

Simulation models for conservative and nonconservative solute transport in streams

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Abstract Solute transport in streams is governed by a suite of hydrologic and chemical processes. Interactions between hydrologic processes and chemical reactions may be quantified through a combination of field-scale experimentation and simulation modeling. Two mathematical models that simulate conservative and nonconservative solute transport in streams are presented. A model for conservative solutes that considers One-Dimensional Transport with Inflow and Storage (OTIS) may be used in conjunction with tracer-dilution methods to quantify hydrologic transport processes (advection, dispersion, lateral inflow and transient storage). For nonconservative solutes, a model known as OTEQ may be used to quantify chemical processes within the context of hydrologic transport. OTEQ combines the transport mechanisms in OTIS with a chemical equilibrium sub-model that considers complexation, precipitation/dissolution and sorption. OTEQ has been used to quantify processes affecting trace metals in two streams in the Rocky Mountains of Colorado, USA.

INTRODUCTION

Many investigators are studying streams and the effect of basin loading on water quality. Of particular interest is the study of streams adversely affected by acid-mine drainage and acid deposition. Because of acidic conditions, these streams often have elevated concentrations of trace metals such as aluminum, copper, zinc and iron. The fate and transport of solutes within these environments is of importance as high concentrations of trace metals may be toxic to fish and other aquatic organisms.

Studies of acidic streams share two goals: (a) to quantify the physical or hydrologic processes controlling solute concentrations, and (b) to quantify the dominant chemical and biological reactions. Both goals are generally addressed through field-scale experimentation and simulation modeling. Tracer-dilution methods, for example, are frequently used to quantify hydrologic transport processes. During a tracer-dilution experiment, a conservative solute (tracer) is injected at the upper end of a stream reach. Tracer concentrations measured at downstream locations are used to determine the volumetric flow rate and the additional flow entering the stream via surface runoff and groundwater. The hydraulic properties of the stream are then determined by applying a conservative solute transport model (e.g. Broshears *et al.*, 1993).

The importance of various chemical and biological reactions is assessed by conducting pH modification experiments (McKnight & Bencala, 1989; Kimball *et al.*,

1994). Within a pH modification experiment, instream pH levels are temporarily altered to allow pH-dependent processes (e.g. precipitation, sorption) to be studied. Data obtained during pH modification experiments may be used to identify the processes controlling solute concentrations. A key step in process identification is interpretation of the complex interactions between hydrologic processes and chemical reactions. Mathematical models for nonconservative or reactive solutes may be used to describe competing processes, such as sorption and precipitation.

This paper presents two models developed to quantify process dynamics for conservative and nonconservative solutes. A model incorporating One-Dimensional Transport with Inflow and Storage (OTIS) is presented for the case of conservative solute transport. The OTIS model may be used to determine the hydrologic and hydraulic characteristics of the stream based on data from tracer-dilution experiments. For non-conservative solute transport, a reactive solute transport model, OTEQ, is presented. OTEQ may be used to quantify the chemical processes responsible for changes in solute concentrations observed during pH modification experiments.

SOLUTE TRANSPORT MODELS

Conservative transport – OTIS

The OTIS solute transport model was developed to simulate the transport of solutes in streams and rivers in which one-dimensional transport may be assumed. Although the model was developed primarily for conservative solutes, nonconservative behavior may be simulated through specification of a first-order decay or production rate. Several physical mechanisms govern the downstream transport of solutes and are considered in the model. These mechanisms include advection, dispersion, lateral inflow and transient storage. Advection, the downstream transport of solute mass at a mean velocity, and dispersion, the spreading of solute mass due to shear stress and molecular diffusion, are considered in most mechanistic models of stream water quality and solute transport. Consideration of these important mechanisms leads to the familiar advection-dispersion equation. Within the OTIS model, additional terms are added to the advection-dispersion equation to account for the effects of transient storage and lateral inflow. Transient storage has been noted in many streams, where solutes may be detained in small eddies and zones of water that are stationary relative to the faster moving water near the center of the channel. In addition, significant portions of the flow may move through the coarse gravel of the stream bed and the porous areas near the stream bank. The travel time for solutes carried through these porous areas may be significantly longer than that for solutes traveling within the water column. Lateral inflow is any water added to the stream due to groundwater inflow, overland flow, interflow or small springs. These flows dilute or concentrate solutes in the stream if they carry solute concentrations that are lower or higher than the stream solute concentration.

The OTIS model is formed by writing mass balance equations for two conceptual areas: the stream channel and the storage zone. The stream channel is that portion of the stream in which advection and dispersion are the dominant transport mechanisms. The storage zone is the portion of the stream that contributes to transient storage, i.e. stagnant pockets of water and porous areas of the stream bed. Water in the storage zone is considered immobile relative to water in the stream channel. The exchange of solute

mass between the stream channel and the storage zone is modeled as a first-order mass transfer process. Conservation of mass for the stream channel and storage zone yields:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} (AD \frac{\partial C}{\partial x}) + \frac{q_{LIN}}{A} (C_L - C) + \alpha (C_S - C) - \lambda C \quad (1)$$

$$\frac{dC_S}{dt} = \alpha \frac{A}{A_S} (C - C_S) - \lambda_S C_S \quad (2)$$

where A is the stream channel cross-sectional area [L^2], A_S is the storage zone cross-sectional area [L^2], C is the in stream solute concentration [$M L^{-3}$], C_L is the solute concentration in lateral inflow [$M L^{-3}$], C_S is the storage zone solute concentration [$M L^{-3}$], D is the dispersion coefficient [$L^2 T^{-1}$], Q is the volumetric flow rate [$L^3 T^{-1}$], q_{LIN} is the lateral inflow rate [$L^3 T^{-1} L^{-1}$], t is the time [T], x is the distance [L], α is the storage zone exchange coefficient [T^{-1}] λ is the in-stream first-order decay coefficient [T^{-1}] and λ_S is the storage zone first-order decay coefficient [T^{-1}] (Bencala & Walters, 1983; Runkel & Broshears, 1991). Equations (1) and (2) describe the spatial and temporal variation in solute concentration within the stream channel and the storage zone.

Several model features provide a flexible and efficient framework from which to consider solute transport problems. Noteworthy features include:

- * *Simulation Flexibility*: The user may request the output of simulation results at any number of arbitrary locations along the stream. Simulations for multiple conservative solutes may be performed during a single program execution. Nonconservative solutes subject to first-order transformations may also be considered. The governing equations may be solved for both dynamic (time-varying) and steady-state conditions.
- * *Consideration of Unsteady Flow Regimes*: Many solute transport models assume steady flow regimes where flow rates and cross-sectional areas are constant in time. OTIS allows for the consideration of unsteady flow regimes where time-varying flows and areas are specified in an external flow file. This allows the transport model to be linked with flow routing models (Runkel & Restrepo, 1993).
- * *User Interface*: OTIS is available as a stand-alone program and as a module within the Modular Modeling System, MMS (Leavesley *et al.*, 1992). MMS is a modeling framework that provides a graphical user interface (GUI). The GUI includes a spreadsheet for data entry and other options for viewing simulation results.
- * *Efficiency*: The governing differential equations are solved using the Crank-Nicolson method and the decoupling procedure described by Runkel & Chapra (1993). These methods provide an efficient solution that results in fast execution times for most solute transport problems.

OTIS is ideally suited for the analysis of tracer data. Broshears *et al.* (1993) present an application of OTIS to a tracer-dilution experiment conducted on a small mountain stream. During the experiment, a solution of lithium chloride was injected into the stream for 52 h. Water samples were collected at several downstream locations. Model parameters were estimated using tracer data and a series of simulation runs as described in Broshears *et al.* (1993). Simulation results and tracer data for two sampling locations are shown in Fig. 1.

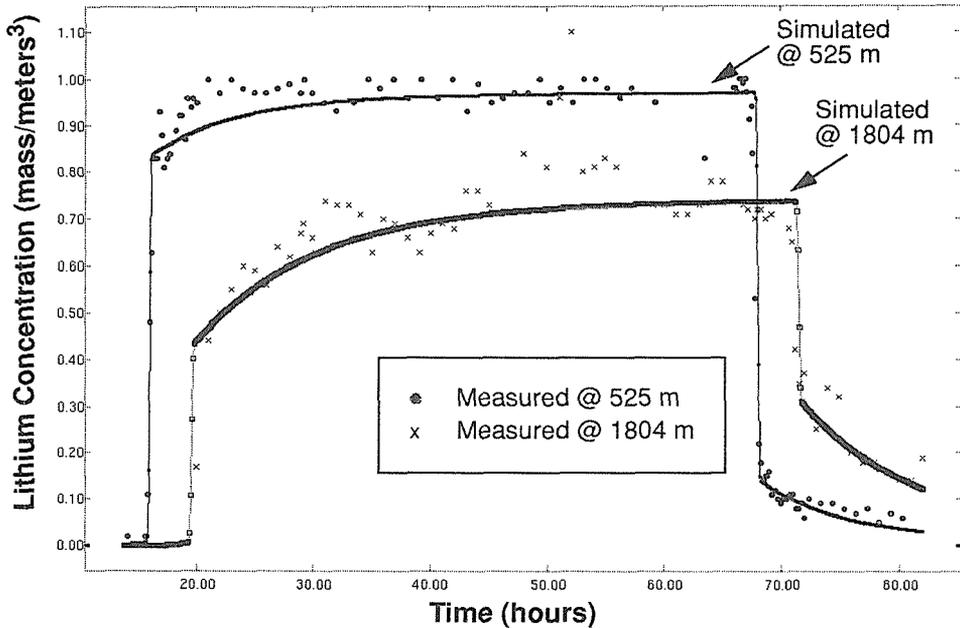


Fig. 1 Simulation of tracer concentrations at two sampling locations using the OTIS solute transport model. Model parameters are estimated using the tracer data.

Nonconservative transport – OTEQ

The OTIS solute transport model provides a tool for analysis of conservative solutes and nonconservative solutes that are subject to simple first-order transformation. Many cases arise, however, in which solutes are affected by chemical and biological processes that are not considered in such a model. Trace metals, for example, may be affected by precipitation/dissolution, sorption and oxidation-reduction reactions. The OTEQ model described in this section was developed to consider these complex reactions within the context of hydrologic transport.

OTEQ is an equilibrium-based transport model formed by combining the physical transport mechanisms in OTIS with a chemical equilibrium sub-model. The sub-model uses the numerical framework of MINTEQ (Westall *et al.*, 1976; Allison *et al.*, 1991), a chemical equilibrium model distributed by the US Environmental Protection Agency. Given total analytical concentrations of chemical components, MINTEQ computes the distribution of chemical species that exist within a batch reactor at equilibrium. Specific reactions considered include complexation, precipitation/dissolution and sorption. Use of the chemical equilibrium sub-model is based on the "Local Equilibrium Assumption", wherein chemical reactions are considered sufficiently fast relative to hydrologic processes (Rubin, 1983). When the assumption of equilibrium is inappropriate, kinetic controls may be placed on specific reactions, such as sorption and dissolution from the stream bed.

A conceptual diagram illustrating the coupling of hydrologic transport and equilibrium chemistry is given as Fig. 2. The stream is represented as a series of segments or control volumes. Hydrologic processes transport solute mass from one segment

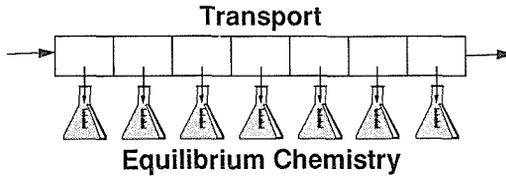


Fig. 2 Conceptual diagram of the coupling between hydrologic transport and equilibrium chemistry.

to the next. This downstream movement is described by the differential equations governing transport (equations (1) and (2)). Within each segment, chemical equilibrium is assumed, and solute mass is distributed among dissolved, sorbed and precipitated forms. This chemical partitioning is described by the chemical equilibrium sub-model.

A complete description of the governing equations and solution techniques underlying the OTEQ model is presented by Runkel (1993). In short, the total solute concentration, T , equals the sum of five distinct phases. The first three phases are the dissolved, precipitated and sorbed concentrations present in the water column (C , P_w and S_w). These phases are mobile and are subject to downstream transport. The final two phases are the precipitated and sorbed concentrations present on the stream bed (P_b and S_b). Dissolved mass in the water column forms precipitates when the solution becomes oversaturated with respect to the defined solid phases. Any precipitated mass resides in the water column until the precipitate settles to the stream bed or redissolution occurs. Precipitates dissolve when the solution becomes undersaturated. Dissolved species sorb (or desorb) to (or from) solid phases present in the water column or on the stream bed.

Model equations for the stream channel are developed by considering conservation of mass for the total solute concentration. This yields:

$$\frac{\partial T}{\partial t} = -\frac{Q}{A} \frac{\partial}{\partial x}(T_w) + \frac{1}{A} \frac{\partial}{\partial x} \left[AD \frac{\partial}{\partial x}(T_w) \right] + \frac{q_{LIN}}{A}(T_{wL} - T_w) + \alpha(T_{wS} - T_w) \quad (3)$$

$$\frac{\partial P_b}{\partial t} = \frac{v_{p1}}{d_1}(P_w) - f_b \quad (4)$$

$$\frac{\partial S_b}{\partial t} = \frac{v_{s1}}{d_1}(S_w) - g_b \quad (5)$$

where T_w is the waterborne solute concentration [$M L^{-3}$], T_{wL} is the waterborne solute concentration in the lateral inflow [$M L^{-3}$], T_{wS} is the waterborne solute concentration in the storage zone [$M L^{-3}$], f_b is a source/sink term describing dissolution from the stream bed [$M L^{-3} T^{-1}$], g_b is a source/sink term describing sorption/desorption from the stream bed [$M L^{-3} T^{-1}$], v_{p1} is the settling velocity for water column precipitates [$L T^{-1}$], v_{s1} is the settling velocity for water column sorbates [$L T^{-1}$], d_1 is the effective settling depth [L], and the model parameters are as defined for the OTIS model.

Equation (3) states that any change in the total solute concentration is due to the physical transport of the waterborne solute concentration. The waterborne solute concen-

tration is equal to the total solute concentration minus the immobile phases (P_b and S_b):

$$T_w = T - P_b - S_b \quad (6)$$

Equations (4) and (5) state that change in the immobile precipitate and sorbed concentrations is due to settling and the effects of chemical reaction (dissolution and sorption/desorption). Source/sink terms describing these chemical reactions are functions of the equilibrium sub-model. Model equations for the storage zone are presented by Runkel (1993).

OTEQ has been used to quantify the dominant processes affecting trace metals in two acidic streams in the Rocky Mountains of Colorado (Runkel, 1993; Broshears *et al.*, 1994). Modeled processes include precipitation/dissolution, degassing and kinetically-controlled sorption/desorption.

SOFTWARE AVAILABILITY

Source code and executable binaries for the OTIS solute transport model are available over the Internet computer network via anonymous file transport protocol. Internet addresses for two anonymous ftp locations are in Table 1. Instructions for obtaining and installing the code are provided in the "readme" file in the "pub/otis" directory at each anonymous ftp location. Executable binaries are provided for several hardware platforms (SUN, Data General, DEC and IBM workstations, MS-DOS-based personal computers). Source code is provided for users with other hardware requirements. Persons without Internet access may obtain the code by contacting the author. To date, the OTEQ solute transport model has been used exclusively as an in-house research tool. Further development, testing and documentation efforts are required prior to releasing the code as a public domain software package.

Table 1 Anonymous ftp locations for the OTIS solute transport model.

ftp location	Internet address
cadswes.colorado.edu	128.138.239.26
otis.cr.usgs.gov	136.177.8.72

Acknowledgement This work was completed as part of the US Geological Survey Toxic Substances Hydrology Program. The author acknowledges the assistance of Kenneth Bencala, Robert Broshears, Briant Kimball and Diane McKnight.

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