Mathematical and numerical modeling of contaminant transport in aqueous systems involving mobile solid phases

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Abstract

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DOCTOR of PHYLOSOPHY in Civil and Environmental Engineering

University of California, Davis

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This dissertation mainly focuses on the mathematical and numerical modeling of colloid or particle facilitated transport of sorbing chemical compounds in aquatic systems including surface water and unsaturated soil. The first and second chapters describe a riverine contaminant fate and transport model that takes into account transport and transformations of contaminants in the water column as well as in the bed sediments of streams. A coupled transport model is used to describe the transport of both dissolved and sorbed-to-suspended-sediments phases of contaminants in the water column and a quasi-two-dimensional model is developed to describe the diffusive transport, burial and solid-water mass exchange of chemicals in the bed sediments. The first chapter focuses mainly on the physical transport processes involved in such a system including advection and dispersion of dissolved and suspended-sediment associated chemicals, suspended sediment-water mass exchange, deposition and resuspension of sediments and bed-water column exchange of contaminants. Also this chapter deals with the mechanical dispersion, diffusion and

burial of contaminants in bed sediments. This model takes into account the effects of sediment compaction, sorption and release of contaminants to the pore water and sediment solid phase in the bed sediments. Solid-water mass exchange is assumed to be governed by a kinetic linear model. A simple river flow and sediment transport model is also developed. At the end of the chapter, a demonstration simulation is presented on transport of a sorbing chemical using the data from Colusa basin drain channel.

The second chapter focuses on the transformation reactions of chemical in the system described in the first chapter. A fully kinetic model capable of handling complicated non-linear reaction rate expressions was developed using a non-iterative explicit method along with a novel variable time step approach for solving reaction ordinary differential equations. The variable time step approach assigns an individual time-step to solve the reaction terms affecting each component based on the magnitude of the rate of reactions they are involved. This enables the model to keep the time step used for solving the physical transport processes controlled solely by the relevant transport mechanisms involved and therefore reduces the computational efforts needed to incorporate fast and near-equilibrium reactions into the model. The model is finally applied to a demonstration case of modeling bacterial mediated biogeochemical transformations of 14 major components in a riverine system.

The third chapter describes a colloid facilitated contaminant transport model in the unsaturated zone. The model has a one dimensional flow module using Richards' equation and a colloid transport module that uses colloid filtration theory along with both random sequential adsorption and Langmuir approaches as options for modeling surface jamming. The flow and colloid transport models are coupled in order to take into account the effects of plugging. The colloid-facilitated contaminant model considers contaminants to be present in five phases including dissolved, sorbed to soil matrix, mobile colloids, immobile entrapped colloids, and colloids entrapped at the air-water interface. A multi-species Langmuir sorption model is used for handling multiple competing contaminants. The model is used for fitting experimental data obtained from the literature and a good agreement was achieved. This chapter has been submitted to the Journal of Contaminant Hydrology for publication.

In the forth chapter, an innovative method for approximating the radial diffusion mass exchange model for a multi-disperse particle mixture with a multiple rate model using a numerical optimization technique is introduced. Multiple rate models are computationally less demanding than radial diffusion models especially for multidisperse mixtures, since various fractions of mass from various sizes can be lumped together and the refinement in particle size bins does not affect the number of unknowns in the system. In the approach explained in this paper, a method is developed to approximate the radial diffusive transport into each particle by several direct mass exchanges with different layers of the same particle through minimization of the difference between the time variations of concentration in each layer of particle predicted by two models. The resulting approximation was then expanded to a multi-disperse particle system. This approximation can reduce the number of unknowns in a radial diffusion representation of a multi-disperse system significantly and make its application for real systems feasible. The model is used to explain

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measured desorption of 1,2 dichlorobenzene from several soil types with known particle size distributions and a good agreement was achieved.

To my lovely wife Tinoosh and my parents

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Chapter I:

Mathematical Modeling of Sediment-Facilitated Transport of Contaminants in Riverine Systems – Physical Processes.

Abstract:

Sediment-water interaction encompasses important process affecting the transport of contaminant in river systems, especially for contaminants with high affinity to sediment materials. River bed sediments can act as a reservoir of contaminants for highly sorbing compounds. These sediments can retain chemical compounds for long periods of times and then release them to the water gradually due to diffusion or due to human activities or natural changes in flow regimes that may lead to transient exposure to the water column. In this research, a quasi two-dimensional numerical model is developed to predict the transport of contaminants in river systems, considering the processes taking place in the top layers of bed sediments and the water column. Burial, consolidation, kinetic water-solid mass exchange and bio and physical diffusion of contaminants in the bed sediments as well as sediment-associated transport of contaminants in the water body due to advection and dispersion of suspended materials and dissolved contaminants are taken into account. This coupling of transport in bed sediments and water column enables the model to simulate long-term fate of contaminants in the ecosystem. The model is solved using a semi-implicit finite difference method. Several demonstration computations were done using suspended sediment transport data in Colusa basin drain in order to investigate the effect of different processes on the distribution of contaminants in the bed sediments and their release into the water column.

1. Introduction

Contamination of water bodies is a problem of continually-growing concern in the state and worldwide. One of the major forms of aquatic contamination that can have adverse effect on the aquatic environment and also can cause human health problems through the food chain is sediment contamination. These sediment particles can be in suspension or they can lie on the bed of the water body and can change states due to deposition and entrainment. The contaminated sediments can also become buried under newly deposited sediments and not exposed to the water body. In this case, bed sediments may serve as a reservoir for contaminants and act as a long-term recalcitrant source of contamination. These contaminated bed sediments may become resuspended due to dredging, dam removal, or any other human activity, in addition to natural stage variations in the water body. For hydrophobic contaminants, suspended particles can act as a vehicle in the transport of contamination to downstream sites in the river. Also due to the possibility of anoxic condition in the sediments many biotic chemical transformations can occur in the bed sediment layers such as redox reactions that mobilize metallic contaminants or render them bioavailable (e.g., methylation). Therefore, to predict the long-term effects of contaminated sediment using mathematical models, the effects of transport of these contaminated sediments and their resuspension, deposition, and burial have to be considered. In this chapter modeling of the physical processes involved in sediment-associated transport of contaminants is discussed. The next chapter describes the modeling approach used to predict the biotic and abiotic *chemical* processes that can transform contaminants in the bed sediments or water column in ways that may affect their mobility or their effect on the environment.

In what follows, various models that have considered the sediment-water exchange processes in contaminant fate and transport are reviewed. Early models have mainly used a linear kinetic mass exchange between the sediments and water column and have overlooked the distribution of contaminants in the bed sediments and therefore the history of contaminant release.

Thomann et al. (1991) constructed a model to describe the physico-chemical fate and transport of chemicals in water-sediment systems. They used a one-dimensional (1-D) advection model with rapid sorption-desorption kinetics between water and bed sediments by assuming an interfacial exchange rate, and solved the resulting systems of equations for the total concentration of the contaminant (dissolved plus particulate). They modeled sediments as one well mixed layer. This model was used to predict the fate and transport of PCBs in the Hudson River, and to simulate the fate of cadmium in Foundry Cove superfund site. Shrestha (1996) used a two-dimensional(2-D) verticallyaveraged model to predict the spatial and temporal distribution of cohesive sediments and associated toxic heavy metals in estuaries. He used an experimental relation obtained by fitting Krone's experimental data (1962) to describe the bulk deposition and aggregation of the particles, and solved the model using the finite elements method. For adsorption, he assumed instant equilibrium using a linear reversible sorption isotherm. This model was used later to simulate heavy metal transport in South San Francisco Bay (Shrestha and Orlob, 1996). Ji et al. (2002) utilized a 2-D/3-D hydrodynamic and sediment transport model (EFDC) (Hamrick, 1992; Hamrick and Wu, 1997) along with an equilibrium assumption between particles and bulk and pore water to model the transport of several metals including cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and lead (Pd) in Blackstone River in Massachusetts.

All of the above mentioned models use an equilibrium assumption between the aqueous and solid phases. However, it has been shown that in many cases, especially for hydrophobic compounds, the rate of release of contaminants from the particles are slow relative to the transport, and equilibrium may not be fully attained when contaminated bottom sediments are resuspended into the water column (Coates and Elzerman, 1986; Young et al., 1987). Perianez et al. (1996) used a disequilibrium model for ionic exchange between water and particles, together with a 2-D hydrodynamic and sediment-transport model. They divided the particles into two size classes and obtained a constant ionic exchange coefficient for each of the classes. Perianez and Martinez-Aguirre (1997) developed a 2-D model including the phases of water, suspended sediments, bed sediments and contaminants, for modeling fate and transport of Uranium(U), Thorium (Th), and Radium (Ra) in an estuarine marsh system. In Perianez (2002) he improved his model by replacing the one-step sorption-desorption kinetics with a two-step kinetic model consisting of two consecutive reaction models.

There have been some modeling efforts also that solely focus on the spatial distribution of contaminants in the sediments. These models have mainly focused on lake systems and have adopted a one-dimensional vertical representation of sediment column. For example Formica et al. (1988) used a vertical transport model considering deposition, diffusion, sorption and decay to predict the fate of polychlorinated biphenyl (PCB) in lake sediments. Smith and Comans (1996) developed a simple 1-D vertical model to predict the diffusive transport and remobilization of cesium (Cs) in sediment. They used a 2-stage model for sorption of Cs to the soil particles and considered the partitioning coefficient as a function of the chemical composition of the water-sediment system. In two stage sorption models, the contaminant sorbed to the solid phase is assumed to be transported from one strongly sorbing phase to a less-strong sorbing phase kinetically, where the less sorbing portion of the solid phase is in equilibrium with the bulk water.

Although there have been many modeling exercises on sediment associated transport of metalloids in rivers that assume a single fully mixed bed sediment layer and also many 1-D vertical contaminant transport models in the sediments for lake and estuaries, no modeling attempt has been found to integrate these two approaches in order to incorporate the effect of the history of deposition of contaminated sediments and consecutive erosion and deposition processes on the release of contaminants from

sediments to overlying waters. This effort considered herein is very important because many contaminants with high affinity to solid materials are present as a distinct high concentration sediment-associated layers buried under newly deposited sediments the water body. These sediments may be re-exposed to the water body due to high erosion rates caused by natural phenomena such as flooding or high turbulence or anthropogenic activities such as dredging or changes in the morphology or hydrology of the river induced by dams, dam removal, diversions, etc. In addition the burial of sediment associated contaminants can be considered as a natural attenuation of contaminants in such cases and an integrated sediment-water model can help in predicting these events and their consequences. In order to take these long-term effects into account it is necessary to model the transformations of contaminants as well as their variation with depth of sediments.

The goal of this research is to develop a model that combines both vertical fate and transport of sediment associated contaminants with their horizontal transport due to water flow. The model includes a 1-D hydrodynamic and sediment transport model. The contaminant transport model has two main components including the horizontal sediment-associated and dissolved contaminant transport and vertical diffusive transport in the bed sediments which are fully coupled. The horizontal transport component models the transport of dissolved and sediment-associated contaminants by using a linear kinetic reversible mass exchange between particles and water body. Airwater exchange, decay, and reaction of multiple species are also considered. The diffusive transport in the bed sediments is considered to be vertical 1-D which means that the horizontal diffusive transport in the bed sediments is neglected. Contaminants are considered to be in solid and pore water phases and the exchange between these two phases is modeled using linear kinetic reversible sorption. Mass exchanges due to bioturbation and bio-irrigation are represented by a Fickian diffusion process. The two main modules of the model for transport in the water body and transport in bed

sediments are coupled using a viscous boundary layer at the water-sediment interface and erosion and deposition of sediments. The schematic of the processes involved in the model is shown in Figure 1. The hydrodynamic model uses the kinematic wave equation along with the Flow-Area-Depth-Velocity rating curves and the sediment transport model uses the relationships for sediment entrainment proposed by Garcia and Parker (1993) and 1-D advection and dispersion equations.

2. Model Development

The model is contained a 1-D transport model representing the flow and transport in the river reach and a quasi 2-D model with neglecting the horizontal mass transfers in the bed sediments. Transport of suspended sediments and dissolved and sediment associated contaminants in the river reach is modeled using an advection dispersion equation with considering the effect of inputs/outputs from/to the bed sediments as source and sink terms. This source and sink terms include the boundary layer exchange, and deposition and re-suspension of sediments and the compounds associated with them. On the other hand the molecular diffusion and burial of contaminants are represented using a 2-D advection dispersion model while the horizontal mass exchanges are neglected. Biodispersion and bioirigation caused by benthic organisms are represented using a diffusive term which vanishes with depth. In the following the derivation of the governing equations developed for this system are explained.

2.1. Sediment-phase and aqueous transport in river

A 1-D model is used for the transport of species in the river. For each species being modeled a set of two coupled 1-D advection-dispersion equations, one for dissolved species and one for particle associated species are used, respectively:

$$\frac{\partial(C_{i})}{\partial t} + \frac{\partial(vC_{i})}{\partial x} = \frac{1}{A} \frac{\partial}{\partial x} \left(D_{h} A \frac{\partial C_{i}}{\partial x} \right) + k_{b} \frac{P}{A} (c_{i}(0) - C_{i}) - C_{s} k_{r} (K_{D} C_{i} - S_{i}) + R_{i} + \frac{Q_{in}}{A} (C_{i,in} - C_{i}) + k_{at} (C_{i,at} - K_{H} C_{i}) - \frac{P}{A} u_{f} \theta_{0} c_{i}(0)$$

$$\frac{\partial C_{s} S_{i}}{\partial t} + \frac{\partial v C_{s} S_{i}}{\partial x} = \frac{1}{A} \frac{\partial}{\partial x} \left(D_{s} A \frac{\partial C_{s} S_{i}}{\partial x} \right) + Er.w_{p} \cdot \frac{P}{A} s_{i}(0) - w_{p} r_{0} \cdot \frac{P}{A} \cdot C_{s} S_{i} + \frac{Q_{in}}{A} (C_{s,in} S_{in} - C_{s} S_{i}) + k_{r} C_{s} (K_{D} C_{i} - S_{i})$$

$$(1)$$

in which, t(s) is time, x(m) is the special coordinate in river axis, $C_i(\mu g/mL)$ is the dissolved concentration of chemical i in bulk water, v(m/s) is the cross-sectional averaged velocity along the river, $D_h(m^2/s)$ is the mechanical dispersion coefficient along the river axis, $k_b(m/s)$ is the sediment-water exchange coefficient for the dissolved species, $c_i(0)(\mu g/mL)$ is the pore-water concentration at the topmost layer of sediments, P(m) is the wetted perimeter of the stream, $k_r(s^{-1})$ is the mass exchange coefficient between suspended particles and water, $C_{i,at}$ (atm) is the partial pressure of the vapor phase of constituent *i*, K_H (atm.m³/g) is the Henry's coefficient, $C_s(\mu g.m^{-3})$ is the concentration of suspended particles, $K_D(L/g)$ is the water-solid distribution coefficient, $S_i(\mu g.gr^{-3})$ is the sorbed phase concentration, R_i is the sum of reaction terms for species i, $q_{in}(m^3 s^{-1})$ is the amount of lateral water flux, $C_{i,in}(\mu g/mL)$ is the concentration of species i in the lateral flux, $k_{at}(s^{-1})$ is the atmospheric exchange rate coefficient, $D_s(m^2/s)$ is the dispersion coefficient for suspended particles, $Er(g.m^{-3})$ is the entrainment coefficient, $w_p(m/s)$ is particle fall velocity, $s_i(0)(\mu g/mL)$ is the sorbed concentration at the topmost layer of the bed sediments, r_0 is the ratio between the concentration of suspended particles at the bed and the average concentration of suspended particles over water depth, $C_{s,in}(\mu g/mL)$ is the concentration of suspended particles in the lateral inflow, $u_t(m/s)$ is pore water velocity in bed sediments due to consolidation (downward defined as positive) and θ_0 is the bed sediment porosity at the sediment water interface.

In Eq. (1) the second term in the left hand side represents the advective transport of dissolved species, the first term from the right hand side is the mechanical dispersion; the second term is the exchange of species with benthic porewater; the third term is the exchange with suspended sediments; the fifth term is the lateral flux of chemicals; and the sixth term represents exchange with atmosphere and the seventh term refers to the effect of flow of pore water to the water column due to consolidation as explained in section 2.1. In Eq. (2), the second term from the left hand side represents advection of chemicals sorbed to particles due to movement of particles; the first term from the right hand side represents the effect of mechanical dispersion and deposition respectively; and fourth and fifth terms are respectively lateral inflow of chemical species associated with suspended solids, and mass exchange with bulk water. These processes are shown schematically in Figure 1.



Figure 1: Processes involved in sediment associated contaminant transport

2.2. Transport in bed sediments

The 1-D transport model described above is coupled with the transport of chemical species in bed sediments. The horizontal diffusive and advective transport of chemicals in bed sediments is ignored due to larger horizontal scale with respect to vertical scales. In addition, in this model it is assumed that the effects of bioturbation can be simulated using a diffusive model with a modified diffusion coefficient corrected to account for the mixing due to bioturbation. In the following two subsections I detail the treatment of consolidation and reactive transport in bed sediments.

2.2.1. Consolidation

When new sediments deposit on top of older layers, the later undergo consolidation so that the top layers of sediments typically have a higher porosity and smaller density than the lower layers. In order to simulate long-term fate of sediment-associated contaminants, the effects of consolidation should be taken into account. These effects can be summarized by the lower burial velocities for the deeper sediments and the upward movement of pore water. In Figure 2 the fluid and solid mass balance for a finite volume of the sediments is depicted.



Figure 2: Mass balance diagram for flows and transport due to sediment consolidation (The directions indicate the assumed positive coordinate for the respective quantities)

The mass balance for solid and fluid phases in consolidating sediments can be written respectively as:

$$\frac{\partial(1-\theta)}{\partial t} = -\frac{\partial[u_s(1-\theta)]}{\partial z^*}$$
(3)

$$\frac{\partial \theta}{\partial t} = -\frac{\partial u_f \theta}{\partial z^*} \tag{4}$$

where u_f and u_s are fluid and solid velocity with respect to a fixed coordinate system (z^*), θ is the porosity of the media. Adding equations (3) and (4) yields:

$$\frac{\partial u_f \theta}{\partial z^*} + \frac{\partial [u_s(1-\theta)]}{\partial z^*} = 0$$
(5)

Or

$$\frac{\partial [(u_f - u_s)\theta]}{\partial z^*} + \frac{\partial u_s}{\partial z^*} = 0$$
(6)

where $(u_f - u_s)\theta$ is the Darcy velocity due to consolidation. Integrating equation (6) and considering that both u_f and u_s are zero at infinitely deep sediment leads to:

$$\left(u_{f}-u_{s}\right)\Big|_{z^{*}}\theta=-u_{s}\Big|_{z^{*}}\tag{7}$$

Here we are using the following relationship for determining porosity versus depth in the sediments suggested by (Boudreau, 1996).

$$\theta(z^*) = (\theta_0 - \theta_\infty)e^{-k_\theta(z_0 - z^*)} + \theta_\infty$$
(8)

where z_0 is the sediment bed surface elevation, k_0 is a compression coefficient, θ_0 is the porosity at the surface and θ_{∞} is the minimum porosity at deep layers. It worth noting that equation (8) does not take into account the hysteresis effects in sediment consolidation and assumes that the porosity and density of sediment materials does not depend on their history of being at different levels. Defining the new coordinate system z which has its origin on the sediment water interface and increases with depth:

$$z(z^*,t) = z_0 - z^*$$
(9)

Equations (3) and (4) can be written respectively as:

$$\frac{\partial(1-\theta)}{\partial t} + \frac{\partial(1-\theta)}{\partial z}\frac{\partial z_0}{\partial t} = -\frac{\partial[u_s(1-\theta)]}{\partial z}$$
(10)

$$\frac{\partial\theta}{\partial t} + \frac{\partial\theta}{\partial z}\frac{\partial z_0}{\partial t} = -\frac{\partial u_f\theta}{\partial z}$$
(11)

Here the positive direction for u_f and u_s is changed according to the new coordinate system for sake of simplicity. Therefore, a positive value indicates downward velocity. Equation (8) with respect to the new coordinate system becomes:

$$\theta(z) = (\theta_0 - \theta_\infty)e^{-k_\theta z} + \theta_\infty \tag{12}$$

whereas in the original coordinates θ derived by Eq. (8) included an implicit dependence on time through z_0 , in the new coordinates θ derived by Eq. (12) is solely space dependent and also the derivative of θ with respect to depth is:

$$\frac{\partial \theta(z)}{\partial z} = -k_{\theta}(\theta_0 - \theta_{\infty})e^{-k_{\theta}z}$$
(13)

with θ only in z now, Equation (10) and (11) lead to:

$$\left(\frac{\partial z_0}{\partial t} + u_s\right)\frac{\partial \theta}{\partial z} = \frac{\partial u_s}{\partial z}(1 - \theta)$$
(14)

or by arranging equation (14):

$$\frac{\partial}{\partial z} \left[\left(J_0 + u_s \right) (1 - \theta) \right] = 0 \tag{15}$$

where $J_0 = \partial z_0 / \partial t$ does not vary with z and is the rate of deposition or erosion plus the effect of consolidation. Or

$$J_{0} = \partial z_{0} / \partial t = \frac{1}{(1 - \theta_{0})\rho_{s}} \Big(w_{p} r_{0} \cdot C_{s} - Er \cdot w_{p} \Big) - u_{s0}$$
(16)

By integrating Equation (15) from z to infinity we can write:

$$\int_{z}^{\infty} \frac{\partial}{\partial z} \left[\left(J_0 + u_s \right) (1 - \theta) \right] dz = \left(J_0 + u_s (\infty) \right) (1 - \theta_{\infty}) - \left(J_0 + u_s \right) (1 - \theta) = C$$
(17)

Since we know that consolidation velocity u_s at infinity is zero and porosity at infinity is equal to θ_{∞} we can calculate C as:

$$C = J_0 \left(1 - \theta_\infty \right) \tag{18}$$

and therefore:

$$u_s = J_0 \left(\frac{\theta - \theta_\infty}{1 - \theta} \right) \tag{19}$$

Substituting into equation (7) we can calculate u_f as:

$$u_f = \frac{u_{s0} - u_s}{\theta} + u_s \tag{20}$$

$$u_f = -J_0 \left(\frac{\theta - \theta_\infty}{\theta}\right) \tag{21}$$

and Darcy velocity $q = (u_f - u_s)\theta$ which is equal to:

$$q = -J_0 \frac{\left(\theta - \theta_\infty\right)}{1 - \theta} \tag{22}$$

As an example the sediment physical properties predicted by the model described above in Eqs (12), (19), and (21) using hypothetical parameters are presented in Figure 3.



Figure 3: Consolidation velocities, Darcy flux, porosity and bulk density versus depth in sediments with $\theta_{\infty} = 0.3$, $\theta_0 = 0.8$, $k_{\theta} = 5$

2.2.2. Reactive Transport

The governing equations for the reactive transport model for dissolved species *i* and its corresponding sorbed phase in the bed sediment at each location of the river can be written as follows with respect to a fixed vertical coordinate system.

$$\frac{\partial(\theta c_i)}{\partial t} = -\frac{\partial(\theta u_f c_i)}{\partial z^*} + \frac{\partial}{\partial z^*} \left(\left(D_m + D_B \right) \theta \frac{\partial c_i}{\partial z^*} \right) - B_d k_r \left(K_D c_i - s_i \right) + R_i$$
(23)

$$\frac{\partial (B_d s_i)}{\partial t} = -\frac{\partial (B_d u_s s_i)}{\partial z^*} + \frac{\partial}{\partial z^*} \left(D_B B_d \frac{\partial c_i}{\partial z^*} \right) + B_d k_r \left(K_D c_i - s_i \right) + R_{s,i}$$
(24)

With boundary conditions:

$$(D_m + D_B)\theta \frac{\partial c_i}{\partial z_*} = k_b (c_i - C_i) \quad \text{at } z^* = z_0$$
(25)

$$\frac{\partial c_i}{\partial z} = 0 \qquad \text{at } z^* = \infty \tag{26}$$

And, for equation (24):

$$s_i \Big|_{z^{*=\infty}} = 0$$
 for $J_0 < 0$ erosion (27)

$$s_i \Big|_{z^{*=\infty}} = S_i$$
 for $J_0 > 0$ deposition (28)

where $c_i = c_i(x, z^*, t)$ is the dissolved concentration in pore water in the bed sediments, $s_i(x, z^*, t)$ (µg/g) is the mass concentration of sorbed species, B_d(g/ml) is the bulk density of the sediment materials, $D_b(\text{cm}^2\text{s}^{-1})$ is the mechanical dispersion coefficient due to inhomogeneity of bed materials and the mixing due to the activities of benthic organisms, D_m(cm²s⁻¹) is the molecular diffusion coefficient, and $R_{s,i}$ is the production or elimination of species *i* due to total intra-phase reaction rate. Imposing the transformed coordinate system $z = z_0 - z^*$ on Equations (23) and (24) yields:

$$\theta \frac{\partial (c_i)}{\partial t} = -\frac{\partial [\theta (u_f + J_0)c_i]}{\partial z} + \frac{\partial}{\partial z} \left((D_m + D_B)\theta \frac{\partial c_i}{\partial z} \right) + B_d k_r (K_D c_i - s_i) + R_i$$
(27)

$$\frac{\partial (B_d s_i)}{\partial t} = -\frac{\partial [B_d (u_s + J_0) s_i]}{\partial z} + \frac{\partial}{\partial z} \left(D_B B_d \frac{\partial c_i}{\partial z} \right) - B_d k_r \left(K_D c_i - s_i \right) + R_{s,i}$$
(28)



Figure 4: A sample simulation of evolution of a sorbing tracer deposited with sediment on the sediment top layers.

Figure 4 shows a sample computation of evolution of concentration due to pure deposition of contaminated sediments with a constant rate with sorbed and dissolved concentration at the bulk water equal to unity and no exchange between sorbed and dissolved phases. The deposition velocity is assumed to be 1.5cm/hr and the bio-dispersion of the solid phase is assumed to be zero. Under and overshooting of the sorbed phase profile near the front is due to use of a high order numerical method for advection.

3. Numerical Solution

3.1. Sediment-Associated transport in the river:

Equations (1) and (2) are solved via the finite difference method using an upwinding scheme for the convective term, a centered scheme for the diffusive terms, both in space and a Crank-Nicholson scheme in time finite difference method. Eqs. (1) and (2) becomes:

$$\frac{A_{k}^{t+1}C_{i,k}^{t+1} - A_{k}^{t}C_{i,k}^{t}}{\Delta t} + \left[\frac{A_{k}v_{k}C_{i,k} - A_{k-1}v_{k-1}C_{i,k-1}}{\Delta x}\right]^{t+1/2} = \left[\frac{D_{h,k+1/2}A_{k+1/2}C_{i,k+1} - (D_{h,k+1/2}A_{k+1/2} + D_{h,k-1/2}A_{k-1/2})C_{i,k} + D_{h,k-1/2}A_{k-1/2}C_{i,k-1}}{(\Delta x)^{2}}\right]^{t+1/2} + \left[k_{b}P_{k}\left(c_{i,k}\left(0\right) - C_{i,k}\right)\right]^{t+1/2} - \left[AC_{s}k_{r}\left(K_{D}C_{i,k} - S_{i,k}\right)\right]^{t+1/2} + \left[A_{k}R_{i,k}\right]^{t+1/2} + \left[q_{in,k}C_{i,in,k}\right]^{t+1/2} + \left[A_{k}k_{at}\left(C_{i,at} - K_{H}C_{i,k}\right)\right]^{t+1/2} - \left[P_{k}u_{f,k}\theta_{0}c_{i,k}\left(0\right)\right]^{t}$$
(29)

$$\frac{A_{k}^{t+1}C_{s,k}^{t+1}S_{i}^{t+1} - A_{k}^{t}C_{s,k}^{t}S_{i}^{t}}{\Delta t} + \left[\frac{v_{k}A_{k}C_{s,k}S_{i,k} - v_{k-1}A_{k-1}C_{s,k-1}S_{i,k-1}}{\Delta x}\right]^{t+1/2} = \left[\frac{D_{h,k+1/2}A_{k+1/2}S_{i,k+1}C_{s,k+1} - (D_{h,k+1/2}A_{k+1/2} + D_{h,k-1/2}A_{k-1/2})S_{i,k}C_{s,k} - D_{h,k-1/2}A_{k-1/2}C_{i,k-1}C_{s,k-1}}{(\Delta x)^{2}}\right]^{t+1/2} + \left[Er.w_{p}.Ps_{i}(0)\right]^{t} - \left[w_{p}r_{0}.P.C_{s}S_{i}\right]^{t+1/2} + \left[q_{in}C_{s,in}S_{in}\right]^{t+1/2} + \left[Ak_{r}C_{s}(K_{D}C_{i} - S_{i})\right]^{t+1/2} \right]^{t+1/2}$$
(30)

Subscripts "*k*" indicate spatial discretization grid cells, subscript "i" indicate constituent or species number and superscript "t" indicate time steps. In the weighted time scheme unknown terms are considered to be weighted average of their values in the current time step t+1 and their previous time step t, therefore:

$$C_{i,k} = \omega C_{i,k}^{t+1} + (1 - \omega) C_{i,k}^{t}$$
(31)

$$S_{i,k} = \omega S_{i,k}^{t+1} + (1 - \omega) S_{i,k}^{t}$$
(32)

Substituting (31) and (32) into (29) and (30) and rearranging equations leads to the following system of equations approximating equations (1) and (2):

$$\Omega_{k,1}C_{i,k-1}^{t+1} + \Omega_{k,2}C_{i,k}^{t+1} + \Omega_{k,3}C_{i,k+1}^{t+1} + \Lambda_k S_{i,k+1}^{t+1} = RHS_{C,k}$$
(33)

$$\Phi_{k,1}S_{i,k-1}^{t+1} + \Phi_{k,2}S_{i,k}^{t+1} + \Phi_{k,3}S_{i,k+1}^{t+1} + \Gamma_k C_{i,k+1}^{t+1} = RHS_{s,k}$$
(34)

where

$$\Omega_{k,1} = -\omega \left[\left(\frac{A_{k-1}v_{k-1}}{\Delta x} + \frac{D_{h,k-1/2}A_{k-1/2}}{(\Delta x)^2} \right) \right]^{t+1/2}
(35a)
\Omega_{k,2} = \left[\frac{A_k^{t+1}C_{i,k}^{t+1}}{\Delta t} \right]^{t+1/2} + \omega \left[\frac{A_k v_k}{\Delta x} \right]^{t+1/2} + \left[\omega k_b P_k \right]^{t+1/2}
+ \omega \left[A_k C_{s,k} k_r K_D \right]^{t+1/2} + \left[\frac{D_{h,k+1/2}A_{k+1/2} + D_{h,k-1/2}A_{k-1/2}}{(\Delta x)^2} \right]^{1/2}$$
(35b)

$$\Omega_{k,3} = -\omega \left[\frac{D_{h,k+1/2} A_{k+1/2}}{(\Delta x)^2} \right]^{t+1/2}$$
(35c)

$$\Lambda_{k} = -\omega \Big[A_{k} C_{s,k} k_{r} K_{D} S_{i,k+1}^{t+1} \Big]^{t+1/2}$$
(35d)

$$RHS_{C,k} = \frac{A_{k}^{t}C_{i,k}^{t}}{\Delta t} + (1-\omega)\frac{\left[A_{k}v_{k}\right]^{t+1/2}C_{i,k}^{t} - \left[A_{k-1}v_{k-1}\right]^{t+1/2}C_{i,k-1}^{t}}{\Delta x} + \omega\left[A_{k}k_{at}\right]^{t+1/2}C_{i,k+1}^{t+1}} \\ (1-\omega)\frac{\left[D_{h,k+1/2}A_{k+1/2}\right]^{t+1/2}C_{i,k+1}^{t} - \left[(D_{h,k+1/2}A_{k+1/2} + D_{h,k-1/2}A_{k-1/2})\right]^{t+1/2}C_{i,k}^{t} - \left[D_{h,k-1/2}A_{k-1/2}\right]^{t+1/2}C_{i,k-1}^{t}}{(\Delta x)^{2}} \\ + k_{b}P_{k}\left(c_{i,k}^{t}(0) - (1-\omega)C_{i,k+1}^{t}\right) - \left[A_{k}\right]^{t+1/2}C_{s,k}k_{r}(1-\omega)\left(K_{D}C_{i,k+1}^{t} - S_{i,k+1}^{t}\right) + \left[A_{k}\right]^{t+1/2}R_{i}^{t} + \\ q_{in,k}C_{i,in,k} + \left[A_{k}\right]^{t+1/2}k_{at}\left(C_{i,at} - (1-\omega)C_{i,k+1}^{t}\right) - P_{k}u_{f,k}\theta_{0}c_{i,k}^{t}(0)$$

$$(35e)$$

$$\Phi_{k,1} = -\omega \left(\frac{\left[v_{k-1} A_{k-1} \right]^{t+1/2} C_{s,k-1}}{\Delta x} + \frac{\left[D_{h,k-1/2} A_{k-1/2} \right]^{t+1/2} C_{s,k-1}}{\left(\Delta x \right)^2} \right)$$
(35f)

$$\Phi_{k,2} = \frac{k}{\Delta t} + \omega \left(\frac{\left[v_k A_k \right]^{t+1/2} C_{s,k}}{\Delta x} w_p r_0 P.C_s + \frac{\left[D_{h,k+1/2} A_{k+1/2} + D_{h,k-1/2} A_{k-1/2} \right]^{t+1/2} C_{s,k}}{(\Delta x)^2} + A_k^{t+1/2} k_r C_s \right)$$
(35g)
$$\Phi_{k,3} = -\omega \frac{\left[D_{h,k+1/2} A_{k+1/2} \right]^{t+1/2} C_{s,k+1}}{(\Delta x)^2}$$
(35h)

$$\Gamma_k = -\omega A_k^{t+1/2} k_r C_{s,k} K_D C_{i,k}^{t+1}$$
(35i)

$$RHS_{s,k} = \frac{A_{k}^{t}C_{s,k}^{t}S_{i}^{t}}{\Delta t} + (1-\omega)\frac{\left[v_{k}A_{k}\right]^{t+1/2}C_{s,k}S_{i,k}^{t} - \left[v_{k-1}A_{k-1}\right]^{t+1/2}C_{s,k-1}S_{i,k}^{t}}{\Delta x} \\ (1-\omega)\frac{\left[D_{h,k+1/2}A_{k+1/2}\right]^{t+1/2}C_{s,k+1}S_{i,k}^{t} - \left[D_{h,k+1/2}A_{k+1/2} + D_{h,k-1/2}A_{k-1/2}\right]^{t+1/2}C_{s,k}S_{i,k}^{t} - \left[D_{h,k-1/2}A_{k-1/2}\right]^{t+1/2}C_{s,k-1}S_{i,k}^{t}}{(\Delta x)^{2}} \\ + Er.w_{p}.P_{k}\left[s_{i}(0)\right]^{t} - (1-\omega)w_{p}r_{0}.P.C_{s}S_{i,k}^{t} + \\ q_{in}C_{s,in}S_{in} + (1-\omega)A_{k}^{t+1/2}k_{r}C_{s,k}\left(K_{D}C_{i,k}^{t} - S_{i,k}^{t}\right)$$

$$(35j)$$

Here all other time varying values including A, v, and D are also considered as their weighted averages at current and previous time steps.

$$\Pi_{s,k}^{t+1/2} = \omega \Pi_{s,k}^{t+1} + (1-\omega) \Pi_{s,k}^{t}$$
(36)

where Π is a generic variable representing *A*, *P*, *C*_s, *D*_h and *v*. The system of algebraic equations (33) and (34) is solved using Bi-Conjugate gradient method. The Crank-Nicholson approximation is second order in time and the first-order backward differencing is first order in space.

3.2. Diffusive transport in bed sediments:

In order to solve the transport in the bed sediments, the computational domain is discretized horizontally into vertical segments or "columns" so that one sediment column is associated with each river segment. Since there is no horizontal connection between adjustment sediment columns (e.g., diffusive exchange or sub-flow is neglected) each column can be solved independently and this reduces the 2-D problem to a set of 1-D problems (Figure 5). In order to reduce the numerical diffusion and to be able to accurately capture the fronts of various species in the sediments a higher order method (QUICKES) is used to solve vertical transport equations.



Figure 5: Computational domain for solving sediment associated transport in the river and bed sediments

The transport equation for each column is solved using a time weighting scheme finite difference method. A central differencing method is used for diffusive terms and the QUICKEST (Wallis and Manson, 1994) method is used for the advective terms. The discretized form of various terms in equations (27) and (28) can be written as follows

$$\theta \frac{\partial(c_i)}{\partial t} \cong \theta_k \frac{c_{i,k}^{t+1} - c_{i,k}^t}{\Delta t}$$
(37)

$$\frac{\partial \left[\theta \hat{u}_{f} c_{i}\right]}{\partial z} \approx \frac{\left[\hat{u}_{f,k+1}\right]^{t+1/2} \theta_{k+1} c_{k+1} - \left[\hat{u}_{f,k-1}\right]^{t+1/2} \theta_{k-1} c_{k-1}}{2\Delta z} \qquad \text{for } \hat{u}_{f,k} < 0 \qquad (38b)$$

$$+ \gamma \frac{\left[\hat{u}_{f,k-1}\right]^{t+1/2} \theta_{k-1} c_{k-1} - 3\left[\hat{u}_{f,k}\right]^{t+1/2} \theta_{k} c_{k} + 3\left[\hat{u}_{f,k+1}\right]^{t+1/2} \theta_{k+1} c_{k+1} - \left[\hat{u}_{f,k+2}\right]^{t+1/2} \theta_{k+2} c_{k+2}}{\Delta z}$$

$$\frac{\partial}{\partial z} \left(D_T \theta \frac{\partial c_i}{\partial z} \right) \cong \frac{\left[D_{T,i+1/2} \right]^{t+1/2} \theta_{i+1/2} c_{i+1} - \left[D_{T,i+1/2} \theta_{i+1/2} + D_{T,i-1/2} \theta_{i-1/2} \right]^{t+1/2} c_i + \left[D_{T,i-1/2} \right]^{t+1/2} \theta_{i-1/2} c_{i-1}}{\Delta z^2}$$
(39)

$$\frac{\partial (B_d s_i)}{\partial t} \cong B_d \frac{s_{i,k}^{t+1} - s_{i,k}^t}{\Delta t}$$
(40)

$$\frac{\partial [B_{d}\hat{u}_{s}s_{i}]}{\partial z} \cong \frac{B_{d,k+1}[\hat{u}_{s,k+1}]^{t+1/2}s_{i,k+1} - B_{d,k-1}[\hat{u}_{s,k-1}]^{t+1/2}s_{i,k-1}}{2\Delta z} \qquad \text{for } \hat{u}_{s,k} > 0 \quad (41a)$$

$$+ \gamma \frac{B_{d,k-2}[\hat{u}_{s,k-2}]^{t+1/2}c_{k-2} - 3B_{d,k-1}[\hat{u}_{s,k-1}]^{t+1/2}c_{k-1} + 3B_{d,k}[\hat{u}_{s,k}]^{t+1/2}c_{k} - B_{d,k-1}[\hat{u}_{s,k-1}]^{t+1/2}c_{k-1}}{\Delta z}$$

$$\frac{\partial [B_{d}\hat{u}_{s}s_{i}]}{\partial z} \approx \frac{B_{d,k+1}[\hat{u}_{s,k+1}]^{t+1/2}s_{i,k+1} - B_{d,k-1}[\hat{u}_{s,k-1}]^{t+1/2}s_{i,k-1}}{2\Delta z} \\
+ \gamma \frac{B_{d,k-1}[\hat{u}_{s,k-1}]^{t+1/2}c_{k-1} - 3B_{d,k}[\hat{u}_{s,k}]^{t+1/2}c_{k} + 3B_{d,k+1}[\hat{u}_{s,k+1}]^{t+1/2}c_{k+1} - B_{d,k+2}[\hat{u}_{s,k+2}]^{t+1/2}c_{k+2}}{\Delta z} \quad \text{for } \hat{u}_{s,k} < 0 \quad (41b)$$

where $\hat{u}_s = u_s + J_0$, $\hat{u}_f = u_f + J_0$, $D_T = D_m + D_B$ and for QUICKEST scheme the weighting factor $\gamma = 1/6$. Similar to the scheme used for solving transport in the river,
the time weighting method is used here, or for all time varying parameters including *s*, *c*, *v*:

$$\left[\Pi_{s,k}\right]^{t+1/2} = \omega \Pi_{s,k}^{t+1} + (1-\omega) \Pi_{s,k}^{t}$$
(42)

where ω is considered to be equal to 0.5. The discretized set of equations can be written as the following algebraic linear system of equations:

$$-\omega\Omega_{k,1}c_{i,k-2}^{t+1} - \omega\Omega_{k,2}c_{i,k-1}^{t+1} + \left(\frac{\theta_k}{\Delta t} - \omega\Omega_{k,3}\right)c_{i,k}^{t+1} - \omega\Omega_{k,4}c_{i,k+1}^{t+1} - \omega\Omega_{k,5}c_{i,k+2}^{t+1} - \omega\Lambda_k s_{i,k+1}^{t+1} = RHS_{C,k}$$
(43)

$$-\omega \Phi_{k,1} s_{i,k-2}^{t+1} - \omega \Phi_{k,2} s_{i,k-1}^{t+1} + \left(\frac{B_d}{\Delta t} - \omega \Phi_{k,3}\right) s_{i,k}^{t+1} -\omega \Phi_{k,4} s_{i,k+1}^{t+1} - \omega \Phi_{k,5} s_{i,k+2}^{t+1} - \omega \Gamma_k c_{i,k+1}^{t+1} = RHS_{s,k}$$
(44)

where

$$\Omega_{k,1} = -\gamma \frac{\hat{u}_{f,k-2}^{t+1/2} \theta_{k-2}}{\Delta z} \qquad \qquad \text{for } \hat{u}_{f,k} > 0$$

$$\Omega_{k,1} = 0 \qquad \qquad \text{for } \hat{u}_{f,k} < 0$$

$$\Omega_{k,2} = (1/2 + 3\gamma) \frac{\hat{u}_{f,k-1}^{t+1/2} \theta_{k-1}}{\Delta z} + \frac{D_{T,k-1/2}^{t+1/2} \theta_{k-1/2}}{\Delta z^2} \qquad \text{for } \hat{u}_{f,k} > 0$$

$$\Omega_{k,2} = (1/2 - \gamma) \frac{\hat{u}_{f,k-1}^{(r+1)/2} \theta_{k-1}}{\Delta z} + \frac{D_{T,k-1/2}^{(r+1)/2} \theta_{k-1/2}}{\Delta z^2} \qquad \text{for } \hat{u}_{f,k} < 0$$

$$\Omega_{k,3} = -3\gamma \frac{\hat{u}_{f,k}^{t+1/2} \theta_k}{\Delta z} - \frac{D_{T,k-1/2}^{t+1/2} \theta_{k-1/2} + D_{T,k+1/2}^{t+1/2} \theta_{k+1/2}}{\Delta z^2} - B_d k_r K_D \qquad \text{for } \hat{u}_{f,k} > 0$$

$$\Omega_{k,3} = 3\gamma \frac{\hat{u}_{f,k}^{t+1/2} \theta_k}{\Delta z} - \frac{D_{T,k-1/2}^{t+1/2} \theta_{k-1/2} + D_{T,k+1/2}^{t+1/2} \theta_{k+1/2}}{\Delta z^2} - B_d k_r K_D \qquad \text{for } \hat{u}_{f,k} < 0$$

$$\Omega_{k,4} = -(1/2 - \gamma) \frac{\hat{u}_{f,k+1}^{t+1/2} \theta_{k+1}}{\Delta z} - \frac{D_{T,k+1/2}^{t+1/2} \theta_{k+1/2}}{\Delta z^2} \qquad \text{for } \hat{u}_{f,k} > 0$$

$$\Omega_{k,4} = -(1/2 + 3\gamma) \frac{\hat{u}_{f,k+1}^{t+1/2} \theta_{k+1}}{\Delta z} - \frac{D_{T,k+1/2}^{t+1/2} \theta_{k+1/2}}{\Delta z^2} \qquad \text{for } \hat{u}_{f,k} < 0$$

$$\Omega_{k,4} = 0 \qquad \qquad \text{for } \hat{u}_{f,k} > 0$$

$$\Omega_{k,4} = \gamma \frac{\hat{u}_{f,k+2}^t \theta_{k+2}}{\Delta z} \qquad \qquad \text{for } \hat{u}_{f,k} < 0$$

 $\Lambda_k = B_d k_r$

$$\Phi_{k,1} = -\gamma \frac{\hat{u}_{s,k-2}^{t+1/2} B_{d,k-2}}{\Delta z} \qquad \text{for } \hat{u}_{s,k} > 0$$

$$\Phi_{k,1} = 0 \qquad \qquad \text{for } \hat{u}_{s,k} < 0$$

$$\Phi_{k,2} = (1/2 + 3\gamma) \frac{\hat{u}_{s,k-1}^{t+1/2} B_{d,k-1}}{\Delta z} + \frac{D_{B,k-1/2} B_{d,k-1}}{\Delta z^2} \qquad \text{for } \hat{u}_{s,k} > 0$$

$$\Phi_{k,2} = (1/2 - \gamma) \frac{\hat{u}_{s,k-1}^{t+1/2} B_{d,k-1}}{\Delta z} + \frac{D_{B,k-1/2} B_{d,k-1/2}}{\Delta z^2} \qquad \text{for } \hat{u}_{s,k} > 0$$

$$\Phi_{k,3} = -3\gamma \frac{\hat{u}_{s,k}^{t+1/2} B_{d,k}}{\Delta z} - \frac{D_{B,k-1/2} B_{d,k-1/2} + D_{B,k+1/2} B_{d,k+1/2}}{\Delta z^2} - B_{d,k} k_r \qquad \text{for } \hat{u}_{s,k} > 0$$

$$\Phi_{k,3} = +3\gamma \frac{\hat{u}_{s,k}^{t+1/2} B_{d,k}}{\Delta z} - \frac{D_{B,k-1/2} B_{d,k-1/2} + D_{B,k+1/2} B_{d,k+1/2}}{\Delta z^2} - B_{d,k} k_r \qquad \text{for } \hat{u}_{s,k} > 0$$

$$\Phi_{k,4} = -(1/2 - \gamma) \frac{\hat{u}_{s,k+1}^{t+1/2} B_{d,k+1}}{\Delta z} - \frac{D_{B,k+1/2} B_{d,k+1/2}}{\Delta z^2} \qquad \text{for } \hat{u}_{s,k} > 0$$

$$\Phi_{k,4} = -(1/2 + 3\gamma) \frac{\hat{u}_{s,k+1}^{t+1/2} B_{d,k+1}}{\Delta z} - \frac{D_{T,k+1/2} B_{d,k+1/2}}{\Delta z^2} \qquad \text{for } \hat{u}_{s,k} > 0$$

$$\Omega_{k,4} = 0 \qquad \qquad \text{for } \hat{u}_{s,k} > 0$$

$$\Omega_{k,4} = \gamma \frac{\hat{u}_{s,k+2}^{t+1/2} B_{d,k+2}}{\Delta z} \qquad \text{for } \hat{u}_{s,k} > 0$$
$$\Gamma_k = B_d k_r K_D$$

And the right hand sides are calculated as follows:

$$RHS_{c,k} = (1 - \omega)\Omega_{k,1}c_{i,k-2}^{t} + (1 - \omega)\Omega_{k,2}c_{i,k-1}^{t} + \left(\frac{\theta_{k}}{\Delta t} + (1 - \omega)\Omega_{k,3}\right)c_{i,k}^{t} + (1 - \omega)\Omega_{k,4}c_{i,k+1}^{t} + (1 - \omega)\Omega_{k,5}c_{i,k+2}^{t} + (1 - \omega)\Lambda_{k}s_{i,k+1}^{t}$$
(43)

$$RHS_{s,k} = (1-\omega)\Phi_{k,1}s_{i,k-2}^{t} + (1-\omega)\Phi_{k,2}s_{i,k-1}^{t} + \left(\frac{B_{d}}{\Delta t} + (1-\omega)\Phi_{k,3}\right)s_{i,k}^{t} + (1-\omega)\Phi_{k,4}s_{i,k+1}^{t} + (1-\omega)\Phi_{k,5}s_{i,k+2}^{t} + (1-\omega)\Gamma_{k}c_{i,k+1}^{t}$$
(44)

Equations (43) and (44) are solved using the Bi-Conjugate Gradient method. As the boundary conditions flux boundary at the top is considered in order for the method to be mass conservative. The symmetrical boundary is used at the bottom boundary.

3.3. Model testing:

To test the mathematical and numerical model, several comparisons and convergence analysis using analytical solutions for pure-advection pure-diffusion in bed sediment and similarly pure advection in a river reach (i.e. erosion-deposition and solid-water mass exchange neglected) have been performed; the model has been confirmed to converge to the analytical solutions for simplified cases. Also, the mass conservation for a case involving all processes was tested and the model was shown to be mass conserving.

A hypothetical demonstration simulation is performed for a 30km river reach considering the top 50cm of sediments with an initial condition representing a layer of high concentration at a certain depth of sediments. The initial suspended sediment concentration over the reach is assumed to be small and a load of sediment with 10g/L concentration is assumed to flow from upstream and deposit on the bed sediments. The parameters involved in this modeling exercise are summarized in Table 1. The variation of contaminant concentration in the river reach is shown in Figure 6 and Figure 7. Figures 6a and 7a show the dissolved and particulate concentrations of contaminant in the reach 21 and 42 hrs after the start of simulations, Figures 6b, 6c, 7b and 7c show the distributions of contaminant concentration in bed sediments 21, and 42 hours after the start of the test. As it can be noticed from the figures, at the upstream of the reach higher deposition rates with respect to erosion due to high concentration of the moving front of sediments causes the high concentration containing layer to move down, whereas downstream the contaminant containing layer moves towards the surface due to higher erosion rates. Also, as the layer shifts up it spreads with a higher rate compared to when it is buried due to the decreasing bio-diffusion rate with respect to depth. The profiles of dissolved and particulate concentrations in the bulk water also show the effect of burial and erosion on the rate of release of contaminants to the water. As the high concentration layer buries under new sediment as is expected the exchange of contaminants between the sediments and water column decreases significantly as expected. In Figure 6, the exchange of species between bed sediments and water is smaller due to the location of the high-concentration layer in a deeper layer. In Figure 7 the suspended sediments have moved downstream and the high concentration layer is further buried at the upstream and has moved further up at the downstream due to erosion. Therefore the mass exchange at the upstream is further decreased whereas it has increased at the down stream.

Table 1: parameters used in the demonstration simulations.

Davamatar	Value
Parth of wordshad as diment laws	
Depth of modeled sediment layer	50 cm
River Reach Length	30Km
River Segment Length	1Km
Flow Velocity	0.1 m/s
Depth of Concentrated Contaminant layer	10 cm
Maximum Porosity θ	0.631
Minimum Porosity θ_{∞}	0.3
Sediment Grains Density	2.16 gr/cm^3
Porosity decrease rate with depth k_{θ}	0.1 m^{-1}
Time step	30 s
Simulation Duration	18 days
Maximum Bioturbation Diffusion	$0.634 \times 10^{-3} \text{ cm}^2/\text{s}$
Bioturbation decay rate with depth	0.1 m^{-1}
Initial Concentration of sediment	1 mg/kg
associated contaminants	
Water-Sediment Mass exchange	$5.00 \text{ x}10^{-6} \text{ m/sec}$
Coefficient k_b	
Desorption rate k_r	$3.17 \times 10^{-6} \text{ sec}^{-1}$
Solid-Water Partitioning Coefficient K_D	10000 L/kg
Molecular Diffusion Coefficient D_m	$10 \times 10^{-6} \text{ cm}^{2/\text{s}}$



Figure 6: Distribution of Contaminant 21 hrs after the start of simulations in a) water column b) pore water in bed sediments and c) sorbed to bed sediments



Figure 7: Distribution of Contaminant 42 hrs after start of simulations in a) water column b) pore water in bed sediments and c) sorbed to bed sediments

4. Model Application

4.1. Steady State simulation

The model is applied to predict fate and transport of a hypothetical conservative compound with high affinity with sediments in the Colusa Basin Drain in northern California. Sediment characteristic and loads data in Colusa basin drain have been measured by Mirbagheri et al. (1988a; b). The Colusa Basin Drain transfers flood runoff and irrigation return flow from agricultural lands in the northern central valley to Sacramento River. In this study a 30km reach of the drain is considered. In order to simulate flow in the drain system a 1-D kinematic wave model is utilized which uses

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flow-cross sectional area-depth rating curve to model transient variations of flow, area and depth of water in a river (Julien, 2006). The kinematic wave equation for a river is written as follows:

$$\frac{\partial A}{\partial t} + \frac{\partial Q}{\partial x} = i(x)$$

with the rating curves of the following forms:

$$A = a_A h^{p_A}, \quad Q = a_Q h^{p_Q}, \quad u = \frac{a_Q}{a_A} h^{p_Q - p_A}$$

where A, Q and u are respectively cross-sectional area, volumetric flow rate and flow velocity. The kinematic wave equation is solved using an upwind semi-implicit finite different method with upwind first order spatial differencing. Rating curves for different sections of the reach is are given by Mirbagheri et al. (1988a). Figure 8 shows measured and modeled velocity and depth along the reach for a constant flow of 42 m³/s in steady state condition. The rating curve parameters for the locations between the observation measurements have been obtained by interpolating the rating curve parameters at the observation locations. For computing the erosion, deposition and transport of suspended sediment a one-dimensional advection-dispersion model of suspended solids is developed. The equation suggested by Garcia and Parker (1991, 1992, 1993) is used for computing sediment entrainment.

$$E_{s} = \frac{AZ_{u}^{5}}{1 + \frac{A}{0.3}Z_{u}^{5}}$$

where

$$Z_{u} = \frac{u_{s}^{*}}{v_{s}} R_{p}^{0.6}, \qquad u_{s}^{*} = \frac{g^{0.5}}{C'} u, \qquad C' = 18 \log \left(\frac{12R_{b}}{3D_{s}}\right)$$

where u_s^* is the shear velocity, v_s is the fall velocity of the particles, R_b is the hydraulic radius, D_s is the mean particle size and R_p is the average particle Reynolds number.



Figure 8: Measured and Modeled depth and velocity for a steady state flow of 42 m³/sec

Measured and modeled suspended sediment concentration over the reach is shown in Figure 9. The discrepancies between measured and modeled values can be due to inhomogeneous sediment particle size and also variation of average particle size over the channel length, which is not taken into account in the model. A multi-disperse sediment transport model can help improving these results. The parameters used in the model are listed in Table 1. The initial conditions used in this simulation were a contaminated layer with sorbed concentration of 1 mg/kg in a layer at 18cm depth with a thickness of 3cm.

In Figure 10 rates of erosion and deposition, respectively calculated from the Garcia and Parker relation and fall velocity and their difference represented by net deposition are shown. Negative net deposition indicates net erosion or net removal of bed materials from the location, and a positive net deposition indicates accumulation of bed materials. The net deposition and erosion in steady state conditions are relatively close

and their difference was at most 18% of their magnitude. As it can be seen in most parts of the reach net deposition takes place except for one location about 11 km downstream from the top boundary condition and at the downstream point. Also the reach is approximately in a local equilibrium in terms of sediment erosion and deposition as the difference between both processes is small compared to erosion and deposition rates themselves. This is an expected observation for steady state conditions.



Figure 9: Measured and Modeled sediment concentration in Colusa Basin drain in a steady state condition



Figure 10: Erosion and Deposition rate over the reach in steady state condition

Figure 11 shows the sorbed and dissolved concentration profiles of contaminants in bulk water at different times after the start of simulation. The rapid increase in the particulate concentration take place at the high erosion zone and the sedimentassociated concentration remains relatively constant to the end of the reach due to small exchange with bulk water. The gradual increase in dissolved concentration is mainly due to desorption from the particulate phase. In Figure 12, the time variation of concentration at the downstream end is shown. Due to a large partitioning coefficient and small desorption rates assumed for the hypothetical compound in the simulation and also small the diffusive flux of dissolved contaminants from the bed sediments to the water column, the dissolved concentration is relatively small compared to sorbed concentration. In Figure 13 the distribution of contaminants in the bed sediments is shown. As it can be seen at the places where the rate of erosion is lower than the rate of deposition the high concentration sediment layer buries under the newly deposited sediments and therefore the exchange between sediment and water diminishes. On the other hand, at locations where the rate of erosion is higher than the rate of deposition the centroid of the concentration distribution moves up and contaminants are released into the water. The high contaminated sediment layer expands as it moves upward due to erosion because of the reverse consolidation. In the pore phase, small concentrations at the top are due to exchange with bulk water with low contaminant concentration, whereas the higher top sorbed phase concentration is due to the deposition of relatively high concentration suspended particles on the top layer of sediments. The bio-diffusion rate is assumed to decrease exponentially with the depth, and therefore the rate of diffusive transport to the lower layers is small.



Figure 11: Bulk water profile of a) contaminant sorbed to suspended sediments b) dissolved at various times after the start of simulation



Figure 12: time variation of dissolved and particulate contaminant concentration at the downstream boundary of the reach

In the previous example the rate of uptake and release by the particles were assumed to be very small compared to typical sediments (i.e., $k_r = 0.27/\text{day}$) so that the behavior of sorbed and dissolved phases can be studied independently. That is the cause of the differences between the patterns of the distributions of solid and pore phases in the bed sediments as shown in Figure 13, since it takes several weeks for the sorbed and pore phases to reach equilibrium. A simulation is also done for a higher value of mass exchange between solid and aqueous phases with $k_r = 25$ hr⁻¹ in order to demonstrate the effect of mass exchange between the solid and aqueous phases. Figure 14 shows the profile of sorbed and dissolved concentrations in the water column along the reach at various times. It is possible to see that the sorbed concentration drops quickly after the region with high erosion rate due to the high mass exchange with the water. This behavior was not observed in the case with low mass exchange rate, as it expected. Figure 15 represents the time variation of dissolved and particle associated contaminants at the end of the reach. As expected, the particulate and dissolved phases show a similar increasing pattern due to exposure of bed sediment contaminants to the water column. The distribution then decreases due to decrease in the available amount of contaminants in the sediments. In Figure 16 the variation of contaminants in the case with small and large solid-water exchange rate cases is the low sorbed and particulate concentrations in top layers of bed sediments.



Figure 13: Distribution of Contaminants in the sediments left column: in pore water and right column: sorbed to bed sediments at various times after the start of simulation

It can be observed in Figure 14 that the concentration sorbed to suspended sediments drops fairly rapidly after the high erosion locations due to fast exchange with the overlying water. Therefore the sediments that deposit on the zones with net deposition do not contain a high concentration as compared to the case with small solid-water exchange.



Figure 14: Bulk water profile of a) sorbed to suspended sediments contaminant b) dissolved at various times after the start of simulation for the case with higher solid-water exchange rate



Figure 15: Time variation of dissolved and particulate contaminant concentration at the downstream of the reach for the high exchange rate case



Figure 16: Distribution of contaminant is the bed sediments at various times for the case with high solid-water exchange rate

4.2. Transient Flow Simulation

A similar simulation as the one explained in the previous section was performed on a case with time varying flow and, therefore with varying sediment erosion rates. Two high flow events were assumed to take place during the simulation event at 7 and 13 days after the start of simulation as shown (see Figure 17). All parameters used in this simulation were the same as those in the previous simulation with $(k_r = 25 \text{ hr}^{-1})$. The erosion and deposition rates and the net deposition rate alongside the reach at various times after the start of simulation are shown in Figure 18 and Figure 19 respectively. The profiles of dissolved and particle-associated concentration in the water column are shown in Figure 20. It can be observed that the concentrations for both particleassociated and dissolved contaminants along the river reach have highest values around the location with net erosion and they drop at the locations with net deposition. The dissolved profile has a smoother shape due to the rate limited desorption. Also, in the time dependent flow case each location may undergo a net erosion or net deposition at different times. Another observation is the expected dependence between suspended sediment-associated contaminants and the net erosion rate. It can be seen that at day 10, which is after the first high flow regime, the particle-associated concentration has its highest values and it drops to lower values at day 20. This behavior can be seen also in Figure 21 which shows high suspended sediment-associated and dissolved concentrations corresponding to high flow. Also, the decrease in the dissolved concentration after the peak flow might be due to high net deposition rates after the flow peak and blockage of the bed sediment layers with higher concentration from the water column. Figure 22 shows the distribution of contaminants in the bed sediments at various times. Similar to the steady-state flow case, the dissolved concentrations at the top layers are small. Due to higher rates of erosion the high concentration layer completely disappears at some locations due to the high erosion rates at particular locations. While these general trends are captured here, in natural rivers, the small scale heterogeneities and the temporal changes in the net erosion or net deposition regimes caused by changes in the morphology of the bed may cause some differences with the results obtained by this modeling study. Simulating the effect of these small scale heterogeneities requires further study or special up-scaling modeling techniques which were beyond the scope of this work.



Figure 17: Flow rate vs. time in the reach for the case with variable flow



Figure 18: Erosion and Deposition rates at various times of time varying flow case



Figure 19: Net Deposition/Erosion rate at different times of simulation in time varying flow case



Figure 20: Profiles of a) particle-associated and b) dissolved contaminants along the river reach at various time for time varying flow condition



Figure 21: Sediment-associated and dissolved concentrations in the bulk water at the down-stream boundary.



Figure 22: Distribution of contaminant concentration in the bed sediments for the time varying flow case at different times after the start of simulation.

5. Conclusion and summary

A quasi two-dimensional numerical model has been developed for the prediction of fate and transport of contaminants in river systems, considering the interactions taking place in the benthic sediments and the water column. Burial, consolidation, kinetic watersolid mass exchange and bio and physical diffusion of contaminants in the bed sediments, as well as sediment-associated transport of contaminants in the water body due to advection and dispersion of suspended materials and dissolved contaminants, have been taken into account. A semi-implicit finite difference method has been used to solve the resulting set of coupled partial differential equations. A demonstration simulation has been presented on flow and sediment transport data obtained for Colusa basin drain in northern California. For this purpose, a simple flow model using a kinematic wave equation and a sediment transport module using the relations offered by Garcia and Parker (1993) has been developed and is linked to the model. The mechanistic formulation in the model is unique as it combines aspects not taken into account by other researchers in an integrated manner. This work puts together a group of processes of contaminant transport in rivers usually spreads over several models including suspended sediment associated transport in river and evolution of sediment associated contaminants in the bed sediments. Although there is no available data to calibrate all processes contained in the model, the individual components of the model have been tested with analytical solutions and satisfactory agreement has been observed. Two demonstration simulations have been performed for two cases with steady state flow and sediment transport conditions, one with high and the other with low solid-water exchange rates and one case with unsteady flow and sediment transport. The results indicate that the model is capable of reproducing expected variations of sediment-associated contaminants in a river system. The model uses a 1-D representation of the river with a quasi 2-D vertical representation of bed sediments; therefore, the effects of dead zones, shores, banks and floodplains with possible higher deposition rates, can not be considered unless very small spatial distribution is used. However, the model also has the capability of being coupled with two and three dimensional water quality models with some slight modifications to enhance its capability of considering benthic sediment processes. Also small scale heterogeneities in the river hydrodynamic, and therefore sediment deposition and erosion regimes can significantly affect the release or burial of contaminants. Since the model can handle only large scale variations alongside the river due to computational setbacks of using small grid cells, taking into account the effect of such heterogeneities the some special up-scaling methods needs to be incorporated into the model.

The next chapter discusses using the model for simulation of fate and transport of multi-species reactive compounds in a river system controlled by biotic and abiotic reactive networks.

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Chapter II:

Mathematical Modeling of Sediment-Facilitated Transport of Contaminants in Riverine Systems – Chemical Processes.

Abstract:

A mechanistic multi-species contaminant reactive transport model in riverine systems which considers the physical processes in the water column and sediments has been presented in the previous chapter. In this chapter the methods used to model biogeochemical reactions and transformations of the species using a fully kinetically controlled approach are introduced. The kinetically-controlled reaction network is solved using a non-iterative sequential (operator splitting) method using an innovative approach that uses variable time steps for each species. This enables the model to simulate both fast and slow reactions with significant computational efficiency. Using the fully kinetic approach frees the user from partitioning reactions into equilibrium and kinetically controlled basis (that is often an approximation) and the associated complexity of basis swapping when some concentrations become small with the multiple time step approach, near equilibrium reactions can be represented by the model via fast kinetics. The code is developed so that various forms of simple, Monod, dual-Monod and multiplicative Monod with inhibiting functional forms of reactions can be introduced into the model. Several demonstration cases including one dimensional sediment columns and two dimensional multi-species reactive transport in the river system are simulated using the model.

1. Introduction:

In the previous chapter, an approach used for modeling physical transport processes in riverine benthic sediments and water column has been introduced. In this chapter the main focus will be on modeling chemical reactions involved in fate of contaminants and other species that may influence the degradation, mobility, and toxicity of contaminants in river sediment systems. The focus is on heavy metals and the biogeochemical reactions governing their fate and transport in such multiphase systems. For many metals including Cobalt (Co), Copper (Cu), Molybdenum (Mo), Nickel (Ni) and Zinc (Zn), the redox state can affect the mobilization of metallic ions significantly. In an oxic condition, these metals may undergo oxidation to their higher oxidized forms. At these states they usually have larger solubility with respect to their solid mineral salt precipitates and thus larger mobility. It is noted that the reverse is true for the ubiquitous earth metals (e.g. Iron and Manganese). Under anoxic conditions, reduced forms of these metals are forms which have smaller solubility and therefore mobility. Since top layers of sediments usually have oxic conditions, heavy metals occurring at the surface of sediments are typically in their higher oxidized form. When these metals undergo burial, the condition becomes anoxic, and reduction can occur due to microbially-mediated oxidation of organic carbon utilizing sulfate and/or Fe (III) as electron acceptor. These phenomena can mobilize metals that can be transported upward to the sediment surface again due to several processes including diffusion and bioturbation, where they are exposed to oxygen, and may undergo oxidation again. The net effect of these processes creates a cycle of oxidation and reduction of the metallic ions that governs transport and bioavailability of metals in water-sediment systems. Several studies have been conducted on modeling these microbially-mediated cycling of metals in aquatic systems, mainly emphasizing biogeochemical processes in marine, oceanic sediments (Boudreau, 1996; Furrer et al., 1990; Maher et al., 2006; Soetaert et al., 1996; Steefel and Yabusaki, 1996; Van Cappellen and Gaillard, 1996; Van

Cappellen et al., 1993; VanCappellen and Wang, 1996) and lakes (Carignan and Lean, 1991). Another important effect of microbial activity in the sediments is methylation of metals (Bryan and Langston, 1992; Odum, 2000). Many heavy metals such as mercury, lead, and arsenic may undergo methylation in the presence of certain types of bacteria in the sediment. The methylated forms of these metals usually have a higher mobility and more importantly are much more bioavailable than their regular state (John, 1989). Biogeochemical models can be highly useful to investigate conditions in which these processes occur in the sediments.

Boudreau (1999) extensively reviewed the approaches to model metal diagenetic cycling in freshwater lacustrine sediments. Theoretically, there is no major difference between the processes involved in diagenetic metal cycling in saline marine waters and freshwaters Boudreau (1999). In both cases the horizontal component of the flow and transport in the pore water is small enough to be ignored and a one-dimensional column is usually considered to represent the sediment layers. However, in riverine systems, due to faster dynamics of sediment resuspension and deposition and the strong horizontal advective component of the flow, horizontal transport of particles and constituents associated with them can play an important role in the whole process. To the best of the author's knowledge there is no integrated modeling approach that considers early diagenetic effects in the sediments as well as transport mechanisms including erosion and sedimentation in a riverine systems for predicting contaminant fate and transport in a coupled manner. This is in spite of the fact that sediment associated contaminants represent a real problem in many water bodies and the redox conditions in sediments can control the biodegradation, bioavailablity, and mobility of many contaminants present in the riverine systems. The goal of this study is to develop and test such a modeling approach by developing a coupled river fate and transport model and a sediment diagenetic model.

1.1. Numerical approaches in reactive transport in porous media

There have been a wide range of approaches in modeling reactive transport in aquatic systems and porous media, ranging from simple first-order biodegradation models to complicated bio-film models. Rittmann and VanBriesen (1996) categorized reactive biogeochemical transport models into four categories, including first-order or biodegradation models, equilibrium models, microbially mediated Monod or dual Monod models and biofilm models. First-order models are the most commonly used models in fate and transport of organic contaminants. In these models, the rates of transformation of contaminants are assumed to be proportional to their concentrations and independent of concentration of other influential agents such as biomass or other constituents. In equilibrium or instantaneous reaction models, biodegradation is assumed to take place instantaneously resulting in equilibrium between the organic electron donor and the electron acceptor. The most commonly used approach in the geochemical modeling has been the full equilibrium approach (Bethke, 1996; Engesgaard and Kipp, 1992; Yeh and Tripathi, 1991). Borden and Bedient (1987) and Rifai and Bedient (1990) used the equilibrium approach to explain the results of their field experiments. Yeh and Tripathi (1991) used an iterative operator splitting approach referred to as sequential iterative approach (SIA) in their well known model HYDROGEOCHEM. In this approach transport and reaction terms are solved iteratively in each time step until convergence is attained. The drawback of the equilibrium and first-order biodegradation models is that it they ignore the fact that the reactions are catalyzed by living organisms and their rate should be controlled by the concentration of the involved organisms. Equilibrium models are basically incapable of handling rate-limited irreversible biodegradation reactions. Also it has been shown recently that in many cases local equilibrium is not attained in timescales relevant to contaminant transport in many aquatic systems, especially in microbially-mediated redox reactions which have slow rates (Steefel and Macquarrie, 1996). Biofilm models

take into account micro-scale processes including diffusive transport of substrates and terminal electron acceptors into and out of the biophase (Molz et al., 1986; Rittmann and McCarty, 1981; Widdowson et al., 1988). Due to the high complexity of these models and the large computational cost of running them for real cases, they have been rarely used for practical large scale modeling efforts.

Microbially-mediated process models have received a significant amount of attention in the recent years. These models are usually built based on a reactive network consisting of main species involved in reductive transformation of the contaminant of interest in the system. These species usually contain sequential terminal electron acceptors such as oxygen, nitrate, iron, manganese and sulfate. Some of these models assume that the biomass concentration of any functional group of bacteria is proportional to the corresponding terminal electron acceptors and ignore the kinetic growth and decay of bacteria (e.g. Macquarrie et al., 1990) whereas in some other models the biomass is predicted by incorporating the kinetics of bacterial growth and decay into the model (e.g. Essaid et al., 1995). The most widely used kinetic relations for modeling the effect of biomass in microbially-mediated reactions are single or multiplicative Monod kinetic models (Bae and Rittmann, 1996a; b)

There have been various approaches in solving the coupled systems of reactive and transport equations involved in microbially-mediated chemical transformation problems. These approaches can be roughly divided into fully kinetic models and hybrid models which are capable of handling both equilibrium and kinetic reactions simultaneously. (Lichtner, 1985; 1996) provided a useful review of the mathematical foundations of time-space continuum model for the reactive transport in the porous media. Among the numerical techniques which have been utilized in solving these types of PDEs, Non-iterative explicit operator splitting method, iterative sequential and fully couple implicit methods can be named.

Many researchers have used fully kinetic approach for microbially mediated reactive transport problems. For example Macquarrie et al. (1990) developed a coupled two dimensional biodegradation model considering the transport of microbial biomass, and terminal electron acceptors as well as the substrate by utilizing dual-monod reaction kinetics. They solved the system of partial differential equations (PDEs) using principal direction Galerkin finite elements method. They treated non-linear reactions using a semi-implicit iterative technique. Wood et al. (1994) solved the nonlinear monod type reactive transport equations of a biodegradation problem using the operator splitting method by using an explicit non-iterative sequential method. Essaid et al. (1995) used a two dimensional model to simulate aerobic and anaerobic biodegradation of organic compounds. They also used a non-iterative explicit method to solve non-linear ODEs representing reactions expressed using monod type kinetics. While an equilibrium assumption may not be appropriate for many reaction networks that include slow reactions (Brusseau et al., 1989; Vanderzee et al., 1989), the use of a kinetic model in systems with both fast and slow reactions has some other problems due to the high stiffness of the governing partial differential equations (Chilakapati et al., 1998). In conventional kinetic models, fast reactions require very small time steps which can significantly increase the computational effort needed to solve the problem (Steefel and Macquarrie, 1996). For this reason, most of the purely kinetic models have been used for systems with relatively slow reactions usually involving bacteria-mediated transformation. However even in relatively slow bacterial-mediated redox reactions there are often some fast secondary reactions involved.

In order to solve this stiffness problem caused by using purely kinetic models, some researchers have attempted to develop combined kinetic-equilibrium models. In this approach, the components involved are categorized into primary and secondary components and the transport equations are solved only for primary components. The concentrations of the secondary components are then calculated by assuming equilibrium with the corresponding primary components and this reduces the number of transport equations to be solved. Friedly and Rubin (1992) proposed a method to formulate and solve a mixed equilibrium-kinetic reactive transport model using a sequential non-iterative technique based on the concept of concentration and stochiometric spaces. Recently, some researchers have used methods that solve the set of transport PDEs and reactions simultaneously (Kee et al., 1985; Oran and Boris, 1987; Steefel and Lasaga, 1994). This approach is called one-step or global implicit method. In this approach the reaction term is calculated from the current time step concentrations, which makes the resulting system of equation fully implicit. In order to solve this system of equations for nonlinear reactions iterative techniques are used. Steefel and Yabusaki (1996) used this approach to develop GIMRT model for onedimensional simulation of diagensis in sediments. They later developed CRUNCH model by improving some of GIMRT features such as adding the effects of erosion, compaction and also adding surface complexation, multicomponent diffusion, and variable porosity due to dissolution and precipitation (Steefel, 2001). Although the Global Implicit approach is observed to work efficiently for one component systems, in systems with large numbers of species the stiffness matrix becomes very large and the computer CPU time for solving such systems increases rapidly. Walter et al. (1994) and Zysset et al. (1994a, b) have used mixed equilibrium and kinetic formulation with the so-called sequential iterative approach (SIA). In SIA approach the transport equation for each species is solved separately but iteration in each time step is performed on transport and reaction terms until convergence is attained. This approach reduces the size of system of equations that need to be solved in each time step with respect to the global implicit approach. Fang et al. (2003) used the mixed equilibrium and kinetic approach to develop a model BIOGEOCHEM for biogeochemical reactions in batch systems.

Although the mixed equilibrium-kinetics approach has the advantage of reducing the number of transport equations to be solved and also of eliminating the stiffness of the

system with respect to a fully kinetic approach, it requires that the model user to specify a priori which reactions to treat as equilibrium and which as kinetically controlled. In most cases, it is possible to predetermine whether a reaction can be treated as equilibrium or kinetic; however this is not always the case, because the rates of nonlinear reactions may vary significantly due to the changes in the concentration of participating species. Therefore in a spatially and temporally variable system one reaction rate may vary from slow to near-equilibrium.

In this research, an innovative developed that uses a fully kinetic approach with multiple time-steps for each reaction. This allows the transport time step not to be influenced by high reaction rates of some of the species. Also, slow reactions can be treated with larger time steps, which saves a significant amount of computational effort. Using a fully kinetic approach eliminates the need to pre-specify the nature of reactions in terms of being kinetically controlled or in equilibrium, as well as any basis switching required during solution of such mixed systems. The model is fully mass-conservative and is capable practically to model instantaneous equilibrium conditions for fast reactions by using smaller time steps with respect to transport time step. The formulation and implementation of the method is described in the next section.

2. Formulation and numerical solution of the reaction Terms

The 1-D reactive transport equations for each species in stream bed with sorption and desorption to the solid phase can be written as follows:

$$\frac{\partial c_i}{\partial t} + L(c_i) = \sum_{j=1}^{nr} \vartheta_{ij} R_{m,j}(\hat{c}, \hat{s}) \qquad \text{for } i=1..nc$$
(1)

$$\frac{\partial s_i}{\partial t} + L(s_i) = \sum_{j=1}^{nr} \vartheta_{ij} R_{\mathrm{Im},j}(\widehat{c}, \widehat{s}) \qquad \text{for } i=1..nc$$
(2)

where *L* represents the transport and solid-aqueous phase mass exchange operator. For example, in the pore water phase on benthic sediments *L* can be written as follows:

$$L(c_i) = \frac{1}{\theta} \frac{\partial v \theta c_i}{\partial z} - \frac{1}{\theta} \frac{\partial}{\partial z} \left(D\theta \frac{\partial c_i}{\partial z} \right) + k_r \left(K_D c_i - s_i \right)$$
 for mobile phase and (3)

$$L(s_i) = -k_r (K_D c_i - s_i)$$
 for immobile phase (4)

 \mathcal{G}_{ij} are stoichiometric coefficients for component *i* in reaction *j*, *nr* is number of reactions *,nc* are number of constituents, $R_{m,j}$ is the reaction rate of reaction *j* which affects mobile phase concentration and $R_{Im,j}$ is the reaction rate of reaction *j* which affects immobile phase and \hat{c} , \hat{s} are concentration vectors for all aqueous and sorbed species respectively. The methods of solving the equation for the transport operator *L* were presented in chapter one and here the focus will be on how to handle the reaction terms. Since each reaction rates can be a function of concentrations of several species, equations (1) and (2) can also be written as follows:

$$\frac{\partial c_i}{\partial t} + L(c_i) = \sum_{j=1}^{nr} \vartheta_{ij} R_{m,j}(\hat{c}, \hat{s}) = g_{m,i}(\hat{c}, \hat{s})$$
(5)

$$\frac{\partial s_i}{\partial t} + L(s_i) = \sum_{j=1}^{nr} \mathcal{G}_{ij} R_{im,j}(\hat{c}, \hat{s}) = g_{\mathrm{Im},i}(\hat{c}, \hat{s})$$
(6)

 \hat{c} and \hat{s} are vectors of species concentrations in mobile and immobile phases respectively and $g_{m,i}$, $g_{\text{Im},i}$ are functions representing all reactions affecting component *i*. An operator splitting technique is used to solve equations (5) and (6) so that the transport part is solved using the techniques explained in the previous chapter and then the concentration changes obtained from the reaction terms is superimposed to it. In the transport stage the intermediate concentrations c^* and s^* are calculated using the implicit finite difference method explained in the previous chapter.

$$\frac{c_i^* - c_i^t}{\Delta t} + L(c_i) = 0 \tag{7}$$

$$\frac{s_i^* - s_i^t}{\Delta t} + L(s_i) = 0 \tag{8}$$

and then the concentration change due to the reaction term is added.

$$c_i^{t+1} - c_i^* = \int_t^{t+\Delta t} g_{m,i}(\hat{c}, \hat{s}) dt$$
(9)

$$s_i^{t+1} - s_i^* = \int_t^{t+\Delta t} g_{im,i}(\hat{c}, \hat{s}) dt$$
(10)

Using first order Taylor series expansion equations (9) and (10) can be written as follows:

$$c_i^{t+1} - c_i^* = \int_t^{t+\Delta t} \left(g_{m,i}(\widehat{c}^t, \widehat{s}^t) + \frac{\partial g_{m,i}(\widehat{c}^t, \widehat{s}^t)}{\partial t} \tau \right) d\tau + O(\Delta t^3)$$
(11)

$$s_i^{t+1} - s_i^* = \int_t^{t+\Delta t} \left(g_{im,i}(\widehat{c}^t, \widehat{s}^t) + \frac{\partial g_{im,i}(\widehat{c}^t, \widehat{s}^t)}{\partial t} \tau \right) d\tau + O(\Delta t^3)$$
(12)

In which \hat{c}^t , \hat{s}^t are concentration vectors evaluated at time *t*. By performing the integration, equations (11) and (12) can be written as:

$$\frac{c_i^{t+1} - c_i^*}{\Delta t} \cong g_{m,i}(\hat{c}^t, \hat{s}^t) + \frac{1}{2} \frac{\partial g_{m,i}(\hat{c}^t, \hat{s}^t)}{\partial t} \Delta t$$
(13)

$$\frac{s_i^{t+1} - s_i^*}{\Delta t} \cong g_{m,i}(\hat{c}^t, \hat{s}^t) + \frac{1}{2} \frac{\partial g_{im,i}(\hat{c}^t, \hat{s}^t)}{\partial t} \Delta t$$
(14)

in order for the second order term to be ignored and the method remain stable and accurate, it should be small compared to the first-order term or the first terms in equations (13) and (14) or:

$$\frac{\left(\partial g_{m,i}(\hat{c}^{t},\hat{s}^{t})/\partial t\right)\Delta t}{g_{m,i}(\hat{c}^{t},\hat{s}^{t})} < \varepsilon \qquad \text{and} \qquad \frac{\left(\partial g_{im,i}(\hat{s}^{t},\hat{c}^{t})/\partial t\right)\Delta t}{g_{im,i}(\hat{c}^{t},\hat{s}^{t})} < \varepsilon \tag{15}$$

where ε is an error tolerance determining the maximum truncation error due to ignoring the second order term. Equation (15) can be calculated analytically as:

$$\frac{1}{g_{m,i}(\hat{c}^{t},\hat{s}^{t})}\frac{\partial g_{m,i}(\hat{c}^{t},\hat{s}^{t})}{\partial c_{j}}\frac{\partial c_{j}}{\partial t}\Delta t < \varepsilon$$
(16)

$$\frac{1}{g_{im,i}(\hat{s}^t,\hat{c}^t)}\frac{\partial g_{im,i}(\hat{s}^t,\hat{c}^t)}{\partial s_j}\frac{\partial s_j}{\partial t}\Delta t < \varepsilon$$
(17)

However calculating the derivative of the reaction functions with respect to the concentration of all constituents at each time step is a computationally costly process especially for nonlinear reactions containing several Monod terms. Therefore the derivatives in equation (15) can be expressed numerically using the first-order approximation:

$$\frac{\partial g_{m,i}(\hat{c}^{t})}{\partial t} \approx \frac{g_{m,i}(\hat{c}^{t+\Delta t}) - g_{m,i}(\hat{c}^{t})}{\Delta t}$$
(18)

$$\frac{\partial g_{im,i}(\hat{s}^{t})}{\partial t} \approx \frac{g_{im,i}(\hat{s}^{t+\Delta t}) - g_{im,i}(\hat{s}^{t})}{\Delta t}$$
(19)

therefore the criteria in expression (15) can be written as:
$$\frac{g_{m,i}(\hat{c}^{t+\Delta t}) - g_{m,i}(\hat{c}^{t})}{g_{m,i}(\hat{c}^{t})} < \varepsilon$$

$$\frac{g_{im,i}(\hat{s}^{t+\Delta t}) - g_{im,i}(\hat{s}^{t})}{g_{im,i}(\hat{s}^{t})} < \varepsilon$$
(20)
(21)

for fast reactions the variation of concentration vs. time and therefore the change in the reaction rates $g_{m,i}$, $g_{im,i}$ can be large so that criteria (20) and (21) may not be satisfied when the transport time step Δt is used for solving reactions. In order to satisfy these criteria, the time step should be decreased. For near equilibrium equations decreasing the time step for the transport equation as well as the reaction time steps for all reactions can make the numerical procedure infeasible. Also each species may have its own appropriate time step satisfying the conditions in equations (20) and (21). In addition, due to the nonlinear dependence of the rates on concentrations of species the appropriate time step can vary during time and with space due to variation in concentrations. To solve problems stemming from the representation of fast reactions using a kinetic approach, an independent and variable time step was used for each species at each grid cell to satisfy rate variation criteria. In the procedure the time step for each species is found at the beginning of each time step by reducing time steps for each species until the terms in equations (20) and (21) become less than a predefined tolerance. This time step can be different for each species. The flowchart in Figure 23 shows the steps taken in the algorithm to compute the reaction term.



Figure 23: The algorithm for using the variable time-step approach in solving reactive transport Firstly the transport time-step Δt is chosen for every reaction then the reaction rate for $g_{m,i}$ is calculated at time t and the concentration vector at time t+ Δt is calculated using first-order Taylor series approximation. Then using the concentration vectors at $t+\Delta t$ the reaction rate function $g_{m,i}$ at time t+ Δt is calculated and criteria (20) and (21) are checked. If the criteria are not satisfied, the reaction time step associated with the species is divided by two. This stage is repeated for each species until the criteria are satisfied for all components. It worth noting that to calculate the reaction functions at time t+ Δt_i (Δt_i being the time step assigned to component *i*) the concentration vectors are required to be known at time $t+\Delta t_i$ for all components. Since each component has its own time-step the concentrations may not be directly calculated at time $t+\Delta t_i$ but the algorithm is arranged so that before calculating the concentration for each species the concentration of all other species at a time at or after $t+\Delta t_i$ are calculated and therefore the concentration vector at $t+\Delta t_i$ can be calculated by interpolation for all species. In advancing the solution within one time-step the least advanced species should be chosen and be advanced at each time step so that the all components of concentration vectors \hat{c} and \hat{s} at the time be specified or can be calculated through linear interpolation. The schematic in Figure 24 shows the sequence of steps of computation in a hypothetical problem. The reaction network Figure 24 is assumed to have three components with components I, II, and III having limiting time steps of ΔT , $\Delta T/2$, and $\Delta T/4$ respectively (ΔT being the time step used to solve the transport PDE). In this case the reaction ODE for component I (with the largest time step) is solved first explicitly by having the concentrations of all components known at time zero; then in the second step the ODE for component II with the largest time-step of the smallest progressed reactions is solved and then component III is solved. In the forth time step component III has the smallest progress therefore is advanced and so fourth. As an example the

following hypothetical reaction network with multi-scale reaction rates are solved using the variable-time step scheme in a batch system.

$$A + B \xleftarrow[k_2]{k_1} C + D \qquad (a)$$

$$A \xrightarrow{\kappa_3} E \tag{b}$$

$$B \xrightarrow{\kappa_4} F \tag{c}$$

It is assumed that the mass-action the ODE describing the concentration of each component's kinetics can be written as:

$$\frac{d[A]}{dt} = -k_1[A][B] + k_2[C][D] - k_3[A]$$

$$\frac{d[B]}{dt} = -k_1[A][B] + k_2[C][D] - k_4[B]$$

$$\frac{d[C]}{dt} = +k_1[A][B] - k_2[C][D]$$

$$\frac{d[D]}{dt} = +k_1[A][B] - k_2[C][D]$$

$$\frac{d[E]}{dt} = k_3[A]$$

$$\frac{d[F]}{dt} = k_4[B]$$

The values of k_1 , k_2 , k_3 and k_4 are chosen respectively to be 100, 200, 0.001, and 0.005 indicating that the first reaction (a) is several orders of magnitude faster than the other two reactions (b) and (c).

The transport time-step is assumed to be 1 second in this problem and the initial conditions are chosen to be $[A]_0 = 1$, $[B]_0 = 1$, $[C]_0 = 0.625$, $[D]_0 = 0.8$, $[E]_0 = 0$, $[F]_0 = 0$. Clearly due to dependence of the kinetics on the concentrations of A, B, C, and D, the state of the reactions in terms of being kinetically controlled or in instantaneous equilibrium depends on their concentrations. Initially within the ranges of the initial concentrations reaction (a) acts in instantaneous equilibrium with respect to the time step of 1 sec. relative to reactions (b) and (c) that are kinetically controlled relative to

reaction (a). Using the algorithm the limiting time-step for components [A], [B], [C], and [D] which are affected by the fast reaction were determined to be 1/1024 seconds and the 1 second transport time-step were found to be appropriate for components, [E] and [F]. Figure 25 shows the solution to the system of ODE using the variable time-step scheme in the first 2 seconds (2 time steps) of simulations. The ticks on the curves represent the times when the concentrations are calculated for the corresponding component. The solution of the problem in 10000 seconds is shown in Figure 26. As expected, eventually all of the components convert to [F] and [E] and the system remains with some unused [C] due to its initial excessive amount and the fact that system runs out of [D]. Also the line representing the magnitude of [A][B]/[C][D] remains constant and equal to the equilibrium constant (0.5) for the most of the simulation except at some period of time when the concentration of [B] is negligibly small and therefore the system is out of equilibrium as is expected. This example shows clearly that even for the reactions that have relatively high rates so that they appear to act in instantaneous equilibrium there may be some circumstances that they are out of equilibrium state due to the small concentration of some of the involved species.



Figure 24: Steps sequence used in computing concentrations using variable time-step method.



Figure 25: Initial solution of the hypothetical reaction network at the first 2 transport time steps.



Figure 26: Solution of the hypothetical multi-scale problem

3. Demonstration simulations

3.1. Demonstration simulation: One dimensional column

As a demonstration simulation, the model is applied to the problem of methylation of mercury in a one-dimensional vertical sediment column. In aquatic systems, major forms of mercury are usually associated with sediment particles and mercury species are mainly transported in sediment-associated forms in rivers and estuaries. Therefore a realistic mercury fate and transport model needs to incorporate sediment transport and also sediment associated species transport.

The most common toxic form of mercury is its methylated form which can be bioaccumulated in biota and biomagnified through the food chain. There is strong evidence that sulfate reducing bacteria (SRBs) are the primary agents for production of methylmercury and thus methylmercury is mostly produced in anoxic sulfidic waters (Gilmour and Henry, 1991; King et al., 2000; King et al., 2001; King et al., 1999). In rivers anoxic sulfate reducing conditions may occur in the sediments. Thus, in order to model the rate of methylation in a riverine system, the rate of sulfate reduction, available reactive mercury, and organic matter concentrations are required to be known in the sediments at different depths. In order to compute the rate of methylation of mercury, the activities of SRBs and concentration of H₂S are required. For this purpose, the fate and transport of some major species affecting the activities of SRB such as O₂, NO_3^{-} , Fe and Mn needs to be modeled as well, since they act as inhibiting agents to SRB activity. Since mercury concentration is usually small compared to other major components such as organic matter, oxygen, nitrate, sulfate, iron, etc., the effect of mercury reactions on the concentration of major components is ignored. The reaction network here is adopted from Berg et al. (2003), Hunter et al. (1998), and VanCappellen and Wang (1996) with some slight modifications and simplifications. The biotic organic matter decomposition reactions are considered as primary reactions and re-oxidation of reduced species resulting from primary reactions are considered secondary reactions. Organic Matter, MnO₂, FeOOH, S⁰, FeS, FeS₂ HgS are considered to be purely associated with solid phases, Mn^{2+} and Fe^{2+} , Hg^{2+} are considered to be partly aqueous and partly associated with the solid phase and the rest of the species were assumed to be purely aqueous. Biomass concentration of each functional group of bacteria is assumed to be in instantaneous equilibrium and proportional to the activity of the terminal electron acceptor associated with that bacterial functional group and therefore the biomass concentration is implicitly considered in the model. Although this approach ignores the population lag following shift in electron acceptor but is a widely

used assumption (Berg et al., 2003; Hunter et al., 1998; VanCappellen and Wang, 1996). The complete reaction network used in the model can be expressed as follows:

$OM + O_2 \xrightarrow[R_1]{} CO_2$	7	
$OM + 0.8NO_3^- + 0.8H^+ \xrightarrow{R_2} CO_2 + 0.4N_2$		
$OM + 2MnO_2 + 4H^+ \xrightarrow{R_3} CO_2 + 2Mn^{2+}$		Primary Bacterial Mediated
$OM + 4FeOOH \xrightarrow{R_4} CO_2 + 4Mn^{2+}$		reductions
$OM + 0.5SO_4^{2-} \xrightarrow{R_5} CO_2 + 0.5H_2S$		
$OM \xrightarrow[R_6]{} CO_2 + 0.5CH_4$		
-	Τ̈́	
$2Mn^{2+} + O_2 \xrightarrow[R_7]{} 2MnO_2 + 4H^+$		
$4Fe^{2+} + O_2 \xrightarrow[-R_8]{} 4FeOOH + 8H^+$		
$2Fe^{2+} + MnO_2 \xrightarrow{R_9} 2FeOOH + Mn^{2+}$		
$2Fe^{2+} + H_2S \xrightarrow{R_{10}} 2FeS + 2H^+$		
$H_2S + 2O_2 \xrightarrow{R_{11}} SO_4^{-2} + 2H^+$		Secondary Redox Reactions
$H_2S + MnO_2 \xrightarrow[R_{12}]{} S_0 + Mn^{2+}$		
$H_2S + 2FeOOH + 4H^+ \xrightarrow{R_{13}} S_0 + 2Fe^{2+}$		
$2O_2 + 2FeS \xrightarrow[R_{14}]{} Fe^{2+} + SO_4^{2-}$		
$FeS + S_0 \xrightarrow[R_{15}]{} FeS_2$		
$7O_2 + 2FeS_2 \xrightarrow[R_{16}]{} 4SO_4^{2-} + 2Fe^{2+}$		
$CH_4 + 2O_2 \xrightarrow[R_{17}]{} CO_2$		
$4S^{0} \xrightarrow{R_{18}} 3H_{2}S + SO_{4}^{2-} + 2H^{+}$	_	
-		
$Hg^{2+} + H_2S \xrightarrow{R_{Hg,f}} HgS + 2H^+$		
$Hg^{2+} + OM \xrightarrow{SRB,R_m} MeHg$		Mercury Transformation reactions
$Hg^{2+} + H_2S \xleftarrow{R_r}{R} HgS + 2H^+$		
$MeHg \xrightarrow{R_d} Hg^{2+}$		
-		

Multiplicative Monod type kinetics with inhibition terms is used as oxidant inhibitor multipliers as suggested by Boudreau (1996) and VanCappellen and Wang (1996).

$$R_{1} = -k_{1}[OM] \frac{[O_{2}]}{K_{O2} + [O_{2}]}$$
(22-a)

$$R_{2} = -k_{2}[OM] \frac{[NO_{3}]}{K_{NO3} + [NO_{3}]} \frac{K'_{O2}}{K'_{O2} + [O_{2}]}$$
(22-b)

$$R_{3} = -k_{3}[OM] \frac{[MnO_{2}]}{K_{MnO_{2}} + [MnO_{2}]} \frac{K'_{NO3}}{K'_{NO3} + [NO_{3}]} \frac{K'_{O2}}{K'_{O2} + [O_{2}]}$$
(22-c)

$$R_{4} = -k_{4}[OM] \frac{[FeOOH]}{K_{FeOOH} + [FeOOH]} \frac{K'_{MnO2}}{K'_{MnO2} + [MnO_{2}]} \frac{K'_{NO3}}{K'_{NO3} + [NO_{3}]} \frac{K'_{O2}}{K'_{O2} + [O_{2}]}$$
(22-d)

$$R_{5} = -k_{5}[OM] \frac{[SO_{4}]}{[SO_{4}] + K_{SO4}} \frac{K'_{FeOOH}}{K'_{FeOOH} + [FeOOH]} \frac{K'_{MnO2}}{K'_{MnO2} + [MnO_{2}]} \frac{K'_{NO3}}{K_{NO3} + [NO_{3}]} \frac{K'_{O2}}{K'_{O2} + [O_{2}]}$$
(22-e)

$$R_{6} = -k_{6}[OM] \frac{[CH_{4}]}{[CH_{4}] + K'_{CH4}} \frac{K'_{SO4}}{[SO_{4}] + K'_{SO4}} \frac{K'_{FeOOH}}{K'_{FeOOH} + [FeOOH]} \frac{K'_{MnO2}}{K'_{MnO2} + [MnO_{2}]} \frac{K'_{NO3}}{K_{NO3} + [NO_{3}]} \frac{K'_{O2}}{K'_{O2} + [O_{2}]}$$
(22-f)

where the rate of organic matter mineralization is assumed to be proportional to the organic matter concentration, and related to the terminal electron acceptor concentration by a Monod term and the inhibiting agents using inverse linear terms. For the secondary reactions simple mass action relationships (e.g. R = k[A][B]) are used. The following relationships are used to compute reaction rates of mercury transformation:

$$R_{Hg,r} = k_{Hg,r} [Hg^{2+}] [H_2 S]$$
(23-a)

$$R_{Hg,f} = k_{Hg,f} \tag{23-b}$$

$$R_m = k_m [SRB] \frac{OM}{K_{OM} + OM} [Hg^{2+}]$$
(23-c)

$$R_d = k_d [MeHg] \tag{23-d}$$

$$R_r = k_r [Hg^{2+}]$$
 (23-e)

$$R_o = k_o [Hg^0]$$
(23-f)

where the [SRB] or the activity of the sulfate reduction bacteria is assumed to be proportional to the sulfate reduction rate:

$$[SRB] = k_{5} \frac{[SO_{4}]}{[SO_{4}] + K_{SO4}} \frac{K'_{FeOOH}}{K'_{FeOOH} + [FeOOH]} \frac{K'_{MnO2}}{K'_{MnO2} + [MnO_{2}]} \frac{K'_{NO3}}{K_{NO3} + [NO_{3}]} \frac{K'_{O2}}{K'_{O2} + [O_{2}]}$$
(24)

The calculation was done on a 50cm vertical sediment column, ignoring the river reach dynamics and assuming a constant rate of deposition of sediments containing fixed amounts of species. The parameters used for the simulation are listed in Tables 1 to 3. Since the initial concentrations of primary elements are adopted from an arctic coastal area, the sulfate concentration is high with respect to a typical freshwater riverine system. The biodispersion is calculated as exponentially decreasing with depth and the compaction effect is taken into account in calculating the diffusion coefficient, dry density and porosity of sediment vs. depth. The profiles are obtained by running the model for two years starting with uniform concentrations of species with depth. Figure 27 and Figure 28 show the concentration of primary components and mercury species at 20 days and 720 days after the start of simulation for the case with low deposition rate (2.6 cm/day burial velocity at top). Oxygen and nitrate diminish quickly with depth whithin the top 5 cm. Also MnO2 and FeOOH disappear within the top 5 cm of the column. On the other hand, the sulfate concentration does not vanish totally in the top 50cm due to its high concentration at the surface and the sulfate reduction condition can be seen at depths larger than 3 cm in the sediments where all sufate prohibiting species including oxygen, nitrate, ferric iron and manganese oxide have vanished, indicating existence of a sulfate reducing condition all over the column in depths below 5 cm. Concentrations of H_2S , FeS, S₀, Hg^{2+} , Hg^0 , and MeHg are assumed to be zero in the water column. The mercury was assumed to be initially concentrated at a 3 cm layer at depth of 20cm with concentration of 1 nmol/g initially as cinnabar which is close to the typical values found in San Fransisco Bay (Choe et al., 2004). FeS and FeS₂ have

increasing concentrations with depth due to their small rates of production and higher concentrations of H_2S in deeper layers. S^0 is mainly created at the interface between the FeOOH front and H₂S and its concentration are depleted with depth afterward due to conversion to SO_4^{2-} . Due to the high net deposition rate the mercury associated layer is almost buried in 20 days and in the simulation results at 720 days no mercury is observed. In real cases this does not happen due to existence of periodic erosiondeposition regimes which makes the net burial rates over a large period of time in a river system much smaller than the instantaneous values considered in this study. After 20 days the concentrations of Hg^{2+} of the in order of pg/ml and the methyl mercury concentration is almost negligible. A simulation with a smaller deposition rate of 0.26 cm/day is also performed and the results are presented in Figure 29 and Figure 30 for 20 and 720 days after the start of the simulation, respectively. In this case, the iron and manganese reducing depths are shortened and sulfate concentration diminishes at the depth of 15 cm. Again, in 720 days the mercury containing layer is completely buried as expected but in 20 days the concentration of mercury species can be seen in the figure and as it can be noticed based on the model prediction bio-available mercury exists in the system mainly in the form of methyl mercury.

 $\frac{1.61 \times 10^{-1} (a)}{6.31 \times 10^{-2} (a)}$ $\frac{4.42 \times 10^{-2} (a)}{1.89 \times 10^{-1} (a)}$ $\frac{7.25 \times 10^{-3} (a)}{9.46 \times 10^{-3} (a)}$ Not used

 4.73×10^{-3} (a)

(estimated)

x10⁻⁵

1.2

		$k_{11} (yr^{-1})$
$k_1 (yr^{-1})$	9.26x10 ^{-2 (a)}	k_{12} (yr ⁻¹)
$k_2 (yr^{-1})$	9.26x10 ^{-2 (a)}	$k_{13} (yr^{-1})$
$k_3 (yr^{-1})$	9.26x10 ^{-2 (a)}	$k_{14} (yr^{-1})$
$k_4 (yr^{-1})$	9.26x10 ^{-2 (a)}	$k_{15} (yr^{-1})$
$k_5 (yr^{-1})$	9.26x10 ^{-2 (a)}	$k_{16} (yr^{-1})$
$k_6 (yr^{-1})$	9.26x10 ^{-2 (a)}	$k_{17} (yr^{-1})$
$k_7 (yr^{-1})$	3.47x10 ^{-1 (a)}	$k_{18} (yr^{-1})$
$k_8 (yr^{-1})$	$3.47 x 10^{+1} $ (a)	1 (1
k ₉ (yr ⁻¹)	2.37x10 ^{-3 (a)}	k _{Hg,f} (yr
$k_{10} (yr^{-1})$	1.48x10 ^{+1 (a)}	

Table 2: Rate coefficients used in the kinetic reaction network

$k_{H\sigma r}(vr^{-1})$	1.58	x10 ⁻
115,1 ()	⁴ (estim	ated
	from b)
$k_m(yr^{-1})$	20.1(b))
$k_d(yr^{-1})$	1.65(b))
$k_r(yr^{-1})$	11(b)	
$k_0(yr^{-1})$	8.76 x1	$0^{2}(b)$
a. (Berg et	al., 2003	5), b. (Kin
et al., 2004	4)	

Table 3: Parameters used for the demonstration calculation on one-dimensional sediment column

Parameter	Value
Burial velocity	First case: 2.6 cm/day,
-	Second case: 0.26 cm/day
Depth of modeled sediment layer	50 cm
Maximum Porosity $ heta$ _	0.631
Minimum Porosity $ heta_{\scriptscriptstyle\infty} $	0.3
Sediment Grains Density	2.16 gr/cm^3
Porosity decrease rate with depth k_{θ}	0.1 m ⁻¹
Time step	1200 s
Simulation Duration	2 yrs
Maximum Bioturbation Diffusion	$0.317 \times 10^{-3} \text{ cm}^2/\text{s}$
Bioturbation decay rate with depth	5 m^{-1}
Initial Concentration of sediment associated	1 mg/kg
contaminants	

Table 4: Chemical and physical parameters for species used in the model

	$D(cm^2s^{-1})$	K'(limiting	Bulk water	Initial	Partitioning	Sou
		concentration)	concentration	Concentration	coefficient	rce
					(K_D)	
$[O_2]_{ini}$	11.7x10 ⁻⁶	20(µmol/ml)	389(µmol/ml)	389(µmol/ml)	N/A	а
[OM] _{ini}	N/A	N/A	250(µmol/gr)	250(µmol/gr)	N/A	а
[NO ₃ ⁻¹] _{ini}	9.8x10 ⁻⁶	N/A	6.2(µmol/ml)	6.2(µmol/ml)	N/A	а
(µmol/ml)						
[N2]	9.5 x10 ⁻⁶	N/A	669(µmol/ml)	669(µmol/ml)	N/A	а
[H2S]	8.7 x10 ⁻⁶	N/A	0(µmol/ml)	0(µmol/ml)	N/A	а
$[SO_4^{-2}]$	5.0 x10 ⁻⁶	1600(µmol ml ⁻¹)	7300(µmol/ml)	7300(µmol/ml)	N/A	b,a
$[MnO_2]$	N/A	10 (µmol g ⁻¹)	333(µmol/gr)	333(µmol/gr)	N/A	а
$[Mn^{2+}]$	3.1 x10 ⁻⁶	N/A	0.2(µmol/gr)	1(µmol/ml)	28cm ³ g ⁻¹	а
[FeOOH]	N/A	20 (µmol g ⁻¹)	6.25(µmol/gr)	625(µmol/gr)	N/A	а
$[Fe^{2^+}]$	$3.4 \text{ x} 10^{-6}$	N/A	27.2 (µmol/gr)	0	268cm ³ g ⁻¹	а
[HgS]	N/A	N/A	0	1(nmol/gr)	6218cm ³ g ⁻¹	с
[Hg2+]	$5 \text{ x} 10^{-6}$	N/A	0	0	N/A	с
[MeHg]	5 x10 ⁻⁶	N/A	0	0	N/A	с
[Hg0]	5 x10 ⁻⁶	N/A	0	0	N/A	с

a. (Berg et al., 2003) b. (VanCappellen and Wang, 1996), c.(Choe et al., 2004)



Figure 27: Profiles of concentration of the involved species 20 days after the start of simulation for the burial velocity of 2.6 cm/day.



Figure 28: Profiles of concentration of the involved species 720 days after the start of simulation for the burial velocity of 2.6 cm/day.

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Figure 29: Profiles of concentration of the involved species 20 days after the start of simulation for the burial velocity of 0.26 cm/day.



Figure 30: Profiles of concentration of the involved species 720 days after the start of simulation for the burial velocity of 0.26cm/day.

3.2. Demonstration Simulation: River system

The second demonstration case consisted of on a 30 km river reach. Flow and sediment characteristics were adopted from the Colusa Basin Drain data (Mirbagheri et al., 1988a; b) similar to the case used in the previous chapter for the single species case. The only difference with the case used in Chapter one is that here 5 tributary inflows are assumed to supply sediments and nutrients to the river at equidistant increments along the river. The tributary inflows were added to the model since it was observed that if no nutrient is supplied along the 30 km reach the nutrients will be depleted quickly at the beginning of the reach which does not reflect most common conditions. The location and effluent concentrations are presented in Figure 31. The sediment concentrations in the tributary inflows are assumed to be relatively high and also the organic carbon concentration associated with the sediments in the tributary flows were assumed to be higher than in the river reach. Table 5 lists flow, sediment concentration and the concentration of species in the main upstream boundary as well as in tributary inflows. Oxygen and nitrogen were assumed to be supplied across the water through air-water interface with a linear boundary layer model as explained in the previous chapter. In this approach Henry's law is used to calculate the equilibrium concentration of the gas in the water using the relation suggested by Chapra (1996). Deposition, erosion and net deposition rates are presented in Figure 32. At intersections with tributaries the net rate of deposition is high due to the supply of high suspended sediment concentration flow. Also, due to inflow of high suspended matter flow the net deposition rate is positive in most of the reach. Distributions of various species in the sediments are depicted in Figure 33 to Figure 48. Oxygen is present at the top sediment layer and it can exist at greater depths when higher net deposition rates exist. Nitrate also diminishes in the top sediment layer and as expected the depth of its front in the sediments is larger close to the tributary inflows due to the large supply of nitrate. The effect of high supply of organics to the water body at tributaries can be observed in Figure 35. The organic content reduces both in sediment and water body but it remains

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higher than 1.4 mg/g all over the sediments because the rate of decomposition of OM is assumed to be directly proportional to the concentration of OM. MnO₂ and FeOOH disappear in the top 20 cm where MnO_2 is mainly converted to Mn^{2+} (Figure 37 and Figure 38) whereas Fe^{2+} converts to FeS and FeS₂ at deeper layers due to the high concentration of H₂S at those layers. For both FeOOH and MnO₂ it can be noticed that their fronts move deeper in the high deposition locations. It should be noted that the solutions presented in Figure 33 Figure 48 do not represent steady state conditions and there may be further changes as the solution evolves even with the identical (steady) boundary conditions. For example the evolution of the concentration profile of organic carbon in the sediments takes a much longer time to reach steady state than the time used for this simulation. SO_4^{2-} , as it can be observed in Figure 41, is converted to H_2S at the top 30 cm when all inhibiting species including O_2 , NO_3^- , FeOOH, and MnO₂ are nonexistent. Figure 46 to Figure 48 represent the evolution of mercury species in the sediment. Due to higher bio-dispersion in the top layers and higher density of the sediments at the bottom layers Mercury diffuses up while it is being buried into the deep sediments due to deposition. Lower concentrations of Hg²⁺ at the bottom layers are due to high concentrations of H_2S , which convert Hg^{2+} to HgS. Methyl mercury is produced in the zones in which SRB activity is high (i.e. sulfate is being converted to H_2S) and an adequate amount of Hg^{2+} and OM exist. This situation occurs at locations with higher deposition rate as expected because OM depletes other electron acceptors forcing sulfate reducing conditions and SRB growth.



Figure 31: Schematic representation of the river reach and tributary inflows used for simulation

	Main flow	Tributary flow
Flow (Qin)	$42.1 \text{ (m}^{3}\text{/s)}$	$0.3 (m^3/s)$
Suspended Sediments	0.078 gr/L	10 gr/L
[O ₂] _{ini}	8890(µmol/ml)	3000(µmol/ml)
[OM] _{ini}	250(µmol/gr)	750(µmol/gr)
$[NO_3^{-1}]_{ini}$	6.2(µmol/ml)	26.2(µmol/ml)
[N2]	15000(µmol/ml)	15000(µmol/ml)
[H2S]	0(µmol/ml)	0(µmol/ml)
$[SO_4^{-2}]$	7300(µmol/ml)	7300(µmol/ml)
[MnO ₂]	33.3(µmol/gr)	70.0(µmol/gr)
$[Mn^{2+}]$	0.2(µmol/ml)	0.7(µmol/ml)
[FeOOH]	62.5(µmol/gr)	62.5(µmol/gr)
$[Fe^{2+}]$	2.72(µmol/gr)	7.2(µmol/gr)
[HgS]	0	0
[Hg2+]	0	0
[MeHg]	0	0
[Hg0]	0	0
Oxygen Air-Water	3.92 m/day	N/A
Exchange coefficient		
Oxygen Saturated	9000 (µmol/ml)	N/A
Concentration		
Nitrogen Air-Water	3.92 m/day	N/A
Exchange coefficient		
Nitrogen Saturated	16000 (µmol/ml)	N/A
Concentration		

 Table 5: Physical and chemical characteristics of tributary and main inflow to the river reach (Berg et al., 2003) with some modifications



Figure 32: Sediment erosion and deposition and net-deposition rates along the reach



Figure 33: O₂ Concentration (µmols/mL) profile after 30 days from the start of the simulation



Figure 34: NO_3^- Concentration (µmols/mL) profile after 30 days from the start of the simulation



Figure 35: Organic Content Concentration (µmol/g) profile after 30 days from the start of the simulation



Figure 36: N₂ Concentration (µmol/mL) profile after 30 days from the start of the simulation



Figure 37: MnO₂ Concentration (µmol/g) profile after 30 days from the start of the simulation



Figure 38: Mn²⁺ Concentration (µmol/g) profile after 30 days from the start of the simulation



Figure 39: FeOOH Concentration (µmol/g) profile after 30 days from the start of the simulation



Figure 40: Fe²⁺ Concentration (µmol/g) profile after 30 days from the start of the simulation



Figure 41: SO_4^{2-} Concentration (µmol/mL) profile after 30 days from the start of the simulation



Figure 42: H_2S Concentration (µmol /mL) profile after 30 days from the start of the simulation



Figure 43: FeS Concentration (µmol/g) profile after 30 days from the start of the simulation



Figure 44: S_0 Concentration (µmol/g) profile after 30 days from the start of the simulation



Figure 45: FeS₂ Concentration (µmol/g) profile after 30 days from the start of the simulation



Figure 46: Hg²⁺ Concentration (µmol/g) profile after 30 days from the start of the simulation



Figure 47: HgS Concentration (µmol/g) profile after 30 days from the start of the simulation



Figure 48: MeHg Concentration (µmol/g) profile after 30 days from the start of the simulation

Figure 49 and Figure 50 show the profiles of concentration of various species in the water column. The concentration of O2 drops at the inlets of tributary flows due to lower concentration of dissolved oxygen assumed in tributary inflows and also the supply of high concentrations of organic content. Organic matter increases immediately at the tributaries and then decreases with distance relatively rapidly. This decrease is partly due to decomposition and partly due to the mixing of suspended sediments with bottom sediments that contain lower organic content. Running the model for a longer time may alter this profile as higher concentrations of organic content accumulate in the bottom sediments and the profile may show a more uniform shape. The source of MnO₂ is bottom sediments and tributary inflows. Therefore, at the locations where there is higher erosion rate due to exposure of bottom layers with higher Mn²⁺ due to reductive condition, less concentrations of MnO₂ are observed. The low concentration of MnO₂ and high concentration of Mn^{2+} at river kilometer 6 can be interpreted to be due to net erosion which exposes Mn²⁺ created in lower layers to the water column. The same behavior can be seen for FeOOH and Fe^{2+} with the difference that the concentration of FeOOH also increases at the high erosion region due to high erosion rate. The initial concentration of FeOOH is considered to have higher values at the top sediment layers

than in the suspended sediments associated with the inflows. Therefore a high erosion rate contributes to the concentration of particle associated FeOOH in the water body. SO_4^{2-} has a uniform concentration along the river where H₂S has higher concentration at the high erosion locations due to its existence in lower layers.



Figure 49: Profiles of Dissolved and Particulate O₂, OM, NO₃-⁻, MnO₂, Mn²⁺ in the river reach



Figure 50: Profiles of Dissolved and Particulate FeOOH, Fe²⁺, SO₄²⁻, H₂S in the river reach

4. Conclusions

Multi-component biotic/abiotic reactive transport model in riverine system considering the processes taking place in both water column and mobile sediment phases is presented in this chapter. The model uses an innovative variable time step method to simulate multiple time scale reaction networks. The multiple time step technique is formulated as a fully kinetic model but is also capable of representing fast and near equilibrium reactions by using smaller time step sizes for species dominated by those particular reactions. Using the fully kinetic approach, the state of the reactions whether they are in equilibrium or kinetically controlled does not need to be specified a priori. Several demonstration cases were simulated using the model. These cases contain several species in a one dimensional sediment column and a hypothetical river system with many tributary inflows. The model appears to be an efficient tool to investigate the migration and transformation of reactive contaminants in river systems and can be particularly used to investigate the fate of sediment associated contaminants and study remediation strategies (e.g. given well defined initial and boundary conditions). Although the model was extensively validated by testing the mass conservation and comparing with available analytical solutions for simple cases, it was not tested with real contaminant transport field data due to lack of extensive data appropriate for such a modeling practice. For such a practice an extensive dataset containing the distribution and preferably time variation of various chemical species involved in a river system both in sediments layers and water column is required. However, the patters of concentration distribution in sediments for different species in the sediments do qualitatively match with literature data and previous 1-D modeling done by other researchers. Combining the model with more sophisticated, hydrodynamic, sediment transport and limnological models can significantly enhance the capability of the model. Limnological models are especially likely to improve the capability of the model to predict the concentrations of the main species such as oxygen, nitrogen

compounds and organic carbon in the water column by more appropriately considering temperature, pH, light and other influencing factors.

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Chapter 3:

Modeling Colloid Facilitated Transport of Multi-species contaminants in Unsaturated Porous Media

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Abstract:

Colloid facilitated transport has been recognized as a potentially important and overlooked contaminant transport process. In particular, it has been observed that conventional two phase sorption models are often unable to explain transport of highly sorbing compounds in the subsurface appropriately in the presence of colloids. In this study a one-dimensional model for colloid facilitated transport of chemicals in unsaturated porous media is developed. The model has parts for simulating coupled flow, and colloid transport and dissolved and colloidal contaminant transport. Richards' equation is solved to model unsaturated flow, and the effect of colloid entrapment and release on porosity and hydraulic conductivity of the porous media is incorporated into the model. Both random sequential adsorption and Langmuir approaches have been implemented in the model in order to incorporate the effect of surface jamming. The concept of entrapment of colloids into the air-water interface is used for taking into account the effect of retardation caused due to existence of the air phase. A non-equilibrium sorption approach with options of linear and Langmuir sorption assumptions are implemented that can represent the competition and site saturation

effects on sorption of multiple-compounds both to the solid matrix and to the colloidal particles. Several demonstration calculations are performed and the conditions in which the non-equilibrium model can be approximated by an equilibrium model are also studied.

1. Introduction:

Colloid facilitated transport of contaminants in subsurface has been suggested as a potential cause of the unexpected appearance of extremely low solubility contaminants at distances from the sources (Kersting et al., 1999; Von Gunten et al., 1988) It is hypothesized that because of the similarity between the chemical composition of colloidal particles and the porous media, contaminants with high affinity to the solid phase can bind to colloidal particles and therefore the colloids can act as a vehicle for transport of contaminants in the porous media (Honeyman, 1999; McCarthy and Zachara, 1989). High specific surface area of the colloidal particles with respect to the porous media also can enhance their ability to absorb contaminants and transport them. McCarthy and Zachara (1989) indicated that ignoring the effect of colloids in transport of the strongly sorbing compounds can cause significant discrepancies between modeled results and reality.

Several models have been developed for predicting colloid facilitated transport in the porous media. The first approaches have been to use the two phase model while incorporating the effect of colloids by modifying the retardation factor in the transport equation (Magee et al., 1991). Since the advection velocity of colloidal particles are different than dissolved chemical (both due to size exclusion effect and the different attachment and release behavior of colloids), and due to the inability of a two phase model to take into account these processes, several researchers have tried to use a three

phase model approach that explicitly considers a colloidal phase. Among the first attempts to model colloid facilitated contamination transport in the porous media using a three phase approach are the works by Enfield and Bengtsson (1988); Jiang and Corapcioglu (1993); Mills et al. (1991), and Corapcioglu and Jiang (1993). Enfield and Bengtsson (1988) developed a colloid facilitated transport model with the three phase approach by assuming equilibrium between aqueous, solid and colloidal phases. They assumed a uniform and constant concentration of colloids in their system and did not take into account the deposition and release of particles. Mills et al. (1991) used the same approach but they also included the effect of various partitioning coefficients associated with various species of one metals by assuming that the ratio of each species remains constant regardless of the metal's total concentration. Jiang and Corapcioglu (1993) developed a three phase model including dissolved, colloidal and sorbed contaminants also with an assumption of instantaneous equilibrium between all three phases. They represented the capture and release of colloids to/from the collector grains by assuming a first-order, kinetically controlled filtration rate. They used colloid filtration theory in order to calculate the attachment rate of colloids and also assumed that entrapped colloids can be released to the pore water later. They solved the governing partial differential equation using a fully implicit finite difference algorithm.

It has been shown that the effect of colloid facilitated transport becomes significant when the desorption rate of contaminants from colloids are relatively slow. This indicates that for compounds with high exchange rate between colloidal and aqueous phase the effect of colloid facilitated transport is less significant. On the other hand slow desorption of chemicals from colloidal particles has been observed in several batch experiments (e.g. Penrose et al., 1990). Therefore an equilibrium assumption is not always justified in modeling the colloid-facilitated transport of highly sorbing compounds. Saiers and Hornberger (1996) developed a 3 phase approach with 2-site

adsorption and desorption approach to model transport of Cs in the presence of colloidal kaolinite in a column experiment. They assumed that the compound sorbs to one site type as in equilibrium with Langmuir sorption isotherm and the other type of sites as kinetically controlled with first order kinetics. Roy and Dzombak (1998) used the same approach to model colloid facilitated transport of hydrophobic organic compounds in porous media.

All of the models discussed above have assumed saturated porous media and linear isotherms for sorption and desorption of contaminants to/from the porous media. Saiers, (2002) expanded on the work of Saiers and Hornberger (1996) to incorporate the effect of heterogeneity in colloid sizes and solid phase by considering various colloid types and different site types on the porous media surface for sorbing colloids and using the Langmuir sorption model to incorporate the effect of site saturation on colloid attachment for each site. They assumed linear isotherms for sorption of metals to the solid phase and colloidal particles and adopted Gamma distribution to represent the distribution of kinetic sorption rate coefficient and also for the distribution of partitioning coefficient for colloidal particles.

Sen et al. (2002) used the same approach as Corapcioglu and Jiang (1993) and incorporated the effects of colloid release on porosity and hydraulic conductivity. However they did not consider the capture of colloids by grains in their model. Sen et al. (2004) modified the model by incorporating the effect of colloid capture. They assumed that the entrapped colloids attach irreversibly to the porous media and considered the source of released colloids to be initially attached colloids located on the solid surfaces of the soil matrix. In a recent paper Sen and Khilar (2006) reviewed various models for colloid transport and colloid facilitated transport in porous media.

In addition to the works done on the modeling of colloid associated transport in porous media there have also been several efforts on modeling these processes in fractured porous media using numerical and analytical methods. These include, Abdelsalam and Chrysikopoulos (1995); Ibaraki and Sudicky (1995); James and Chrysikopoulos (1999a); James and Chrysikopoulos (1999b); James and Chrysikopoulos (2000); James and Chrysikopoulos (2003).

Since in many cases colloids and contaminants associated with them may pass through the unsaturated zone to reach to the groundwater, the capability of modeling colloid facilitated transport in unsaturated zone is necessary. In addition since the rate of deposition and release of colloidal particles to/from the porous media depends on many factors including hydrodynamic forces, in the unsaturated zone the assumption of a constant deposition and release rate may not be appropriate. The main mechanisms involved in the retardation of colloids in the presence of an air-phase has been the subject of some discussions. Corapcioglu and Choi (1996) and Lenhart and Saiers (2002) attributed the retardation effect to air-water interface and film straining. Crist et al. (2004) reported that hydrophilic and negatively charged colloids were mainly retained within but not attached to the thin film of water between the air phase and the solid phase. McCarthy and McKay (2004) and DeNovio, et al. (2004) reviewed the evolution of the views about the effect of air phase on colloid transport in porous media and the mechanisms involved. Wan and Wilson (1994) did some experimental studies on the effect of air phase in the porous media in increasing the rate of entrapment of colloids. Some Wan and Tokunaga (1997) suggested a model for estimating the film straining coefficient for various colloid characteristics and saturation contents. Wan and Tokunaga (1998) measured the partitioning coefficient of colloids at air-water interfaces using a bubble column method and assuming instantaneous and linear sorption of colloids to air-water interface. Wan and Tokunaga (2002) used the same

technique to estimate the partitioning coefficient of several types of clay colloids at airwater interface.

Not many colloid-facilitated transport models have addressed the unsaturated zone. Choi and Corapcioglu (1997) developed a model for colloid facilitated transport in unsaturated porous media. They assumed that in unsaturated condition a part of colloids will reversibly attach to the water-air interface. Therefore, they considered colloids to be in 3 distinct form or regions; attached to the solid phase, mobile in the pore water or captured in the air-water interface.

They used fixed rates of deposition and release of colloid to both solid phase and airwater interface and used a first-order kinetically controlled model to describe deposition and release from both phases.

Many of the different aspects of colloid-facilitated transport modeling have been studied as isolated phenomena. To our knowledge no modeling effort has been attempted that integrates all these processes in a coupled manner.

In this research a wholly kinetically controlled model is developed for colloidfacilitated transport of contaminants in the unsaturated porous media. The model can handle both linear and site saturation Langmuir models for competitive sorption of multiple metals. The same concept of attachment of colloids to air-water interface as Choi and Corapcioglu (1997) is used for considering the effect of unsaturated conditions on colloid transport. Unsaturated flow governed by Richard's equation is linked to the model and the effects of variability in hydraulic conductivity and porosity due to entrapment and release of colloidal particles onto the surface is explicitly taken into account. Here as in the work by Sen et al. (2004) it is assumed that colloidal particle release takes place from a different source of colloids than the captured ones and that the captured colloids are irreversibly retained. Also in this work the colloid entrapment formula developed by Johnson and Elimelech (1995) is used to compute the rate of capture of colloids. Both Langmuir and RSA dynamic blocking approaches are incorporated into the model incorporating the effect of surface saturation on colloid deposition as options. Also the equilibrium equivalents to the model are presented and the numerical conditions in which the kinetic model can be effectively replaced by various equilibrium approximations are studied.

2. Model Development

The goal of this research is to develop an integrated flow, colloid transport, and contamination transport model in order to take into account colloid-facilitated transport and plugging effects as well as hydrodynamic effects of unsaturated flow on colloid transport. The model includes three main modules including an unsaturated flow model that solves Richard's equation, a colloid transport model using the colloid filtration model developed and summarized by Johnson and Elimelech (1995), the concept of entrapment of colloid into air-water interface suggested by Wan and Wilson (1994), and a multi-species colloid facilitated transport model considering competitive kinetic sorption to both porous media and colloidal particles.

2.1. Flow Model

Richard's equation is used for modeling unsaturated flow in terms of water content in the porous media:

$$\frac{\partial \theta}{\partial t} = -\frac{\partial K(\theta)}{\partial z} + \frac{\partial}{\partial z} \left[K(\theta) \left(\frac{\partial \psi}{\partial z} \right) \right]$$
(1)

in which z is the vertical coordinate (The positive direction is assumed to be downward), θ is the volumetric water content, written as $\theta(z,t)$ as a function of depth and time, $K(\theta)$ [L/T] hydraulic conductivity, dependent on water content, ψ [L] matric

potential in the soil defined as the negative of pressure head. The van Genuthten's soil retention relationships van Genuchten, (1980) were used for calculating matric potential and hydraulic conductivity based on saturation content:

$$K(\theta) = K_s S_e^{1/2} [1 - (1 - S_e^{1/m})^m]^2$$
⁽²⁾

where K_s [L/T] is the vertical saturation hydraulic conductivity which is a function of concentration of colloids entrapped at the location it is being calculated, *m* is the van Genuchten retention parameter that is related to the uniformity of pore-size distribution and is usually specified by the soil type and S_e is the effective saturation which is expressed as:

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \tag{3}$$

in which θ_s and θ_r are respectively the saturated, and residual water contents. The pressure-water content in van Genuchten model is expressed as:

$$\psi = \frac{1}{\alpha} \left(S_e^{-1/m} - 1 \right)^{1/n} \tag{4}$$

where n is the parameter related to the uniformity of pore size distribution and is usually calculated as 1/(1-m), and α [1/L] is a parameter related to mean pore size. Two cases of boundary conditions are implemented at the top boundary of the column:

$$Q(0) = K(\theta) \left[1 - \partial \psi / \partial z \right]_{z=0} = F(t) \quad \text{in flow dominated condition/no ponding}$$
(5a)

$$\theta|_{z=0} = \theta_s$$
 in head dominated condition/ponding (5b)

where F(t) the flux of water available at the surface in terms of rain intensity or other sources. Governing equation (1) with relationships (2) to (4) and boundary condition (5) is solved using a semi-implicit Crank-Nicholson finite difference scheme.

2.2. Colloid Transport Model

An advection-dispersion model with kinetic capture and release to/from porous media is used here. It is assumed that the source of colloid release in the porous media is different than the captured colloids as in Sen et al. (2004). This assumption is reasonable since colloid re-entrainment rates are often observed to be much smaller than filtration rates unless a significant change in the chemistry takes place. Also as opposed to Choi and Corapcioglu (1997) here it is assumed that capture and release of colloids at the air-water interface takes place instantaneously, following the more simplified approach of Wan and Wilson (1994). It worth noting that more recently the important effect of electrostatic interactions of colloids with the air-water interface have been demonstrated (Wan and Tokunaga, 2002); however, for dilute conditions this effect can be taken into account using the present equilibrium assumption by specifying the partitioning coefficient between water and air-water interface to represent the effect of electrostatic charges. Therefore in our model colloids can be in four distinct phases: mobile in pore-water G, irreversibly filtered G_{sf} , initially attached to grains and available for release G_{si} , and captured at the air-water interface G_a . Also the air-water interface area is assumed to be proportional to the volume of air phase and therefore the concentration of colloids captured in air-water interface is expressed as mass of colloids divided by volume of air. The bulk volumetric mass balance equation for mobile colloids, captured, attached available, and captured in water-air interface can be written respectively as:

$$\frac{\partial(\theta G)}{\partial t} + \frac{\partial\theta v_p G}{\partial z} = \frac{\partial}{\partial z} \left(D_c \theta \frac{\partial G}{\partial z} \right) - B_d k_p G + B_d k_{rp} G_{si} - k_{fa} (\theta_s - \theta) G + k_{ra} (\theta_s - \theta) G_a$$
(6)

$$\frac{\partial G_{sf}}{\partial t} = k_p G \tag{7}$$

$$\frac{\partial G_{si}}{\partial t} = -k_{rp}G_{si} \tag{8}$$

$$\frac{\partial [(\theta_s - \theta)G_a]}{\partial t} = k_{fa}(\theta_s - \theta)G - k_{ra}(\theta_s - \theta)G_a$$
(9)

where $G[M/L^3]$ is the concentration of mobile colloids in pore water, $v_p[L/T]$ is the colloidal average velocity which is calculated from the equation suggested by DiMarzio and Guttman, (1970) :

$$v_p = \frac{Q}{\theta} \left[2 - \left(1 - \frac{a_p}{r_0} \right) \right]$$
(10)

 $a_p[L]$ is the colloid radius and $r_0[L]$ is the average pore radius, This model is applicable when $a_p/r_0 \ll 1$. $D_c[L^2/T]$ is the mechanical dispersion coefficient for colloids, B_d [M/L³] is the bulk density, k_p [L³/MT] and k_{rp} [1/T] are capture and release coefficients respectively, k_{fa} [1/T] and k_{ra} [1/T] are capture and release rates to the air-water interface, G_{si} [M/M] is the concentration of initially attached and available colloids expressed as mass of colloid per dry mass of solids, G_{sf} [M/M] is the concentration of irreversibly captured colloids and G_a [M/L³] is the concentration of colloids captured in the air water interface expressed as mass of colloids to the air-water interface takes place instantaneously and also that the surface area of the air-water interface is proportional to the air phase volume, so that $G_a = K_a G$, where $K_a = k_{ra}/k_{fa}$ is the equilibrium airwater partitioning coefficient for colloidal particles which depends on colloids hydrophobicity Wan and Wilson (1994). Incorporating this equilibrium relationship, we can write equation (6) as follows:

$$\frac{\partial \{ \left[\theta + \left(\theta_s - \theta \right) K_a \right] G \}}{\partial t} + \frac{\partial \theta v_p G}{\partial z} = \frac{1}{\theta} \frac{\partial}{\partial z} \left(D \theta \frac{\partial G}{\partial z} \right) - B_d k_p G + B_d k_{rp} G_{si}$$
(11)

with the boundary conditions,

$$G|_{z=0} = G_0$$
 Top boundary condition (12a)

and

$$\frac{\partial G}{\partial z}\Big|_{z=L} = 0$$
 Bottom boundary condition (12b)

While filtration is assumed irreversible, we do allow the rates of filtration to be limited by site blocking due to presences of initially attached and irreversibly attached colloids on the collector surface. The surface area limitation for colloid capture is taken into account using the monolayer coverage assumption and the capture rate coefficient, (k_p) is found using the following relationship (Adamczyk et al., 1992; Privman et al., 1991; Schaaf and Talbot, 1989):

$$k_{p} = \frac{1}{4} f \alpha_{p} \eta Q B(G_{s})$$
⁽¹³⁾

where $f [L^2/M]$ represent the specific surface area of the porous media expressed as the porous media surface area per unit dry mass of porous media, α_p is the particle attachment efficiency, η is the collection efficiency (i.e. the frequency with which colloids encounter surfaces) $G_s = G_{sf} + G_{si}$, and *B* is a function than takes into account the blocking effect by attached particles called *dynamic blocking function*. Two approaches have been used to define dynamic blocking function in Johnson and Elimelech, (1995). The first approach is a simple Langmuir model:

$$B(G_s) = \frac{G_{s\max} - G_s}{G_{s\max}}$$
(14)

in which G_{smax} is the surface jamming limit. The second approach is via using the nonlinear function suggested by Schaaf and Talbot, (1989) based on random irreversible deposition of particles onto a surface assuming a monolayer coverage, called random sequential adsorption (RSA), In RSA approach the blocking function is found using the following polynomial that represent fractional surface area remaining given G_s attached colloids:

$$B(G_{s}) = 1 - 4\left(\frac{G_{s}}{G_{s\max}}\right) + 3.308\left(\frac{G_{s}}{G_{s\max}}\right)^{2} + 1.40\left(\frac{G_{s}}{G_{s\max}}\right)^{3} \qquad \text{for } G_{s} < 0.8G_{s\max} (15a)$$
$$B(G_{s}) = 8.97 \cdot (G_{s\max} - G_{s})^{3} \qquad \qquad \text{for } G_{s} > 0.8G_{s\max} (15b)$$

Both Langmuir and RSA options are implemented into the model as alternatives.

The rate of release of initially immobile colloids is given by the modified version of the equation suggested by Arulanandan, (1975) to reflect hydrodynamic entrainment as a poison process with frequency proportional to shear stress.

$$k_{rp} = \alpha_h \cdot f \cdot (\tau_w - \tau_c) = \alpha_{hm} \cdot f \cdot (v_w - v_c)$$
(16)

In the above equation the shear stress is assumed to be proportional to the flow velocity v_w and the proportionality constant is factored into the coefficient α_{hm} . As opposed to Arulanandan, (1975) who assumed that release rate is independent of colloid availability on the surface, here we assumed that the rate of release is proportional to available attached colloids G_{sf} . Considering the rate of release proportional to the availability of colloids on the surface provides the option to specify the rate of release of colloids based on the soil texture type or other characteristics which affect the availability of colloidal particles to be released.

For computing the effect of clogging hydraulic conductivity the empirical relationship suggested by Khilar and Fogler, (1998) is adopted

$$K_s = K_{s\max} e^{\left(-k_{perm}G_s\right)} \tag{17}$$

where k_{perm} is an adjustable parameter indicating the influence of captured colloids on the permeability of the media.

2.3. Colloid-Facilitated Transport

The transport equations for dissolved and colloid associated contaminants for the mobile phase can be written respectively as:

$$\frac{\partial(\theta C)}{\partial t} + \frac{\partial(QC)}{\partial z} = \frac{\partial}{\partial z} \left(D\theta \frac{\partial C}{\partial z} \right) - B_d k_r \left(K_D C - C_s \right) - G\theta k_{rG} \left(K_{DG} C - C_G \right)$$

$$-B_d G_{si} k_{rG} \left(K_{DG} C - C_{Gsi} \right) - B_d G_{sf} k_{rG} \left(K_{DG} C - C_{Gsf} \right) - (\theta_s - \theta) G_a k_{rG} \left(K_{DG} C - C_{Ga} \right)$$
(18)

and

$$\frac{\partial(\theta GC_G)}{\partial t} + \frac{\partial(v_p \theta GC_G)}{\partial z} = \frac{\partial}{\partial z} \left(D_c \theta \frac{\partial(GC_G)}{\partial z} \right) - B_d k_p GC_G + B_d k_{rp} G_{si} C_{Gsi} - k_{fa} (\theta_s - \theta) GC_G + k_{ra} (\theta_s - \theta) G_a C_{Gsa} + Gk_{rG} \theta (K_{DG} C - C_G)$$
(19)

where $D[L^2/T]$ is mechanical dispersion coefficient for dissolved species which is equal to hydrodynamic dispersion and molecular diffusion $\alpha_d v + D_m$, α_d is diffusivity, D_c is dispersion coefficient for colloidal particles, $k_r[1/T]$ is mass exchange rate between pore-water and solid phase, $K_D[L^3/M]$ is soil-water partitioning coefficient, $k_{rG}[1/T]$ is the mass exchange coefficient between water and colloidal particle which is assumed to be constant for all colloids regardless of their phase since they have similar physical characteristics, $K_{DG}[L^3/M]$ is the colloid-water partitioning coefficient, $C_G[M/M]$ is concentration of contaminants sorbed to mobile colloidal particles expressed as mass of contaminant over mass of colloids, and $C_{Gsi}[M/M]$ and $C_{Gsf}[M/M]$ are the mass concentration of contaminants sorbed to reversibly attached and irreversibly attached colloidal particles respectively. The mass balance equation for immobile sorbed phase contamination respectively to, colloids captured on the soil matrix, available colloids, and captured by air-water interface are:

$$\frac{\partial (G_{si}C_{Gsi})}{\partial t} = k_{rG}G_{si}(K_DC - C_{Gsi}) - k_{rp}G_{si}C_{Gsi}$$
(20)

$$\frac{\partial \left(G_{sf} C_{Gsf}\right)}{\partial t} = k_{rG} G_{sf} \left(K_D C - C_{Gsf}\right) + k_p G C_G$$
(21)

$$\frac{\partial [(\theta_s - \theta)G_a C_{Ga}]}{\partial t} = k_{rG} (\theta_s - \theta)G_a (K_D C - C_{Ga}) -k_{fa} (\theta_s - \theta)G_a C_{Ga} + k_{ra} (\theta_s - \theta)G C_G$$
(22)

Incorporating the instantaneous equilibrium between mass density of aqueous and airwater interface associated colloids into (19) we get $C_{Ga} = C_G$. It worth noting that this equality due to high rate of exchange of colloids between the two phases and not due to high rate of contaminant exchange. Then substituting equation (22) into equation (19) we can write equation (16) as follows:

$$\frac{\partial \{ \left[\theta + (\theta_s - \theta) K_a \right] G C_G \}}{\partial t} + \frac{\partial \left(v_p \theta G C_G \right)}{\partial z} = \frac{\partial}{\partial z} \left(D_c \theta \frac{\partial (G C_G)}{\partial z} \right) - B_d k_p G C_G + B_d k_{rp} G_i C_{Gsi} + k_{rG} G \left[(\theta_s - \theta) K_a + \theta \right] (K_{DG} C - C_G)$$
(23)

Equations (19) and (23) reveal that the equilibrium exchange of colloids between water and air-water interface acts as a retardation factor on colloid transport as well as colloid facilitated transport as depicted by Wan and Tokunaga (1997). Also the mass balance for the sorbed phase concentration to the immobile solid matrix is:

$$\frac{\partial C_s}{\partial t} = k_r (K_D C - C_s) \tag{24}$$

The boundary condition for equations (18) and (23) can be written as:

- $C\big|_{z=0} = C_0 \tag{25a}$
- $\left. \frac{\partial C}{\partial z} \right|_{z=L} = 0 \tag{25b}$

$$C_G\Big|_{z=0} = C_{G0} \tag{25c}$$

$$\left. \frac{\partial C_G}{\partial z} \right|_{z=L} = 0 \tag{25d}$$

As long as the exchange rates are small in comparison to transport for each phase (i.e. Damkohler number is small) equations (18), and (20-23) can be effectively solved numerically and used for contaminants with relatively small desorption rate. However when mass exchange rates of either water-solid (k_r) or water-colloid (k_{rG}) are large, then the above mentioned equations become numerically stiff and require small time steps which increases the computational intensity of the model. Therefore some levels of simplifications such as assuming equilibrium conditions between various phases can be implemented to reduce this computational burden. The first level of simplification is that of equilibrium between aqueous and colloidal phase concentrations. This simplification can be used in cases where the exchange rate between colloidal material and pore water is significantly high with respect to the transport process. Then this equilibrium assumption can be expressed as:

$$C_G = C_{Ga} = C_{Gsi} = C_{Gsf} = K_{DG}C$$
⁽²⁹⁾

Substituting this assumption into equations (18) and (20-23) yields the following set of governing equations.

$$\frac{\partial \left\{ \theta + \left[\theta + \left(\theta_{s} - \theta \right) K_{a} \right] G K_{DG} C + B_{d} \left(G_{sf} + G_{si} \right) K_{DG} C \right\}}{\partial t} + \frac{\partial \left[Q C + v_{p} \theta G K_{DG} C \right]}{\partial z}$$

$$= \frac{\partial}{\partial z} \left(D \theta \frac{\partial C}{\partial z} + D_{c} \theta \frac{\partial \left(G K_{DG} C \right)}{\partial z} \right) - B_{d} k_{r} \left(K_{D} C - C_{s} \right)$$

$$(30)$$

$$\frac{\partial C_s}{\partial t} = k_r (K_D C - C_s) \tag{31}$$

For the case where the exchange rate between pore-water and immobile solid matrix is also large, sorption to the solid phase can be considered in equilibrium too, (i.e., $C_s = K_D C_s$) and therefore Eqs. (23) and (24) reduce to the following equation:

$$\frac{\partial \left\{ \theta + (\theta + (\theta_s - \theta)K_a)GK_{DG} + B_d(G_{si} + G_{sf})K_{DG} + B_dK_D \right\} + \frac{\partial [Q(C + \theta GK_{DG}C)]}{\partial z}}{\partial z} = \frac{\partial}{\partial z} \left(D\theta \frac{\partial C}{\partial z} + D_c\theta \frac{\partial (GK_{DG}C)}{\partial z} \right)$$
(32)

2.4. Multiple-contaminant competitive sorption model:

Metal sorption is usually described as the binding of metallic ions to some limited number sites available on porous media or colloids. Because the density of sites on the surface is finite, metals compete in capturing these sites. Therefore when multiple species of metals occur, these coupled interaction effects have to be considered. In order to take this coupling effect into account we used the Langmuir approach. In this case K_D and K_{DG} are functions of sorbed phase concentrations and are expressed as:

$$K_D^i = K_I^i P_{av} \tag{33a}$$

$$K_{DG}^{i} = K_{IG}^{i} P_{G,av}$$
(33b)

In the above equations, $K_I^i[L^3/M]$, and $K_{IG}^i[L^3/M]$ are intrinsic partitioning coefficients for metal species *i*, and $P_{av}[M/M]$ and $P_{G,av}[M/M]$ are mass concentrations of sites available (not occupied by metal ions) respectively on soil matrix and colloidal phase expressed as equivalent mass of sites over mass of dry solid or colloidal phase. Similar equations can be written for reversibly attached, irreversibly attached and airwater interface colloidal phases. The concentration of available sites are equal to:

$$P_{av} = P_0 - \sum_{i=1}^{nm} \psi_i C_s^i$$
(34a)

$$P_{G,av} = P_{G,0} - \sum_{i=1}^{nm} \psi_i C_G^i$$
(34b)

where ψ_i is the stoichiometric coefficient, or the mass concentration of sites captured by a unit mass concentration of the metal i, C_s^i and C_G^i are sorbed concentration of metal species *i* to solid phase and colloidal phase respectively, P_0 and $P_{G,0}$ are initial site availability on soil matrix and colloidal particles, and *nm* is number of compounds involved. Equations (33a-b and 34a-b) are substituted into equations (18) and (20-23) and for each constituent a set of equations is generated which are solved in a coupled manner. In equilibrium conditions we can write $C_s^i = K_I^i P_{av} C^i$, and $C_G^i = K_{IG}^i P_{G,av} C^i$. Substituting this into equations (24a-b) we can calculate P_{av} and $P_{G,av}$ as:

$$P_{av} = P_0 / (1 + \sum K_I^i C^i)$$
(35a)

$$P_{G,av} = P_{G,0} / (1 + \sum K_{IG}^{i} C^{i})$$
(35b)

The above mentioned equations should be substituted into equations (30)-(31) or (32) for each constituent and then the resulting equations should be solved in a coupled manner.

3. Numerical Solution

Unsaturated flow model is solved using a semi-implicit finite difference method with Crank-Nicholson time weighing scheme with saturation content θ as the main variable. Due to non-linearity of $K(\theta)$ and $\partial \psi / \partial \theta$ with respect θ their values is calculated explicitly from the previous time step. The colloid facilitated transport model (equations (6)-(9) are also solved using a fully coupled implicit finite difference scheme with dynamic blocking function *B* evaluated explicitly from the previous time step. The transport and colloid facilitated transport component of the model represented by equations (18) and (20)-(24) are solved in a fully coupled form using an implicit finite difference method again with Crank-Nicholson time weighing. In case of competitive

sorption, the set of equation are solved for each species of metal separately using the K_D and K_{DG} and P_{av} , $P_{G,av}$ values estimated from the previous time step.

4. Results

4.1. Comparison with experimental data

The model is compared with data presented by Roy and Dzombak, (1997) for transport of phenanthrene in steady and saturated flow in porous media in a column with the presence of silica, clay minerals and iron oxide colloids. In this experiment a solution of 1 mg/L phenanthrene with 0.1M NaCl was injected to the column for 61 pore volumes (PV) and then the influent solution was changed to no phenantherene with 0.001 M NaCl for the rest of the experiment. The low ionic strength was intended to induce the colloids attached to collector grains to be released. To model this phenomena the detachment rate coefficient α_h is assumed to be zero in the presence of high ionic strength solution and is set to a finite value after presence of the low ionic strength solution. The parameters used in the model are listed in Table 1.

Figure 1 shows the comparison between data and model prediction breakthrough curves for both colloidal particles and total phenanthrene concentration ($Ct = C + G.C_G$). As it can be seen good agreement between measured and predicted values can be seen. The parameters used in the prediction are mainly obtained from Roy and Dzombak, (1997 and 1998). For prediction of colloid transport (Fig. 1a) the values of v_{crit} and α_{hm} have been estimated so that k_{rp} becomes equal to the value 0.3/hr as suggested by Roy and Dzombak, (1998). Also partitioning coefficient between water and colloidal particles (k_{DG}) was found by calibration since Roy and Dzombak, (1998) did not explicitly mention a value obtained from direct measurement. In addition the value of G_{max} were calculated using estimated mass and surface area of a single colloid and the surface area of porous media using typical surface jamming limits considered in Johnson and Elimilech, (1995). A reasonable agreement between the observed and modeled breakthrough curves was achieved for both colloids and the compound total concentration. However a tail is observed in the colloid concentration breakthrough curve which the single rate attachment model used in this research is unable to reproduce it appropriately. Using multiple or distributed rate models for colloid transport may improve this behavior.

a)

b)



Figure 51: Model results compared to data obtained by Roy and Dzombak, (1997) a) Breakthrough curve for colloidal particle concentration b) Total contaminant concentration

4.2. Single component simulation

A few simulations were also performed to show the capability of the model to capture the effects of unsaturated condition and kinetic sorption-desorption to colloidal particles. The same parameters used in the model verification stage with Roy and Dzombak, (1997) data as listed in Table 1 where used for demonstration except that a smaller colloid detachment rate k_{rp} was used since the high value in Roy and Dzombak, (1997) results in all attached colloids being washed out quickly. For these simulations it is assumed that a 33 hrs (equivalent of 60 pore volumes) of wet condition is followed by a 22 hrs (40 pore volumes) of dry conditions. The wet and dry conditions were dictated by specifying the top boundary conditions (i.e. Eq 5a with F=0 for dry condition and Eq 5b for wet condition). The colloid-associated concentration in the inflow is calculated by assuming it to be in equilibrium with the inflow water. Also the initial concentration of colloids attached to the solid phase is assumed to be smaller than in the Roy and Dzombak since the goal is to examine the effect of colloids in the influent and not the release of colloids from the media. A larger value is also used for the colloid-water partitioning coefficient in order to present the behavior of highly sorbing compounds in the system. Air-water partitioning coefficient is calculated from the values obtained by Wan and Tokunaga, (2001). Since these values are based on the surface area of air phase they have been converted in terms of volume of colloids by assuming the volume of air bubbles to be in the same order of magnitude of the media grain sizes. Figure 2 shows the water content profile at some intervals after the start of wet and dry period and the flow rate and the concentration of colloidal particles at the bottom of the column. The reason for the decrease of the colloidal concentration while the flow is reduced is due to the dependency of colloid release on flow velocity.

Parameter Value Simulation Time 55 hrs (61 p.v.) ^(a) Duration of wet period, (low ionic strength in verification 22 hrs (40 p.v.)^(a) stage) Time step 5 sec $10 \text{ cm}^{(f)}$ Length of the Column Number of Grid points 20 1650 (kg/cu.m)^(f) Dry Bulk density of solid phase 0 376^(a) Initial porosity Verification: 0.376 (saturated)^(a) Initial Saturation content simulations: 0.1 $14.5(1/m)^{(b)}$ van Genuchten parameter α 2.67^(b) van Genuchten parameter n 0.625^(b) van Genuchten parameter m 6.85 (cm/hr)^(a) Initial saturation hydraulic conductivity/Flow velocity 0.045^(b) Residual water content 1.1418 $(kg/kg)^{calculated from (c)}$ Surface jamming limit Neglected 0.0 (kg/g) Hydraulic conductivity reduction parameter 250(µm)^(a) Average radius of media grains a_c 1.0(µm)^(a) Average radius of colloidal particles a_n 1.2^(d) Partitioning coefficient of colloids between water and air-water interface K_a $19 (g/kg)^{(a)}$ Initial concentration of colloids available 0.1 (g.kg) on the surface G_{s2} 1.0(mg/l)^(a) Inflow concentration of dissolved compound Verification: 0^(a) Inflow concentration of colloidal particles Simulation: 20 mg/L Colloid water mass exchange coefficient k_G $1.2 (1/hr)^{(a)}$ $0.12 (1/day)^{(a)}$ Solid water mass exchange coefficient k_s 5×10^{-3 (e)} Collection efficiency η 3×10^{-3} estimated from ^(a) so that Attachment efficiency α same attachment rate is obtained $3000 (m^2/kg)^{(f)}$ Specific surface area of porous media fVerification: 50 (L/kg)^(calibration) Partitioning coefficient between water and colloidal particle Simulation: 500 (L/kg)^(calibration) K_{DG} 5.8 (L/kg)^(f) Partitioning coefficient between water and solid phase K_D Diffusivity α_d 0(cm), assumed 2×10^{-3} Detachment rate coefficient α_{hm} (kg/m^3) , calculated from ^(a) Detachment threshold velocity v_{crit} 1.17(cm/hr), assumed

Table 6: Base values of the parameters used in comparison to Roy and Dzombak, (1997) and demontration simulations

a) Roy and Dzombak, (1998), b) Leij et al., (1996), c) Johnson and Elimelech, (1995)

d) Wan and Tokunaga, (2001), e) Nelson and Ginn, (1997), f) Roy and Dzombak, (1997)

Figure 3 present profiles of dissolved (*C*), sorbed (*C_s*), mobile colloidal (*C_G*) and the Sorbed concentration to irreversibly attached colloids (*C_{Gsi}*). As it is seen the colloidal concentration front grows ahead of dissolved concentration indicating that colloidal particles move faster than dissolved compound due to their slower capture/sorption rate and smaller retardation and therefore they can carry the chemicals bound to them faster. Figure 3c is 4.5 hrs after the flow stops. As the flow rate decreases in unsaturated condition (Figure 3c) mass exchange between colloidal particles and aqueous phase causes the concentration associated with the colloids to decrease and approach to the equilibrium concentration with dissolved compounds.



Figure 52: a) Water content profile in the column at some time intervals after rain (a.r.) and after drought (a.d.) and b) flow and aqueous colloid concentration (G) at the bottom of the column.



Figure 53: Concentration profiles for Dissolved, Sorbed soil matrix, Sorbed to colloids, and sorbed to captured colloids at a) 12.5 hrs, b) 25 hrs and c) 37.5 hrs after simulation start. Flow is stopped at 33 hrs after the start of simulation.

4.3. Multiple compound simulation with competitive sorption

A similar simulation is done on colloid-facilitated transport of multiple metals with competitive sorption. Metal I is assumed to have lower partitioning coefficient (K_I = 0.5 L/µg, $\Psi_I = 1$) and metal II is assumed to have a higher partitioning coefficient (K_{II} = 5 L/µg, Ψ_{II} = 1) for both colloidal and immobile solid phase. Initial available site concentration is assumed to be (1 mg/kg) for colloidal particles including attached or mobile, and (0.1 mg/kg) for immobile solid phase. Inflow dissolved concentrations are 5 and 2µg/L respectively for metal I and II. Colloidal concentrations are assumed to be at equilibrium with dissolved aqueous phase at the inlet. All remaining flow and colloid transport related parameters have been chosen as listed in table 1. Figure 4 presents the profile of dissolved and colloidal metals at various times. As it can be noticed the transport of dissolved metals with higher affinity to the solid phase is slower while its colloid-facilitated transport is faster than the metal with lower affinity to soil particles. This is an expected result since the metal with higher affinity sorbs to the colloid phase more persistently and can travel with them to farther distances. Another point that can be realized from Figure 4 is that at the locations where both metals have relatively high concentrations in aqueous phase the metal with higher affinity occupies the majority of sites, maintaining the concentration of the metal with lower affinity in the aqueous phase. This phenomenon causes the concentration of the metal with lower affinity to increase to a level higher than its inflow concentration at the locations where the front of the metal with higher affinity moves. This process is seen more clearly by looking at the colloidal concentrations of both metals. In this case, the adsorption capacity of colloidal particles for the low affinity metal decreases significantly when in the presence of the second metal. Also the drop in the colloidal concentrations of the metal with higher affinity is due to the mobile-immobile colloid exchange.



Figure 54: Profiles and dissolved and colloidal concentration of metals with high and low partitioning coefficients in at a) 12.5 hrs, b) 25 hrs and c) 37.5 hrs after simulation start. Flow is stopped at 33 hrs (60 p.v.) after the start of simulation.



Figure 55: Breakthrough curves of a) colloid associated metals at the first 20 hrs and b) dissolved and colloidal concentrations at 300 p.v. steady flow experiment.

In order to demonstrate the complete breakthrough of metals in the column system a simulation with steady and continuous flow for 300 (p.v.) was performed. All parameters were chosen same as the ones used for the previous simulation for two

(a)

metals except that there were no dry period and the duration of the simulation was longer. Figure 5 presents breakthrough curves obtained from the simulations. In Figure 5a the colloidal concentrations of metals at the first 20 pore volumes of the simulation are shown. As it is noticed the metal with higher affinity to the colloidal particles reaches the end of the column earlier. In Figure 5b it is noticed that both colloidal and dissolved concentrations of the metal with smaller affinity to the solid phase reaches to a concentration higher than the inflow concentration before the front of the metal with higher affinity reaches the bottom of the column. The reason for this phenomenon is the remobilization of metals with low affinity due to their replacement by metal with higher affinity in the column.

4.4. Criteria for using equilibrium approach

Figures 6 and 7 show the breakthrough curves obtained by running the single compound simulations with various exchange rate coefficients (k_r). As is expected by increasing the exchange rate coefficient the breakthrough curve (BTC) approaches to the BTC obtained by using the equilibrium assumption between the colloidal and dissolved species. As it can be noticed for small Damkohler numbers ($Da=k_r.L/v$) the colloid associated metal appears relatively rapidly at the effluent with respect to its retardation factor (e.g. $K_{rG} = 0.012/hr$, $Da = 6.6 \times 10^{-3}$). As Damkohler number increases the behavior of the system gets closer to the one predicted by the equilibrium assumption between colloids and pore water phase. For Damkohler number equal to 66 ($K_{rG} = 120/hr$) the breakthrough curve predicted by the kinetic model can be approximated by the equilibrium model satisfactory well. Generally it can be suggested that for a Damkohler number greater than 20, equilibrium assumption can produces satisfactory results in a 1-D column.



Figure 56: Breakthrough curves for colloid associated and dissolved metals with various exchange rate coefficients between colloidal and solid phase for a metal with K_D =5.8 L/kg and K_{DG} = 500 L/kg

5. Discussion and Conclusions

In this paper the development of a colloid-facilitated contamination transport model in unsaturated zone is presented. Four different colloidal phases including, mobile, initially reversibly attached, irreversibly attached and attached to air-water interfaces are considered in the model. Reversible kinetic sorption of contaminants to each phase is also taken into account. The model uses filtration theory with a dynamic blocking approach to simulate removal of colloids by the porous media. Colloid release is assumed to be proportional to the shear stress exerted by the flow onto the grain which was assumed to be proportional to flow velocity. The concept of exchange between aqueous phase and air-water interface is used in order to take into account the effect of drying and wetting on colloid transport. The exchange of colloid with porous media surface is assumed to be kinetically controlled and the exchange to the air-water interface is assumed to be instantaneous. A linear kinetic sorption and Langmuir competitive sorption assumptions for multiple metals are implemented in the model. Several demonstration simulations are presented in order to show the capability of the model to represent various aspects of colloid-facilitated transport. Also the applicability of equilibrium assumption between colloidal and aqueous phase was tested for various exchange rate coefficient and it was found that for a Damkohler number greater than 20, an equilibrium model can represent the system reasonably well. The model can be used for prediction of leaching of various contaminants specially the ones with high affinity to colloidal matter from upper ground sources to the groundwater through vadose zone such as in storm-water infiltration basins and leaching from underground tanks.

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Chapter 4:

Approximation of a radial diffusion model with a multiple rate model for heterodisperse particle mixtures

Abstract:

An innovative method is proposed for approximation of the set of radial diffusion equations governing mass exchange between aqueous bulk phase and immobile intraparticle phase for a heterodisperse mixture of particles. For this purpose the temporal variation of concentration at several uniformly distributed points within a normalized representative particle with spherical, cylindrical or planar shape is fitted with a 2domain linear reversible mass exchange model. The approximation method is then superposed in order to generalize the model to a heterodisperse mixture of particles. The method can reduce the computational effort needed for solving the intra-particle mass exchange to a heterodisperse mixture of particles significantly and also the error due to the approximation is shown to be relatively small. The method is applied to describe desorption batch experiment of 1,2-Dichlorobenzene from four different soils with known particle size distributions and it could produce good agreement with experimental data.

Keywords: Radial Diffusion model, Multiple-rate model, Sorption, Desorption, Modeling, Heterodisperse particles

1. Introduction

One of the most common models to simulate rate-limited mass transfer between the immobile zone within a particle and the surrounding bulk concentration is the radial diffusion model (e.g., Villermaux, 1974; Rao et al., 1980; Wu and Gschwend, 1986).

Radial diffusion models often consider mass transfer resistances imposed by an aqueous boundary layer surrounding the particles, diffusion into intra-particle pore spaces,, with the particle and pore geometry typically approximated by ideal forms such as spherical or cylindrical. These particle scale diffusive resistances are often combined with sorption to the intra-particle walls, and many adsorption processes involving mono-disperse particles have been analyzed using radial diffusion models (Neretnieks, 1976a; Neretnieks, 1976b; Vrentas and Vrentas, 1998; Wiberg and Harris, 2002).

There have been some efforts to solve the radial diffusion equation for hetero-disperse systems. For example Ruthven and Loughlin (1971) and Cooney and Adesanya. (1983) used the analytical solution for the uptake rate by a single sphere to obtain the uptake rate of a hetero-disperse particles for a batch system in which the bulk concentration is held constant. Cooney and Adesanya. (1983) also used a finite difference method to solve the non-linear site saturation model by approximating the particle size distribution using 17-31 intervals. Rasmuson (1985), found an analytical solution for modeling the breakthrough curve for columns containing hetero-disperse particles with fixed boundary and initial conditions. Fong and Mulkey (1990) suggested a method for calculating a representative radius for a particle size distribution that can be used to approximate adsorption rates for the hetero-disperse mixture using a mono-disperse radial diffusion model. Pedit and Miller (1995) solved the complete set of radial diffusion equations in a batch system using a numerical the method. They used the method of lines to reduce the governing system of partial differential equations to a system of ordinary differential equations, and then used the Bubnor-Galerkin finite element method with a third order shape functions to solve the resulting set of equations. Karapanagioti et al. (2001) also used a finite difference method for modeling the mass exchange, biodegradation and sorption in a batch system with hetero-disperse particles. Basagaoglu et al. (2002) used a finite-difference method to solve the radial diffusion model for a hetero-disperse mixture of particles with non-linear site limited

sorption reactions. They tested their model with a mixture of three spherical particle sizes in a batch system and also a mixture of three different shapes of particles (spherical, cylindrical and planar), each with a single size class.

Although the solution of the system of equations obtained from radial diffusion equation for a hetero-disperse mixture in a batch system is tractable, the computational effort needed for solving macroscopic transport problems in 1,2 or 3 dimensions explicitly is rather large (e.g. Dietrich et al., 2003). For a domain with homogenous media, using the method of temporal moments can reduce the computational effort significantly. Cunningham and Roberts (1998) and Neretnieks (1976a) used this method to investigate the impact of a distribution of time scales as an indicator of particle sizes and intra-particle effective diffusion on the transport of sorbing solute. They ignored the film resistance between aqueous phase and particles. This method can be used for determining the spatial moments of solute concentration in homogeneous columns. In practical applications other simplified models such as one-site models (Bahr and Rubin, 1987; Lapidus and Amundson, 1952; Oddson et al., 1970; Rao et al., 1980), two-site models (Cameron and Klute, 1977; Selim et al., 1976, and Nkedi-Kizza et al., 1984) or multiple rate models (Haggerty and Gorelick, 1995) are used. Rao et al. (1980) also showed the failure of one-site models manifested as an apparent time dependence of the exchange rate coefficient. Log-normal or Gamma distributions are often assumed to govern the rate distribution for the multiple rate models (Connaughton et al., 1993; Culver et al., 1997; Pedit and Miller, 1994). However because these simplified models are not directly based on the mechanisms involved in the sorption process, there is no way to relate the rates of adsorption-desorption with the system's physical characteristics such as particle size distribution of the media, diffusivity of the contaminants, pore size distribution in the particle and the tortuosity factor associated with the intra-particle pores. Thus the parameters involved in such models are usually treated as fitting parameters and therefore these models usually lack the capability of

being generalized to other soil media and chemical properties than the one to which they have been fitted.

In order to take into account the physical characteristics of the media in multiple-rate serial models, there have been some efforts to find the link between multiple rate models and radial diffusion models. Haggerty and Gorelick (1995) suggested a method for extracting the equivalent multiple rate model from a normalized radial diffusion model by setting equal the bulk water concentrations obtained by a radial diffusion model and a multiple rate model with an infinite number of sites. They used Laplace transformation of time dependent bulk dissolved concentrations and found the exchange rate distributions as infinite series so that the resulting multiple-rate model could predict exactly the bulk water concentrations associated with radial diffusion. However they used an assumption of no boundary layer between the grain and bulk water (i.e. the concentration in the outermost part of the grain were assumed to be exactly equal to the bulk water concentration). Also in their approximation they matched the bulk concentrations obtained from the radial diffusion and its multiple rate approximations, and therefore in their model although the bulk water concentration predicted by the radial diffusion model and its equivalent multiple rate model are exactly equal, the rates they obtained as an infinite series do not represent any physical exchange rate between any part of the solid phase and bulk water. In addition in case of hetero-disperse mixtures of particle sizes, using an infinite series for the exchange rate and the mass associated with each exchange rate leads to having as many infinite series as the number of particle size classes, which will multiply the computational effort needed for solving the problem by the number of particle size classes selected.

The goal in the present study is to use a numerical method to obtain the multiple-rate model that can best approximate a radial diffusion model in terms of intra-particle concentration for hetero-disperse mixtures. In other words, we seek to approximate a serial mass transfer process with an effective set of parallel linear reversible reactions to incorporate the effect of distributed particle sizes on mass transfer controlled by radial diffusion (Figure 1). Our parallel reaction model uses a rate distribution associated with a multiple rate model and requires significantly smaller computational effort compared to a comparable radial diffusion model for hetero-disperse particle mixtures. The advantage of this model with respect to previous multiple rate models is that the exchange rate distribution here is obtained directly from the diffusive characteristics of the grains. Also because a numerical technique is used to solve the radial diffusion equation in this study, the model can be extended further for non-linear cases, various shape factors and different boundary conditions.

Each particle is conceptualized as a symmetric grain surrounded by a diffusive boundary layer. The exchange process is controlled by intra-particle diffusion and film resistance due to the boundary layer. The model produces a continuous distribution for the rate coefficient instead of a discontinuous series since the exchange rate obtained for a distance from the center of a grain is a continuous function of distance from the center of the grain.



Figure 57. Schematic of a) Radial diffusion model b) Multiple rate approximation

For obtaining the exchange rate coefficient associated with any point (or distance from the center of the grain) inside a particle, the normalized radial diffusion method is solved numerically and then the optimal multiple exchange rate at each point is calculated by minimizing the sum of squared differences between the two over an appropriate time range.

2. Solution approach:

2.1. Radial diffusion model:

The equation for reactive (sorbing) diffusion of a dissolved compound within porous particles can be written as follows (Wu and Gschwend, 1986).

$$\beta \frac{\partial C_r}{\partial t} + (1 - \beta) \rho_s \frac{\partial S_r}{\partial t} = \frac{\beta D_m}{r^{\nu - 1}} \frac{\partial}{\partial r} \left(r^{\nu - 1} \frac{\partial C_r}{\partial r} \right)$$
(1)

in which S_r is the total local volumetric concentration in the porous sorbent (M/L³), C_r is the intraparticle contaminant concentration in the dissolved phase (M/L³), β is the porosity of the sorbent (-), D_m is the pore fluid diffusivity of the sorbate (L²/T), *r* is the radial distance from the center of a grain (L), and *v* is shape factor which is equal to 1 for planar, 2 for cylindrical, and 3 for spherical grains (-).

We assume that the sorption process inside the particle is fast, linear and reversible, in which case $S_r = K_D C_r$ and eq. 1 can be written as:

$$\frac{\partial C_r}{\partial t} = \frac{D_e}{r^{\nu-1}} \frac{\partial}{\partial r} \left(r^{\nu-1} \frac{\partial C_r}{\partial r} \right)$$
(2)

where

$$D_e = \frac{\beta D_m}{(1-\beta)\rho_s K_p + \beta} f(\beta, \lambda)$$
(3)

in which D_e is the sorption-retarded effective intra particle diffusivity (L²/T), K_p is the equilibrium partition coefficient (L³/M), ρ_s is the bulk density (M/L³), and $f(\beta, \lambda)$ is a correction factor in the diffusion coefficient (Wu and Gschwend, 1986) that includes the effect of tortuosity and intra-aggregate porosity.

For the purpose of finding the generic multiple rate model, it is assumed that initially particles are clean, therefore the initial and boundary conditions for the intraparticle contaminant concentration in a dissolved phase can be expressed as:

$$C_r(r,0) = 0 \tag{4}$$

A symmetry boundary condition is used on the center of the grain.

$$\frac{\partial C_r(r,t)}{\partial r} = 0 \quad at \, r = 0 \tag{5}$$

and a film resistance boundary condition is imposed at the surface of the grain also assuming for the purpose of obtaining the generic multiple rate distribution that the bulk concentration is maintained constant.

$$D_{e} \frac{\partial C_{r}(r,t)}{\partial r} = k_{b} \left[C_{bulk} - C_{r}(R,t) \right] \quad at \ r = R \tag{6}$$

in which k_b is the film resistance coefficient (L/T).

The normalized form of Eq. 2 can be written as follows.

$$\frac{\partial \chi}{\partial \tau} = \frac{1}{\xi^{\nu-1}} \frac{\partial}{\partial \xi} \left(\xi^{\nu-1} \frac{\partial \chi}{\partial \xi} \right)$$
(7)

where the dimensionless variables are defined as follows:

$$\xi = \frac{r}{R} \tag{8}$$

$$\tau = \frac{tD_e}{R^2} \tag{9}$$

$$\chi(\xi,\tau) = \frac{C(\xi,\tau)}{C_{bulk}} \tag{10}$$

$$Bi = \frac{Rk_b}{D_e} \tag{11}$$

Where ξ is dimensionless distance from the center of the grain, τ is the dimensionless time, χ is the dimensionless concentration and *Bi* is the Biot number which indicates the importance of intra-particle diffusion with respect to film resistance coefficient.

It worth noting that the simplified boundary and initial conditions in Eqs. 4 and 5 and the assumption of fixed bulk concentration are imposed solely for obtaining the generic exchange-rate coefficient distribution. Having the generic exchange rate distribution, the multiple rate model can be used for different boundary and initial conditions, including a variable bulk concentration. The normalized boundary conditions can be written as:

$$\left. \frac{\partial \chi}{\partial \xi} \right|_{\xi=1} = B_i \left(1 - \chi(1, \tau) \right) \tag{12}$$

$$\left. \frac{\partial \chi}{\partial \xi} \right|_{\xi=0} = 0 \tag{13}$$

and the normalized initial condition is

$$\chi(0,\tau) = 0 \tag{14}$$

Now the solution to Eq. 7 can be expressed for any particle size, via the stretching normalizations in eqs. 8 through 11.

The solution to the PDE in eq. 7 with boundary conditions 8 and 9 and initial condition 14 is obtained using an implicit finite difference method (Appendix A) and can be expressed as a function of normalized time τ , normalized distance from the center ξ , and *Bi*. For sake of simplicity the numerical solution to the PDE is called χ , however it has some differences with the exact solution due to truncation errors and other types of possible errors in using a numerical technique. So from this point of the paper χ refers to the numerical solution to the normalized radial diffusion equation.

$$\chi = \chi(\xi, \tau; Bi) \tag{15}$$

To obtain the generic rate coefficient distribution for a multiple rate model that can represent the mass exchange to the normalized grain, the normalized radial diffusion model for the normalized grain is solved and then for each point among the set of points inside the grain within radius increments, the exchange rate coefficient that can best represent the concentration variation at that point is obtained by minimizing the difference between the solutions found from radial diffusion and the linear reversible sorption model.

The normalized radial diffusion PDE is solved for a large range of Bi with logarithmic increments (i.e. it is solved in range of 10^{-5} to 10^{5} with increments of 1.2 as a multiplier). The time increments and radial grid sizes should be specified so that the computational intensity remains affordable while satisfying the stability conditions of the numerical method. In particular, insufficient resolution of the intra-granular dimension can lead to serious mass balance errors (Basagaoglu et al., 2002). So the

radius is discretized into 100 grid points and the increment for τ is considered dependent on *Bi*. The simulation for each increment of *Bi* is continued until the average concentration inside the particle reaches 0.99 of the saturation concentration (i.e. the situation where the average normalized concentration (χ) inside the grain is greater than 0.99).

Figure 2 represents the solution of the normalized radial diffusion equation for four different *Bi* values as an example. It can be noticed from the figure that for *Bi* values greater than about 100 the limiting process is not boundary layer exchange but intraparticle diffusion. On the other hand for small Bi values (i.e. below 0.1) the effect of intra particle diffusion becomes negligible and the controlling process becomes the film resistance.



Figure 58. Numerical solution of the radial diffusion equation vs. τ and ξ for Bi equal to a) 10^{-2} , b) 10^{0} , c) 10^{2} , and d) 10^{4}

2.2. Multiple-rate model:

As outlined above, the goal is to fit the best possible single rate exchange model to each layer with identical distance from the center and to obtain a multiple rate model by superposing all single rate models. In the multiple rate approximation the intra-particle zones are treated as if they are directly exchanging mass with the bulk solvent (Figure 1b). Each intra-particle zone is associated explicitly with its own rate coefficient, the value of which drops with decreasing normalized radial coordinate value. The net diffusive reactive behavior is obtained by linear superposition (summation) of the individual mass transfers. The utility of this explicit linear approximation is suggested by the linearity of the governing differential eq 1. Thus the approximate parallel domain multiple-rate model can be written as follows:

$$\frac{\partial C_i}{\partial t} = k_{f,i} \left(C_{bulk} - \widehat{C}_i \right) \qquad \qquad i=1..M$$
(16)

 \hat{C} is the intra-particle concentration found by the multiple-rate model approximation, M is the number of intra-particle zones in the multiple rate model, and $k_{f,i}$ is the exchange rate (1/T) associated with the intraparticle zone *i*.

The normalized form of eq. 16 for the fixed pore water concentration can be written as follows:

$$\frac{\partial \hat{\chi}_i}{\partial \tau} = \kappa_{f,i} \left(1 - \hat{\chi}_i \right) \tag{17}$$

in which the normalized variables are defined as:

$$\hat{\chi}_i = \frac{\hat{C}_i}{C_{bulk}} \tag{18}$$

$$\kappa_{f,i} = k_{f,i} \frac{R^2}{D_e} \tag{19}$$

Now if we consider that each zone *i* in the multiple rate model corresponds to a layer (or a range of distances from the center) in the discretized radial diffusion model, then for each layer *i*, $\kappa_{f,i}$ is clearly a function of B_i and ξ_i as

$$\kappa_{f,i} = \kappa_f(\xi_i, B_i) \tag{20}$$

Now for any specified Bi value and point inside the grain (i.e., ξ) $\kappa_{f,i}$ is a constant and equation 17 can be solved analytically.

$$\widehat{\chi} = 1 - e^{-\kappa_{f,i}\tau} \tag{21}$$

To determine the function $\kappa_f(\xi, B_i)$ which makes the approximate solution $\hat{\chi}$ as close as possible to the numerical solution of the radial diffusion equation χ , it is necessary that for each particular value of B_i and ξ_i the value of κ_f be estimated such that it minimizes the difference between $\hat{\chi}$ and χ over the specified time span.

$$\min_{\kappa_f(\xi,Bi)} \int_0^\infty \left(\chi - \widehat{\chi}\right)^2 d\tau$$
(22)

or

$$\min_{\kappa_f(\xi,B_i)} \int_0^\infty \left(\chi(\xi,\tau,B_i) - (1 - e^{-\kappa_f \tau}) \right)^2 d\tau$$
(23)

The optimization problem in eq. 23 is solved using the steepest descent method for a range of Bi between 10^{-5} and 10^{5} with logarithmic increments and ξ between 0 and 1 with increments of 0.01.

The result of the numerical solution of the optimization problem in eq. 23 is presented in Figure 3. As can be noticed from the figures for $B_i > 10$ the dependence on B_i is small indicating that the dominant factor in the sorption to the grain is intra-particle diffusion, on the other hand for $B_i < 0.1$ the κ_f variation with respect to ξ is small indicating that the dominant process in controlling the sorption is boundary layer diffusion. For most environmental systems the Biot number is greater than 100 (Ko et al., 2003) which indicates that usually film resistance does not control the mass exchange between water and particles.



a)

Figure 59. κ_f versus Bi and ξ for a) v=3 and b) v=2 obtained by minimizing the difference between the multiple rate and radial diffusion solutions

For the special case of no film resistance, $Bi = \infty$, the analytical solution of eq. 7 can be used instead of the numerical solution. Adopting the method by Crank (1975) the analytical solution to eq. 7 with boundary conditions (9) and $\chi(1) = 1$ can be obtained from the following infinite series:

$$\chi = 1 + \frac{2}{\pi\xi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin(n\pi\xi) \exp(-n^2\pi^2\tau) \quad \text{for shape factor } v=3$$
(24)

So in that case, substituting eq. 24 into eq. 23, the following expression should be minimized:

$$\int_{0}^{\infty} \left(\frac{2}{\pi\xi} \sum_{n=1}^{\infty} \frac{(-1)^{n}}{n} \sin(n\pi\xi) e^{-n^{2}\pi^{2}\tau} - e^{-k\tau} \right) d\tau$$
(25)

Eq. 25 was used to verify of the results obtained from the numerical solution of the normalized radial diffusion equation. The average concentration and flux versus time obtained from the radial diffusion solution is compared with those estimated with the multiple-rate model for Bi=100 in figure 4. It can be seen that there is a good agreement between two models for most values of τ_i . However, there are some degrees of discrepancies between the fluxes predicted by the multiple rate and radial diffusion models for smaller flux estimates. Those discrepancies may arise either from the numerical errors involved in the method or the approximations introduced.

The solutions to the normalized radial diffusion model and the multiple rate model for the case of Bi = 100 at ξ =0.1, 0.5, 0.9 respectively, for a spherical particle (v=3) versus time are shown in figure 5. Here the discrepancies are clear and their reason is the fundamental differences between the RD and MR models (i.e., in the serial models there will be a lag until the compounds reach the internal zones while in the parallel model no such lag exists.)



Figure 60. Radial diffusion and estimated multiple rate model a) mass flux and b) average concentration versus time for a spherical particle with Bi = 100



Figure 61. Local intra-particle concentration versus time obtained by radial diffusion and its equivalent multiple-rate model for a spherical grain with Bi = 100 at ξ =0.1, ξ =0.5, and ξ =0.9.

The variation in the bulk aqueous phase concentration with time is shown for a single size mixture using the RD and MR models in figure 6. when the bulk water concentration is not fixed. It can be noticed that the agreement is as good as for fixed pore water concentration (Figure 4) although the exchange rate distribution is obtained using a fixed bulk concentration assumption.



Figure 62. Bulk water concentration for a single size media obtained by radial diffusion and multiple rate models for porosity $\varepsilon = 0.5$, $K_D = 1$ and grain radius R=1.

2.3. Solution technique for media with hetero-disperse particles:

If a media with particle size distribution $\psi(R)$ is considered, (i.e., the fraction of mass with the particle size R is equal to $\psi(R)$) the objective will be to find the distribution of k_f values, $\theta(k_f)$ (i.e. the fraction of mass that has exchange rate of k_f with the bulk solution) that provides the best agreement between the MR and RD models of the system.

To calculate the exchange rate distribution, the k_f domain is first divided into different bins k_{f,1}-k_{f,2}, k_{f,2}-k_{f,3}, ... k_{f,n-1}-k_{f,n}. The mass associated with each bin (i.e. k_{f,i}-k_{f,i+1}) can be calculated by summing the masses associated with the exchange rates between κ_{f_i} and κ_{f_i+1} for each particle size where $\kappa_{f,i} = k_{f,i}R^2/D$. This is possible because from the solution of the minimization problem we obtained kf as a monotonically decreasing function of normalized distance from the center ξ_i . Therefore ξ can be expressed as a function of κ_f for a specified value of Biot number as follows:

$$\xi = \xi(\kappa_f, B_i) = \xi(k_f \frac{R^2}{D}, \frac{Rk_b}{D})$$
(26)

where k_b can be determined by the thickness of boundary layer and molecular diffusion coefficient of the contaminants.

The mass associated with the exchange rate bin $k_{f,i}$ - $k_{f,i+1}$, M_i , can be calculated as:

$$\frac{M_i}{\sum M} = \int_0^\infty \left(\xi(k_{f,i+1} \frac{R^2}{D}, \frac{Rk_b}{D})^\nu - \xi(k_{f,i} \frac{R^2}{D}, \frac{Rk_b}{D})^\nu \right) \psi(R) dR$$
(27)

Or if a measured (discrete) particle size distribution is available:.

$$\frac{M_i}{\sum M} = \sum_{j=0}^{R_{\text{max}}} \left(\xi(k_{f,i+1} \frac{R_j^2}{D}, \frac{R_j k_b}{D})^{\nu} - \xi(k_{f,i} \frac{R_j^2}{D}, \frac{R_j k_b}{D})^{\nu} \right) \psi(R_j) \Delta R_j$$
(28)

in which R_j is the representative particle radius of the particle size bin and ΔR_j is the increment of the bin.

The exchange rate distribution can therefore be obtained by computing the integral in eq. 26 numerically and the multiple rate batch sorption system can be written as follows:

$$\frac{\partial C_{bulk}}{\partial t} = -\sum_{0}^{k_{f,max}} \theta(k_{f,i}) k_{fi} (C_{bulk} - C_i)$$
(29)

$$\frac{\partial C_i}{\partial t} = k_{f,i} (C_{bulk} - C_i) \qquad \qquad for \ i=1....i_{max}$$
(30)

where C_i is the intra-particle concentration associated with exchange rate $k_{f,i}$ and C_{bulk} is the concentration in bulk aqueous phase.

In Figure 7 the exchange rate distribution obtained by the present method is compared with the one suggested by Haggerty and Gorelick (1995). It should be noted that the columns in the Haggerty and Gorelick distribution are representing dirac-delta functions multiplied by the values on the y axis because in their model exchange rates are expressed as infinite discrete series.



Figure 63. Exchange rate distribution for a sphere with unit radius in comparison with the distribution suggested by Haggerty and Gorelick (1995)

3. Application:

To illustrate the model's application for describing adsorption rates in hetero-disperse systems, it is used to describe batch adsorption rate curves for 1,2 dichlorobenzene (1,2-DCB) on four natural sorbents: Yolo soil, Forbes soil, Ohio Shale and Pahokee Peat. Experimental procedures and results of 1,2-DCB adsorption and desorption rates on these sorbents have been previously reported, including application of a multiple rate model baesd on the γ -distribution (Ju and Young, 2005a). Table 1 summarizes the relevant properties of the sorbents and experimental conditions for each of them. The particle size distribution for each sorbent was determined by a laser-based particle counter (0.2-20µm: Particle Measurement Systems, Liquilaz) and a coulter counter (20-2000µm) and the cumulative particle size distributions are shown in Figure 8.



Figure 64. Cumulative particle size mass distribution for four sorbents

Table 7. Summary of batch adsorption experimental conditions and fitted values of D_e , K_D , and $K_{D,\infty}$.

Sorbent	Average	Average	Distribution	Estimated	Estimated
	sorbent mass	Initial 1,2-	Coefficient	Theoretical	intra-
	concentration	DCB	measured at	partitioning	particle
	(mg/cm^3)	concentration	34 days	coefficient	Diffusion
		(mg/L)	$(K_D) (L/kg)$	$(K_{D,\infty})$	Coefficient
				(L/kg)	$(D_e) (cm^2/s)$
Yolo	0.1017	0.107	11.34	21.55	4.5x10 ⁻¹¹
Forbes	0.0104	0.104	161.87	355.75	1.2x10 ⁻¹²
Pahokee peat	0.00195	0.103	665.54	1431.26	4.2x10 ⁻¹¹
Ohio Shale	0.00098	0.104	1505.7	4069.45	5.7x10 ⁻¹³

The lower limit of the correlation suggested by Harriot, (1962) for the case of no externally supplied mixing was used to estimate k_f :

$$\frac{2Rk_f}{D_l} = 2 + 0.64 \,\mathrm{Re}^{1.182} \,Sc^{0.333} \tag{31}$$

where D_l is the free liquid diffusivity (L²/T), Sc is the Schmidt number (-), and Re is the Reynolds number (-) associated with the particles, which are calculated using the following equations:

$$Sc = \frac{\mu}{\rho_l D_l} \tag{32}$$

$$\operatorname{Re} = \frac{(2R)^{2/3}}{\left(\frac{\mu}{\rho_l}\right)^{1/2}} \left(\frac{P}{\rho_l V}\right)^{1/6}$$
(33)

where ρ_l is liquid density, v is settling velocity of the particles that can be found by Stokes' law ε is porosity of the media, μ is the viscosity and P is the power dissipation rate which is set equal to zero here since the only mixing process is falling of particles under their own weight during end-over-end tumbling of the batch reactors.

For each sorbent the intra-particle diffusivity (D_e) and theoretical ultimate distribution coefficient $(K_{D,\infty})$ are found so that the mean-squared difference between the measured and computed pore water distributions is minimized. K_D is calculated from the experimental data using the following equation and is the ratio between the sorbed and bulk concentrations when all parts of solid phase reaches equilibrium.

$$K_D = (1 - \beta)\rho_s K_p + \beta$$

The results are presented in Figure 9. λ shown on the figure legend is $K_D/K_{D,\infty}$. In Figure 9 the time axis is shifted by 0.001 sec for plotting purposes. The effective intraparticle diffusion rates and theoretical partitioning coefficients for the four sorbents are summarized in Table 1.



Figure 65. Computed and measured pore water concentration for a) Yolo, b) Forbes, c) Pahokee peat and d) Ohio shale



Figure 10. Relationship between the hard carbon fraction of the sorbents and the fitted values of D_e and $K_D/K_{D,\infty}$ for the four sorbents.

The fitted values of the effective diffusion coefficient for the four sorbents span a range of nearly two orders of magnitude ($\sim 6 \times 10^{-13}$ to $\sim 5 \times 10^{-11}$ cm²/s). These fitted values are within the wide range observed previously for natural sorbents such as uptake of chlorinated benzenes by river sediments (8×10^{-12} to 1×10^{-9} cm²/s; Wu and Gschwend, 1986) and desorption of "aged" 1,2-dibromoethane by subsurface materials (2×10^{-17} to 8×10^{-17} cm²/s; Steinberg et al., 1987). In particular, the values obtained for Yolo soil and Pahokee peat are within the range of values observed for chlorinated benzenes on Charles River sediment by Wu and Gschwend (1986). The smaller values of D_e observed for the other two sorbents are consistent with their much higher organic carbon normalized adsorption capacities (Ju and Young, 2005b), which would contribute to increased intraparticle retardation. The unusual sorption characteristics of these materials were previously hypothesized to result from their higher hard carbon contents, where hard carbon is defined as organic carbon remaining after low temperature chemical oxidation (Ju and Young, 2005b). Figure 10 shows that both the effective diffusivity and the value of $K_D/K_{D,\infty}$ tend to decrease with increasing hard carbon fraction of the sorbents. These findings are consistent with the hypothesis that the locus of high capacity and rate-limited sorption in natural sorbents is the hard carbon domain. According to this hypothesis, the larger the fraction of a sorbent's organic carbon that is operationally defined as "hard" the slower will be the rate of approach to sorptive equilibrium and the larger the ultimate organic normalized distribution coefficient. Obviously, the exact configuration of the hard and soft carbon domains relative to one another and to the sorbent's mineral phases will impact the effective diffusion coefficient, too; determination of this configuration is beyond current capabilities but its variability may account for some of the scatter in Figure 10.

4. Conclusions:

A computationally efficient and reasonably accurate approximation of the radial diffusion model was presented for describing sorption reaction rates in hetero-disperse particle suspensions. Although there are some discrepancies at early times between the measured and computed solute concentrations during adsorption (Figure 9) these arise from a combination of laboratory limitations (e.g., inaccuracies in measuring concentration at early times) and modeling approximations (e.g.,instant sorption to the outer surface of particles is ignored in the RD model). Further refinement of the model would require sorption rate data that was more nearly continuous at early times, such as from a differential batch adsorber, With such data in hand, the model could be modified to estimate the mass which sorbs to the surface of each particle.

The model fitting procedure employed here showed that a shape factor (ν) equal to 3 provided the best fit of the data. However, the physical characteristics of the particles suggest that the actual shape factor is smaller than 3. This discrepancy arises because, in reality, the internal porosity and thus the intra-particle diffusivities and sorptive surface areas are higher at outer layers of particles than in inner zones. Therefore another approach that could improve the results is to use an intra-particle diffusion rate that varies as a function of radial position.

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6. Supplemental Information:

A-Stability analysis for radial diffusion numerical solver

Eq. (7) is solved using second order, implicit, finite difference scheme with Crank-Nicholson time weighting:

$$\frac{\chi_i^{t+1} - \chi_i^t}{\Delta \tau} = \frac{1}{\xi_i^{\nu-1}} \frac{1}{\Delta \xi} \left(\xi_{i+1/2}^{\nu-1} \frac{\chi_{i+1} - \chi_i}{\Delta \xi} - \xi_{i-1/2}^{\nu-1} \frac{\chi_i - \chi_{i-1}}{\Delta \xi} \right)$$
(A.1)

Writing the right hand side of equation (A.1) as weighted sum of the values obtained in time steps t and t+1 and arranging the equations yields:

$$\left(\frac{1}{\Delta\tau} + \frac{\xi_{i+1/2}^{\nu-1} + \xi_{i-1/2}^{\nu-1}}{\xi_{i}^{\nu-1}} \frac{\omega}{\Delta\xi^{2}}\right) \chi_{i}^{t+1} - \frac{\omega}{\Delta\xi^{2}} \frac{\xi_{i+1/2}^{\nu-1}}{\xi_{i}^{\nu-1}} \chi_{i+1}^{t+1} - \frac{\omega}{\Delta\xi^{2}} \frac{\xi_{i+1/2}^{\nu-1}}{\xi_{i}^{\nu-1}} \chi_{i-1}^{t+1} \\
= \frac{\chi_{i}^{t}}{\Delta\tau} + \frac{1}{\xi_{i}^{\nu-1}} \frac{1-\omega}{\Delta\xi^{2}} \left(\xi_{i+1/2}^{\nu-1} \chi_{i+1}^{t} - \left(\xi_{i+1/2}^{\nu-1} + \xi_{i-1/2}^{\nu-1}\right) \chi_{i}^{t} + \xi_{i-1/2}^{\nu-1} \chi_{i-1}^{t}\right) \tag{A.2}$$

Equation (A.2) is solved using TDML method.

For analyzing the stability of the finite difference scheme, von Neumann method is used. If we consider evolution of a Fourier mode of wave-number k,

$$\chi(x,t) = \tilde{\chi}(t)e^{jkx}$$
(A.3)

Substituting (A.3) into (A.2) yields:

$$\begin{split} &\left(\frac{1}{\Delta\tau} + \frac{\xi_{i+1/2}^{\nu-1} + \xi_{i-1/2}^{\nu-1}}{\xi_i^{\nu-1}} \frac{\omega}{\Delta\xi^2}\right) \widetilde{\chi}(t+1) e^{jkx} \\ &- \frac{\omega}{\Delta\xi^2} \frac{\xi_{i+1/2}^{\nu-1}}{\xi_i^{\nu-1}} \widetilde{\chi}(t+1) e^{jkx} e^{jk\Delta\xi} - \frac{\omega}{\Delta\xi^2} \frac{\xi_{i+1/2}^{\nu-1}}{\xi_i^{\nu-1}} \widetilde{\chi}(t+1) e^{jkx} e^{-jk\Delta\xi} \\ &= \left(\frac{1}{\Delta\tau} - \frac{\xi_{i+1/2}^{\nu-1} + \xi_{i-1/2}^{\nu-1}}{\xi_i^{\nu-1}} \frac{1-\omega}{\Delta\xi^2}\right) \widetilde{\chi}(t) e^{jkx} + \frac{1-\omega}{\Delta\xi^2} \frac{\xi_{i+1/2}^{\nu-1}}{\xi_i^{\nu-1}} \widetilde{\chi}(t) e^{jkx} e^{-jk\Delta\xi} \end{split}$$

or

$$\frac{\widetilde{\chi}(t+1)}{\widetilde{\chi}(t)} = \frac{\left(\frac{1}{\Delta\tau} - \frac{\xi_{i+1/2}^{\nu-1} + \xi_{i-1/2}^{\nu-1}}{\xi_i^{\nu-1}} \frac{1-\omega}{\Delta\xi^2}\right) + 2\frac{1-\omega}{\Delta\xi^2} \frac{\xi_{i+1/2}^{\nu-1}}{\xi_i^{\nu-1}} \cos(jk\Delta\xi)}{\left(\frac{1}{\Delta\tau} + \frac{\xi_{i+1/2}^{\nu-1} + \xi_{i-1/2}^{\nu-1}}{\xi_i^{\nu-1}} \frac{\omega}{\Delta\xi^2}\right) - 2\frac{\omega}{\Delta\xi^2} \frac{\xi_{i+1/2}^{\nu-1}}{\xi_i^{\nu-1}} \cos(jk\Delta\xi)}$$

For the method to be stable $\left|\frac{\widetilde{\chi}(t+1)}{\widetilde{\chi}(t)}\right| < 1$ or
$$\frac{\widetilde{\chi}(t+1)}{\widetilde{\chi}(t)} < 1 \quad and \quad \frac{\widetilde{\chi}(t+1)}{\widetilde{\chi}(t)} > -1$$

First condition is always true regardless of the value of ω , second condition is always true for Crank-Nicholson scheme $\omega = 0.5$. Thus the scheme is unconditionally stable when $\omega = 0.5$. So the controlling stability condition may stem from the boundary condition.

If we assume that Biot number is much larger than 1, then we can consider the outer layer as an isolated layer from other internal layer for the purpose of stability analysis. The mass balance for the outermost layer can be written as:

$$\chi_{ni}^{t+1} = \frac{\frac{\chi_{ni}^{t}}{\Delta \tau} - (1 - \omega)B_{i}\chi_{ni}^{t} + B_{i}}{\frac{1}{\Delta \tau} + \omega B_{i}}$$

For stability $\chi_{ni}^{t} < \chi_{ni}^{t+1} < 1$

$$\frac{1}{\Delta \tau} < \frac{\left(-\omega - (1-\omega)\chi_{ni}^{t} + 1\right)B_{i}}{(1-\chi_{ni}^{t})}$$

In the worst case when $\chi_{ni}^t = 0$

$$\Delta \tau > \frac{1}{\left(1 - \omega\right)B_i}$$