

An Integrated Media, Integrated Processes Watershed Model – WASH123D: Part 6 – Sediment and Reactive Chemical Transport in Stream/River Networks

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ABSTRACT

A watershed system includes river/stream networks, overland regions, and subsurface media. This paper presents a numerical model of sediment and reactive chemical transport in river/stream networks of watershed systems. The distribution of mobile suspended sediments and immobile bed sediments is controlled by hydrological transport as well as erosion and deposition processes. The distribution and fate of chemical species with a variety of chemical and physical processes is mathematically described by a system of advective-dispersive-reactive species-transport equations. To circumvent the stiff problem associated with fast reactions, a matrix decomposition procedure is performed via the Gauss-Jordan column reduction of the reaction network. After the decomposition, the system of species-transport equations is transformed to a system of reaction extent-transport equations each contains one and only one linearly independent reaction rate or no reaction rates. A reaction-extent transport equation with fast reaction is then approximated with an algebraic equation. Thus the system of reaction-extent transport equations is reduced to three subsets: (1) algebraic equations, (2) kinetic-variable transport equations containing slow reaction rates, and (3) component transport equations containing no reaction rates. A variety of numerical methods are investigated for solving the mixed differential and algebraic equations (DAE). Two verification examples are compared with analytical solutions to demonstrate the correctness of and to emphasize the need of implementing various numerical methods for application-dependent simulations. A hypothetical example is employed to demonstrate the capability of the model to simulate both sediment and reactive chemical transport and to handle complex reaction networks involving both slow and fast reactions.

1. INTRODUCTION

Due to the development of computer technology in the past two decades, water quality models have become popular assessing tools for studying the contaminant distributions. Our study involves the development of water quality models to simulate (1) river/stream networks, (2) overland regions, and (3) subsurface media. This paper considers the sediment and chemical transport modeling in river/streams. The transport and fate of water quality constituents in overland water and subsurface systems will be addressed in separate communications.

Most of the existing surface water quality models simulate either specific systems (Park and Lee, 2002 and Lopes et al., 2004) or systems containing specific chemicals or reactions (Ambrose et al., 1993 and Park et al, 2003). Models considering interactions among chemicals

based on reaction mechanism have a better potential for application to other systems (Steeffel and Cappellen, 1998). In the transport simulation, biogeochemical reactions can be divided into two classes: (1) fast/equilibrium reactions, and (2) slow/kinetic reactions. Although a few reaction-based watershed models can handle contaminant transport subject to kinetic reactions (Cheng et al., 2000; and Yeh et al., 2005), no existing river/stream water quality model, to our knowledge, has used a fully mechanistic approach to estimate both kinetic and equilibrium reactive chemical transport in river/streams.

This paper presents a general numerical model simulating sediment and reactive chemical transport in river/stream networks. In the model, we include mobile suspended sediments and immobile bed sediments. The dissolved chemicals in the mobile water phase, particulate in the suspended sediment phase and precipitates in the suspension precipitate phase are usually considered mobile. Dissolved chemicals in the immobile water phase, particulates in the bed sediment phase, and precipitates in the bed precipitate phase are considered immobile. Five numerical options are provided to solve transport equations and three coupling strategies are given to deal with reactive chemistry. The main objective of this paper is to emphasize the need of implementing various numerical options and coupling strategies to deal with different types of problems for different application circumstances.

2. MATHEMATICAL BASIS

The distribution of suspended sediment and bed sediment is controlled through hydrological transport as well as erosion and deposition processes. The distribution of chemical species with chemical and physical processes is mathematically described the following equation with hydrology transport and the production rate from all reactions contributing to the species.

$$\frac{\partial(A\rho_i C_i)}{\partial t} + \alpha_i L(\rho_i C_i) = A \sum_{k=1}^N [(v_{ik} - \mu_{ik})r_k], \quad i \in M \quad (1)$$

where A is the river/stream cross-sectional area, ρ_i is the density of the phase associated with species i, C_i is the concentration of species i, t is the time, α_i is 0 for immobile species and 1 for mobile species, v_{ik} and μ_{ik} are the reaction stoichiometry of species i in the k-th reaction associated with the products and reactants, respectively, r_k is the rate of the k-th reaction, and

$$L(\rho_i C_i) = \frac{\partial(Q\rho_i C_i)}{\partial x} - \frac{\partial}{\partial x} \left[AK_x \frac{\partial(\rho_i C_i)}{\partial x} \right] - M_i^s \quad (2)$$

where Q is the river/stream flow rate, x is the axis coordinate along the river/stream direction, K_x is the dispersion coefficient, and M_i^s is the source term other than that due to reactions.

The system described by equation (1) is very stiff if some of reactions are very fast; in the limit with infinite rates. To circumvent the stiff problem, we will take a diagonalization approach through decomposition. A Gauss-Jordan column reduction of the reaction network will transform the M species transport equations into three subsets:

Algebraic Equations for Equilibrium Reactions

$$\begin{aligned} \frac{\partial(AE_i)}{\partial t} + L(E_i^m) &= A\gamma_{kk}r_k + A \sum_{j \in N_{KD}} \gamma_{ij}r_j, \quad k \in N_E, i \in M : \\ \frac{\partial(AE_i)}{\partial t} + L(E_i^m) &\approx A\gamma_{kk}r_k = \infty \exists \quad \text{a thermodynamically} \\ &\quad \text{consistent equation} \end{aligned} \quad (3)$$

Reactive Transport Equations for Kinetic-Variables

$$\frac{\partial(AE_i)}{\partial t} + L(E_i^m) = A\gamma_{kk}r_k + A \sum_{j \in N_{KD}} \gamma_{ij}r_j, k \in N_{KI}, i \in M \quad (4)$$

Transport Equations for components

$$\frac{\partial(AE_i)}{\partial t} + L(E_i^m) = 0; \text{ donating } T_k = E_i, k \in N_C, i \in M. \quad (5)$$

where N_E is the number of linear independent fast reactions, N_{KI} and N_{KD} are the number of linear independent and dependent slow reactions, respectively, $N_C = M - N_E - N_{KI}$ is the number of components, E_i is the total concentration of a reaction extent, which is a linear combination of species concentrations, E_i^m is the mobile part concentration of a reaction extent, and γ is the decomposed reaction matrix.

After matrix decomposition, the system of species-transport equations is transformed to a system of reaction extent-transport equations that each contains one and only one linearly independent reaction rate or no reaction rate. A reaction-extent transport equation with fast reaction is then approximated with an algebraic equation and its reaction-extent is called an equilibrium variable. This facilitates the decoupling of fast reactions from slow reactions and allows robust and efficient numerical integration.

In order to enable the model for both research and practical applications, five options are provided to solve the advective-dispersive transport equation: (1) Option 1 – the application of finite element methods (FEM) to the conservative form of transport equations (CFTE), (2) Option 2 – the application of FEM to the advective form of transport equations (AFTE), (3) Option 3 – the application of the modified Lagrangian-Eulerian (LE) approach, (4) Option 4 - LE approach for all interior nodes and downstream boundary nodes but with FEM applied to CFTE for the upstream flux boundary, and (5) Option 5 - LE approach for all interior and downstream boundary nodes with FEM applied to AFTE for upstream flux boundary. Three coupling strategies are provided to deal with reactive chemistry: (1) Strategy 1 - the fully-implicit scheme, (2) Strategy 2 - the mixed predictor-corrector/operator-splitting method, and (3) Strategy 3- the operator-splitting method.

3. EXAMPLES

3.1 Comparison of options to solve the advective-dispersive transport equations

A 50 km-long river/stream with uniform width of 10 m is discretized into 1,000 equal size elements. We assume the water depth is 5 m and flow velocity is 0.4 m/s. A dissolved chemical in the mobile water phase CMW and a dissolved chemical in the immobile water phase CIMW are considered to undergo the following reaction.



Initially, no chemical exists in the domain of interest. Variable boundary conditions are applied to both the upstream and downstream boundary nodes. At the upstream boundary node, the incoming concentration of CMW is 1 g/m³. The molecular diffusion coefficient is assumed to be zero. Three cases with different dispersivities of 3.125 m, 62.5 m, and 1000 m were considered. Simulations were performed with fixed time step size of 36 s and total simulation time of 1,800 s.

Using the same coupling strategy, the fully-implicit scheme, to deal with reactive chemistry, simulations were performed with the five numerical options to solve the advective-

dispersive equation. In Figure 1, simulation results of CMW are compared with the analytical solutions given by Lindstrom and Freed, 1967.

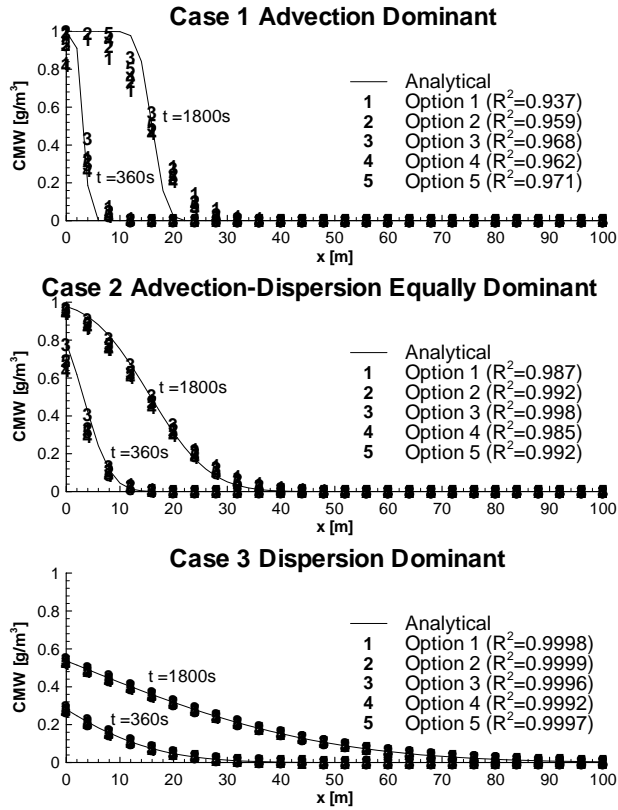


FIGURE 1. Concentration profiles of CMW of example 3.1.

It is seen that: (1) for advection dominant cases, Options 3 through 5 give more accurate simulation than the other two; (2) for advection-dispersion equally-dominant cases, Option 3 giving slightly better results than Option 2 and 5, and Option 2 and 5 yielding slightly better results than Option 1 and 4; (3) for dispersion dominant cases, Option 1 and 2 giving slightly better results than the other three. Therefore, for advection dominant problems for research applications when accuracy is the primary concern, Options 3 through 5 are preferred. For dispersion dominant problems for research applications, Options 1 and 2 may be preferred. For practical applications when the efficiency is the primary concern, Option 3 is preferred because it gives the most efficient computation in term of CPU time. The efficiency results from the fact that one can use a much larger time step size without having to worry about the limitation of time-step sizes imposed by advective transport.

3.2 Comparison of coupling strategies to deal with reactive chemistry

A 4 km-long river/stream with uniform width of 10 m is discretized into 400 equal size elements. We assume the water depth is 2 m and flow velocity is 1.0 m/s. The same two species as in previous example are considered to undergo the following reactions.

$$\text{Case1 : CMW} = \text{CIMW} \quad K_{eq} = 1.0 \quad (7)$$

$$\text{Case2 : CMW} = \text{CIMW} \quad K_f = 3 \text{ h}^{-1}, K_b = 3 \text{ h}^{-1} \quad (8)$$

$$\text{Case3 : CMW} = \text{CIMW} \quad K_f = 1.0 \times 10^{-2} \text{ h}^{-1}, K_b = 1.0 \times 10^{-2} \text{ h}^{-1} \quad (9)$$

Initially, no chemical exists. Dirichelet and Variable boundary conditions are applied to the upstream and downstream boundary nodes, respectively. At the upstream boundary node, the concentration of CMW is 1 mg/kg. Simulations were performed with fixed time step sizes of 360 s and total simulation time of 1,800 s. The molecular diffusion coefficient and longitudinal dispersivity are assumed to be zero. Option 3 is used to solve the transport equations. With integral mesh Courant numbers, the numerical error is zero in solving the advective transport equation, thus numerical errors due to coupling strategies are isolated.

Using the same numerical option, the Modified LE approach, to solve the advective-dispersive equation, simulations were performed with three coupling strategies to deal with the reactive chemistry. In Figure 2, simulation results of CMW are compared with the analytical solutions (Quezada et al, 2004).

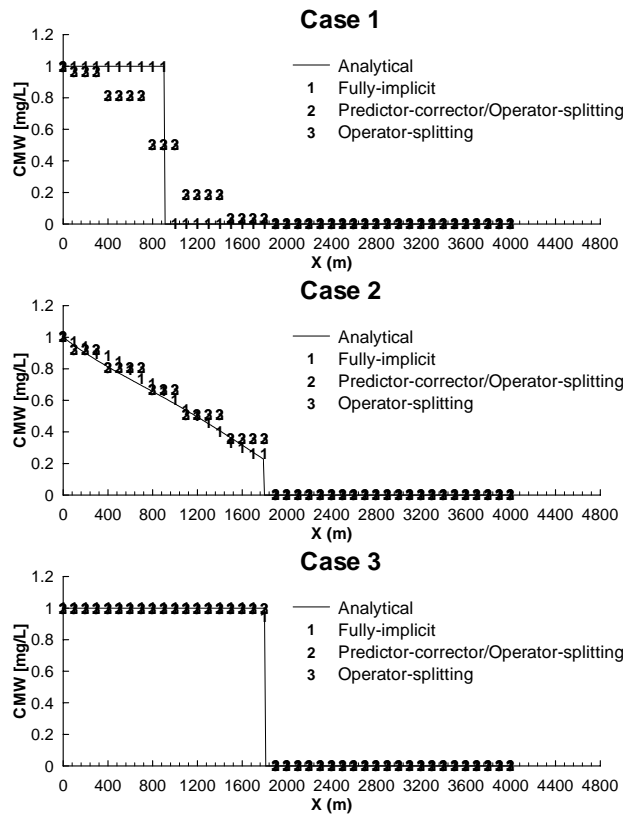


FIGURE 2. Concentration profiles of CMW at time = 1,800 s in example 3.2.

It is seen that the Strategy 1 gives accurate solution for all three cases although solution for Case 2 is less accurate than the other two. However, simulation accuracy using Strategy 2 and 3 varies for the three cases. For Case 1, in which an equilibrium reaction involves, calculation results of these two strategies are far from the analytical values. For Case 2, in

which a kinetic reaction with faster rate involves, simulations of these two strategies are close to the exact solution although less accurate than Strategy 1. For Case 3, in which a kinetic reaction with slower rate involves, accurate simulations are obtained with these two strategies.

For problems involving only kinetic reactions with slower rates, all the three strategies can generate accurate solution. Because Strategy 1 takes more time to achieve convergent simulations due to iteration, the other two strategies are recommended. For problems with involving equilibrium reactions, Strategy 1 is recommended for both research and practical applications because the other two strategies simply cannot give enough accurate simulations. For problems involving only kinetic reactions with faster rates, Strategy 1 is recommended when accuracy is the primary concern; on the other hand, Strategy 2 and 3 are recommended for practical applications when efficiency is the primary concern.

TABLE 1. Reaction network for example 3.3.

Reaction	Reaction parameters	No.
$M \leftrightarrow C_1 - 3C_2$	Rate= 5.787e-7M	R1
$M \leftrightarrow S_1$	$0.0047M=S_1+S_2+S_3+S_4+S_5+S_6+S_7+S_8$	R2
$C_3 \leftrightarrow C_4 + C_5$	$\text{Log } K_3^e = -17.97$	R3
$C_6 + C_5 \leftrightarrow C_7$	$\text{Log } K_4^e = 12.32$	R4
$C_2 + C_5 + C_6 \leftrightarrow C_8$	$\text{Log } K_5^e = 15.93$	R5
$C_6 \leftrightarrow C_2 + C_9$	$\text{Log } K_6^e = -12.6$	R6
$C_1 + C_5 \leftrightarrow C_{10}$	$\text{Log } K_7^e = 22.57$	R7
$C_1 + C_2 + C_5 \leftrightarrow C_{11}$	$\text{Log } K_8^e = 29.08$	R8
$C_1 + C_5 \leftrightarrow C_2 + C_{12}$	$\text{Log } K_9^e = 19.65$	R9
$C_1 + C_5 \leftrightarrow 2C_2 + C_{13}$	$\text{Log } K_{10}^e = -36.3$	R10
$C_1 \leftrightarrow C_2 + C_{14}$	$\text{Log } K_{11}^e = -2.19$	R11
$C_1 \leftrightarrow 2C_2 + C_{15}$	$\text{Log } K_{12}^e = -5.67$	R12
$C_1 \leftrightarrow 3C_2 + C_{16}$	$\text{Log } K_{13}^e = -13.6$	R13
$C_1 \leftrightarrow 4C_2 + C_{17}$	$\text{Log } K_{14}^e = -21.6$	R14
$2C_1 \leftrightarrow 2C_2 + C_{18}$	$\text{Log } K_{15}^e = -2.95$	R15
$C_2 + C_4 + C_5 \leftrightarrow C_{19}$	$\text{Log } K_{16}^e = 21.4$	R16
$C_4 \leftrightarrow C_2 + C_{20}$	$\text{Log } K_{17}^e = -9.67$	R17
$C_4 \leftrightarrow 2C_2 + C_{21}$	$\text{Log } K_{18}^e = -18.76$	R18
$C_4 \leftrightarrow 3C_2 + C_{22}$	$\text{Log } K_{19}^e = -32.23$	R19
$C_2 + C_5 \leftrightarrow C_{23}$	$\text{Log } K_{20}^e = 11.03$	R20
$2C_2 + C_5 \leftrightarrow C_{24}$	$\text{Log } K_{21}^e = 17.78$	R21
$3C_2 + C_5 \leftrightarrow C_{25}$	$\text{Log } K_{22}^e = 20.89$	R22
$4C_2 + C_5 \leftrightarrow C_{26}$	$\text{Log } K_{23}^e = 23.1$	R23
$\leftrightarrow C_2 + C_{27}$	$\text{Log } K_{24}^e = -14.0$	R24
$S_1 \leftrightarrow S_2 + C_2$	$\text{Log } K_{25}^e = -11.6$	R25
$S_1 + C_2 \leftrightarrow S_3$	$\text{Log } K_{26}^e = 5.6$	R26
$S_1 + 3C_2 + C_5 \leftrightarrow S_4$	$\text{Log } K_{27}^e = 30.48$	R27
$S_1 + C_1 + C_2 + C_5 \leftrightarrow S_5$	$\text{Log } K_{28}^e = 37.63$	R28
$S_1 + C_2 + C_4 + C_5 \leftrightarrow S_6$	$\text{Log } K_{29}^f = 25.0, \text{Log } K_{29}^b = -3.49$	R29
$S_1 - C_2 + C_4 \leftrightarrow S_7$	$\text{Log } K_{30}^f = -5.99, \text{Log } K_{30}^b = -3.30$	R30
$S_1 + C_2 + C_5 + C_6 \leftrightarrow S_8$	$\text{Log } K_{31}^f = 20.0, \text{Log } K_{31}^b = -3.81$	R31
$C_{29} + 2\text{Site-C}_{30} \leftrightarrow \text{Site-C}_{29} + 2C_{30}$	Rate= $10^{-5.75}C_{29}(a_{30}\text{Site-C}_{30})^2 - 10^{-5.5}a_{29}\text{Site-C}_{29} \cdot C_{30}^2$	R32
$C_6 + 2\text{Site-C}_{30} \leftrightarrow \text{Site-C}_6 + 2C_{30}$	Rate= $10^{0.6}C_6(a_{30}\text{Site-C}_{30})^2 - a_6\text{Site-C}_6 \cdot C_{30}^2$	R33

3.3 Chemical transport with complexation, sorption and dissolution reactions

A 20 km-long river/stream containing a uniform width of 20 m is discretized into 100 equal size elements. We assume water depth is 2 m and flow velocity is 1 m/s. As shown in Table 1, 41 chemical species are involved in the complex reaction network with 33 reactions.

As simulation starts, variable boundary conditions are applied to both the upstream and downstream boundary nodes. Initial concentrations are: $C_1 = C_3 = 1.0 \times 10^{-7}$ mol/Kg, $C_2 = C_4 = C_5 = C_6 = C_{10} = C_{29} = C_{30} = 1.0 \times 10^{-5}$ mol/Kg, $M = 1.0 \times 10^{-5}$ mol/Kg, Site- $C_6 = 1.4 \times 10^{-4}$ mol/g, Site- $C_{29} = 7.0 \times 10^{-4}$ mol/g, and Site- $C_{30} = 1.5 \times 10^{-4}$ mol/g. Coming-in boundary concentrations are $C_1 = 1.0 \times 10^{-7}$ mol/Kg, $C_2 = C_4 = C_5 = C_{10} = C_{29} = 1.0 \times 10^{-5}$ mol/Kg, and $C_3 = C_6 = C_{30} = 1.0 \times 10^{-4}$ mol/Kg. The longitudinal dispersivity is 80 m. A 90,000-second simulation is performed with a fixed time step size of 150-seconds.

The concentration distributions of M, C_1 , and S_1 at different simulation time are plotted in Figure 3. Due to the dissolution reaction R1, bed precipitate M gradually dissolves into dissolved chemical C_1 in the mobile water phase. Therefore, we observe decreasing concentration of M with time and increasing concentration of C_1 along the down stream direction. Due to the sorbing site forming reaction R2, the concentration of S_1 decreases with time as the surface area of M decreases along with dissolution. Since S_1 involves in seven sorption reactions R25~R31, its concentration distribution is also affected by these reactions and related species.

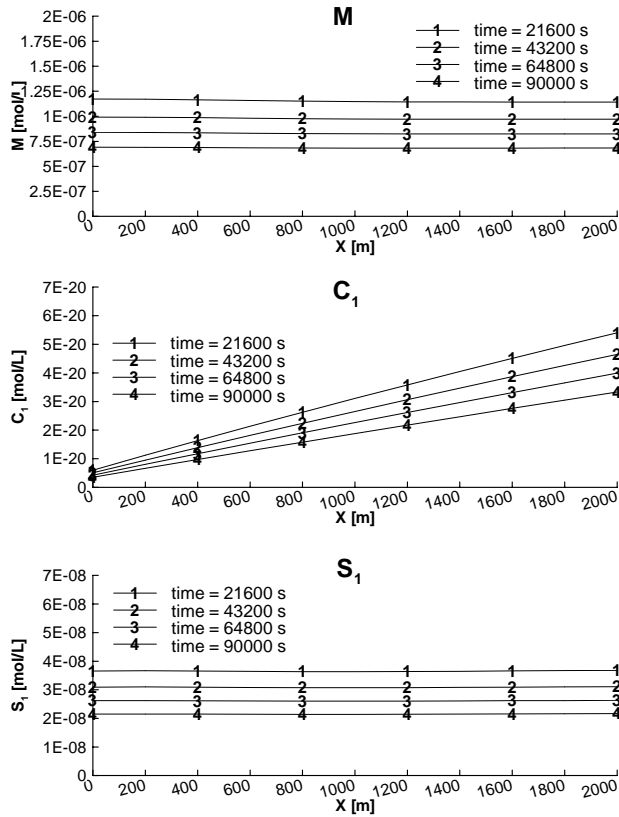


FIGURE 3. Concentration profiles for example 3.3.

4. SUMMARY

This paper presents the development of a numerical model for transient simulation of sediment and biogeochemical transformation of chemical species as they are transported in the river/stream networks. Transport equations based on the principle of mass balance are used to describe temporal-spatial distributions of sediments and water qualities. Through the decomposition of the system of species transport equations via Gauss-Jordan column reduction of the reaction network, fast reactions and slow reactions are decoupled, which enables robust numerical integrations. In order to provide accurate, efficient and robust computations, a variety of numerical methods are provided to solve the mixed differential and algebraic equations. Application of the code to two verification problems demonstrates the preferences and recommendations of numerical options under different conditions. Application of the code to a hypothetical problem illustrates the ability of the model to simulating transport of chemicals under complex reaction networks.

5. ACKNOWLEDGEMENTS

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