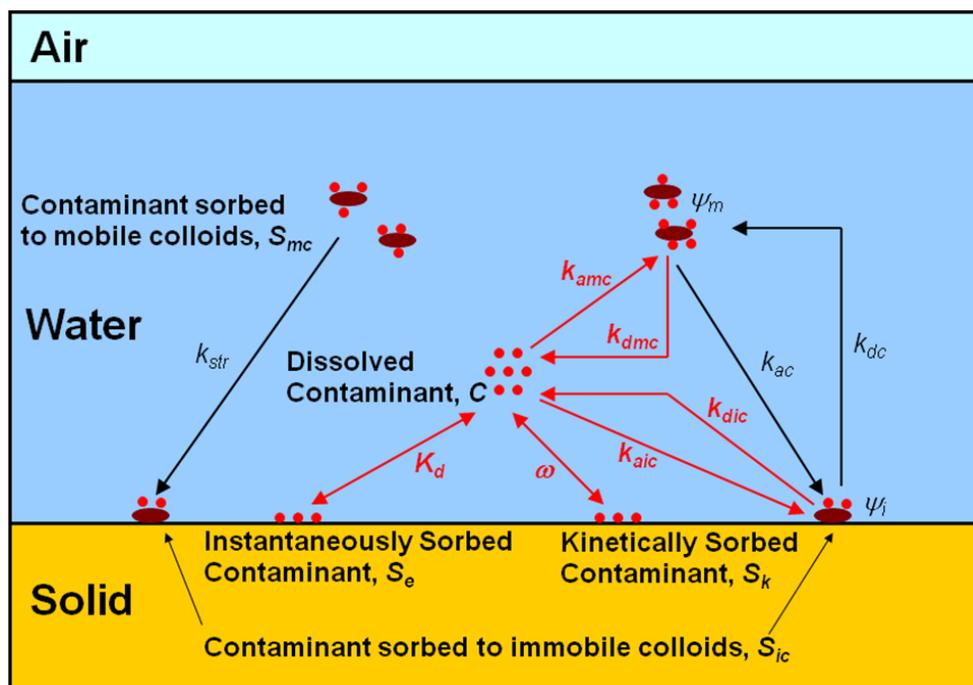# The C-Ride Module

for HYDRUS

Simulating One- and Two-Dimensional Colloid-Facilitated Solute Transport in Variably-Saturated Porous Media

Version 2.0

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Abstract

Šimůnek, J., M. Šejna, and M. Th. van Genuchten, The C-Ride Module for HYDRUS Simulating One- and Two-Dimensional Colloid-Facilitated Solute Transport in Variably-Saturated Porous Media, Version 2.0, PC Progress, Prague, Czech Republic, 47 pp., 2022.

Strongly sorbing contaminants (e.g., heavy metals, radionuclides, pharmaceuticals, pesticides, and explosives) in porous media are associated predominantly with the solid phase, which is commonly assumed to be stationary. However, recent field- and laboratory-scale observations have shown that mobile colloidal particles (e.g., microbes, humic substances, suspended clay particles, and metal oxides) can act as pollutant carriers and thus provide a rapid transport pathway for strongly sorbing contaminants. To address this problem, we have developed a two-dimensional numerical module **C-Ride** for the **HYDRUS** software package that incorporates various processes associated with colloid and **C**olloid-**F**acilitated **S**olute **T**ransport (**CFSTr**) in variably-saturated porous media. The model accounts for transient variably-saturated water flow, and for both colloid and solute movement due to advection, diffusion, and dispersion, as well as for solute movement facilitated by colloid transport. The colloid transport module additionally considers the processes of attachment/detachment to/from the solid phase and straining. Various blocking and depth-dependent functions can be used to modify the attachment and straining coefficients. The solute transport module uses the concept of two-site sorption to describe nonequilibrium adsorption-desorption reactions to the solid phase. The module further assumes that contaminants can be sorbed onto surfaces of both deposited and mobile colloids, thus fully accounting for the dynamics of colloid transfer between different phases. Applications of the model are demonstrated using several test examples.

The purpose of this report is to document the **C-Ride** module for the **HYDRUS** software package [*Šimůnek et al.*, 2011; *Šejna et al.*, 2011] simulating two-dimensional variably-saturated water flow, colloid transport, and colloid-facilitated solute transport in porous media. The module, as well as the description of the module in this report, is largely based on the theoretical development of *Šimůnek et al.* [2006]. The report serves as both a **Technical Manual** and a **User Manual**, as well as a reference document of the **Graphical User Interface** of **C-Ride**-related parts of the **HYDRUS** software package.

DISCLAIMER

The C-Ride module was developed as a supplemental module of the HYDRUS (2D/3D) software package to simulate the transport and reactions of colloid and colloid-facilitated transport in soils and ground water. The software has been verified against selected test cases. However, no warranty is given that the program is completely error-free. If you do encounter problems with the code, find errors, or have suggestions for improvement, please contact the senior author at

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1. Introduction

Colloidal particles (e.g., humic substances, suspended clay particles, metal oxides, and microorganisms) are commonly found in subsurface environments [*Kretzschmar et al*., 1999]. Many contaminants can sorb onto colloids in suspension, thereby increasing their concentrations in solution beyond thermodynamic solubilities [*Kim et al*., 1992]. Experimental evidence now exists that many contaminants are transported not only in a dissolved state by water, but also sorbed to moving colloids. This colloid-facilitated transport has been illustrated in the literature for numerous contaminants, including heavy metals [*Grolimund et al*., 1996; *Šimůnek et al*., 2006], radionuclides [*Von Gunten et al*., 1988; *Noell et al*., 1998], pesticides [*Vinten et al*., 1983; *Kan and Tomson*, 1990; *Lindqvist and Enfield*, 1992], pharmaceuticals [*Tolls*, 2001; *Thiele-Bruhn*, 2003], hormones [*Hanselman et al*., 2003], and other contaminants [*Magee et al*., 1991; *Mansfeldt et al*., 2004]. Since mobile colloids often move at rates similar or faster as non-sorbing tracers, the potential of enhanced transport of colloid-associated contaminants can be very significant (e.g., *McCarthy and Zachara*, 1989). Failure to account for colloid-facilitated solute transport can severely underestimate the transport potential and risk assessment for these contaminants. Models that can accurately describe the various mechanisms controlling colloid and solute transport, and their mutual interactions and interactions with the solid phase, are essential for improving predictions of colloid-facilitated transport of solutes in variably saturated porous media.

The transport behavior of dissolved contaminant species has been studied for many years. By comparison, colloid transport and the many interactions among contaminants, colloids, and porous media are less well understood. While colloids are subject to similar subsurface fate and transport processes as chemical compounds, they are also subject to their own unique complexities [*van Genuchten and Šimůnek*, 2004; *Flury and Qiu*, 2008]. Since many colloids and microbes are negatively charged, they are electrostatically repelled by negatively-charged solid surfaces. This will lead to an anion exclusion process that can cause slightly enhanced transport relative to fluid flow. The advective transport of colloids may similarly be enhanced by size exclusion, limiting their presence to the larger pores [*Bradford et al*., 2003, 2006]. In addition to being subject to adsorption-desorption at solid surfaces, colloids are also affected by straining [*Bradford et al*., 2003, 2006] and may accumulate at air-water interfaces [*Wan and Wilson*, 1994; *Thompson and Yates*, 1999; *Wan and Tokunaga*, 2002; *Crist et al*., 2005; *Torkzaban et al.,* 2008; *Lazouskaya et al*., 2011]. All of these complexities require colloid transport models to be more flexible than regular solute transport models.

Models that consider colloid-facilitated transport are based upon mass balance equations for all colloid and contaminant species. The various colloid-facilitated transport models that have appeared in the literature differ primarily in how colloid transport and contaminant interactions are implemented. For example, *Mills et al*. [1991] and *Dunnivant et al*. [1992] assume that colloids are non-reactive with the solid phase, *Corapcioglu and Jiang* [1993] and *Jiang and Corapcioglu* [1993] consider a first-order kinetic attachment of colloids, *Saiers and Hornberger* [1996] assume irreversible nonlinear kinetic attachment of colloids, and *van de Weerd and Leijnse* [1997] describe colloid attachment kinetics using the Langmuir equation. All colloid-facilitated transport models account for interactions between the contaminants and colloids. Various equilibrium and kinetic models have been used for this purpose.

Although already relatively complex, no existing model for colloid-facilitated contaminant transport to our knowledge includes all of the major processes contributing to colloid and colloid-facilitated transport. For example, most models for colloid-facilitated transport consider flow and transport only in fully saturated groundwater systems, usually for steady-state flow, and thus do not account for colloid interactions with the air-water interface. Also, no colloid-facilitated transport model has considered straining and size exclusion as mechanisms of colloid retention and transport, respectively. These two processes, and especially straining, have recently received much attention since classical colloid transport models are often unable to describe simultaneously both breakthrough curves versus time and concentration profiles versus depth [*Bradford et al*., 2003, 2006; *Li et al*., 2004; *Tufenkji and Elimelech*, 2005].

Straining involves the entrapment of colloids at grain-grain contact points, surface roughness locations, and in down-gradient pores that are too small to allow particle passage. The critical pore size for straining will depend on the size of the colloid and the pore-size distribution of the medium [*McDowell-Boyer et al.*, 1986; *Bradford et al*., 2002, 2003]. Straining may have significant implications for colloid-facilitated solute transport, as illustrated by *Bradford et al.* [2006]. Considering average capillary pressure-saturation curves for the 12 major soil textural groups given by *Carsel and Parrish* [1988], they calculated that a 2 μm colloid, which is the size of a clay particle, will be excluded or strained in 10 to 86% of the soil pore space for various soil textures [*Bradford et al.*, 2006]. These percentages should significantly increase if soil becomes unsaturated.

Size exclusion, a process closely related to straining, affects the mobility of colloids by constraining them to flow domains and pore networks that are physically accessible [*Ryan and Elimelech*, 1996; *Ginn*, 2002]. Electrostatic forces also play an important role in the distribution (and mobility) of colloids. Anionic colloids will be excluded from locations adjacent to negatively charged solid surfaces; similar to the much-reported anion exclusion process for anionic solutes [*Krupp et al.*, 1972; *Gvirtzman and Gorelick*, 1991; *Ginn*, 1995]. In case of size or anion exclusion, colloids will tend to reside in larger pores and in more conductive parts of the flow domain. As a result, colloids will be transported faster than a conservative solute tracer [*Reimus*, 1995; *Cumbie and McKay*, 1999; *Harter et al*., 2000; *Bradford et al*., 2004]. Differences in the dispersive flux for colloids and a conservative solute tracer are also anticipated as a result of exclusion [*Scheibe and Wood*, 2003]. *Bradford et al*. [2002] observed that the dispersivity of 3.2 μm carboxyl latex colloids was up to 7 times greater than bromide in saturated aquifer sand. Conversely, *Sinton et al*. [2000] found in a field microbial transport experiment that the apparent colloid dispersivity decreased with increasing particle size.

Colloid and colloid-facilitated contaminant transport in partially saturated porous media is even more complex than in water-saturated systems. In addition to all of the processes and difficulties discussed above, colloid transport in partially saturated porous media is further complicated by the presence of an air phase, thin water films, and the air-water-solid contact line, in addition to the solid and water phases present in saturated media. *Wan and Wilson* [1994] observed that colloidal particles deposit preferentially on the air-water interface and that particle transport was tremendously retarded since the air-water interface acted as a strong sorption phase. Another physical restriction on colloid transport in unsaturated systems is imposed by thin water films;

this process is often referred to as film straining [*Wan and Tokunaga*, 1997; *Saiers and Lenhart*, 2003]. *Wan and Tokunaga* [1997] proposed that colloid transport in unsaturated systems depends on the ratio of colloid size to water film thickness. The air-water-solid contact line has also been recognized to significantly influence colloid retention and release [*Crist et al.*, 2004 and 2005; *Chen and Flury*, 2005]. *Corapcioglu and Choi* [1996] developed a mathematical model describing colloid transport in unsaturated porous media and also studied the effects of colloids on volatile contaminant transport and air-water partitioning in unsaturated porous media.

Most current models for colloid-facilitated transport assume that the number of colloids with respect to the contaminant is large and that kinetic reactions coefficients are not dependent on the number of colloids in the system. Although this may be true for some systems, the number of colloids (or concentrations) is often highly variable, with colloids being mobilized (or immobilized) due to changing chemical or hydrological conditions. Thus the reaction coefficients need to be adjusted to the number of colloids in the system in different phases (i.e., mobile, immobile, attached to the air-water interface). This adjustment needs to be carried out also for numerical stability reasons. For example, if the number of colloids in the system decreases dramatically and the sorption constants for the solute to colloids are assumed to be constant, this may lead to large sorbed concentrations, and hence numerical instabilities.

The main purpose of this report is to document a two-dimensional numerical module **C-Ride** that incorporates processes associated with colloid and colloid-facilitated solute transport in variably-saturated porous media. **C-Ride** (which refers to **C**olloids providing a **ride** for solutes) was developed specifically for the HYDRUS (2D/3D) software package [*Šimůnek et al.*, 2022ab; *Šejna et al.*, 2022]. The general conceptual basis of the module is discussed in a paper by *Šimůnek et al.* [2006], and restated here for multi-dimensional systems. The module accounts for both colloid and solute transport due to advection, diffusion, and dispersion in variably-saturated media, as well as for solute movement facilitated by colloid transport. The colloid transport module additionally considers the processes of attachment/detachment to/from the solid phase, straining, and/or size exclusion. The module allows for different pore water velocities and dispersivities for the colloids and the solute. However, the module does not describe all of the processes discussed above, such as attachment/detachment to the air-water interface. These processes likely will be added in future versions of the module.

The documentation in this report focuses mostly only on the colloid and colloid-facilitated transport features of the C-Ride module. All processes related to variably-saturated water flow and heat transport are described in detail in the HYDRUS documentation [*Šimůnek et al.*, 2022ab], and will not be repeated here.

The **C-Ride** module may be used to analyze one- and two-dimensional water and solute movement in unsaturated, partially saturated, or fully saturated porous media. **C-Ride** can handle flow domains delineated by irregular boundaries. The flow region itself may be composed of nonuniform soils having an arbitrary degree of local anisotropy. Flow and transport can occur in the vertical plane, the horizontal plane, or in a three-dimensional region exhibiting radial symmetry about a vertical axis. The water flow part of the model considers prescribed head and flux boundaries, as well as boundaries controlled by atmospheric conditions.

The governing flow and transport equations are solved numerically using standard Galerkin-type linear finite element schemes. The **C-Ride** module is fully supported by the HYDRUS graphical user interface [*Šejna et al.*, 2022]. Applications of the **C-Ride** module are demonstrated later in this report on several examples.

2. Conceptual Model

The conceptual model of colloid and colloid facilitated solute transport (Fig. 1) is based on several assumptions. We assume that the porous medium consists of three phases (i.e., solid phase, air, and water). Following *van der Weerd and Leijnse* [1997], we assume that (a) only one type of colloid exists in the system, and that these colloids can be described by their mean behavior, (b) colloids are stable and that their mutual interactions in the liquid phase may be neglected, (c) immobile colloids do not affect the flow and transport properties of the porous medium because of their clogging of small pores, and (d) the transport of colloids is not affected by sorption of contaminants on colloids. Colloids are assumed to exist in three states: mobile (suspended in water), attached to the solid phase, and strained by the solid phase (Fig. 1, Table 1). Colloid phase changes are described in terms of nonlinear first-order processes.
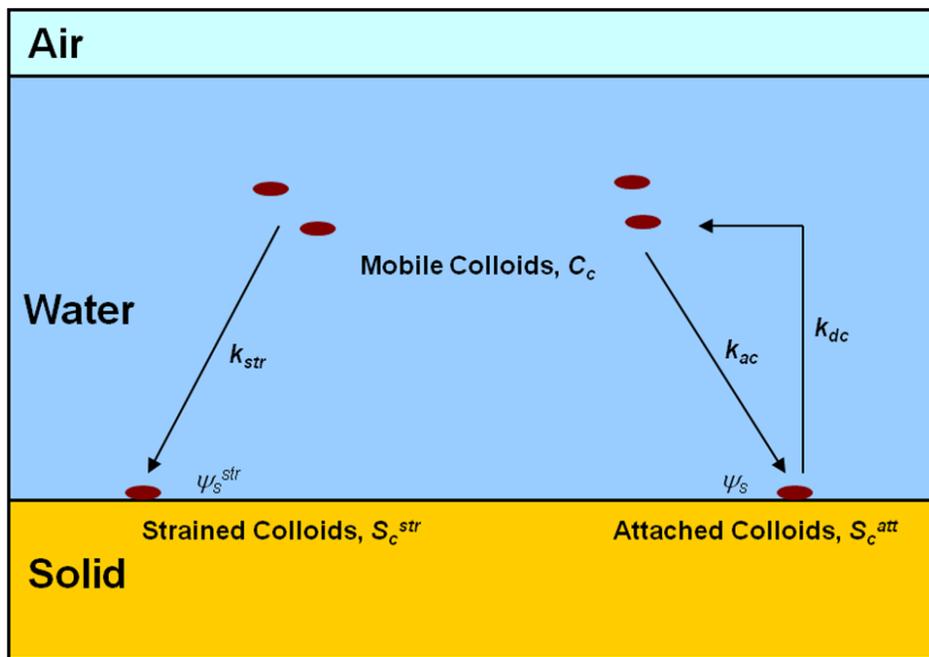
Figure 1. Schematic of the colloid transport model.

We further assume that contaminants can be dissolved in the liquid phase, as well as can be sorbed instantaneously and kinetically to the solid phase, and to colloids in all of their states. We thus distinguish six different states of contaminants (Fig. 2; Table 1): dissolved, instantaneously or kinetically sorbed to the solid phase, and sorbed to mobile or immobile colloids (the latter either strained or attached to the solid phase). The coefficients k in Figures 1 and 2 (Table 2) represent various first-order attachment/detachment or sorption/desorption rates, the coefficients K_d and ω represent instantaneous and kinetic solute sorption to the solid phase, respectively, while the factors ψ account for nonlinearity of various processes.

Table 1. Species considered in the colloid and colloid-facilitated solute transport model (L is the length unit, M is the mass unit, and n is the number of colloids).

Species description	Variable	Units
Colloid species		
Mobile colloids	C_c	nL^{-3}
Colloids attached to the solid phase	S_c^{att}, S_{c1}	nM^{-1}
Strained colloids	S_c^{str}, S_{c2}	nM^{-1}
Solute (contaminant) species		
Dissolved contaminant	C	ML^{-3}
Contaminant instantaneously sorbed to the solid phase	S_e	MM^{-1}
Contaminant kinetically sorbed to the solid phase	S_k	MM^{-1}
Contaminant sorbed to mobile colloids	S_{mc}	Mn^{-1}
Contaminant sorbed to immobile colloids (attached)	S_{ic1}	Mn^{-1}
Contaminant sorbed to immobile colloids (strained)	S_{ic2}	Mn^{-1}
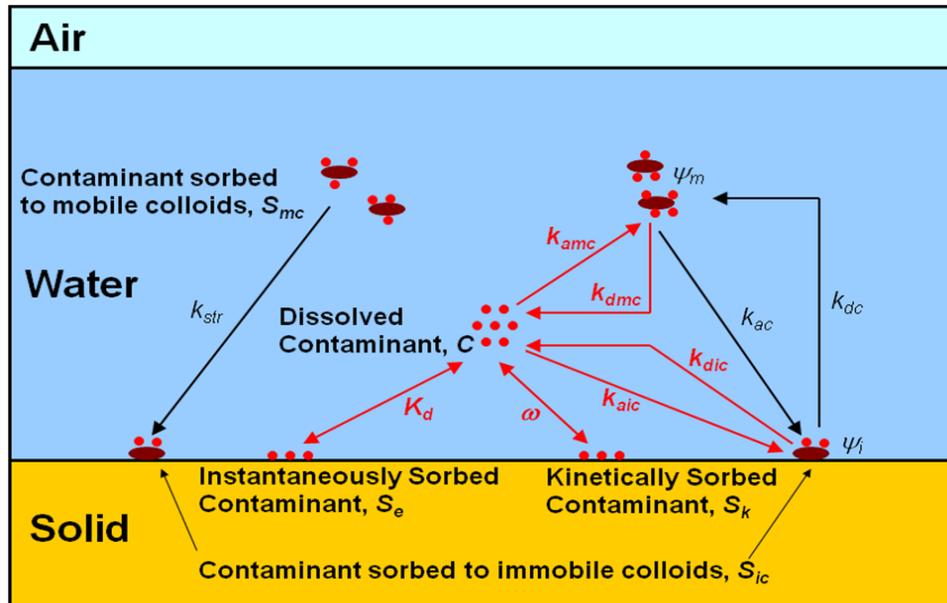
Figure 2. Schematic of the colloid-facilitated solute transport model.

Table 2. Kinetic reactions considered in the colloid and colloid-facilitated solute transport model (T is the time unit).

Reaction description	Variable	Units
Colloid species		
Colloids attachment coefficient	k_{ac}	T^{-1}
Colloids detachment coefficient	k_{dc}	T^{-1}
Colloids straining coefficient	k_{str}	T^{-1}
Solute (contaminant) species		
Solute adsorption rate to mobile colloids	k_{amc}	T^{-1}
Solute desorption rate from mobile colloids	k_{dmc}	T^{-1}
Solute adsorption rate to immobile colloids	k_{aic}	T^{-1}
Solute desorption rate from immobile colloids	k_{dic}	T^{-1}
Solute sorption rate to the solid phase (soil)	ω	T^{-1}

3. Colloid Transport

3.1. *Colloid Transport Equation*

Colloid fate and transport models are commonly based on the advection-dispersion equation, but modified to account for colloid filtration [*Harvey and Garabedian*, 1991; *Hornberger et al.*, 1992; *Corapcioglu and Choi*, 1996; *Bradford et al.*, 2003]. A very general equation for colloid transport describing colloid/matrix mass partitioning in multi-dimensional form is given by:

$$\frac{\partial \theta_c C_c}{\partial t} + \rho \frac{\partial S_{c1}}{\partial t} + \rho \frac{\partial S_{c2}}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}^c \frac{\partial C_c}{\partial x_j}\right) - \frac{\partial q_{ic} C_c}{\partial x_i} - \mu_{cw} \theta C_c - \mu_{cs} \rho S_c \tag{1}$$

where:

C_c colloid concentration in the liquid phase (mobile colloids) [nL^{-3}]

S_c colloid concentration in the solid phase (attached, immobilized, immobile colloids; two sites are considered and there may have different interpretations; for example, S_{c1} may be represented as colloids attached to the solid phase, and S_{c2} may be represented as strained colloids) [nM^{-1}]

θ_c volumetric water content accessible to colloids [L^{3}L^{-3}] (due to ion or size exclusion, θ_c may be smaller than the total volumetric water content θ)

ρ bulk density [ML^{-3}]

q_{ic} Darcy's flux for colloids [LT^{-1}]

D_{ij}^c dispersion coefficient for colloids [L^{2}T^{-1}]

t time [T]

x_i spatial coordinate [L]

μ_{cw} colloid decay in the liquid phase [T^{-1}]

μ_{cs} colloid decay in the solid phase [T^{-1}]

The second and third terms on the left side of Eq. (1) represent the mass transfer of colloids between the aqueous and solid phase [nL^{-3}T^{-1}]. Some researchers have attributed attachment/detachment and straining mechanisms of colloid retention to sites 1 and 2, respectively (e.g., *Bradford et al.*, 2003; *Gargiulo et al.*, 2007, 2008). However, additional microscopic information is frequently needed to substantiate this assumption. Here we do not attempt to attribute specific colloid retention mechanisms to a given site without other experimental evidence. Rather, Eq. (1) is viewed as a simple and flexible approach to describe colloid breakthrough curves and retention profiles that are not exponential with depth. For example, the first kinetic site can represent reversible retention, whereas the second kinetic site can represent irreversible, depth-dependent retention.

The first two terms on the right side of Eq. (1) represent dispersive and advective colloid fluxes, respectively. The value of θ_c is defined as

$$\theta_c = \theta - \theta_{im} \tag{2}$$

where θ is the total water content [L^3L^{-3}] and θ_{im} is the water content that is not accessible to mobile colloids [-] due to size exclusion [*Bradford et al.*, 2006].

3.2. *Colloid Mass Transfer*

Colloid mass transfer between the aqueous and solid phases is traditionally described using attachment-detachment models of the form:

$$\rho \frac{\partial S_{c1}}{\partial t} = \theta_c \psi_c k_{ac} C_c - \rho k_{dc} S_{c1} - \mu_{cs} \rho S_{c1} \qquad (3)$$

where:
$\quad$ k_{ac} $\quad$ colloid deposition (attachment) coefficient [T^{-1}]
$\quad$ k_{dc} $\quad$ colloid entrainment (detachment) coefficient [T^{-1}]
$\quad$ ψ_c $\quad$ dimensionless colloid retention function or blocking coefficient

The attachment coefficient is generally calculated using filtration theory [*Logan et al.*, 1995], a quasi-empirical formulation in terms of the median grain diameter of the porous medium (often termed the collector), the pore-water velocity, and collector and collision (or sticking) efficiencies accounting for colloid removal due to diffusion, interception and gravitational sedimentation [*Rajagopalan and Tien*, 1976; *Logan et al.*, 1995; *Tufenkji and Elimelech*, 2004]. The first-order detachment coefficient in Eq. (3) accounts for colloid mobilization. While in reality, this coefficient is presumably affected by changes in pore-water chemistry (ionic strength, ionic composition, and pH) and physical perturbations in flow, including changes in the flow rate and the water content, it is an input constant in the C-Ride module.

To simulate reductions in the attachment coefficient due to filling of favorable sorption sites, ψ_c is sometimes assumed to decrease with increasing colloid mass retention. Random sequential adsorption [*Johnson and Elimelech*, 1995] and *Langmuirian dynamics* [*Adamczyk et al.*, 1994] equations have been proposed for ψ_c to describe this blocking phenomenon, with the latter equation given by:

$$\psi_c = 1 - \frac{S_{c1}}{S_{c1}^{max}} \qquad (4)$$

in which S_{c1}^{max} is the maximum solid-phase colloid concentration [nM^{-1}]. Conversely, enhanced colloid retention during porous-medium ripening can theoretically be described using a functional form of ψ_c that increases with increasing mass of retained colloids [*Tien*, 1989; and *Tien and Chiang*, 1985; *Deshpande and Shonnard*, 1999] We refer to several recent studies [*Ginn*, 2002; *DeNovio et al.*, 2004; *Rockhold et al.*, 2004] for more detailed discussions of the attachment and detachment coefficients in Eq. (3). The attachment coefficient in Eq. (3) has been found to depend strongly upon water content, with attachment significantly increasing as the water content decreases. This has been attributed to a variety of processes, including interfacial

attachment and film straining. *Bradford et al*. [2002, 2003, 2006] hypothesized that the influence of straining and attachment mechanisms on colloid retention should be separated into two distinct components: attachment and detachment per se, and straining (being the entrapment of colloids in pore throats that are too small to allow passage). They modeled the influence of straining using an irreversible first-order expression as follows:

$$\rho \frac{\partial S_{c2}}{\partial t} = \theta_c \psi_{str} k_{str} C_c \tag{5}$$

where:

k_{str} colloid straining coefficient $[T^{-1}]$

ψ_{str} dimensionless straining blocking coefficient

Application of the first-order attachment-detachment model given by Eq. (3) typically leads to exponential colloid distributions versus depth. *Bradford et al*. [2003] showed that such exponential distributions are often inconsistent with experimental data. They obtained much better results using a depth-dependent straining coefficient ψ_s^{str} in Eq. (5) of the form

$$\psi_{str} = \left(\frac{d_{50} + x}{d_{50}} \right)^{-\beta} \tag{6}$$

where d_{50} is the median grain size of the porous media $[L]$, β is a fitting parameter $[-]$, and x is distance from the porous-medium inlet $[L]$. Data from *Bradford et al*. [2002, 2003] for different colloid diameters (d_p) and porous media median grain sizes showed an optimal value of 0.43 for β, while k_{str} could be described using a unique increasing function of the ratio of d_p/d_{50}. Subsequent studies with layered soils [*Bradford et al*., 2005] showed the importance of straining at and close to textural interfaces when flow occurs in the direction of coarse-textured to medium- and fine-textured media. Straining was found to be a significant mechanism for colloid retention for values of d_p/d_{50} greater than 0.005.

4. Colloid-Facilitated Solute Transport

4.1. *Transport Equation for Colloid-Facilitated Solute Transport*

The colloid-facilitated solute transport model requires knowledge of colloid transport, dissolved contaminant transport, and colloid-facilitated transport, and of various interactions between colloids, solute, and soil. Transport and/or mass-balance equations must therefore be formulated for the total contaminant, for contaminant sorbed kinetically or instantaneously to the solid phase, and for contaminant sorbed to mobile colloids as well as to colloids attached to the soil solid phase, i.e., for contaminant in all different phases or pools.

Our colloid-facilitated transport model closely follows the formulation of many other models (e.g., *Corapcioglu and Jiang*, 1993; *Jiang and Corapcioglu*, 1993; *Saiers and Hornberger*, 1996; *van de Weerd and Leijnse*, 1997; and *Bekhit and Hassan*, 2005). New features of our model include consideration of water contents, and water and solute fluxes, that may change in time and space (i.e., transient variably-saturated water flow), and adjustment of all kinetic rates to the number of colloids present in the system.

The mass-balance equation for the total contaminant. The combined dissolved and colloid-facilitated contaminant transport equation is given by:

$$\frac{\partial \theta C}{\partial t} + \rho \frac{\partial S_e}{\partial t} + \rho \frac{\partial S_k}{\partial t} + \frac{\partial \theta_c C_c S_{mc}}{\partial t} + \rho \frac{\partial S_c S_{ic}}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij} \frac{\partial C}{\partial x_i}\right) - \frac{\partial q_i C}{\partial x_i} +$$
$$+ \frac{\partial}{\partial x_i}\left(\theta_c D_{ij}^c \frac{\partial C_c S_{mc}}{\partial x_j}\right) - \frac{\partial q_{ic} C_c S_{mc}}{\partial x_i} - R_{s1}$$

(7)

where:
   C contaminant concentration of the liquid phase [ML^{-3}]
   S_e contaminant concentration sorbed to equilibrium (type 1) sites [MM^{-1}]
   S_k contaminant concentration sorbed to kinetic (type 2) sites [MM^{-1}]
   S_{mc} contaminant concentration sorbed to mobile colloids [MM^{-1}]
   S_{ic} contaminant concentration sorbed to immobile colloids [MM^{-1}]. Note that there are two types of immobile colloids: attached (S_{ic1}) and strained (S_{ic2}) colloids
   R_{s1} reactions/degradation of a contaminant in all phases combined (dissolved, sorbed to the solid phase, and sorbed to colloids) [ML^{-3}T^{-1}]

For numerical convenience, equation (7) can be divided into two separate transport equations, one for the dissolved solute and one for the solute associated with the colloids being transported in the liquid phase. The dissolved solute transport equation is as follows

$$\frac{\partial \theta C}{\partial t} + \rho \frac{\partial S_e}{\partial t} + \rho \frac{\partial S_k}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial q_i C}{\partial x_i} - \theta k_{amc}\psi_m C - \theta k_{imc}\psi_{im}C +$$
$$+\theta_c k_{dmc}C_c S_{mc} + \rho k_{dic}S_c S_{ic} - R_{s2} \tag{8}$$

while the transport equation for solute associated with the transport of colloids is given by

$$\frac{\partial \theta_c C_c S_{mc}}{\partial t} + \rho \frac{\partial S_c S_{ic}}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta_c D_{ij}^c \frac{\partial C_c S_{mc}}{\partial x_j}\right) - \frac{\partial q_{ic}C_c S_{mc}}{\partial x_i} - \theta_c k_{dmc}C_c S_{mc} - \rho k_{dic}S_c S_{ic} +$$
$$+\theta k_{amc}\psi_m C + \theta k_{aic}\psi_{im}C - R_{s3} \tag{9}$$

which is similar to Eq. (1), but with colloid concentrations multiplied by solute concentration, augmented with the additional processes of solute adsorption/desorption from colloids (particles) and possible degradation.

In equations (8) and (9):

k_{dmc} desorption rate coefficient from mobile colloids [T^{-1}]

k_{dic} desorption rate coefficient from immobile colloids [T^{-1}]

k_{amc} adsorption rate coefficient to mobile colloids [T^{-1}]

k_{aic} adsorption rate coefficient to immobile colloids [T^{-1}]

ψ_m parameter adjusting the sorption rate to the number of mobile colloids present. k_{amc} is the optimum rate for the maximum amount of mobile colloids sorbed. If fewer colloids are present, then k_{amc} is reduced by ψ.

$$\psi_m = \frac{C_c}{C_c^{ref}}$$

C_c^{ref} reference concentration of mobile colloids for which sorption rate k_{amc} is valid [ML^{-3}]

ψ_i parameter adjusting the sorption rate to the number of immobile colloids present. k_{aic} is the optimum rate for the maximum amount of immobile colloids sorbed. If fewer colloids are present, then k_{aic} is reduced by ψ.

$$\psi_i = \frac{S_c}{S_c^{max}}$$

S_c^{ref} reference concentration of immobile colloids for which sorption rate k_{aic} is valid [-]

R_{s2} reactions/degradation of contaminant (dissolved and sorbed to solid phase) [ML^{-3}T^{-1}]

R_{s3} reactions/degradation of contaminant (sorbed to colloids) [ML^{-3}T^{-1}]

Reactions/degradation terms R_{s1}, R_{s2}, and R_{s3} from equations (7), (8), and (9) are defined as follows, respectively:

$$R_{s1} = \mu_w \theta C + \mu_s \rho f S_e + \mu_s \rho S_k + \mu_m \theta_c C_c S_{mc} + \mu_i \rho S_c S_{ic}$$
$$R_{s2} = \mu_w \theta C + \mu_s \rho f S_e + \mu_s \rho S_k \tag{10}$$
$$R_{s3} = \mu_m \theta_c C_c S_{mc} + \mu_i \rho S_c S_{ic}$$

where:

μ_w degradation rate for contaminant dissolved in the liquid phase [T^{-1}]

μ_s degradation rate for contaminant sorbed to the solid phase [T^{-1}]

μ_m degradation rate coefficient for contaminant sorbed onto mobile colloids [T^{-1}]

μ_i degradation rate coefficient for contaminant sorbed onto immobile colloids [T^{-1}]

4.2. *Solute Interactions with the Solid Phase*

Equations (7) and (8) invoke the concept of two-site sorption for modeling nonequilibrium adsorption-desorption reactions (e.g., *van Genuchten and Wagenet*, 1989). The two-site sorption concept assumes that total sorption, *S*, can be divided into two fractions:

$$S = S_e + S_k \tag{11}$$

with sorption S_e [MM^{-1}] on one fraction of the sites (type-1 sites) assumed to be instantaneous, and sorption S_k [MM^{-1}] on the remaining sites (type-2 sites) being time-dependent according to

$$\rho \frac{\partial S_k}{\partial t} = \omega \left[(1-f)\Psi(C) - S_k \right] - \mu_s S_k \tag{12}$$

where ω is the first-order rate constant [T^{-1}], *f* is the fraction of exchange sites assumed to be in equilibrium with the solution phase [-], $\Psi(C)$ is the adsorption isotherm [MM^{-1}] that can be expressed using Freundlich, Langmuir, Freundlich-Langmuir, or linear adsorption models, and R_{sk} represents various chemical and biological reactions of the kinetically sorbed contaminant [ML^{-3}T^{-1}].

4.3. *Solute Interactions with Immobile Colloids*

The mass-balance equation for contaminant sorbed to immobile colloids can be written as follows

$$\rho \frac{\partial S_c S_{ic}}{\partial t} = \theta \psi_c k_{ac} C_c S_{mc} - \rho k_{dc} S_c S_{ic} - \rho k_{dic} S_c S_{ic} + \theta k_{aic} \psi_{im} C - \mu_i \rho S_c S_{ic} \tag{13}$$

All terms have been defined above.

5. Numerical Implementation

For numerical convenience, colloid transport and colloid-facilitated solute transport is simulated by considering the transport of three different species:

a) Colloids (transport equation (1) and mass transfer equation (3))
b) Solute associated with colloids (transport equation (9) and mass transfer equation (13))
c) Solute (transport equation (8) and mass transfer equation (12))

The colloid transport is a nonequilibrium transport (since it involves kinetic processes of attachment and detachment). It can also be nonlinear when blocking functions (for attachment or straining) are considered. The same is true for a solute associated with colloids, which mirrors the transport processes of colloids. Finally, solute transport can be nonequilibrium (i.e., one can consider kinetic sorption using the two-site model, in addition to kinetic desorption from colloids). It can also be nonlinear, considering Freundlich or Langmuir isotherm.

Numerical schemes used to solve the transport equations (both linear and nonlinear) are the same as in the standard HYDRUS module. These numerical schemes are described in detail in the technical manual [*Šimůnek et al.*, 2011]. Additional details about the numerical implementation can be found in *Šimůnek et al*. [2006].

6. Preprocessing and Input Data

6.1. *Main Processes*

The **C-Ride** module is activated in the **Main Processes** window (Fig. 3) by selecting the **Solute Transport** check box and the **Colloid-Facilitated Solute Transport** radio button.
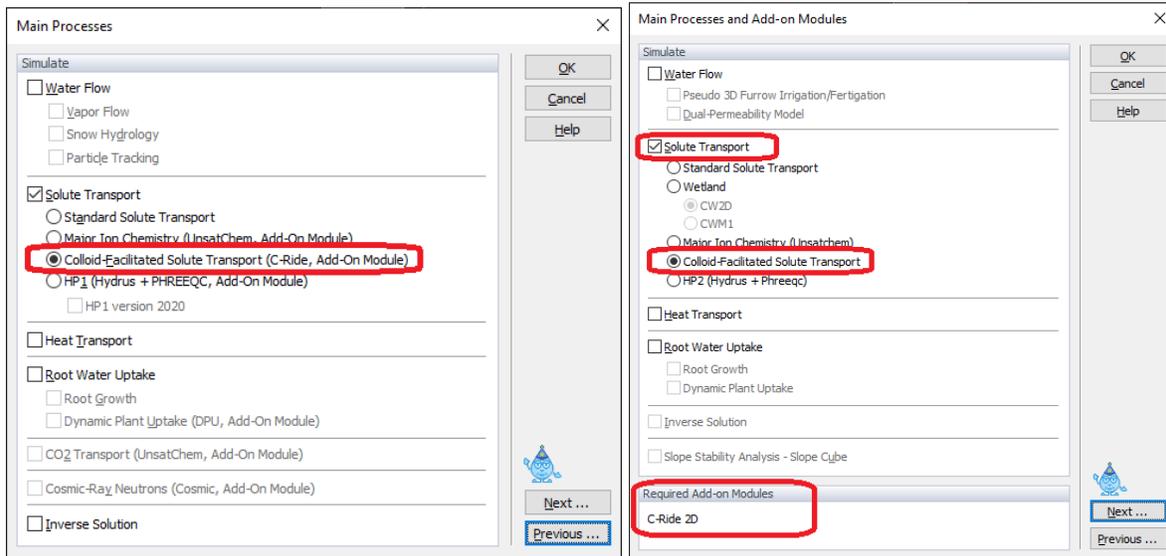

Figure 3. The Main Processes dialog window (1D – left, 2D - right).

6.2. *Solute Transport - General Information*

When the **C-Ride** module is used, basic information needed for defining the solute transport problem is entered in the **Solute Transport** dialog window displayed in Figure 4. In this window, users specify again the **Space** and **Time Weighting Scheme**s, and additional **Solute Information** such as mass units. Note that only one type of mass units can be specified here, while colloids and solute concentrations may clearly use different mass units. The text specified in this edit box is used only in texts in graphs and is not involved in any calculations, and thus it is inconsequential what is specified here. It is important that mass units used for colloids and for solute are consistent.

The "**Two Kinetic Sites Model (Particle Transport Using Attachment/Detachment, Chemical Nonequilibrium**)" or "**Attachment/Detachment Concept (Virus, Bacteria Transport**)" check box needs to be checked (in 1D and 2D, respectively) for the **C-Ride** Module to be active. Users have to set the "**Number of Solutes**" to 3 (colloids, solute attached to colloids, and solute).
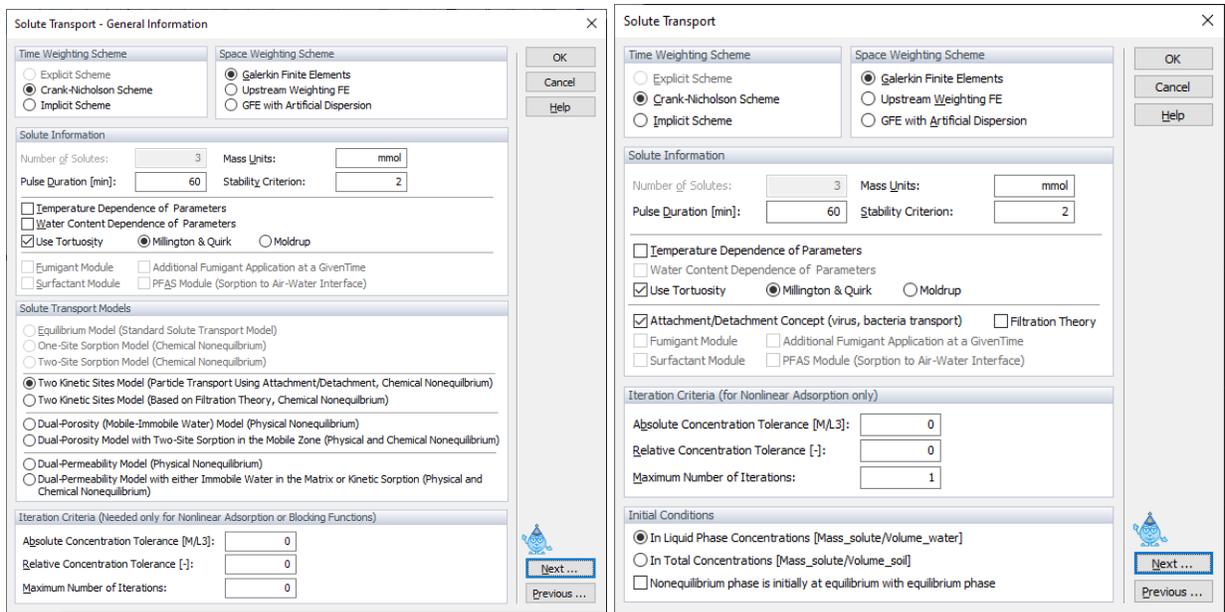
Figure 4. The Solute Transport dialog window (1D – left, 2D - right).

6.3. *Solute Transport Parameters*

The standard structure of HYDRUS input parameters is also preserved for the colloid-facilitated solute transport module. The input parameters for individual components (colloids, solute associated with colloids, and solute) are described below. Figure 5 shows the Solute Transport Parameters dialog window, in which both soil-specific and solute-specific transport parameters are specified.

Figure 5. The Solute Transport Parameters dialog window.

a) Soil Specific Parameters

These parameters are common for all three components, but different for different soil layers.

Table 3. Soil-specific solute transport parameters.

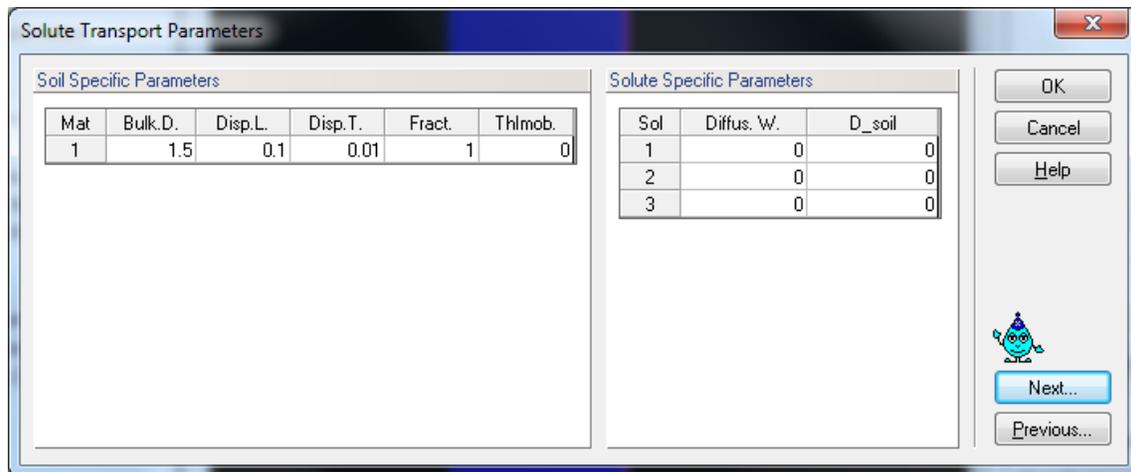| Parameter	Notation	Description
Bulk. D.	ρ	Bulk density [M/L^3]
Disp.L.	λ_L	Longitudinal dispersivity [L]
Disp.T.	λ_T	Transverse dispersivity [L]
Fract.	f	Fraction of sorption sites in equilibrium with the soil solution [-]. This parameter is used only for the third component (solute).
ThImob.	θ_{im}	Immobile water content. In the C-Ride module, this parameter can be used to account for colloid exclusion (water content from which colloids are excluded). Immobile water content for the third component (i.e., solute) is in each case (even when colloids are considered to be excluded from some fraction of water) considered to be zero.

b) Solute Specific Parameters

These parameters are common for different soil layers, but may be different for different components.

Table 4. Solute-specific solute transport parameters.

Parameter	Notation	Description
Diffus. W.	D_w	Molecular diffusion in the liquid phase [LT^{-2}]
D_soil	d_{50}	Diameter of soil grains [L]. This parameter is used only in the Bradford blocking straining function for colloids.

6.4. *Solute Reaction Parameters*

When the C-Ride module is used, the *Solute Reaction Parameters* are specified in the **Reaction Parameters** dialog window displayed in Figures 6, 7, and 8, for the first, second, and third solute components, respectively. The **Reaction Parameters** for the first, second, and third solute components are listed in Tables 5, 6, and 7, respectively.

Table 5. Reaction parameters for the first component (colloids).

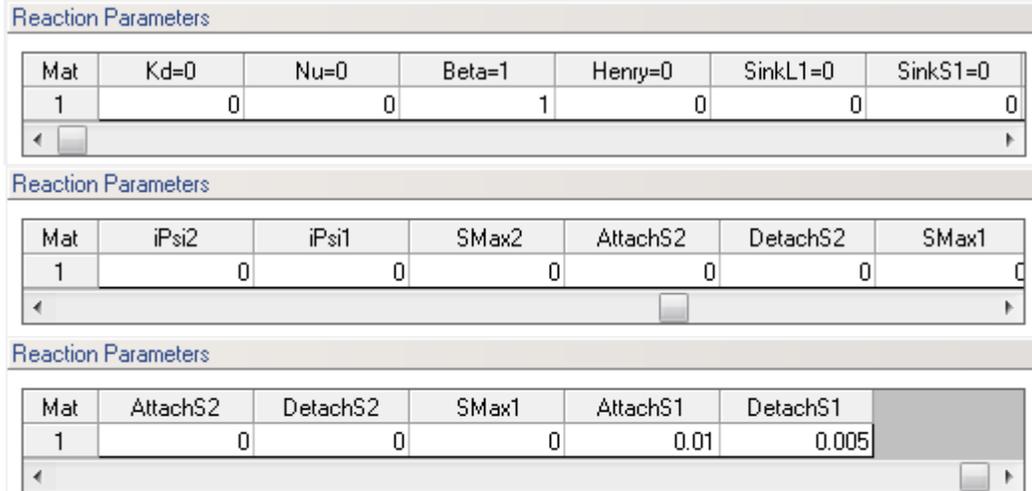| No	Parameter	Notation	Description
1	Kd	K_d	Should be equal to 0. This parameter is usually reserved for the sorption parameter K_d, which is not used with colloid transport [L^3/M].
2	Nu	η	Should be equal to 0 (commonly used for Langmuir η [L^3/M]).
3	Beta	β	Should be equal to 1 (commonly used for Freundlich exponent β).
4	Henry	K_H	Should be equal to 0 (commonly used for Henry's law constant K_H, which is not used with colloid transport).
5	SinkL1	μ_{cw}	Should be equal to 0 (commonly used for colloid immobilization in the liquid phase μ_{cw}). This parameter should not be used when the colloid-facilitated solute transport is considered.
6	SinkS1	μ_{cs}	Should be equal to 0 (commonly used for colloid immobilization in the solid phase μ_{cs}).
7	iPsi2	–	Type of blocking on the second sorption sites (=0; no blocking; =1: Langmuirian dynamics; =3: random sequential adsorption model; =4: depth-dependent blocking coefficient).
8	iPsi1	–	The same for the first sorption sites.
9	SMax2	S_{max}	Parameter in the blocking function for the second sorption sites.
10	AttachS2	k_{ac}	First-order deposition (attachment) coefficient, k_{ac} (or k_{str}) [T^{-1}], for the second sorption sites.
11	DetachS2	k_{dc}	First-order entrainment (detachment) coefficient, k_{dc} [T^{-1}], for the second sorption sites.
12	SMax1	S_{max}	Parameter in the blocking function for the first sorption sites.
13	AttachS1	k_{ac}	First-order deposition (attachment) coefficient, k_{ac} (or k_{str}) [T^{-1}], for the first sorption sites.
14	DetachS1	k_{dc}	First-order entrainment (detachment) coefficient, k_{dc} [T^{-1}], for the first sorption sites.

Figure 6. Parts of the "Reaction Parameters for Solute -1" (colloids) dialog window.

Table 6. Reaction parameters for the second component (solute on colloids).

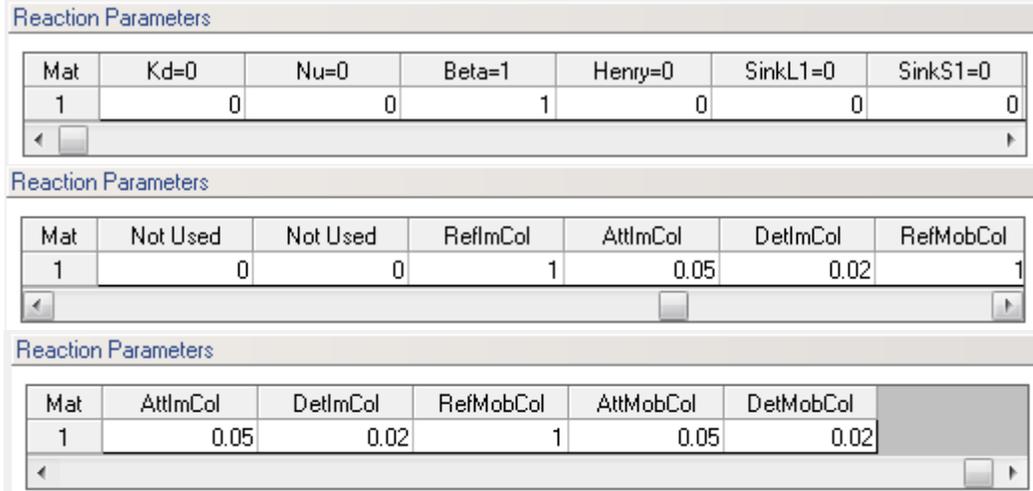| No	Parameter	Notation	Description
1	Kd	K_d	Should be equal to 0. This parameter is usually reserved for the sorption parameter K_d, which is not used with colloid transport [L^3/M].
2	Nu	η	Should be equal to 0 (commonly used for Langmuir η [L^3/M]).
3	Beta	β	Should be equal to 1 (commonly used for Freundlich exponent β).
4	Henry	K_H	Should be equal to 0 (commonly used for Henry's law constant K_H, which is not used with colloid transport).
5	SinkL1	μ_{cw}	Should be equal to 0 (commonly used for colloid immobilization in the liquid phase μ_{cw}).
6	SinkS1	μ_{cs}	Should be equal to 0 (commonly used for colloid immobilization in the solid phase μ_{cs}).
7	Not used		Not used.
8	Not used		Not used.
9	RefImCol	S_c^{ref}	Reference concentration of immobile colloids for which sorption rate k_{aic} is valid [-].
10	AttImCol	k_{aic}	Solute adsorption rate to immobile colloids [T^{-1}].
11	DetImCol	k_{dic}	Solute desorption rate from immobile colloids [T^{-1}].
12	RefMobCol	C_c^{ref}	Reference concentration of mobile colloids for which sorption rate k_{amc} is valid [ML^{-3}].
13	AttMobCol	k_{amc}	Solute adsorption rate to mobile colloids [T^{-1}]
14	DetMobCol	k_{dmc}	Solute desorption rate from mobile colloids [T^{-1}].

Figure 7. Parts of the "Reaction Parameters for Solute -2" (solute on colloids) dialog window.

Table 7. Reaction parameters for the third component (solute).

No	Parameter	Notation	Description
1	Kd	K_d	The sorption distribution parameter K_d [L^3/M].
2	Nu	η	The sorption (Langmuir) parameter η [L^3/M].
3	Beta	β	The sorption (Freundlich exponent) parameter β.
4	Henry	K_H	Henry's law constant K_H.
5	SinkL1	μ_w	Degradation rate for contaminant dissolved in the liquid phase [T^{-1}].
6	SinkS1	μ_s	Degradation rate for contaminant sorbed to the solid phase [T^{-1}].
7	Not used		Not used
8	Not used		Not used
9	Not used		Not used
10	Not used		Not used
11	Not used		Not used
12	Not used		Not used
13	Not used		Not used
14	Alpha	ω	First-order rate coefficient for one-site or two-site nonequilibrium adsorption [T^{-1}].

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Figure 8. Parts of the "Reaction Parameters for Solute -3" (solute) dialog window.

When the depth-dependent straining coefficient ψ_s^{str} is defined using Eq. (6), *cBnd6* and *cBnd7* values in the *Boundary Condition* vector are interpreted as *z*-coordinates of the inlets to materials 1 and 2, respectively. This depth-depending function can thus be used only for up to two materials.

6.5. *Initial Conditions*

Since three solutes are considered when using the C-Ride module, the initial conditions have to be given for all three solutes (i.e., colloids, solute on colloids, and solute). Initial conditions need to be specified for (mobile) colloids suspended in the liquid phase (Concentration 1, C_c) and (immobile) colloids attached to the solid phase (Sorbed Noneq. Conc. 1, S_c^{att}), for solute on mobile colloids (Concentration 2, $S_{mc}C_c$), for solute on immobile colloids (Sorbed Noneq. Conc. 2, $S_{ic}S_c^{att}$), for the solute in the liquid phase (Concentration 3, C), and for the kinetically sorbed solute to the solid phase (Sorbed Noneq. Conc. 3, S_k) (Figure 9).
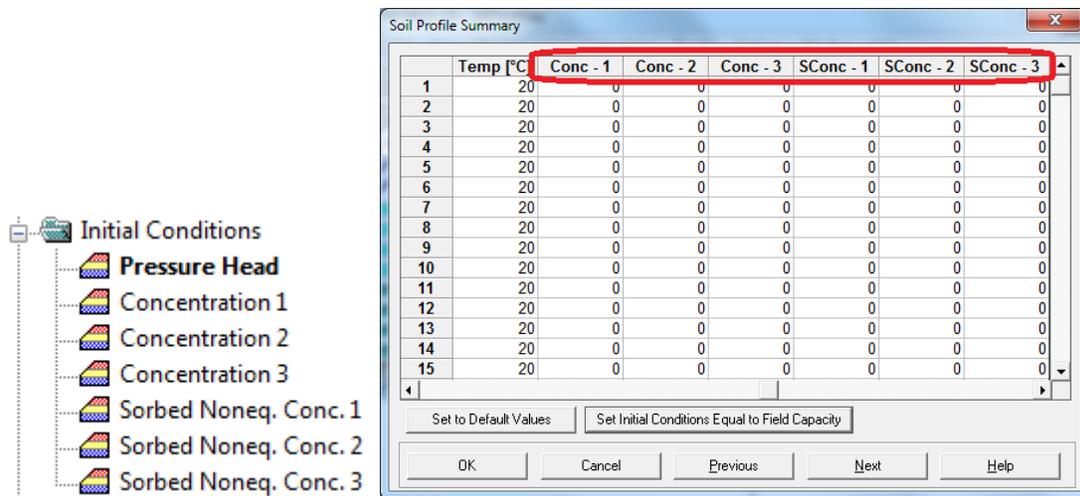
Figure 9. The "Initial Conditions" part of the Data Tab of the Navigator Bar (left) and the Soil Profile Summary dialog window (right) for the C-Ride module.

7. Post-processing

7.1. *Results – Graphical Display*

The output for the C-Ride module is the same as the output for the standard HYDRUS module. Multiple variables (all three main components) can be displayed in the View window (Figure 10).

Figure 10. The "Results - Graphical Display" part of the Data Tab of the Navigator Bar for the C-Ride module.

Other concentration modes (e.g., total concentration; concentration at sorption sites 2, total sorbed concentration) can be selected at the View Tab of the Navigator bar (Figure 10).
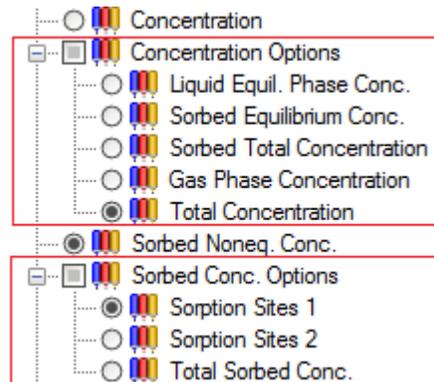
Figure 11. The "Concentration Options" part of the View Tab of the Navigator Bar for the C-Ride module.

7.2. *Results – Other Information*

a) Profile Information

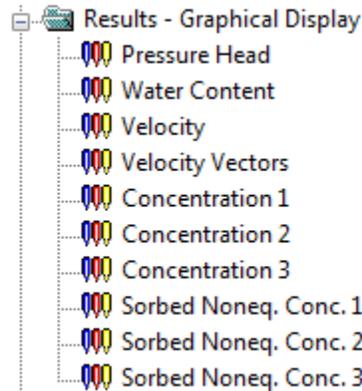The output for the C-Ride module (for one-dimensional applications) is the same as the output for the standard HYDRUS module. Multiple variables (all three main components) can be displayed with the Post-Processing (Results) - Profile Information command (Figure 12).
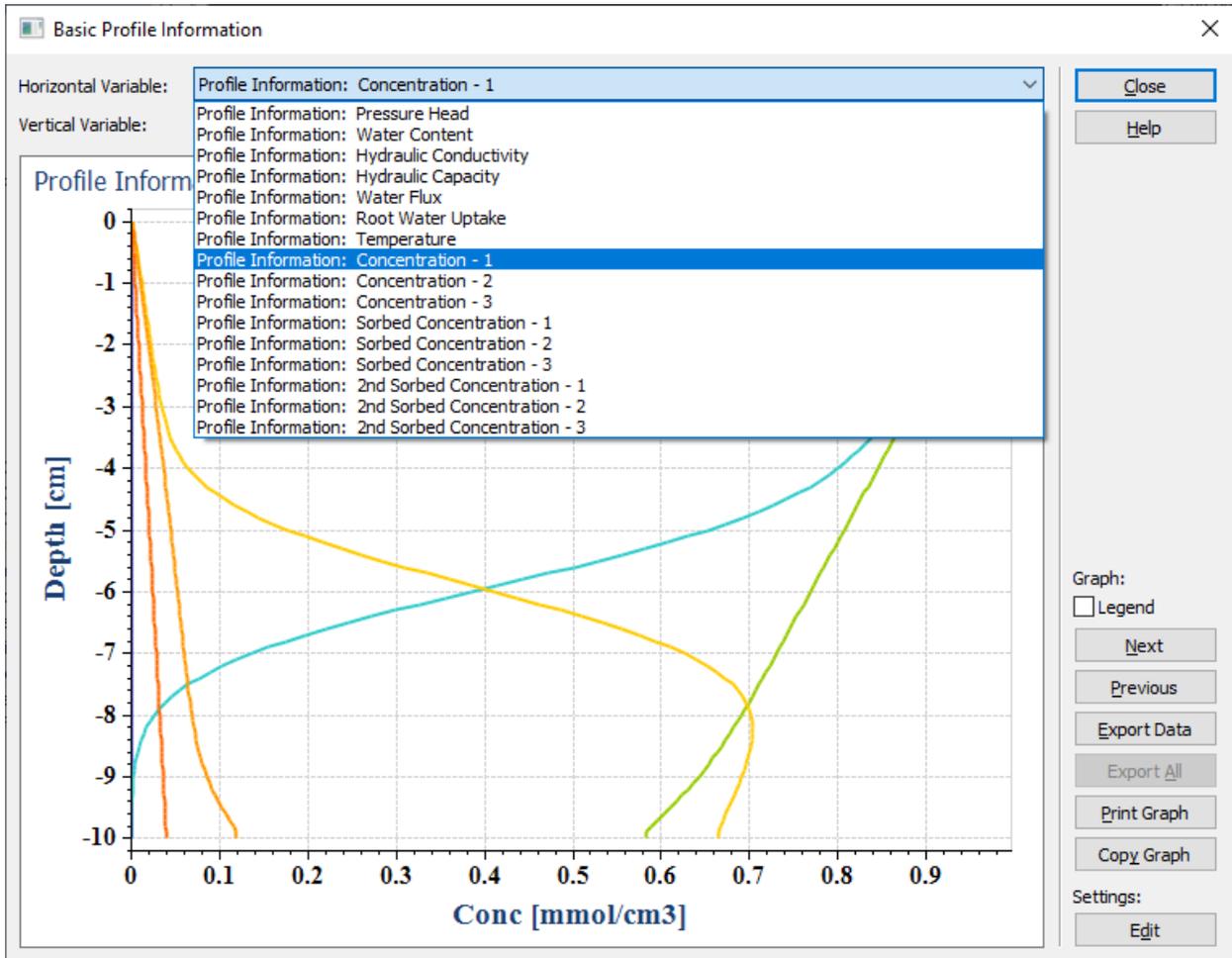
Figure 12. The "Profile Information" graph for the C-Ride module.

b) Solute Fluxes

Similarly, solute fluxes across boundaries and mass transfers between different phases are displayed for all three components. In addition to actual and cumulative boundary fluxes, of special interest is "**Cumulative Non-Equil. Mass Transfer**", which provides information about the mass transfer between the mobile and immobile colloids (for the first component - colloids), about the solute mass transfer associated with the mass transfer of mobile and immobile colloids (for the second component - solute on colloids), and about kinetically sorbed solute (for the third component -

solute). For the second component (i.e., solute on colloids), "**Cumulative Zero-Order Reaction**" and "**Cumulative First-Order Reaction**" give solute mass adsorbed and desorbed to/from colloids, respectively. Finally, for the third component (i.e., solute), "**Cumulative Zero-Order Reaction**" and "**Cumulative First-Order Reaction**" give solute mass desorbed and adsorbed from/to colloids, respectively. "**Cumulative First-Order Reaction**" additionally also includes any first-order degradation, if considered.

8. Example Problems

The C-Ride module supplements the standard HYDRUS program, which includes variably-saturated water flow and solute transport model, and thus the water flow, solute transport, and colloids transport parts of the model have been tested earlier. Therefore, verification and test examples presented in this section concentrate on the demonstration of the new features of the model.

Table 8. List of various test examples used to verify various new options of the C-Ride module.

Name	Flow[+]	Description
Test01a	No	Only mobile colloids, desorption from mobile colloids.
Test01b	No	Only mobile colloids, sorption/desorption from mobile colloids.
Test02a	No	Mobile (initially) and immobile colloids, sorption/desorption from colloids.
Test02b	No	Mobile and immobile (initially) colloids, sorption/desorption from colloids.
Test02c	No	Mobile (initially) and immobile colloids, sorption/desorption from water to colloids.
Test02d	No	Mobile (initially) and immobile (nonlinear) colloids, sorption/desorption from colloids.
Test02e	No	Mobile (initially) and immobile colloids, nonequilibrium sorption/desorption from colloids.
Test02f	No	Mobile and immobile (initially) colloids, sorption/desorption from colloids, root water uptake.
Test03a	SSF	Colloids and solute enter the column independently.
Test03b	SSF	Solute enters the column attached to colloids.
Test03c	SSF	Solute enters the column attached to colloids, Colloid exclusion.
Test04a	TF	Infiltration of mobile colloids, solute desorption from mobile colloids.
Test04b	TF	Infiltration of mobile colloids (attachment/detachment), solute desorption from colloids.
Test04c	TF	Infiltration of mobile colloids (attachment/detachment), solute sorption/desorption from colloids.
Test04d	TF	Infiltration of mobile colloids (attachment/detachment - 2nd site), solute sorption/desorption from colloids.
Test04e	TF	Infiltration of mobile colloids (attachment/detachment), solute sorption/desorption from colloids, root water uptake.
Test04f	TF	Infiltration of mobile colloids (attachment/detachment), solute sorption/desorption from colloids, nonequilibrium sorption to soil.
Test04g	TF	Infiltration of mobile colloids (attachment/detachment), solute sorption/desorption from colloids, nonlinear sorption to soil.
Test05	TF	Transient water flow and CFSTr in a field soil profile under grass.

[+]No - no flow, SSF - steady-state flow, TF - transient flow

The new module and most of its new features have been extensively tested on test problems of increasing complexity. The first set of examples (Test01 and Test02; see Table 8) described in Section 8.1 was run to evaluate correct mass transfers between different phases, such as colloids

between mobile and immobile phases, while solute was transferred between liquid and sorbed phases, between mobile and immobile colloids, and between colloids and liquid phase. This set of examples did not consider water flow. The second set of examples (Test03a and Test03b; see Table 8) described in Section 8.2 considered steady-state water flow conditions, and solute entering the soil column either sorbed to mobile colloids (Test03a) or independently of colloids (Test03b).

8.1. *Example Set 1 - Transfer Between Different Phases Without Flow*

A set of test examples was run to evaluate correct mass transfer between different phases, considering colloids being mobile and immobile (considering attachment, detachment, and straining), solute being sorbed and desorbed to/from colloids from/into the liquid phase, and being sorbed both instantaneously and kinetically to the solid phase. Selected results for selected test runs (Test02a, Test02b, and Test02e) are provided below.

In the Test02a example, colloids were initially in the liquid phase (mobile) and underwent both attachment (k_{ac} =0.01 min^{-1}) and detachment (k_{dc} =0.005 min^{-1}). Solute was initially sorbed to the mobile colloids, and was sorbing and desorbing from both mobile and immobile colloids at a rate of $k_{amc} = k_{aic} = 0.05$ min^{-1} and $k_{dmc} = k_{dic} = 0.05$ min^{-1}, respectively. Once in the liquid phase, solute was instantaneously distributed between the liquid and solid phase with a K_D equal to 1.
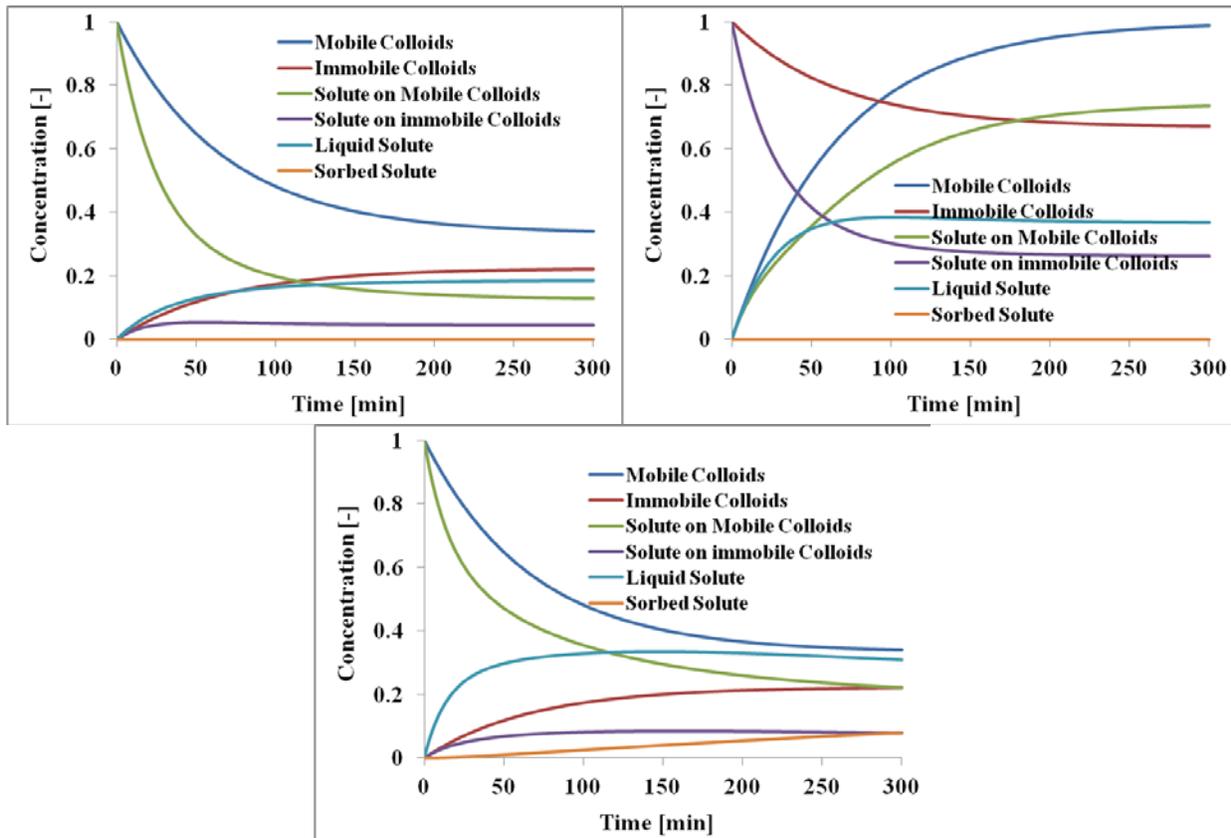

Figure 13. Colloid (mobile and immobile) and solute (liquid, sorbed, and on colloids) concentrations for examples Test02a (top left), Test02b (top right), and Test02e (bottom).

The same rate and distribution coefficients were used in the Test02b example. The only difference was that colloids were initially attached to the solid phase (immobile). In the Test02e example, solute was considered to be sorbed kinetically (rather than instantaneously) to the solid phase with a rate coefficient ω=0.001 min^{-1}.

Figure 13 shows concentrations of mobile and immobile colloids, and solute in the liquid phase, kinetically sorbed to the solid phase, and sorbed to mobile and immobile colloids for the test examples Test02a, Test02b, and Test02e. Table 9 provides mass balance calculations for these test examples at the beginning and end of the simulations. It provides concentrations for different phases, solute mass in different phases, as well as the total mass in the entire system for both colloids and solute.

Table 9. Mass balance calculations for test examples Test02a, Test02b, and Test02e.

	Variable	Test02a Initial	Test02a Final	Test02b Initial	Test02b Final	Test02e Initial	Test02e Final
	K_d	1					
	θ	0.5					
	ρ	1.5					
	f	1		1		0	
Colloids	C_c	1	0.3407	0	0.9889	1	0.3407
	$M_w= \theta C_c$	0.5	0.17035	0	0.49445	0.5	0.17035
	S_c	0	0.2198	1	0.6704	0	0.2197
	$M_s= \rho s_c$	0	0.3297	1.5	1.0056	0	0.32955
	Total$= M_w + M_s$	**0.5**	**0.50005**	**1.5**	**1.50005**	**0.5**	**0.4999**
Solute	C	0	0.1846	0	0.3686	0	0.3075
	$M_w= \theta C$	0	0.0923	0	0.1843	0	0.15375
	$S_e= K_d C$	0	0.1846	0	0.3686	0	0.3075
	$M_{se}= \rho S_e$	0	0.2769	0	0.5529	0	0
	S_k	0	0	0	0	0	0.07953
	$M_{sk}= \rho S_k$	0	0	0	0	0	0.119295
	$C_c S_{mc}$	1	0.1287	0	0.7349	1	0.2221
	$M_{cw}= \theta C_c S_{mc}$	0.5	0.06435	0	0.36745	0.5	0.11105
	$S_c S_{ic}$	0	0.04428	1	0.2634	0	0.07713
	$M_{cs}= \rho S_c S_{ic}$	0	0.06642	1.5	0.3951	0	0.115695
	Total$=M_w+M_{se}+M_{sk}+M_{cw}+M_{cs}$	**0.5**	**0.49997**	**1.5**	**1.49975**	**0.5**	**0.49979**

8.2. *Example Set 2 - Colloid and Solute Transport Under Steady-State Flow Conditions*

A 10 cm long soil column, with a porosity of 0.5 and a saturated hydraulic conductivity of 0.1 cm/min was considered in this set of examples. The flow was considered to be saturated at a flow rate of 0.1 cm/d. The pore volume was thus equal to 50 ($L\theta_s /q = 10*0.5/0.1 = 50$). Colloid and

solute were applied for 60 minutes. In the Test03a example, colloids and solute entered the soil column independently. In the Test03b example, solute entered the soil column sorbed to the colloids. The same rate and distribution coefficients as in examples Test02 were used (i.e., k_{ac} =0.01 min^{-1}, k_{dc} =0.005 min^{-1}, k_{amc} = k_{aic} = 0.05 min^{-1}, k_{dmc} = k_{dic} = 0.05 min^{-1}, and K_D = 1). The retardation factor for colloids is equal to 1 and for solute to 4 ($R=1+\rho K_d/\theta=1+1.5*1/0.5=4$).

Breakthrough curves for colloids, solute sorbed to colloids, and dissolved solute for examples Test03a and Test03b are shown in Figure 14. In the Test03a example, in which colloids and solute entered the column independently, colloids reached the bottom of the column after about 50 minutes (one pore volume), solute concentrations at colloids (blue line) increased only gradually due to sorption and showed long tailing (corresponding to tailing of colloids), and most solute mass appeared mostly at later times, corresponding to the retardation factor of 4. There was only a small increase in dissolved concentrations earlier because of the solute transported by colloids. In the Test03b example, in which solute entered the column sorbed to colloids, solute concentration at colloids mostly mirrored colloid concentrations. Solute concentrations at colloids were slightly lower due to desorption. The solute mass appeared at the end of the column earlier than in the previous example, mainly because solute was for the most part transported adsorbed to mobile colloids.
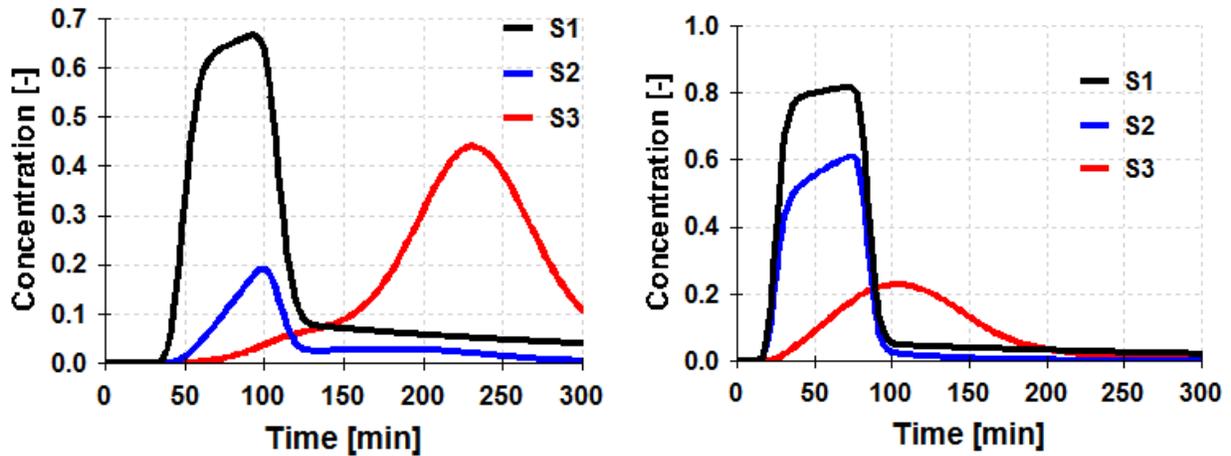

Figure 14. Breakthrough curves for colloids (black line), solute sorbed to colloids (blue line), and solute (red line) for examples Test03a (left) and Test03b (right).

8.3. *Other Examples - Colloid and Solute Transport Under Transient Flow Conditions*

Additional test examples were run for transient water flow conditions. Test04 examples involved water, colloids, and solute infiltrating into the soil profile. In all cases, solute was initially sorbed to infiltrating colloids. Colloids (except for Test04a) underwent processes of attachment/detachment, while solute was sorbing and desorbing to/from both mobile and immobile colloids. Additional processes, such as root water uptake (Test04e), kinetic sorption (Test04f), and nonlinear sorption (test04g), were also evaluated.

Finally, the Test05 example considered complex, 6-month long, transient flow conditions with daily values of precipitation and evapotranspiration and the presence of groundwater in the soil profile.

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