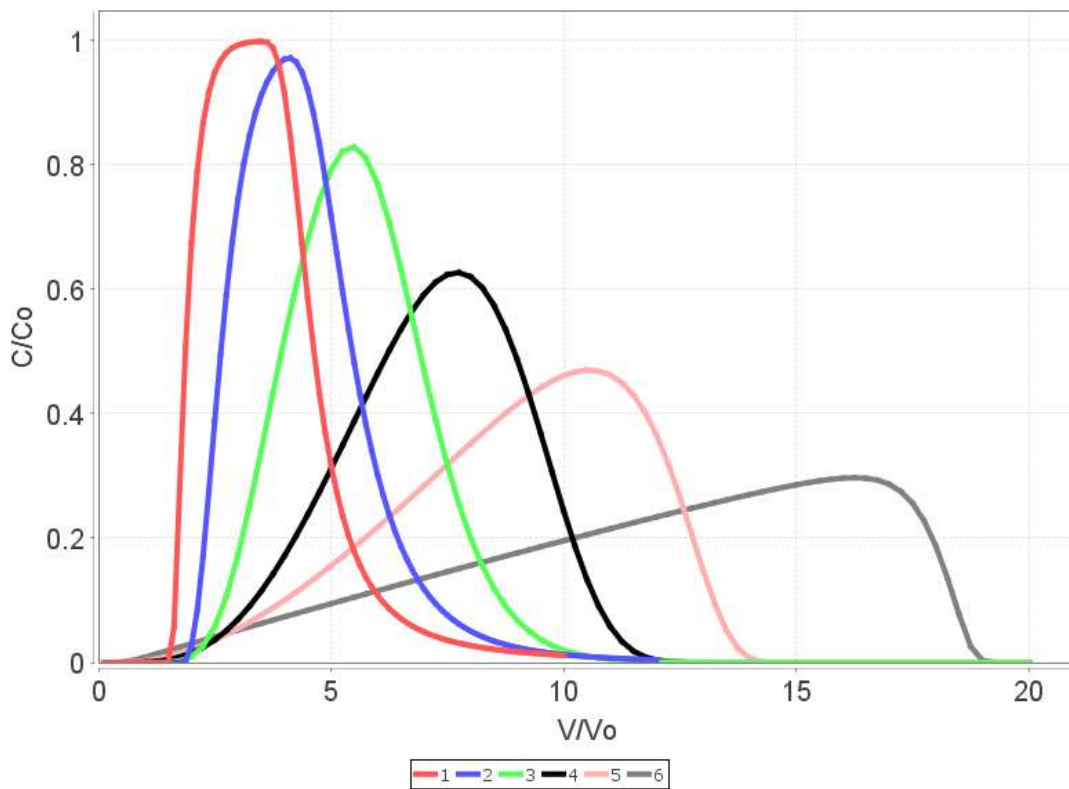
Multireaction and Transport Fitting Model (MRTM-FIT)

This model is that of the multireaction transport (MRTML) model described earlier. However, the model is capable of inverse action; that is to describe a data set or a set of observations based on best estimates of model parameters. Specifically, experimental results are fitted to the multireaction model described above using Levenberg-Marquardt nonlinear least square optimization method (Press et al., 1992). Statistical criteria used for estimating the goodness-of-fit of the models to the data were the coefficients of determination r^2 and the root mean square error (RMSE). The model carries out all mass calculations for soil column experiments and thus requires a complete accounting of the weights of the soil and solution (input and output or effluent) with time. Other necessary constrains include the length of the soil column, soil bulk density and the flux density. A constant or variable flux density can be specificed. If a retention process in the model to be ignored , the associated rate coefficient(s) must be set equals to zero. Parameters that estimates are being sought must be identified (by choosing 1) and their initial estimates must be given. The model will carry out nonlinear-least approximation for the entire data set, that is all initial concentrations versus time and are thus represent overall parameter fit. A user may wish to test the capability of the model for only one input concentration versus time and thus compare individual versus overall fitting.

Input and Output Data Files

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

      a. Manual entry by filling out the template provided below.

      b. As an external ASII file (,dat or txt).

A sample of the input data file referred as MRM –FIT-INPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. For a given initial concentration (Ci) and input concentration (Cs) at time t > 0, the model provides results of concentration, and the amount sorbed versus time. Measured data are indicated by various symbols and continuous curves are model calculations. Model output is given in txt format and must be named and saved by the user. Graphics of simulations are also generated which can be saved by the user.

      The model carries out all mass calculations for a batch experiment and thus requires a complete accounting of the weights of the soil and solution (added as well as decanted) at each

time step. For each input concentration (Co), the model requires the weight of the soil and the solution, the weight of decanted solution, and experimental measured final concentration (C_f) for each time step. Moreover, the number of time steps and the time of sorption and desorption must be given. The user must provide values for all model parameters. If a process is not to be considered, the associated rate coefficient(s) must be set equals to zero. Parameters that estimates are being sought must be identified (by choosing 1) and their initial estimates must be given. The model will carry out nonlinear-least approximation for the entire data set, that is all initial concentrations versus time and are thus represent overall parameter fit. A user may wish to test the capability of the model for only one input concentration versus time and thus compare individual versus overall fitting. The example shown is sliver (Ag) results from miscible displacement experiments for a Winsor soil (not published; available in MS thesis, Liyun Zhang, LSU, 2014). . The transport results are shown by the effluent results of concentration versus pore volume (time) shown in the plot below.

Template for the MRTM-FIT model

Model selected is MRTM-FIT

Tittle SILVER TRANSPORT Colum For Liyun , Windsor soil mixed K3 K4 k5

Input parameters		Fit = 1 No fit = 0
MOISTURE CONTENT (CM3/CM3) (THETA)	0.559	0
BULK DENSITY (G/CM3) (ROE)	1.156	0
COLUMN LENGTH (CM) (LENGTH)	5.0	0
INITIAL SOLUTE CONCENTRATION (UO/ML) (C0)	0.000	0
DIFFUSION COEFF. IN WATER (CM2/HR) (DIFWATER)	0.0005472	0
INTERATION STEP IN TIME (HR) (DT)	0.5	0
INTERATION STEP IN LENGTH (CM) (DZ)	0.4	0
OUTPUT FREQUENCE (HOURS) (FREQOUT)	10	0
MAXIMUM ITERATION NUMBER (MIT)	35	0
DISPERSION COEFFICIENT (D)	0.754	0
EQUILIBRIUM COEFFICIENT KE	0.00	0
NONLINEAR EQUILIBRIUM PARAMETER (NE)	0.426	0
IRREVERSIBLE COEFF. KIRR (C-->SIRR)	0.00	0
RATE COEFFICIENT K1 (C-->S1)	0.00	0
RATE COEFFICIENT K2 (S1-->C)	0.00	0
NONLINEAR KINETIC PARAMETER (U)	0.426	0
RATE COEFFICIENT K3 (C-->S2)	0.8	1
RATE COEFFICIENT K4 (S2-->C)	0.08	1
NONLINEAR KINETIC PARAMETER (W)	0.426	0
RATE COEFFICIENT K5 (S2-->S3)	0.005	1
RATE COEFFICIENT K6 (S3-->S2)	0.00	0
NUMBER OF FITTED PARAMETERS (NP)	3	
NUMBER OF APPLIED PULSES (DSET)	1	
INPUT CONCEVTR (UG/ML)	207.9000	
DARCY FLUX (CM/HR)	0.310000	
PULSE START P.V.(#.P.V.)	0.000000	
PULSE STOP P.V. (#.P.V.)	35.31000	
FLOW INTERRUPTION STARTS AT (#.P.V.)	32.20000	
DURATION OF FLOW INTERRUPTION (HOURS)	48.00000	

NEXT

Screen 2

MEASURED DATA

NUMBER OF OBSERVATION DATA POINTS: 109   [BACK] [OK]

V/V0	C/C0	
0.110301011	0.000443848	
0.551505057	0.000366211	
0.992709103	0.000356445	
1.433913149	0.000329102	
1.654515172	0.00029834	
1.875117195	0.000539551	
2.095719218	0.008828125	
2.316321241	0.03359375	
2.536923264	0.065771484	
2.757525287	0.094042969	
2.978127309	0.110595703	
3.198729332	0.139501953	
3.419331355	0.173925781	
3.860535401	0.218212891	
4.301739447	0.258789063	
4.742943493	0.295410156	
5.184147539	0.3203125	
5.404749562	0.330566406	
5.845953607	0.352050781	
6.287157653	0.373535156	
6.728361699	0.399414063	
7.169565745	0.425292969	
7.390167768	0.430175781	
7.610769791	0.442871094	
8.051973837	0.456054688	

MRTM-FIT ION SIMULATION

65
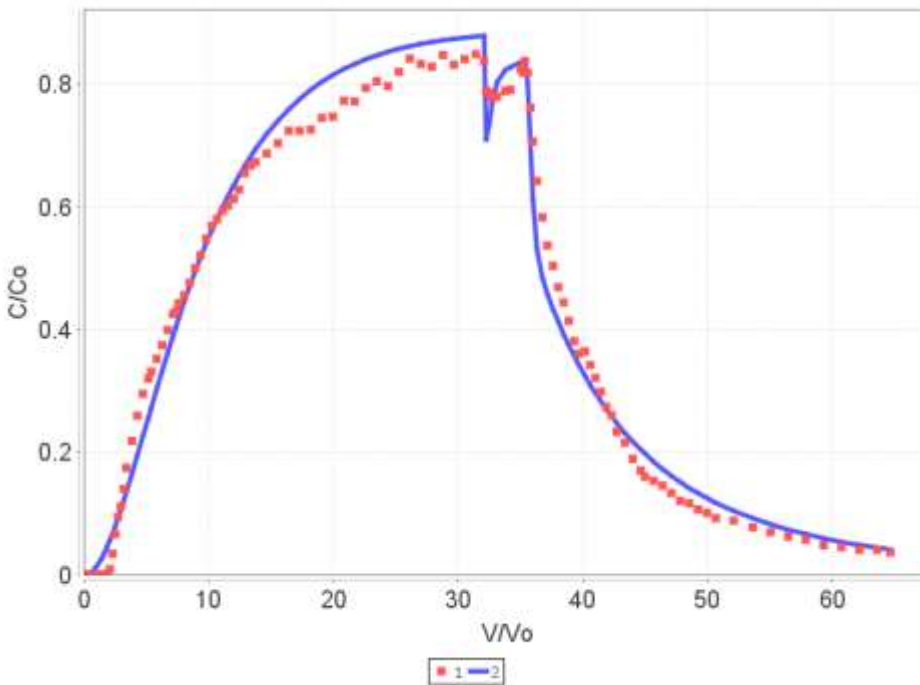
Second-Order Two-Site Transport Model in Layered Soils (SOTSL)

In this model, the sorption term of the convective-dispersive equation (CDE) is based on second-order-two-site formulation. The solute transport equation used is that for multilayered soils where for the *i*th layer (see Figure 1) is given by Equation (1)

$$\rho_i \frac{\partial S_i}{\partial t} + \theta_i \frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \theta_i D_i \frac{\partial C_i}{\partial x} - q \frac{\partial C_i}{\partial x} \qquad where \qquad (0 \leq x \leq L_i, i = 1, 2)$$

where (omitting the *i*):

  C = resident concentration of solute in soil solution (μg cm^{-3}),

  S = amount of solute adsorbed by the soil matrix (μg g^{-1}),

  ρ = soil bulk density (g cm^{-3}),

  θ = volumetric soil water content (cm^3 cm^{-3}),

  D = solute dispersion coefficient (cm^2 d^{-1}),

  q = Darcy soil-water flow velocity (cm d^{-1}),

  Q = a sink or source for irreversible solute interaction (μg cm^{-3} d^{-1}),

  x = distance from the soil surface (cm), and

  t = time (d).

The above equation is subject to the initial and boundary conditions as described under model MRTML.

In this model solute sorption reactions as expressed by the term $(\partial S / \partial t)$ in the above convection-dispersion equation was represented here by the second-order two site model where, In this model, it is assumed that a soil contains a maximum adsorption or total retention capacity or sites (S_{max}). Furthermore, the total sites can be partitioned into two types such that,

$$S_{max} = (S_{max})_1 + (S_{max})_2$$

where (S_{max})$_1$ and (S_{max})$_2$ are the total amount of type 1 sites and type 2 sites, respectively. If F represents the fraction of type 1 sites to the total amount of sites or the adsorption capacity for an individual soil, we thus have

$$(S_{max})_1 = F\ S_{max} \qquad and \qquad (S_{max})_2 = (1 - F)\ S_{max}$$

Based on second order formulation, the retention reaction of each site is

$$\rho \frac{\partial S_1}{\partial t} = k_1 \Theta (S_{max1} - (S_1)C - k_2 \rho S_1 \qquad \textit{for type 1 sites}$$

and

$$\rho \frac{\partial S_2}{\partial t} = k_3 \Theta (S_{max2} - S_2)C - 4 \rho S_2 \qquad \textit{for type 2 sites}$$

where k_1 and k_2 (h^{-1}) are forward and backward rate coefficients for type 1 sites, whereas k_3 and k_4 are rate coefficients for type 2 reaction sites, respectively. In addition, Θ is the soil water content (cm^3 cm^{-3}), ρ is the soil bulk density (g cm^{-3}), and t is time (h). This model also accounts for irreversible sorption or a sink of the linear type,

$$\rho \frac{\partial S_s}{\partial t} = k_s \theta C$$

where S_s is the amount irreversible sorbed (mg/g soil) and k_s is the rate of irreversible retention.

Input and Output Data Files

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

 a. Manual entry by filling out the template provided below.

 b. As an external ASII file (,dat or txt).

A sample of the input data file referred as SOTSL-INPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. For a given initial concentration (Ci) and input concentration (Cs) at time t > 0, the model provides results of concentration, and the amount sorbed versus time. Model output is given in txt format and must be named and saved by the user. Graphics of simulations are also generated which can be saved by the user. The model carries out all mass calculations for a batch experiment and thus requires a complete accounting of the weights of the soil and solution (added as well as decanted) at each time step. For each input concentration (Co), the model requires the weight of the soil and the solution, the weight of decanted solution, and experimental measured final concentration (C_f) for each time step. Moreover, the number of time steps and the time of sorption and desorption must be given. The user must provide values

for all model parameters. If a process is not to be considered, the associated rate coefficient(s) must be set equals to zero. Parameters that estimates are being sought must be identified (by choosing 1) and their initial estimates must be given. The model will carry out nonlinear-least approximation for the entire data set, that is all initial concentrations versus time and are thus represent overall parameter fit. A user may wish to test the capability of the model for only one input concentration versus time and thus compare individual versus overall fitting. A sample of the input data file referred as SOTSL-INPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. Samples of input files in a template format are included in this package. Model output is given in txt format and must be named and saved by the user. Graphics of simulations and experimental measurements are also generated which can be saved by the user. Graphics include breakthrough curves, time-dependent sorption and desorption. The example shown demonstrates the influence of the sorption capacity or the total amount of available sites on the shape of the breakthrough (BTC) curve. . The transport results are shown by the effluent results of concentration versus pore volume (time) shown in the plot below. Six values (cases) were selected for this sensitivity analysis namely; 50, 100, 200, 400, 600, and 800 mg/kg.

Template for the SOTSL model

Model selected is SOTSL

Title TWO-SITE MODEL SENSITIVITY ANALYSIS   NUMBER OF CASES 6

Input parameters	Case 1	Case 2	Case 3 ADD CASE
MOISTURE CONTENT,CM3/CM3 (TH)	0.40000	0.40000	0.40000
BULK DENSITY,G/CM3 (ROU)	1.20	1.20	1.20
COLUMN LENGTH,CM (COL)	10.00E00	10.00E00	10.0
WATER FLUX,CM/HR (WFLX)	1.00000	1.00000	1.00000
INITIAL CONCENTRATION,MG/L (CI)	0.000E00	0.000E00	0.000E00
CONCEN.IN INPUT PULSE,MG/L (CS)	100.00	100.00	100.00
DISPERSION COEFFICIENT,CM2/HR (D)	10.00000	10.00000	10.00000
TOTAL AMOUNT OF AVAIALBLE SITES,ST (ST)	50.00000	100.00000	200.00000
FRACTION OF SITES, F (F)	0.500	0.500	0.500
FORWARD RATE REACTION, 1/(CM3.MG.HR) (K1)	0.0200	0.0200	0.0200
BACKWARD RATE REACTION, K2,HR-1 (K2)	1.0000	1.0000	1.0000
FORWARD RATE REACTION, 1/(CM3.MG.HR) (K3)	0.005	0.005	0.005
BACKWARD RATE REACTION, K4,HR-1 (K4)	0.100	0.100	0.100
IRREVERSIBLE REACTION RATE,KS,HR-1 (KS)	0.005	0.005	0.005
NUMBER OF ITERATIONS (IT)	010	010	010
INPUT PULSE DURATION,HRS (TPULSE)	100.	100.	100.
TOTAL SIMULATION TIME,HRS (TTOTAL)	300.	300.	300.
PRINTOUT TIME DESIRED,HRS (TPRINT)	2.0000	2.0000	2.0000
INCREMENTAL TIME STEP, HRS (DT)	0.10000	0.10000	0.10000
INCREMENTAL DISTANCE, CM (DZ)	0.2000	0.2000	0.2000

OK

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SOTSL Simulation
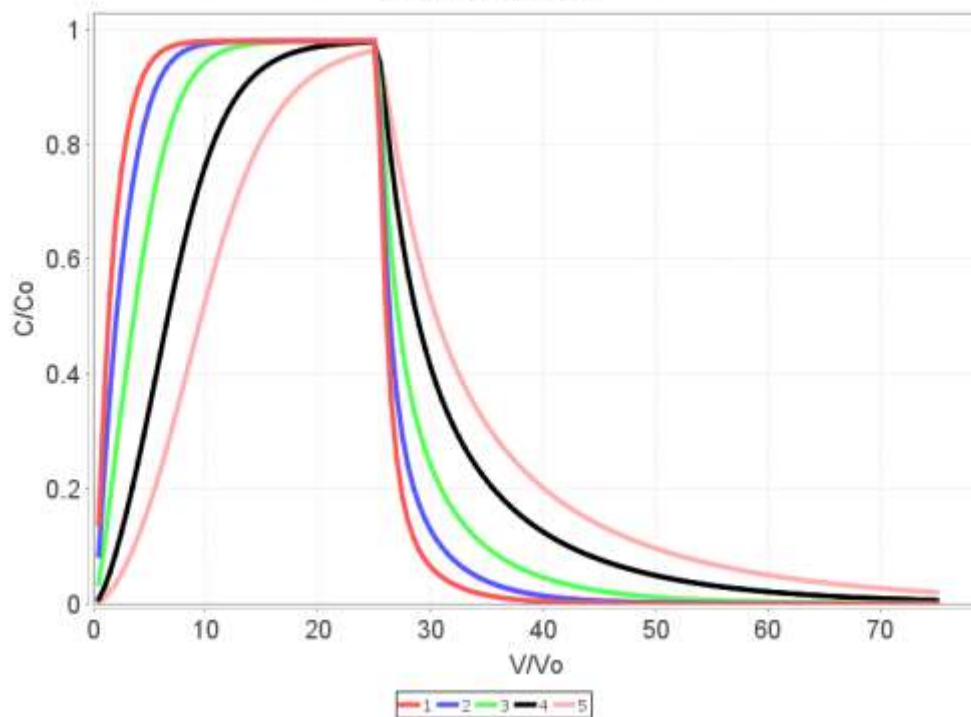
Second-Order and Transport Fitting Model (SOT-FIT)

This model is basically that of the second-order (SOTSL) model described earlier. However, the model is capable of inverse action; that is to describe a data set or a set of observations based on best estimates of model parameters. Specifically, experimental results are fitted to the second-order transport model described above using Levenberg-Marquardt nonlinear least square optimization method (Press et al., 1992). Statistical criteria used for estimating the goodness-of-fit of the models to the data were the coefficients of determination r^2 and the root mean square error (RMSE). This fitting model is tailored to the adsorption-desorption kinetic batch method.

The model carries out all mass calculations for soil column experiments and thus requires a complete accounting of the weights of the soil and solution (input and output or effluent) with time. Other necessary constrains include the length of the soil column, soil bulk density and the flux density. A constant or variable flux density can be specified. If a retention process in the model to be ignored, the associated rate coefficient(s) must be set equals to zero. Parameters that estimates are being sought must be identified (by choosing 1) and their initial estimates must be given. The model will carry out nonlinear-least approximation for the entire data set, that is all initial concentrations versus time and are thus represent overall parameter fit. A user may wish to test the capability of the model for only one input concentration versus time and thus compare individual versus overall fitting.

Input and Output Data Files

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

a. Manual entry by filling out the template provided below.

b. As an external ASII file (,dat or txt).

A sample of the input data file referred as SOT-FIT -INPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. For a given initial concentration (Ci) and input concentration (Cs) at time t > 0, the model provides results of concentration, and the amount sorbed versus time. Measured data are indicated by various symbols and continuous curves are model calculations. Model output is given in txt format and must be named and saved by the user. Graphics of

simulations are also generated which can be saved by the user. Graphics include time-dependent sorption-desorption.

The model carries out all mass calculations for a batch experiment and thus requires a complete accounting of the weights of the soil and solution (added as well as decanted) at each time step. For each input concentration (Co), the model requires the weight of the soil and the solution, the weight of decanted solution, and experimental measured final concentration (C_f) for each time step. Moreover, the number of time steps and the time of sorption and desorption must be given. The user must provide values for all model parameters. If a process is not to be considered, the associated rate coefficient(s) must be set equals to zero. Parameters that estimates are being sought must be identified (by choosing 1) and their initial estimates must be given. The model will carry out nonlinear-least approximation for the entire data set, that is all initial concentrations versus time and are thus represent overall parameter fit. A user may wish to test the capability of the model for only one input concentration versus time and thus compare individual versus overall fitting.

The example shown represents atrazine results from miscible displacement experiments for a Sharkey soil published in the Soil Sci. Amer. Journal (2005, vol . 66, pp 318-327). The transport results are shown by the effluent results of concentration versus pore volume (time) shown in the plot below.

Ma, L. and H. M. Selim. 2005. Predicting pesticide transport in mulch amended soils: A two compartment model. Soil Sci. Soc. Am. J. 69: 318-327.

Template for the SOT-FIT model
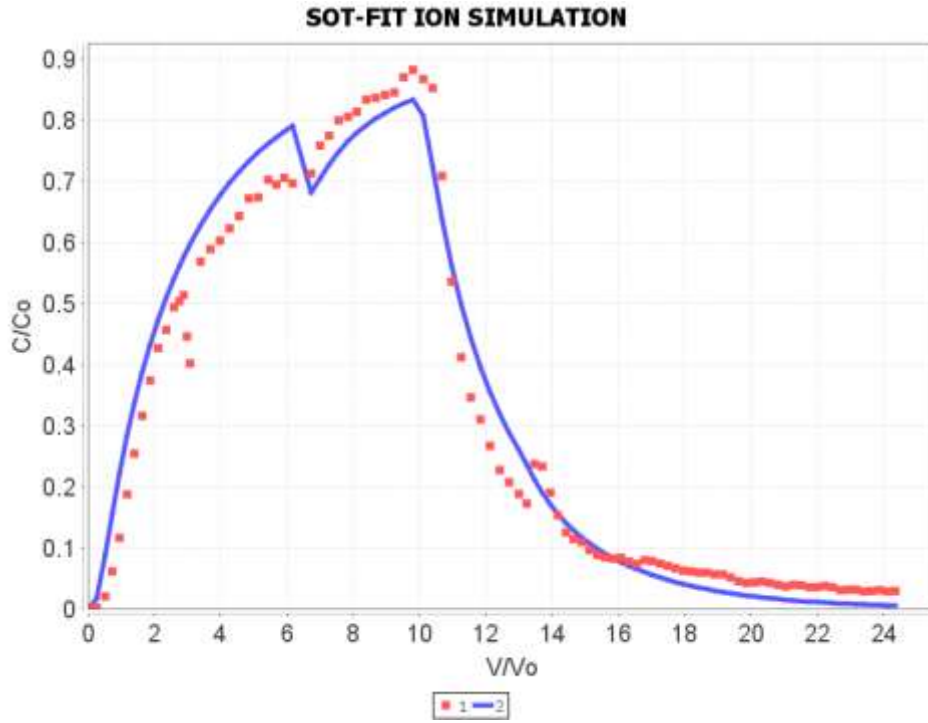
Model selected is SOT-FIT

Tittle: Atrazine BTC, Sharkey+match Fig 7, SSSAJ 2005,69:318-327

Input parameters — Fit = 1 / No fit = 0

Parameter	Value	Fit
MOISTURE CONTENT (CM3/CM3) (THETA)	0.538	0
BULK DENSITY (G/CM3) (ROE)	0.966	0
COLUMN LENGTH (CM) (LENGTH)	10.0	0
INITIAL SOLUTE CONCENTRATION (UG/ML) (C0)	0.000	0
WATER DIFFUSIVE COEFFICIENT (CM2/HR) (DIFWATER)	0.0005472	0
INTERATION STEP IN TIME (HR) (DT)	0.5	0
INTERATION STEP IN LENGTH (CM) (DZ)	0.2	0
OUTPUT FREQUENCE (HOURS) (FREQOUT)	10	0
MAXIMUM ITERATION NUMBER (MIT)	20	0
DISPERSION COEFFICIENT (D)	3.80	0
SORPTION CAPACITY (CAP)	278.83	1
EQUILIBRIUM COEFFICIENT (KE)	0.003507	0
IRREVERSIBLE COEFF. KIRR (C-->SIRR)	0.00	0
RATE COEFFICIENT K1 (C-->S1)	0.00	0
RATE COEFFICIENT K2 (S1-->C)	0.00	0
RATE COEFFICIENT K3 (C-->S2)	0.000472	1
RATE COEFFICIENT K4 (S2-->C)	0.151549	1
RATE COEFFICIENT K5 (S2-->S3)	0.001974	1
RATE COEFFICIENT K6 (S3-->S2)	0.00	0
FITTED PARAMETERS (NP)	4	
NUMBER OF APPLIED PULSES (DSET)	1	
INPUT SOLUTE CON.(UG/ML)	10.30000	
DARCY FLUX (CM/HR)	0.218400	
PULSE START (#.P.V.)	0.000000	
PULSE STOP (#.P.V.)	9.775000	
FLOW INTERRUPTION #1 STARTS AT (#.P.V.)	6.500000	
DURATION OF FLOW INTERRUPTION #1 (HOURS)	96.00000	
FLOW INTERRUPTION #2 STARTS AT (#.P.V.)	13.00000	
DURATION OF FLOW INTERRUPTION #2 (HOURS)	96.00000	

NEXT

Screen 2

SOT-FIT ION SIMULATION

Second-Order Mobile-Immobile Transport Model (SOMIM)

The equations describing the movement for a reactive solute through a porous media having mobile and immobile water fractions are:

$$\Theta^m \frac{\partial C^m}{\partial t} + f\rho \frac{\partial S^m}{\partial t} = \Theta^m D \frac{\partial^2 C^m}{\partial x^2} - v^m \Theta^m \frac{\partial C^m}{\partial x} - \alpha(C^m - C^{im}) - Q^m$$

and:

$$\Theta^{im} \frac{\partial C^{im}}{\partial t} + (1-f)\rho \frac{\partial S^{im}}{\partial t} = \alpha(C^m - C^{im}) - Q^{im}$$

This is a modified version of the convection-dispersion equation where D is the hydrodynamic dispersion coefficient in the mobile water region (cm^2 h^{-1}), Θ^m and Θ^{im} are mobile and immobile water fractions (cm^3 cm^{-3}), respectively. The terms C^m and C^{im} are the concentrations in the mobile and immobile water (μg cm^{-3}), and v^m is the average pore-water velocity in the mobile region (cm h^{-1}). Also ρ is soil bulk density (g cm^{-3}), x is depth (cm) and t is time (h). It is also assumed that the immobile water (Θ^{im}) is located inside aggregate pores (inter-aggregate) where solute transfer occurs by diffusion only. The term α is a mass transfer coefficient (h^{-1}) which governs the transfer of solutes between the mobile- and immobile-water phases in analogous manner to a diffusion process. In addition, it is assumed that the soil matrix is divided into two regions (or sites) where a fraction f is a dynamic or easily accessible region and the remaining fraction is a stagnant or less accessible region (see Figures 2). The dynamic region is located close to the mobile phase whereas the stagnant region is in contact with the immobile phase. Moreover, S^m and S^{im} are the amounts of solutes sorbed in the dynamic and stagnant regions (μg per gram soil), respectively. Also Q^m and Q^{im} are sink (or source) terms associated with the mobile and immobile water regions, respectively. Therefore, Q^m and Q^{im} represent rates of irreversible type reactions. These terms must be distinguished from S^m and S^{im} which represent reversible sorbed solutes in the dynamic and stagnant regions, respectively.

Input and Output Data Files

      An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

      a. Manual entry by filling out the template provided below.

      b. As an external ASII file (.6dat or txt).

A sample of the input data file referred as SOTSL-INPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. For a given initial concentration (Ci) and input concentration (Cs) at time t > 0, the model provides results of concentration, and the amount sorbed versus time. Model output is given in txt format and must be named and saved by the user. Graphics of simulations are also generated which can be saved by the user. The example shown demonstrates the influence of the fraction of sites (F) on the shape of the breakthrough (BTC) curve. The effluent results of concentration versus pore volume (time) shown in the plot below. Six values (cases) were selected for this sensitivity analysis namely F values of 0, 0.2, 0.2, 0.3., 0.4, and 0.5.

Template for the SOMIM model

Model selected is SOMIM

Title: SOMIM TRANSPORT – SENSITIVITY ANALYSIS   NUMBER OF CASES: 6

Input parameters	Case 1	Case 2	Case 3
MOISTURE CONTENT,CM3/CM3 (TH)	0.400E00	0.400E00	0.400E00
BULK DENSITY,G/CM3 (ROU)	1.200E00	1.200E00	1.200E00
COLUMN LENGTH,CM (COL)	10.000E00	10.000E00	10.000E00
WATER FLUX,CM/HR (WFLX)	1.000E00	1.000E00	1.000E00
INITIAL CONCENTRATION,MG/L (CI)	0.000E00	0.000E00	0.000E00
CONCEN.IN INPUT PULSE,MG/L (CS)	10.000E00	10.000E00	10.000E00
DISPERSION COEFFICIENT,CM2/HR (D)	1.000E00	1.000E00	1.000E00
TOTAL AMOUNT OF AVAIALBLE SITES,ST (ST)	200.000E00	200.000E00	200.000E00
FRACTION OF SITES, F (F)	0.00E00	0.100E00	0.200E00
FRACTION OF WATER, FTH (FTH)	0.500E00	0.500E00	0.500E00
FORWARD RATE REACTION, K1,HR-1 (K1)	0.007500	0.007500	0.007500
BACKWARD RATE REACTION, K2,HR-1 (K2)	0.250E-0	0.250E-0	0.250E-0
IRREVERSIBLE REACTION RATE,KS,HR-1 (KS)	0.000E-0	0.000E-0	0.000E-0
TRANSFER COEFFICIENT, TR (TR)	0.050E-0	0.050E-0	0.050E-0
NUMBER OF ITERATIONS (IT)	010	010	010
INPUT PULSE DURATION,HRS (TPULSE)	12.00E00	12.00E00	12.00E00
TOTAL SIMULATION TIME,HRS (TTOTAL)	48.00E00	48.00E00	48.00E00
PRINTOUT TIME DESIRED,HRS (TPRINT)	1.00E00	1.00E00	1.00E00
INCREMENTAL TIME STEP, HRS (DT)	0.10E00	0.10E00	0.10E00
INCREMENTAL DISTANCE, CM (DZ)	0.50E00	0.50E00	0.50E00

OK

SOMIM Simulation
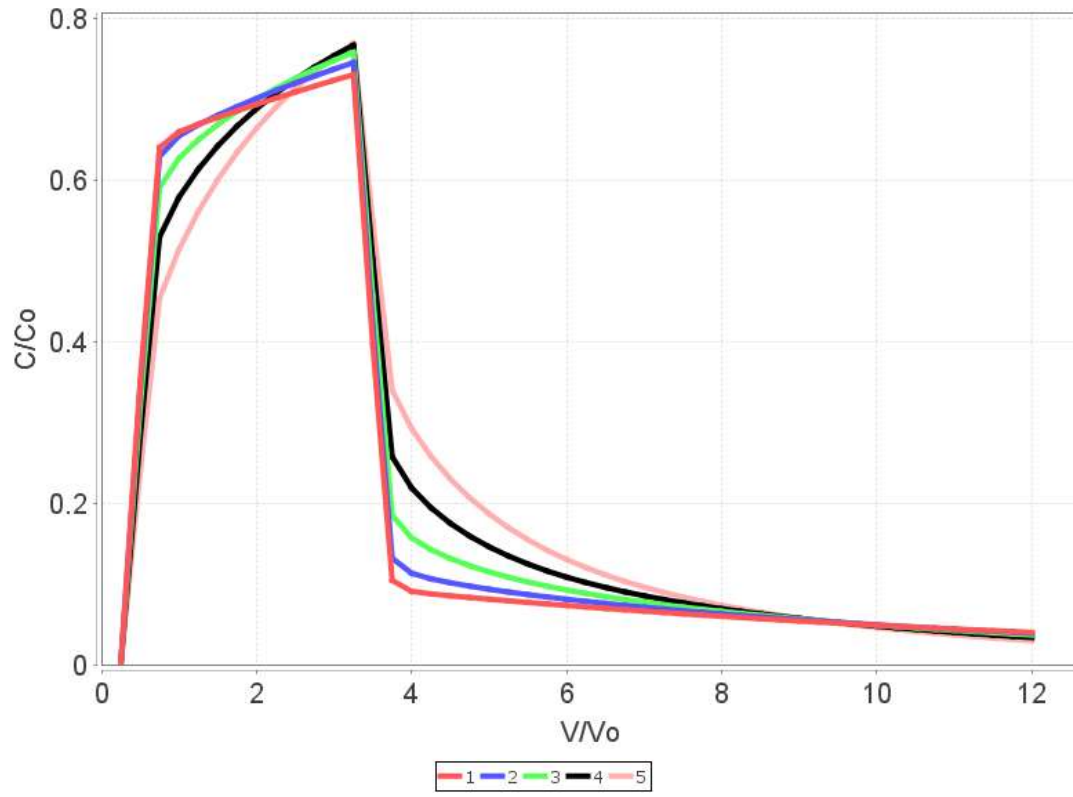
Second-OrderMOBIL-IMMOBILE FIT (SOMIM-FIT)

This model is basically that of the SOMIM-FIT (SOMIM) model described earlier. However, the model is capable of inverse action; that is to describe a data set or a set of observations based on best estimates of model parameters. Specifically, experimental results are fitted to the second-order transport model described above using Levenberg-Marquardt nonlinear least square optimization method (Press et al., 1992). Statistical criteria used for estimating the goodness-of-fit of the models to the data were the coefficients of determination r^2 and the root mean square error (RMSE). This fitting model is tailored to the adsorption-desorption kinetic batch method.

Input and Output Data File

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

a. Manual entry by filling out the template provided below.

b. As an external ASII file (.dat or txt).

A sample of the input data file referred as SOMIM-FIT-IPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. Samples of input files in a template format are included in this package. Model output is given in txt format and must be named and saved by the user. Graphics of simulations and experimental measurements are also generated which can be saved by the user.

The model carries out all mass calculations for a batch experiment and thus requires a complete accounting of the weights of the soil and solution (added as well as decanted) at each time step. For each input concentration (Co), the model requires the weight of the soil and the solution, the weight of decanted solution, and experimental measured final concentration (C_f) for each time step. Moreover, the number of time steps and the time of sorption and desorption must be given. The user must provide values for all model parameters. If a process is not to be considered, the associated rate coefficient(s) must be set equals to zero. Parameters that estimates are being sought must be identified (by choosing 1) and their initial estimates must be given. The model will carry out nonlinear-least approximation for the entire data set, that is all initial concentrations versus time and are thus represent overall parameter fit. A user may wish to test the capability of the model for only one input concentration versus time and thus compare individual versus overall fitting. The example shown represent experimental and predicted atrazine results of two consecutive pulses from miscible displacement experiments for a Sharkey

soil (2 mm aggregate size) (Ma and Selim, 1997). The transport results are shown by the effluent concentration versus pore volume (time) shown in the plot below.

Ma, L. and H. M. Selim. 1997. Evaluation of nonequilibrium models for predicting atrazine transport in soils. Soil Sci. Soc. Am. J. 1299-1307.

Template for the SOMIM-FIT model

Model selected is SOMIM-FIT

Title `****** ATRAZINE BTC COLUMN #1 & 2, SHARKEY (2-4MM)*****`

Input parameters

MOISTURE CONTENT (CM3/CM3) (THETA)	0.6000	
MOBILE WATER FRACTION (FM)	0.338	
SOIL AGGREGATE SIZE (CM) (RADIUS)	0.107	
BULK DENSITY (G/CM3) (ROE)	1.059	
COLUMN LENGTH (CM) (LENGTH)	10.0	
INITIAL SOLUTE CONCENTRATION (UG/ML) (C0)	0.000	
WATER DIFFUSIVE COEFFICIENT (CM2/HR) (DIFWATER)	0.0005472	
INTERATION STEP IN TIME (HR) (DT)	0.5	
INTERATION STEP IN LENGTH (CM) (DZ)	0.2	
OUTPUT FREQUENCE (HOURS) (FREQOUT)	10	
MAXIMUM ITERATION NUMBER (MIT)	10	
X(1)=D	1.994991	0
X(4)=CAP	184.62	0
X(5)=KF	0.016040	1
X(7)=KIRR (C-->SIRR)	0.00	0
X(8)=K1 (C-->S1)	0.00	0
X(9)=K2 (S1-->C)	0.00	0
X(11)=K3 (C-->S2)	0.000107	1
X(12)=K4 (S2-->C)	0.009465	1
X(14)=K5 (S2-->S3)	0.001628	1
X(15)=K6 (S3-->S2)	0.00	0
NUMBER OF FITTED PARAMETERS (NP)	4	
NUMBER OF APPLIED PULSES (NPULSE)	2	
PULSE1 INPUT SOLUTE CON.(UG/ML)	10.47000	
PULSE1 DARCY FLUX (CM/HR)	0.312500	
PULSE1 START P.V.(#.P.V.)	0.000000	
PULSE1 STOP P.V. (#.P.V.)	9.030000	
PULSE1 STOPFLOW STARTS (#.P.V.)	0.000000	
PULSE1 DURATA STOPFLOW (HOURS)	0.000000	
PULSE2 INPUT SOLUTE CON.(UG/ML)	5.295000	
PULSE2 DARCY FLUX (CM/HR)	0.314100	
PULSE2 START P.V.(#.P.V.)	23.06000	
PULSE2 STOP P.V. (#.P.V.)	32.08000	
PULSE2 STOPFLOW STARTS (#.P.V.)	0.000000	
PULSE2 DURATA STOPFLOW (HOURS)	0.000000	

NEXT

Screen 2
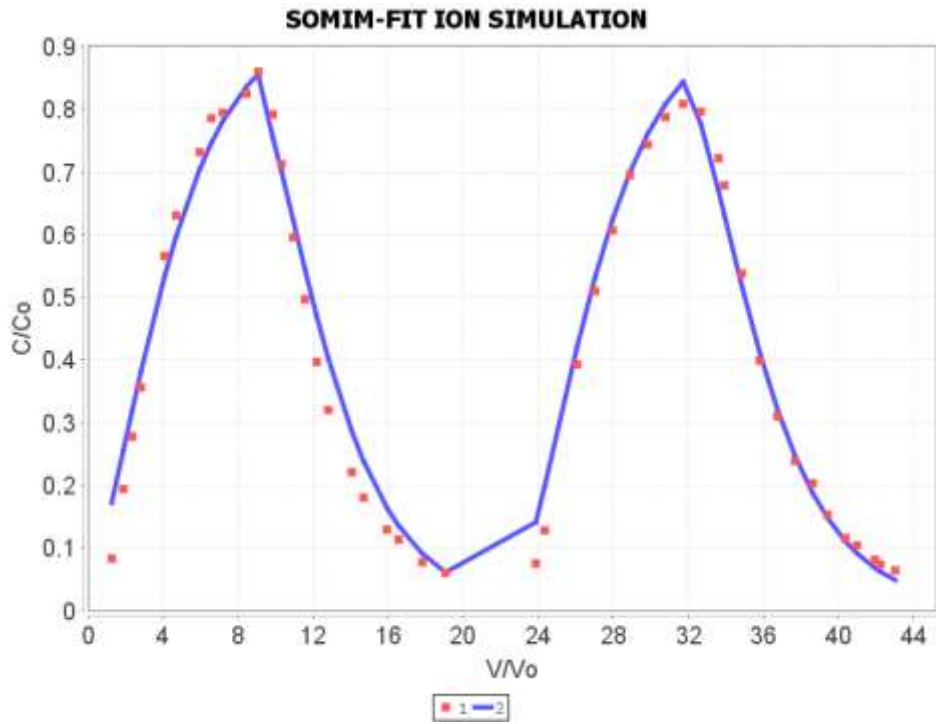
Competitive Transport Model (CMRTM)

Competitive sorption of interacting ions often results in complex breakthrough patterns during their transport in soils and geological media. Therefore, describing heavy metal transport requires retention models that account for their governing mechanisms. The one-dimensional reactive convective-dispersive transport equation is the most frequently used model of describing the transport of dissolved chemicals in soils (Selim, 1992)

$$\frac{\partial \theta C_i}{\partial t} + \rho \frac{\partial S_i}{\partial t} = \frac{\partial}{\partial z} \theta D \frac{\partial C_i}{\partial z} - \frac{\partial q C_i}{\partial z}$$

where S_i is the amount of adsorption (mg kg^{-1}), C_i is the dissolved concentration (mg L^{-1}), i indicates *i*-th component in the system, D is the dispersion coefficient (cm^2 h^{-1}), θ is the soil moisture content (cm^3 cm^{-3}), ρ is the soil bulk density (g cm^{-3}), z is distance (cm), and t is reaction time (h). Retention reactions of a solute by from the soil solution by the matrix of soils and geological media is accounted for by the term ($\frac{\partial S_i}{\partial t}$) and can be quantified based on several approaches. A number of transport models simulate heavy metal sorption based on the local equilibrium assumption (LEA). Here one assumes that the reaction of an individual solute species in the soil is sufficiently fast and that an apparent equilibrium may be observed in a time scale considerably shorter than that of the transport processes. The local equilibrium assumption is the basis for several commonly used models including ion-exchange, surface complexation, Freundlich, and Langmuir models. A discussion of the various models in the perspective of competitive sorption and transport is given in subsequent sections. In contrast to the LEA, for most heavy metals time-dependent retention in soils has been commonly observed as discussed in previous chapters. As a result, a number of formulations were introduced to describe their kinetic sorption behavior in soils. Examples of kinetic models include the first-order model, Freundlich kinetic model, irreversible and second-order models.

The competitive model was developed to describe competitive equilibrium sorption for multicomponent systems where the sorption isotherms of single component follow the Freundlich equation. A general form of the competitive equation can be written as

$$S_i = K_i C_i \left(\sum_{j=1}^{l} \alpha_{i,j} \, C_j \right)^{n_i - 1}$$

where the subscripts i and j denote metal component i and j, l is the total number of components, and $\alpha_{i,j}$ is a dimensionless competition coefficient for the adsorption of component i in the presence of component j. The parameters K_i and n_i are the Freundlich parameters representing a single component system i as described in eq. (14) above. By definition, $\alpha_{i,j}$ equals 1 when $i = j$. If there is no competition, i.e., $\alpha_{i,j} = 0$ for all $j \neq i$, eq. (15) yields a single species Freundlich equation for component i identical to eq. (14). The Competitive MRM model presented here accounts for competitive Freundlich type retention along with MRM formulation discussed earlier such that,

$$(S_e)_i = K_{e,i} C_i \left(\sum_{j=1}^{l} \alpha_{i,j} C_j \right)^{n_i - 1}$$

$$\frac{\partial (S_1)_i}{\partial t} = k_{1,i} \frac{\theta}{\rho} C_i \left(\sum_{j=1}^{l} \alpha_{i,j} C_j \right)^{n_i - 1} - k_{2,i} (S_1)_i$$

$$\frac{\partial (S_2)_i}{\partial t} = k_{3,i} \frac{\theta}{\rho} C_i \left(\sum_{j=1}^{l} \alpha_{i,j} C_j \right)^{n_i - 1} - (k_{4,i} + k_{s,i}) (S_2)_i$$

$$\frac{\partial (S_s)_i}{\partial t} = k_{s,i} (S_s)_i$$

$$\frac{\partial (S_{irr})_i}{\partial t} = k_{irr,i} \frac{\theta}{\rho} C_i$$

When competition is ignored, i.e., $\alpha_{i,j}$ for all $j \neq i$, eq. (21) to a single species nth- order kinetic sorption.

Input and Output Data File

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

     a. Manual entry by filling out the template provided below.

     b. As an external ASII file (.dat or txt).

A sample of the input data file referred as SOMIM-FIT-IPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. Model output is given in txt format and must be named and saved by the user. Graphics of simulations measurements are also generated which can be saved by the user. The user must provide values for all model parameters. If a process is not to be considered, the associated rate coefficient(s) must be set equals to zero. The

transport results are shown by the effluent concentration versus pore volume (time) shown in the plot below. The transport of the two ions are shown by the effluent results of concentration versus pore volume (time) shown in the plot below.

Template for the CMRTM model

Model selected is C-MRTM

Title SIMULATION OF CEMPETITIVE ADSORPTION-DESORPTION WITH SRS EQUTION

Input parameters

NONLINEAR COEFFICIENT FOR COMPONENT 1 (N_1)	0.31
COMPETITIVE COEFFICIENTS OF C1 FOR C2 (A12)	1.04
DISTRIBUTION COEFFICIENT OF COMPONENT 1 (KE_1)	0.40
FORWARD REACTION RATE OF COMPONENT 1 (K1_1)	0.0106
BACKWARD REACTION RATE OF COMPONENT 1 (K2_1)	0.027
CONECUTIVE REACTION RATE OF COMPONENT 1 (K3_1)	0.0019
IRREVERSIBLE REACTION RATE OF COMPONENT 1 (KI_1)	0.00
NONLINEAR COEFFICIENT FOR COMPONENT 2 (N_2)	0.46
COMPETITIVE COEFFICIENTS OF C2 FOR C1 (A21)	0.28
DISTRIBUTION COEFFICIENT OF COMPONENT 2 (KE_2)	1.52
FORWARD REACTION RATE OF COMPONENT 2 (K1_2)	0.0202
BACKWARD REACTION RATE OF COMPONENT 2 (K2_2)	0.0390
CONECUTIVE REACTION RATE OF COMPONENT 2 (K3_2)	0.0011
IRREVERSIBLE REACTION RATE OF COMPONENT 2 (KI_2)	0.00
SIMULATION SETTING	
WATER FLUX, CM/HOUR (WFLX)	1.00
DISPERSION COEFF. OF LAYER 1, CM2/HOUR (D)	1.0
SOIL BULK DENSITY (ROU)	1.19
SATURATED MOISTURE CONTENT (THETA)	0.55
COLUMN LENGTH (L)	20
INITIAL SOLUTION COMPONENT 1 CONCENTRATION (C0_1)	0.00
INITIAL SORBED COMPONENT 1 CONCENTRATION (S0_1)	0.00
INITIAL SOLUTION COMPONENT 2 CONCENTRATION (C0_2)	0.00
INITIAL SORBED COMPONENT 2 CONCENTRATION (S0_2)	0.00
TOTAL SIMULATION TIME, HOURS (TTOTAL)	400.0
PRINTOUT TIME DESIRED, HOURS (TPRINT)	5
NUMBER OF APPLIED PULSES (NPULSE)	1
PULSE1 STARTED AT HOURS (PSTART)	0
PULSE1 STOPPED AT HOURS (PSTOP)	80
PULSE1 SUPPLIED COMPONENT 1 CONCENTRATION (CI_1)	1
PULSE1 SUPPLIED COMPONENT 2 CONCENTRATION (CI_2)	1
NUMBER OF FLOW INTERRUPTIONS (NIN)	1
INCUMBATION1 START AT (ISTART)	150
DURATION OF INCUMBATION 2 (IDURA)	298

OK

CMRTM Simulation
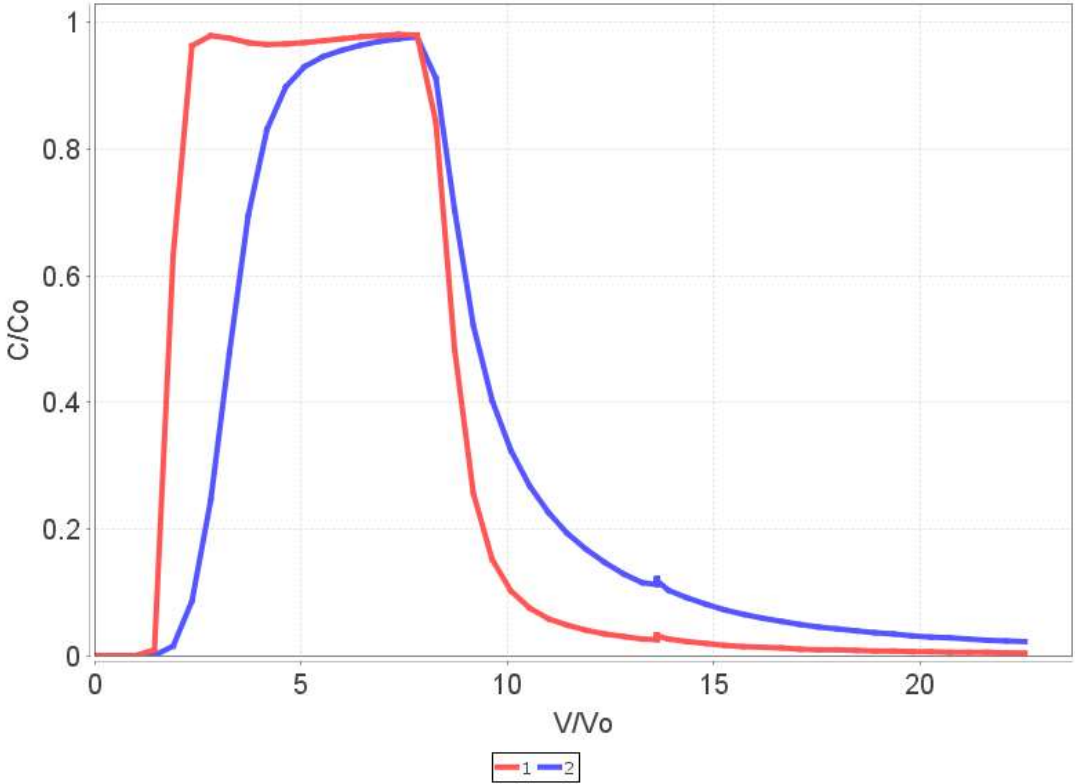
Competitive Transport Fitting Model (CMRTM-FIT)

The competitive transport model described earlier is used here. Specifically, the model deals the transport and reactivities of two competing solute species based on the kinetic approach as outlined above. The model is capable of inverse action; that is to describe a data set or a set of observations based on best estimates of model parameters. Specifically, experimental results are fitted to the multireaction model described above using Levenberg-Marquardt nonlinear least square optimization method (Press et al., 1992). Statistical criteria used for estimating the goodness-of-fit of the models to the data were the coefficients of determination r^2 and the root mean square error (RMSE). This fitting model is tailored to the adsorption-desorption kinetic batch method.

Input Data File

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

       a. Manual entry by filling out the template provided below.

       b. As an external ASII file (,dat or txt).

A sample of the input data file referred as CMRTM-FIT-IPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. Samples of input files in a template format are included in this package. Model output is given in txt format and must be named and saved by the user. Graphics of simulations and experimental measurements are also generated which can be saved by the user. The model deals with only two competitive ions simultaneously and carries out all mass calculations for a batch experiment and thus requires a complete accounting of the weights of the soil and solution (added as well as decanted) at each time step. For each input concentration (Co) for each ion, the model requires the weight of the soil and the solution, the weight of decanted solution, and experimental measured final concentration (C_f) for each time step. Moreover, the number of time steps and depth increments must be given. The user must provide values for all model parameters. If a process is not to be considered, the associated rate coefficient(s) must be set equals to zero. Parameters that estimates are being sought must be identified (by choosing 1) and their initial estimates must be given. The model will carry out nonlinear-least approximation for the entire data set, that is all initial concentrations versus time and are thus represent overall parameter fit. A user may wish to test the capability of the model for only one input concentration versus time and thus compare individual versus overall fitting.

The example shown here represents experimental and prediction of two consecutive pulses of arsenate and phosphate from miscible displacement experiments (Zhang and Selim, 2007). Here the transport of the two ions are shown by the effluent results of concentration versus pore volume (time) shown in the plot below.

Zhang, H. and H. M. Selim. Modeling arsenate-phosphate retention and transport in soils: A multi-component approach. Soil Sci. Soc. Amer. J. 71:1267-1277.

Template for the CMRTM-FIT model

Model selected is CMRTM-FIT

Title [NENT MULTIREACTION TRANSPORT MODEL, COLUMN 13,COMPONENT 1 AND COMPONENT 2 ON OLIVIER]

Input parameters — Fit =1 / No fit = 0

Parameter	Value	Fit
NONLINEAR COEFFICIENT FOR COMPONENT 1 (N_1)	0.31	0
COMPETITIVE COEFFICIENTS OF C1 FOR C2 (A12)	1.04	1
FREUNDLICH COEFFICIENT OF COMPONENT 1 (KE_1)	0.40	0
FORWARD REACTION RATE OF COMPONENT 1 (K1_1)	0.0106	0
BACKWARD REACTION RATE OF COMPONENT 1 (K2_1)	0.027	0
CONECUTIVE REACTION RATE OF COMPONENT 1 (K3_1)	0.0019	0
IRREVERSIBLE REACTION RATE OF COMPONENT 1 (KI_1)	0.00	0
NONLINEAR COEFFICIENT FOR COMPONENT 2 (N_2)	0.46	0
COMPETITIVE COEFFICIENTS OF C2 FOR C1 (A21)	0.28	1
FREUNDLICH COEFFICIENT OF COMPONENT 2 (KE_2)	1.52	0
FORWARD REACTION RATE OF COMPONENT 2 (K1_2)	0.0202	0
BACKWARD REACTION RATE OF COMPONENT 2 (K2_2)	0.0390	0
CONECUTIVE REACTION RATE OF COMPONENT 2 (K3_2)	0.0011	0
IRREVERSIBLE REACTION RATE OF COMPONENT 2 (KI_2)	0.00	0

SIMULATION SETTING

Parameter	Value
WATER FLUX, CM/HOUR (WFLX)	1.00
DISPERSION COEFF., CM2/HOUR (D)	1.0
SOIL BULK DENSITY (ROU)	1.19
SATURATED MOISTURE CONTENT (THETA)	0.55
COLUMN LENGTH (L)	20
INITIAL SOLUTION COMPONENT 1 CONCENTRATION (C0_1)	0.00
INITIAL SORBED COMPONENT 1 CONCENTRATION (S0_1)	0.00
INITIAL SOLUTION COMPONENT 2 CONCENTRATION (C0_2)	0.00
INITIAL SORBED COMPONENT 2 CONCENTRATION (S0_2)	0.00
NUMBER OF ITERATIONS (NIT)	20
NUMBER OF APPLIED PULSES (NPULSE)	3
PULSE1 STARTED AT (PSTART - hrs)	0
PULSE1 STOPPED AT (PSTOP - hrs)	87
PULSE1 SUPPLIED COMPONENT 1 CONCENTRATION (CI_1)	1.335
PULSE1 SUPPLIED COMPONENT 2 CONCENTRATION (CI_2)	0
PULSE2 STARTED AT (PSTART - hrs)	87
PULSE2 STOPPED AT (PSTOP - hrs)	167
PULSE2 SUPPLIED COMPONENT 1 CONCENTRATION (CI_1)	0
PULSE2 SUPPLIED COMPONENT 2 CONCENTRATION (CI_2)	3.23
PULSE3 STARTED AT (PSTART - hrs)	287
PULSE3 STOPPED AT (PSTOP - hrs)	370
PULSE3 SUPPLIED COMPONENT 1 CONCENTRATION (CI_1)	0
PULSE3 SUPPLIED COMPONENT 2 CONCENTRATION (CI_2)	0
NUMBER OF FLOW INTERRUPTIONS (NIN)	1
FLOW INTERRUPTION1 START AT (ISTART - hrs)	167
DURATION OF FLOW INTERRUPTION (IDURA - hrs)	287

NEXT

Screen 2

MEASURED DATA

NUMBER OF OBSERVATION DATA POINTS 42   [BACK]   [OK]

Time	C_1	C_2
	0.0117	0.0000
9	0.0974	0.0000
15	0.3241	0.0149
21	0.5278	0.0203
27	0.6954	0.0252
33	0.7902	0.0252
39	0.8729	0.0245
45	0.9704	0.0234
51	0.9994	0.0209
57	1.0278	0.0191
63	1.0958	0.0194
69	1.1012	0.0198
75	1.1666	0.0194
81	1.0879	0.0231
87	1.2533	0.0194
93	0.7007	1.6019
99	0.5902	2.0934
105	0.4430	2.2718
111	0.3723	2.4286
117	0.3219	2.5369
123	0.2774	2.5999
129	0.2555	2.7007
135	0.2403	2.8338
141	0.2094	2.7666
147	0.2173	3.0843

CMRTM-FIT ION SIMULATION

ION EXCHANGE TRANSPORT MODEL (ION EXCH)

In this model, sorption of ions are accounted for by ion exchange only; i.e., ion exchange is regarded as the dominant sorption mechanism for ions during transport in soils. Here we account for a simple binary homovalent system where two competitive ions with similar valency are considerd. The ion exchange mechanism is based on Vanselow affinity or selectivity coefficients. The model provides concentrations for the two ions versus time and depth in the soil. The model assumes the soil to be either uniform (one layer) or having several layers, with different properties for each layer.

The simplified Vanselow affinity equation, for the simple case of a binary homovalent ions, i.e., $v_i = v_j = v$, and assuming similar ion activities in the solution phase ($\gamma_i = \gamma_j = 1$), we have,

$$K_{12} = \left(\frac{s_i}{C_i}\right) / \left(\frac{s_j}{C_j}\right) \qquad (5)$$

where K_{ij} represents the affinity of ion i over j or a separation factor for the affinity of ions on exchange sites. Rearrangement of eq. (5) yields the following isotherm relation for equivalent fraction of ion 1 as a function of c_1 as

$$s_1 = \frac{K_{12}\, c_1}{1 + (K_{12} - 1)\, c_1} \qquad (6)$$

and c_1 relative concentration (dimensionless) and C_T (mmol$_c$ L^{-1}) represents the total solution concentration,

$$c_i = \frac{C_i}{C_T} \qquad and \qquad C_T = \sum_i C_i \qquad (7)$$

The respective isotherm equation for ion 2 (i.e., s_2 versus c_2) can be easily deduced.

Input Data File

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

   a. Manual entry by filling out the template provided below.

   b. As an external ASII file (,dat or txt).

A sample of the input data file referred as ION-EXCHANGE-IPUT.DAT and is given in INPUTFILES folder to be downloaded by the user. In thhe example given here ion 1 is being replaced by a pulse of ion 2. The transport of the two ions are shown by the effluent results of concentration versus pore volume (time) shown in the plot below.

Template for the ION-EXCHANGE model

Model selected is ION_EXCH

Title: | ION EXCHANGE TRANSPORT (SEE FIG 11 OF ZHOU AND SELIM 2001.SSSAJ 65:1056-1064)

Input parameters

WATER FLUX, CM/DAY (WFLX)	5.625
INITIAL CONCENTRATION OF ION 1, REL. (CI)	1.0
CONCENTRATION OF ION 1 IN PULSE, REL. (CS)	0.0
CONC. OF ION 1 AFTER PULSE, REL. (CA)	1.0
TOTAL CONCENTRATION OF IONS IN SOLUTION, MEQ/L (CT)	0.05
TOTAL TIME LENGTH OF SIMULATION, DAYS (TTOTAL)	40.0
PULSE DURATION, DAYS (TPULSE)	18.0
PRINT OUT TIME INTERVAL, DAYS (TPRINT)	0.5
INITIAL TIME STEP INTERVAL, DAYS (DT)	0.025
INITIAL DEPTH INTERVAL, CM (DX)	0.25
NUMBER OF SOIL LAYERS (NX)	2
NUMBER OF ITERATIONS DESIRED (IT)	1
INPUT DATA FOR LAYER 1	
SOIL THICKNESS, CM (CL)	7.500
SOIL WATER CONTENT, CM3/CM3 (TH)	0.486
SOIL BULK DENSITY, G/CM3 (ROU)	1.365
DISPERSION COEFFICIENT, CM2/DAY (D)	40.00
CATION EXCHANGE CAPACITY, MEQ/G (CEC)	0.000
SELECTIVITY COEFFICIENT (K12)	0.1950
INPUT DATA FOR LAYER 2	
SOIL THICKNESS, CM (CL)	7.500
SOIL WATER CONTENT, CM3/CM3 (TH)	0.375
SOIL BULK DENSITY, G/CM3 (ROU)	1.414
DISPERSION COEFFICIENT, CM2/DAY (D)	40.0
CATION EXCHANGE CAPACITY, MEQ/G (CEC)	0.000
SELECTIVITY COEFFICIENT (K12)	0.1950
INPUT DATA FOR LAYER 2	
SOIL THICKNESS, CM (CL)	7.500
SOIL WATER CONTENT, CM3/CM3 (TH)	0.375
SOIL BULK DENSITY, G/CM3 (ROU)	1.414
DISPERSION COEFFICIENT, CM2/DAY (D)	40.0
CATION EXCHANGE CAPACITY, MEQ/G (CEC)	0.2100
SELECTIVITY COEFFICIENT (K12)	0.195

OK

IONEXCH Simulation
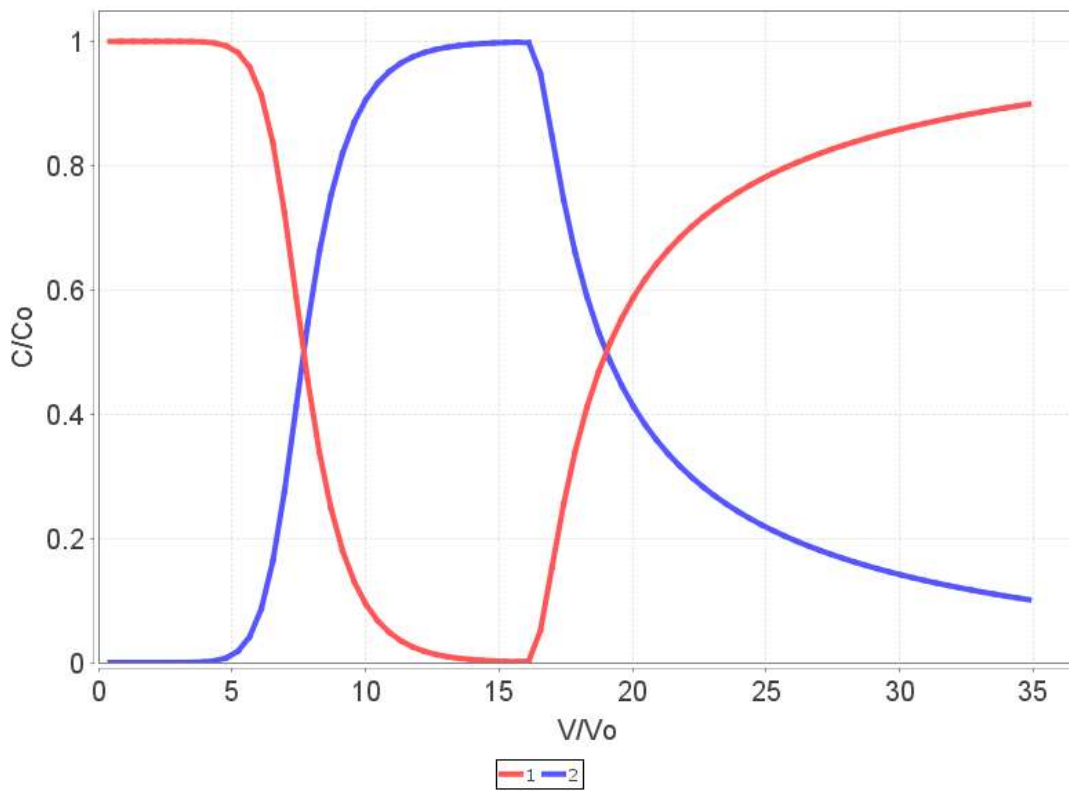
5. Solute Transport Model in Mixed Media (MRTM-MIXED)

The transport model is similar to the MRTM described above except that the transport of a reactive solute is taking place in mixed soil systems. A mixed system consists of two or more porous media, where each medium has distinct physical and chemical properties. When two media are mixed and the resultant properties depend on the relative proportion of each medium in the mixed matrix as well as the properties of each medium. This model also accounts for flow interruption or stop flow. When stop flow takes place, diffusion becomes the dominant process during such time.

The multireaction and transport model MRTM was assumed for the mixed media model. The model accounts for equilibrium and kinetic reactions of both the reversible and irreversible types. The model used in this analysis can be presented in the following formulations:

$$\frac{\rho}{\theta}\frac{\partial S}{\partial t} + \frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z}$$

$$S_e = K_e\left(\frac{\theta}{\rho}\right)C^n$$

$$\frac{\partial S_k}{\partial t} = k_1(\frac{\theta}{\rho})C^n - (k_2 + k_3)S_k$$

$$\frac{\partial S_i}{\partial t} = k_3 S_k$$

Here C is the concentration in solution (mg L^{-1}), S_e is the amount retained on equilibrium sites (mg kg^{-1}), S_k is the amount retained on kinetic type sites (mg kg^{-1}), S_i is the amount retained irreversibly (mg kg^{-1}). Moreover, K_e is a dimensionless equilibrium constant, k_1 and k_2 (h^{-1}) are the forward and backward reaction rate associated with kinetic sites, respectively, k_3 (h^{-1}) is the irreversible rate coefficient associate with the kinetic sites, n is the dimensionless reaction order, θ is the soil water content (cm^3 cm^{-3}), ρ is the soil bulk density (g cm^{-3}), and t is the reaction time (h). At any time t, the total amount of a chemical retained on all sites is:

$$S_T = S_e + S_k + S_i$$

We now extend MRTM formulation to a mixed soil system where two or more geologic media or soil where each medium is having distinct physical, chemical, and microbiological properties

(see Figure 12). Such parameters include θ the soil water content $(\text{cm}^3 \text{ cm}^{-3})$, ρ is the soil bulk density (g cm^{-3}), soil-hydraulic conductivity, and soil-water and solute retention parameters. If one assumes that each medium competes concurrently for retention sites for a specific ion species present in the solution phase, S_T can thus be expressed as;

$$S_T = f_1 S_{T1} + f_2 S_{T2} + f_3 S_{T3} + ... + f_m S_{Tm}$$

Here S_{T1}, S_{T1}, S_{T1}, S_{T1}, and S_{Tm} represent the sorption capacity for geologic medium 1, 2, 3, and n, respectively. For simplicity, we assume the mixed system is composed of n-medium and the dimensionless parameter f (omitting subscripts) represents the fraction of medium 1, 2, 3, etc., to that of the entire mixed medium (on mass per unit bulk volume basis). This parameter is necessary in order to account for the proportion of each geologic medium per unit bulk volume of the mixed soil system.

Based on MRTM formulation, we can express S_T for each respective medium such that for medium 1, we have

$$S_{T1} = S_{e1} + S_{k1} + S_{i1}$$

And the respective S_T for the m-th medium can expressed as

$$S_{Tm} = S_{em} + S_{km} + S_{im}$$

Consequently, the amounts sorbed by the equilibrium sites of the much and the soils are

$$S_e = \sum_{l=1}^{m} f_l \, [S_e]_l$$

Or more explicitly we have

$$S_e = \sum_{l=1}^{m} f_l [K_e]_l \left(\frac{\theta_l}{\rho_l} \right) C^{[n]_l}$$

Similarly, the amounts of solute adsorbed by the kinetic sites of both compartments are:

$$S_k = \sum_{l=1}^{m} f_l \, [S_k]_l$$

where

$$\frac{\partial [S_k]_r}{\partial t} = \sum_{l=1}^{m} f_l [k_1]_l \left(\frac{\theta_l}{\rho_l} \right) C^{[n]_l} - ([k_2]_l + [k_3]_l) \, [S_k]_l$$

In addition, the corresponding irreversible reactions are:

$$\frac{\partial S_{irr}}{\partial t} = \sum_{l=1}^{m} f_l [k_3]_l [S_k]_l$$

The above formulation was incorporated into the convective-dispersive equation (CDE) was solved subject to the following initial and boundary (third type) conditions:

$$C = 0 \qquad t = 0 \qquad 0 < x < L$$

$$S_e = S_k = S_{irr} = 0 \qquad t = 0 \qquad 0 < x < L$$

$$vC_o = -D \frac{\partial C}{\partial x} + vC \qquad x = 0 \qquad t \leq t_p$$

$$0 = -D \frac{\partial C}{\partial x} + vC \qquad x = 0 \qquad t > t_p$$

$$\frac{\partial C}{\partial x} = 0 \qquad x = L \qquad t > 0$$

where t_p is the duration of applied atrazine pulse (hour), L is column length (cm), C_o is atrazine concentration in applied pulse (µg/mL). The CDE can be solved using numerically of the implicit-explicit finite difference approximation.

Input and Output Data File

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

       a. Manual entry by filling out the template provided below.

       b. As an external ASII file (,dat or txt).

A sample of the input data file referred as CMRTM-FIT-IPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. For a given initial concentration (Ci) and input concentration (Cs) at time t > 0, the model provides results of concentration, the amount sorbed versus time. Measured data are indicated by various symbols and continuous curves are model calculations. Model output is given in txt format and must be named and saved by the user. Graphics of simulations and experimental measurements are also generated which can be saved by the user. The model deals with only two competitive ions simultaneously and carries out all mass calculations for a batch experiment and thus requires a complete accounting of the weights of the soil and solution (added as well as decanted) at each time step. For each input concentration (Co) for each ion, the model requires the weight of the soil and the solution, the weight of decanted solution, and experimental measured final concentration (C_f) for each time step. Moreover, the number of time steps and depth increments must be given. The user must

provide values for all model parameters. If a process is not to be considered, the associated rate coefficient(s) must be set equals to zero. Parameters that estimates are being sought must be identified (by choosing 1) and their initial estimates must be given. The model will carry out nonlinear-least approximation for the entire data set, that is all initial concentrations versus time and are thus represent overall parameter fit. A user may wish to test the capability of the model for only one input concentration versus time and thus compare individual versus overall fitting. In the example presented here miscible displacement of a solute pulse in a mixed media made up of a mixture of two soils. Miscible displacement of a solute pulse in a mixed medium made up of a mixture of two soils is considered. Solute retention properties of soil A include irreversible, nonlinear kinetic, and nonlinear equilibrium reactions. Soil A was considered reactive and soil B wss considered as nonreactive. The effluenece of the fraction of soil (on a mass basis) is depicted by f where f values selected were f =0, 0.25, 0.5, 0.75, and 1. The BTC on the far right is for a fully reactive medium (f=1.0) whereas the one onthe right is a fully nonreactive matrix.

Template for the MRTM-MIXED model

Model selected is MRTM_MIXED

Title: R. MIXED MEDIA (2-COMPARTMENS) SENSITIVITYANALY (SEE. FIG 9-15 SELIM 2015)   NUMBER OF CASES   6

Input parameters	Case 1	Case 2	Case 3 ADD CASE
MOISTURE CONTENT,CM3/CM3 (TH)	0.400E00	0.400E00	0.400E00
BULK DENSITY,G/CM3 (ROU)	1.250E00	1.250E00	1.250E00
COLUMN LENGTH,CM (COL.)	10.000E00	10.000E00	10.000E00
WATER FLUX,CM/DAY (WFLX)	1.000E00	1.000E00	1.000E00
INITIAL CONCENTRATION,PPM (CI)	0.000E00	0.000E00	0.000E00
CONCEN.IN INPUT PULSE,PPM (CS)	10.000E00	10.000E00	10.000E00
DISPERSION COEFFICIENT,D,CM2/HOUR (D)	1.000E00	1.000E00	1.000E00
DISTRIB. COEFF. FOR EQL. SORP,CM3/G (KD)	1.000E00	1.000E00	1.000E00
NONLINEAR PARAM.FOR EQUL. MECH. (NEQ)	0.7500E00	0.7500E00	0.7500E00
FORWARD RATE REACTION, K1,HR-1 (K1)	0.100E00	0.100E00	0.100E00
BACKWARD RATE REACTION, K2,HR-1 (K2)	0.0100E00	0.0100E00	0.0100E00
NONLINEAR KINETIC PARAMETER , W, (W)	0.500E00	0.500E00	0.500E00
FORWARD RATE REACTION, K3,HR-1 (K3)	0.000E00	0.000E00	0.000E00
BACKWARD RATE REACTION, K4,HR-1 (K4)	0.000E00	0.000E00	0.000E00
NONLINEAR KINETIC PARAMETER , U, (U)	0.500E00	0.500E00	0.500E00
FORWARD RATE REACTION, K5,HR-1 (K5)	0.000E00	0.000E00	0.000E00
BACKWARD RATE REACTION, K6,HR-1 (K6)	0.000E00	0.000E00	0.000E00
IRREVERSIBLE REACTION RATE,KS,HR-1 (KS)	0.000E00	0.000E00	0.000E00
NUMBER OF ITERATIONS IF B IS NOT 1.0 (IT)	000	000	000
INPUT PULSE DURATION, PORE VOL. (VPULSE)	1.000	1.000	1.000
TOTAL SIMULATION TIME,PORE VOL. (VTOTAL)	7.0000	7.0000	7.0000
PRINTOUT TIME DESIRED,PORE VOL. (VPRINT)	0.20000	0.20000	0.20000
INCREMENTAL TIME STEP, DAYS (DT)	0.02000	0.02000	0.02000
INCREMENTAL DISTANCE, CM (DZ)	0.2500E00	0.2500E00	0.2500E00
DIFFUSION IN WATER (BR 0.052) (DW)	0.084E00	0.084E00	0.084E00
TORTOUSITY COEFFICIENT (LESS THAN 1) (TAU)	0.700E00	0.700E00	0.700E00
NUMBER OF STOP FLOWS OR INTERRUPTONS (NS)	001	001	001
INITIATION OF STOP FLOW #1, P.V. (VSTOPF)	14.0000	14.0000	14.0000
DURATION OF STOP FLOW #1, DAYS (STOPDURA)	2.000	2.000	2.000

OK

MRTM_MIX Simulation
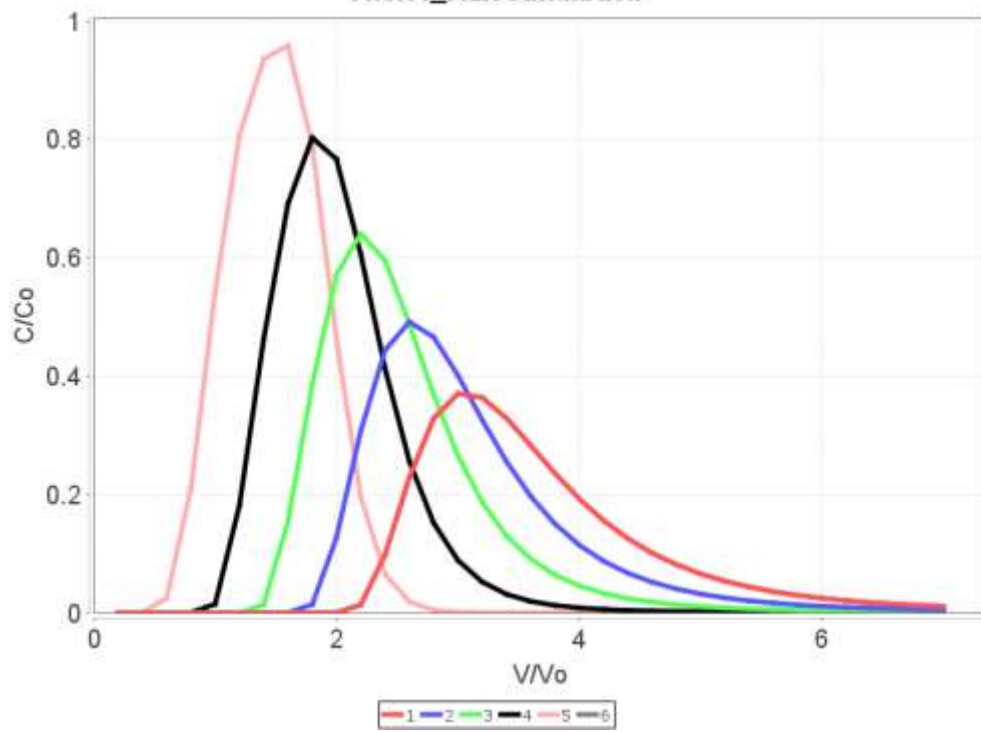
Model for Tracer Transport (TRACER)

This model is a special case for describing the transport of tracer solutes such as tritium, bromide, etc. Here a retardation factor is the only reaction mechanism. The transport is the mobile-immobile approach. The model also accounts for flow interruption or stop flow during such time diffusion becomes the dominant process. Reactive solutes based on the mobile-immobile approach assumes that the soil matrix is dynamic and stagnant soil regions in the soil as a continuum, and connected to one another. Moreover, the water content (θ) is divided into two fractions, a mobile fractions θ^m and an immobile soil water fraction θ^{im}. The immobile fraction may be considered, for transport purposes, to be stagnant and residing in the intra-aggregate domain, or within the micropores of the matrix.

The general mobile-immobile formulation for the convective-dispersive transport of reactive solutes may be expressed as,

$$\Theta^m \frac{\partial C^m}{\partial t} + f\rho \frac{\partial S^m}{\partial t} = \Theta^m D \frac{\partial^2 C^m}{\partial x^2} - v^m \Theta^m \frac{\partial C^m}{\partial x} - \alpha\,(\,C^m - C^{im}\,)$$

and:

$$\Theta^{im}\frac{\partial C^{im}}{\partial t} + (1 - f\,)\rho \frac{\partial S^{im}}{\partial t} = \alpha(\,C^m - C^{im}) \qquad (4)$$

Here the terms C^m and C^{im} are the concentrations in the mobile and immobile water ($\mu g\ cm^{-3}$), and v^m is the average pore-water velocity in the mobile region ($cm\ h^{-1}$). Similarly, the terms S^m and S^{im} refer to the amount sorbed by the dynamic and stagnant regions, respectively, and f is the fraction of the dynamic sites. The term α is a mass transfer coefficient (h^{-1}) which governs the transfer of solutes between the mobile- and immobile-water phases in analogous manner to a diffusion process.

When equilibrium conditions are assumed and linear adsorption to govern the retention of a reactive solute, the transport equations become,

$$R^m \frac{\partial C^m}{\partial t} = D\frac{\partial^2 C^m}{\partial x^2} - v^m \frac{\partial C^m}{\partial x} - \frac{\alpha}{\theta}(\,C^m - C^{im}\,)$$

$$R^{im}\frac{\partial C^{im}}{\partial t} = \frac{\alpha}{\theta}(\,C^m - C^{im}\,)$$

where

$$R^m = 1 + K_d\, f\, \frac{\rho}{\theta^m} \qquad\qquad and \qquad\qquad R^{im} = 1 + K_d\,(1 - f\,)\frac{\rho}{\theta^{im}}$$

where R^m and R^{im} as know as the retardation factors associated with the dynamic and stagnant regions, respectively. The term K_d is the distribution coefficient describing linear sorption between solute in solution and that sorbed by matrix surfaces $(S = K_d \, C)$.

Initial and Boundary Conditions:

The corresponding initial and boundary conditions associated with the second-order mobile-immobile model can be expressed as

$$C^m = C^{im} = C_i \qquad\qquad (t = 0, 0 < x < L) \qquad\qquad (47)$$

$$S^m = S^{im} = S_i \qquad\qquad (t = 0, 0 < x < L) \qquad\qquad (48)$$

$$v\,C_o = vC^m - \Theta^m D \frac{\partial C^m}{\partial x} \qquad\qquad (x = 0, t < t_p) \qquad\qquad (49)$$

$$0 = vC^m - \Theta^m D \frac{\partial C^m}{\partial x} \qquad\qquad (x = 0, t > t_p) \qquad\qquad (50)$$

$$\frac{\partial C^m}{\partial x} = 0 \qquad\qquad (x = L, t \geq 0) \qquad\qquad (51)$$

These conditions are similar to those described earlier for the transport of a solute pulse (input) in a uniform soil having a finite length L where a steady water flux v was maintained constant. The soil column is considered as having uniform retention properties as well as having uniform ρ and θ. It is further assumed that equilibrium conditions exist between the solute present in the soil solution of the mobile water phase (i.e. interaggregate) and that present in the immobile (or intera-aggregate) phase. During flow interruption or stop flow, the convective-dispersive transport reduces to that of the diffusion equation.

Input Data File

An input file must be provided by the user for the selected model. The input model specifies initial and boundary conditions and can be provided in two different ways:

a. Manual entry by filling out the template provided below.

b. As an external ASII file (,dat or txt).

A sample of the input data file referred as TRACER-INPUT.DAT and is given in the INPUTFILES folder to be downloaded by the user. Samples of input files in a template format are included in this package. Model output is given in txt format and must be named and saved by the user. Graphics of simulations are also generated which can be saved by the user. The example given

here is based on experimental data of Reedy et al. (1996) where a bromide pulse was introduced in a small column of fractured saprolite and subject to six flow interruptions. The purpose was to assess the extent of physical nonequilibrium in this material.

Reedy, O.C., P.M. Jardine, G.V. Wilson, and H.M. Selim. 1996. Quantifying the diffusive mass transfer of nonreactive solutes in columns of fractured saprolite using flow interruption. Soil Sci. Soc. Am. J. 60:1376-1384.

Template for the TRACER model

Model selected is TRACER

Title | R-MOBILE IMMOBILE IN SOIL OR FRACTURED MEDIA WITH FLOW INTERRUPTIONS (

Input parameters

Parameter	Value
MOISTURE CONTENT,CM3/CM3 (TH)	0.150E00
BULK DENSITY,G/CM3 (ROU)	2.400E00
COLUMN LENGTH,CM (COL)	40.60000
WATER FLUX,CM/DAY (WFLX)	0.8519E00
INITIAL CONCENTRATION,PPM (CI)	0.000E00
CONCEN.IN INPUT PULSE,PPM (CS)	1.000E00
DISPERSION COEFFICIENT,CM2/DAY (DS)	200.00000
DIFFUSION IN WATER (DW)	0.29520
TORTOUSITY COEFFICIENT (LESS THAN 1) (TAU)	0.500E00
FRACTION OF MOBILE WATER, WF (WF)	0.050E00
RETARDATION FACTOR, RF (RF)	5.0000
TRANSFER COEFFICIENT, TR, DAY-1 (TR)	0.01000
INPUT PULSE DURATION, PORE VOL. (VPULSE)	2.88350
TOTAL SIMULATION TIME,PORE VOL. (VTOTAL)	6.00000
PRINTOUT TIME DESIRED,PORE VOL. (VPRINT)	0.05000
INCREMENTAL TIME STEP, DAYS (DT)	0.10000
INCREMENTAL DISTANCE, CM (DZ)	1.000E00
NUMBER OF STOP FLOWS OR INTERRUPTONS (NS)	006
INITIATION OF STOP FLOW #1, P.V. (VSTOPF)	0.48580
DURATION OF STOP FLOW #1, DAYS (STOPDURA)	1.16300
INITIATION OF STOP FLOW #2, P.V. (VSTOPF)	1.07000
DURATION OF STOP FLOW #2, DAYS (STOPDURA)	2.78100
INITIATION OF STOP FLOW #3, P.V. (VSTOPF)	1.93130
DURATION OF STOP FLOW #3, DAYS (STOPDURA)	6.94800
INITIATION OF STOP FLOW #4, P.V. (VSTOPF)	2.88350
DURATION OF STOP FLOW #1, DAYS (STOPDURA)	1.16300
INITIATION OF STOP FLOW #2, P.V. (VSTOPF)	1.07000
DURATION OF STOP FLOW #2, DAYS (STOPDURA)	2.78100
INITIATION OF STOP FLOW #3, P.V. (VSTOPF)	1.93130
DURATION OF STOP FLOW #3, DAYS (STOPDURA)	6.94800
INITIATION OF STOP FLOW #4, P.V. (VSTOPF)	2.88350
DURATION OF STOP FLOW #4, DAYS (STOPDURA)	16.1560
INITIATION OF STOP FLOW #5, P.V. (VSTOPF)	3.50170
DURATION OF STOP FLOW #5, DAYS (STOPDURA)	0.96180
INITIATION OF STOP FLOW #5, P.V. (VSTOPF)	4.79250
DURATION OF STOP FLOW #5, DAYS (STOPDURA)	105.0000

OK

TRACER Simulation