Modeling Solute Transport and Geochemistry in Streams and Rivers Using OTIS and OTEQ

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ABSTRACT

Solute transport in streams is governed by a suite of hydrologic and geochemical 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 are used to simulate solute transport in streams are presented here. A model 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, and transient storage). Additional applications of OTIS include analyses of nonconservative solutes that are subject to sorption processes and (or) first-order decay. A second model, OTEQ (One-dimensional Transport with EQulibrium chemistry), combines the transport mechanisms in OTIS with a chemical equilibrium submodel that considers complexation, precipitation/dissolution, and sorption. OTEQ may be used to quantify the geochemical processes affecting trace metals.

INTRODUCTION

Many investigators are currently studying streams and the effect of basin loading on stream-water quality. Studies of streams share two common goals: (1) to quantify the hydrologic transport processes controlling solute concentrations, and (2) to quantify the dominant chemical reactions. Both goals may be addressed through a combination of field-scale experimentation and simulation modeling. Tracer-dilution methods, for example, are frequently used to quantify hydrologic transport. During a tracer-dilution experiment, a conservative tracer is injected at the upstream end of a stream reach. Tracer concentrations measured at several downstream locations are used to determine the volumetric flow rate and the additional inflow entering the stream from surface runoff and ground water. Other hydrologic properties, such as traveltime and mixing, are then determined by applying a conservative solute transport model.

Geochemical processes may be identified by analyzing field data that describe the spatial and (or) temporal distribution of solute concentration. A key step in process identification is interpretation of the complex interactions between hydrologic transport and chemical reactions. Given a description of hydrologic transport, reactive transport models may be used to investigate the underlying geochemical processes.

This paper presents two models that are used to simulate the fate and transport of solutes in streams and rivers. Several applications illustrate how the models may be used with field data to identify the dominant processes affecting solute concentrations.

SOLUTE TRANSPORT MODELS

One-Dimensional Transport with Inflow and Storage (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 is used primarily for conservative solutes, nonconservative solutes that are subject to sorption processes and (or) first-order decay may also be simulated. Several hydrologic processes that govern the downstream transport of solutes are considered in the model. These processes include advection, dispersion, lateral

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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 streamwater quality and solute transport. Consideration of these important mechanisms leads to the familiar advection-dispersion equation (see Runkel and Bencala, 1995, p. 144). 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 temporarily detained in small eddies and stagnant pools 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 streambed and the porous areas within the streambank. The traveltime 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 that is added to the stream due to ground-water inflow, overland flow, interflow, or small springs. These flows act to dilute (or concentrate) solutes in the stream channel 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 main channel and the storage zone. The main channel is defined as that portion of the stream in which advection and dispersion are the dominant transport mechanisms. The storage zone is defined as the portion of the stream that contributes to transient storage; that is, stagnant pools of water and porous areas of the streambed. Water in the storage zone is considered immobile relative to water in the stream channel. The exchange of solute mass between the main channel and the storage zone is modeled as a first-order mass transfer process. Consideration of the hydrologic processes discussed above gives rise to mass conservation equations for the main channel and the storage zone (Bencala and Walters, 1983; Runkel, 1998)[1]:

[1]The fundamental units of Mass (M), Length (L), and Time (T) are used throughout this paper.

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

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

where

- A main channel cross-sectional area (L^2),
- A_S storage zone cross-sectional area (L^2),
- C main channel solute concentration ($M\ L^{-3}$),
- C_L lateral inflow solute concentration ($M\ L^{-3}$),
- C_S storage zone solute concentration ($M\ L^{-3}$),
- D dispersion coefficient ($L^2\ T^{-1}$),
- Q volumetric flow rate ($L^3\ T^{-1}$),
- q_{LIN} lateral inflow rate ($L^3\ T^{-1}\ L^{-1}$),
- t time (T),
- x distance (L), and
- α storage zone exchange coefficient (T^{-1}).

These equations describe the hydrologic processes affecting solutes and are therefore applicable to conservative (nonreactive) solutes such as tracers. Nonconservative (reactive) solutes are considered by adding terms to equations (1) and (2). OTIS includes two types of chemical reactions: kinetic sorption and first-order decay. Sorption may take place directly on the streambed or within the storage zone. Addition of terms representing sorption and decay yields:

$$\frac{\partial C}{\partial t} = L(C) + \rho\hat{\lambda}(C_{sed} - K_d C) - \lambda C \quad (3)$$

$$\frac{dC_S}{dt} = S(C_S) + \hat{\lambda}_S(\hat{C}_S - C_S) - \lambda_S C_S \quad (4)$$

where

- $\hat{C}_S$ background storage zone solute concentration ($M\ L^{-3}$)
- C_{sed} sorbate concentration on the streambed sediment ($M\ M^{-1}$)
- K_d distribution coefficient ($L^3\ M^{-1}$)

λ main channel first-order decay coefficient (T^{-1})

λ_S storage zone first-order decay coefficient (T^{-1})

$\hat{\lambda}$ main channel sorption rate coefficient (T^{-1})

$\hat{\lambda}_S$ storage zone sorption rate coefficient (T^{-1})

ρ mass of accessible sediment/volume water ($M\ L^{-3}$)

and $L(C)$ and $S(C_S)$ represent the hydrologic processes in the main channel and storage zone, respectively (the right-hand sides of equations (1) and (2)). The sorption parameters introduced here ($\hat{C}_S$, K_d, $\hat{\lambda}$, $\hat{\lambda}_S$ and ρ) are discussed in detail by Bencala (1983). Equation (3) introduces, C_{sed}, a third concentration variable for which a mass balance is required. The streambed sediment concentration (sorbate concentration on the streambed sediment) is governed by:

$$\frac{dC_{sed}}{dt} = \hat{\lambda}(K_d C - C_{sed}) \qquad (5)$$

Equations (3)-(5) describe the spatial and temporal variation in solute concentration as a function of several hydrologic and geochemical parameters. As discussed by Runkel (1998), parameter estimates may be obtained by nonlinear regression using a modified version of OTIS known as OTIS-P.

One-Dimensional Transport with Equilibrium Chemistry (OTEQ)

The OTIS solute transport model provides a framework for the analysis of conservative solutes and nonconservative solutes that are subject to relatively simple chemical reactions. Many cases arise, however, in which solutes are affected by chemical processes that are not considered in such a simple model. Trace metals, for example, may be affected by pH-dependent processes such as precipitation/dissolution and sorption. The OTEQ model described in this section considers these complex reactions within the context of hydrologic transport.

OTEQ is formed by coupling the OTIS solute transport model with a chemical equilibrium submodel. The chemical equilibrium submodel is based on MINTEQ (Allison and others, 1991), a model that computes the distribution of chemical species that exist within a batch reactor at equilibrium. The coupled model considers a variety of processes including advection, dispersion, transient storage, transport and deposition of water-borne solid phases, acid/base reactions, complexation, precipitation/dissolution, and sorption.

Governing equations for OTEQ are formulated in terms of chemical components. The total component concentration (T) consists of dissolved (C), mobile precipitate (P_w), immobile precipitate (P_b), mobile sorbed (S_w), and immobile sorbed (S_b) phases. Processes considered for each phase are depicted in figure 1, where the system is represented as two compartments. The water column compartment contains the three mobile phases, C, P_w and S_w. Immobile substrate (that is, the streambed or debris) constitutes the second compartment, containing the two immobile phases, P_b and S_b. The three mobile phases are subject to hydrologic transport, as represented by the transport operator, L. The dissolved phase, C, takes part in precipitation/dissolution and sorption/desorption reactions that occur within the water column (interactions with P_w and S_w). The dissolved phase is also affected by dissolution of precipitate from the immobile substrate and by sorption/desorption from immobile sorbents (interactions with P_b and S_b). Finally, C may increase or decrease due to external sources and sinks, as denoted by s_{ext}. The precipitated and sorbed phases in the water column settle in accordance with settling velocity ν ($L\ T^{-1}$).

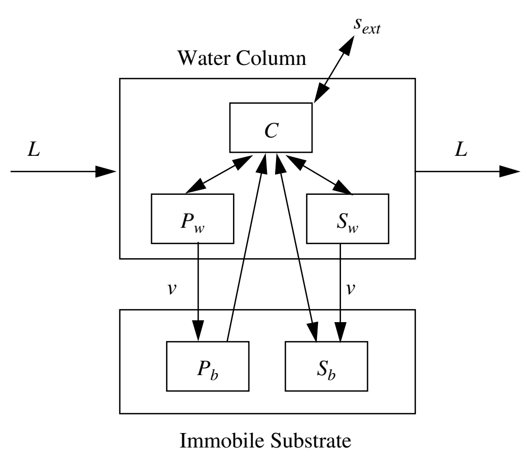

Figure 1. Conceptual surface-water system used to develop the governing differential equations. The total component concentration consists of dissolved (C), mobile precipitate (P_w), immobile precipitate (P_b), mobile sorbed (S_w) and immobile sorbed (S_b) phases. The dissolved and mobile phases are subject to transport, as denoted by L.

Runkel and others (1996a) developed a general mass balance equation for each component by considering the mass associated with each of the five component phases. The mass balance equation for the total component concentration is given by:

$$\frac{\partial T}{\partial t} = L(T) - L(S_b + P_b) + s_{ext} \qquad (6)$$

where the transport operator is as defined in equation (3). Inspection of (6) reveals that T is a function of P_b and S_b. The immobile precipitated and sorbed concentrations are governed by:

$$\frac{\partial P_b}{\partial t} = \frac{v}{d}(P - P_b) - f_b \qquad (7)$$

$$\frac{\partial S_b}{\partial t} = \frac{v}{d}(S - S_b) - g_b \qquad (8)$$

where

- f_b source/sink term for dissolution from the immobile substrate ($M\ L^{-3}T^{-1}$),
- g_b source/sink term for sorption/desorption from the immobile substrate ($M\ L^{-3}T^{-1}$),
- d settling depth (L),
- P total precipitate component concentration ($= P_w + P_b$; $M\ L^{-3}$), and
- S total sorbed component concentration ($= S_w + S_b$; $M\ L^{-3}$).

The governing equation set consists of three differential equations for each component (for T, P_b, and S_b) and the set of algebraic equations representing chemical equilibria. This equation set is solved using a Crank-Nicolson approximation of the differential equations and the sequential iteration approach (Runkel and others, 1996a).

MODEL APPLICATIONS

Several OTIS and OTEQ applications are presented below. Additional OTIS applications are described by Broshears and others (1993), Morrice and others (1997), Harvey and Fuller (1998), and Runkel and others (1998); additional OTEQ applications are described by Broshears and others (1995, 1996), Runkel and others (1996b), and Ball and others (this volume).

Mixing and Traveltime (OTIS)

Data from tracer-injection studies are frequently used to quantify mixing and traveltime in streams and rivers. These hydrologic characteristics are of importance to water-resource managers who are responsible for protecting water supplies from contamination. Given data from tracer-injection studies, stream transport models may be used to estimate the timing, magnitude, and duration of a pollutant cloud that enters a stream due to an accidental spill.

In addition to providing management information, hydrologic parameters derived from tracer-injection data provide insight into the physical characteristics of streams. Values of the transient storage parameters (A_s, α), for example, indicate the degree of mixing due to stagnant pools and flow through porous areas of the streambed. Further, model-derived estimates of traveltime indicate the relevant time scales over which chemical reactions can potentially affect solute concentrations.

In this section we illustrate the use of OTIS to quantify hydrologic processes using tracer-injection data. Our first example uses data from Uvas Creek, a small pool-and-riffle stream in northern California. Bencala and Walters (1983) described a continuous, constant-rate injection of chloride into Uvas Creek. Concentrations were monitored at several downstream locations and streamflow was estimated by tracer dilution.

Application of OTIS to the Uvas Creek chloride injection requires estimates of stream cross-sectional area (A), transient storage (A_s, α) and dispersion (D) for each stream reach. Estimates of stream cross-sectional area are related to traveltime as they control the timing of the chloride profile, whereas estimates of the transient storage parameters represent instream mixing as reflected by the shape of the chloride profile. During a series of simulations, Bencala and Walters (1983) varied A, A_s, α, and D to obtain a match between observed and simulated concentrations. Final simulation results at two sampling locations are shown in figure 2.

Reach-specific parameter estimates developed from tracer-injection data represent integrated or average conditions for a given length of stream. As noted by Bencala and Walters (1983), physical stream characteristics such as cross-sectional area vary substantially over short spatial scales. As such, estimates of A based on tracer-injection data are preferable to estimates based on surveyed transects that may not be representative of the reach under study.

Estimates of A and A_s developed from the tracer data are consistent with the pool-and-riffle description of Uvas Creek given by Bencala and Walters (1983). The pools act to produce transient storage by temporarily detaining some of the chloride. A dimensionless measure of this storage effect is obtained by calculating the ratio of storage zone cross-sectional area to main channel cross-sectional area (A_s/A). Values of A_s/A for various reaches of Uvas Creek range from 1.0 to 3.0. These values indicate that the pool areas are large relative to the main channel.

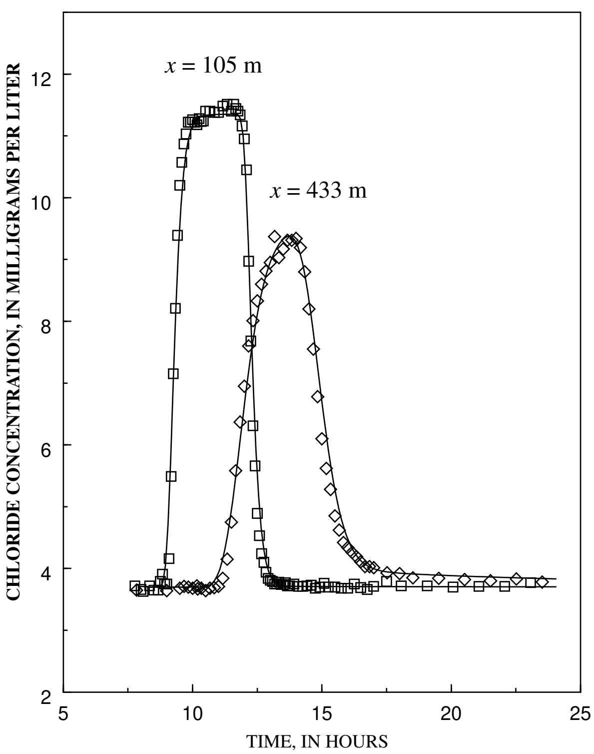

Figure 2. Simulated (solid lines) and observed (symbols) chloride concentrations in Uvas Creek, California (Data and parameter values from Bencala and Walters, 1983).

Analysis of Uvas Creek data relied on a trial-and-error approach wherein parameter estimates were manually adjusted to produce an acceptable match between simulated and observed tracer concentrations. In the following example, parameter estimates are obtained by nonlinear regression using OTIS-P. Laenen and Risley (1997) described several studies in Oregon streams where rhodamine WT was used to determine traveltime. In July 1992, a slug of rhodamine WT was added to the Clackamas River at river mile 13.3 (RM 13.3). Water samples were collected at river miles 11.0, 9.5 and 8.0. Because rhodamine WT was introduced as a slug (as opposed to a continuous injection), data at the first sampling location (RM 11.0) are used to define the upstream boundary condition (fig. 3). Given the boundary condition, the traveltimes (as given by A) and mixing characteristics (as given by A_S, α, D) for the two reaches ending at river miles 9.5 and 8.0 may be determined.

Use of OTIS-P requires a set of initial estimates for the parameters of interest. Here we set A and D for both reaches equal to 50 m^2 and 10 m^2/s, respectively. The exchange coefficient, α, is initially set to 0.0 such that transient storage is not considered. Preliminary OTIS results based on these initial parameter estimates are shown as dashed lines in figure 3. These preliminary profiles indicate that our initial estimates of stream cross-sectional area are too large; the simulated traveltime is overestimated at both RM 9.5 and RM 8.0. In addition, the symmetric simulation profile at RM 8.0 is in contrast to the asymmetry of the observed data. This observation suggests that transient storage may be an important mixing mechanism. Both of these discrepancies may be addressed by developing parameter estimates using OTIS-P. As expected, application of OTIS-P results in an improved simulation (solid lines, fig. 3) and a revised set of parameter estimates (for example, A= 30.4 and 48.1 m^2 for the two reaches).

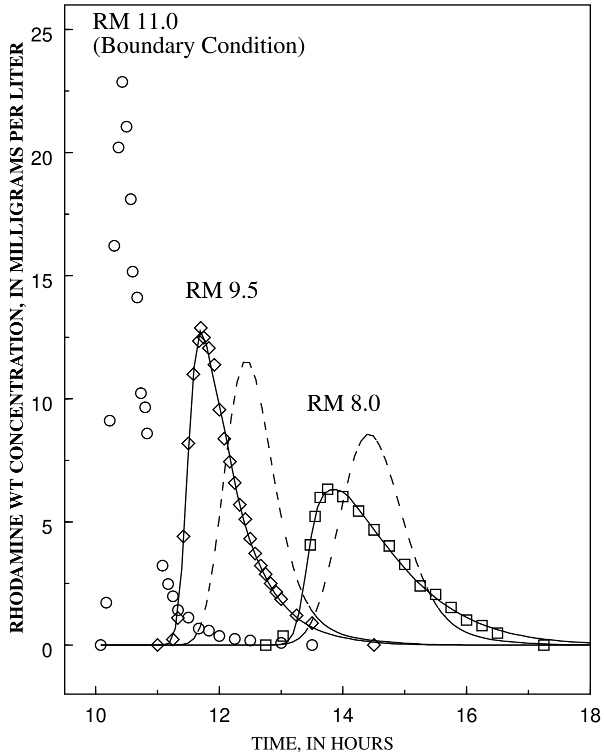

Figure 3. Upstream boundary condition (RM 11.0), observed concentrations (symbols), simulated concentrations based on initial parameter estimates (dashed lines), and simulated concentrations based on final parameter estimates (solid lines) for the Clackamas River, Oregon.

Nutrient Uptake (OTIS)

The examples above illustrate the use of OTIS to quantify hydrologic processes. In this example we show how OTIS may be used to identify chemical reactions. McKnight and Duff (1995) described an experimental addition of lithium chloride (LiCl), phosphate, and nitrate into Green Creek, a glacial meltwater stream in Antarctica. The objective of the study was to quantify stream hydrology and to study nutrient uptake by algal mats that cover the bed of Green Creek. As in the previous examples, a conservative tracer (LiCl) is used to define the hydrologic system. Hydrologic parameters based on the analysis of LiCl transport are then used to evaluate the conservative transport of nitrate and phosphate. A conservative simulation of nitrate is shown as a dashed line in figure 4. As shown in the figure, observed nitrate concentrations are substantially lower than simulated concentrations based on conservative transport. This discrepancy indicates that nitrate concentrations are attenuated by geochemical processes.

Under the assumption that nutrient uptake is a first-order process, the first-order decay coefficients (λ, λ_s) in OTIS are used to quantify the loss of nitrate. Given the hydrologic characterization, OTIS-P is used to estimate uptake in the main channel (λ) and in the storage zone (λ_s). Reach-specific estimates of λ range from $4x10^{-5}$ to $4x10^{-4}$ /s; estimates of λ_s range from $3x10^{-6}$ to $2x10^{-3}$ /s. Simulation results based on these parameter estimates are shown as a solid line in figure 4. Additional mass balance calculations based on λ and λ_s indicate that 84-93 percent of the nitrate loss occurs in the main channel where algal uptake is the likely mechanism of nitrate loss. The remaining loss occurs in the storage zone where possible mechanisms include microbial uptake and nitrate reduction. In contrast, similar analyses indicate that phosphate loss occurs only in the main channel ($\lambda_s = 0$). OTIS thus provides a framework for quantifying the processes that control nutrient concentrations in Green Creek.

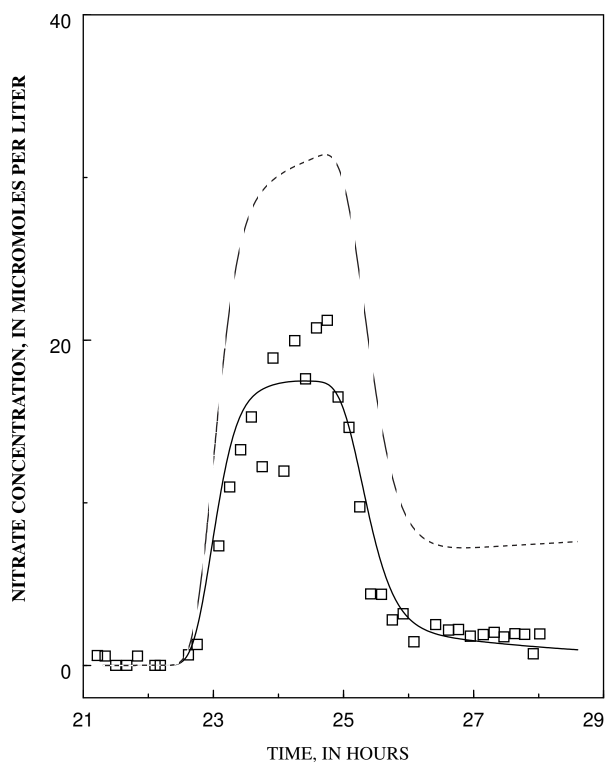

Figure 4. Observed (symbols) and simulated nitrate concentrations in Green Creek, Antarctica, 226 m from the injection point. Simulation results are shown for conservative transport (dashed line) and first-order loss (solid line).

Trace Metal Removal (OTIS and OTEQ)

In addition to the time-variable simulations shown in the previous examples, OTIS may be used to determine the steady-state solute concentrations that result from a constant loading scenario. In this application, we consider the spatial concentration profile of dissolved iron in a small stream. The stream is Saint Kevin Gulch, a headwater stream in the Rocky Mountains of Colorado. Saint Kevin Gulch receives acidic, metal-rich waters from a series of springs that emanate from the toe of a large mine dump. Instream metal concentrations increase and pH levels decrease in the vicinity of the dump. Kimball and others (1991) described a synoptic study conducted in August 1986. During the study, water samples were collected at numerous instream locations and the metal-rich springs. Figure 5 depicts the observed profile of dissolved iron concentration. Two features of the spatial profile are of interest. First, a large increase in dissolved iron occurs at about 400 m; a second feature is the abrupt decrease in dissolved iron concentration below 500 m. The purpose of this application is to quantify the processes responsible for the changes in dissolved iron concentration.

The first step in the analysis is to define the hydrology of the system. Broshears and others (1993) describe the addition of a conservative tracer that coincided with the synoptic study. Data from the tracer addition is used to determine the flow rates and the hydrologic parameters. Observed data from the springs are used to set the lateral inflow concentrations, C_L. OTIS is then used to develop a spatial profile under the assumption that dissolved iron is conservative (nonreactive). Results from this simulation are shown in figure 5 (thick solid line). The close correspondence between observed and simulated iron concentrations in the upper portions of Saint Kevin Gulch (0-500 m) indicates that the initial increase in iron is due to strictly hydrologic factors; that is, iron loading from the metal-rich springs. Simulated iron concentrations decrease downstream after 500 m due to the addition of water from a relatively dilute tributary, but do not match the decrease in the observed data. This discrepancy indicates that chemical reactions affect dissolved iron concentrations below 500 m.

A simple approach to quantifying the chemical reactions is to determine the first-order rate at which iron is lost from the system. Here we use OTIS-P to estimate a first-order decay coefficient for the main channel (λ). A first-order decay rate of $1x10^{-4}$ /s results in the simulated profile shown in figure 5 (thin solid line). Although the decay-rate approach yields an excellent fit to the data, it provides little insight into the mechanisms responsible for the iron loss. Inspection of the spatial pH profile indicates an increase in pH after 500 m that could result in the precipitation of hydrous iron oxides (pH= 3.3 and 4.0 at 464 and 526 m, respectively). To investigate this possibility, a steady-state OTEQ simulation was conducted. Because OTEQ uses the geochemical data base of MINTEQ, precipitation of ferrihydrite [$Fe(OH)_3$] may be explicitly modeled. OTEQ results reflecting ferrihydrite precipitation are shown as a dashed line in figure 5. These results support the hypothesis that iron is precipitating below 500 m.

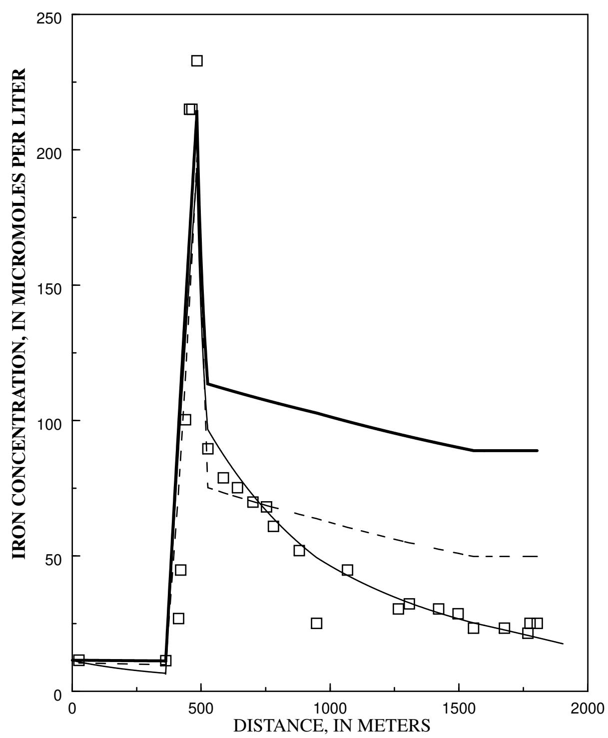

Figure 5. Observed (symbols) and simulated iron concentrations in Saint Kevin Gulch, Colorado. Simulation results are shown for conservative transport (thick solid line), first-order loss (thin solid line) and ferrihydrite precipitation (dashed line).

pH-Dependent Sorption (OTEQ)

OTEQ may also be used to simulate the time-variable behavior of trace metals and pH. As described by Broshears and others (1996), a pH-modification experiment was conducted at Saint Kevin Gulch to determine the effects of pH variation on trace-metal chemistry. During the experiment, a concentrated solution of sodium carbonate was injected to increase instream pH. Instream pH increased to 4.0-4.2 during the initial step of the injection and 5.0-5.8 during the second step. This increase in pH resulted in decreased concentrations of dissolved iron, aluminum, and copper. Model simulations by Broshears and others (1996) indicate that changes in dissolved iron and aluminum are attributable to the precipitation and dissolution of hydrous metal oxides. In this section we extend the work of Broshears and others (1996) to consider the effects of the pH modification on dissolved copper.

As shown in figure 6, dissolved copper concentrations decreased during the second step of the pH modification experiment. Several characteristics of the data point to specific mechanisms responsible for the loss of dissolved copper. First, formation of copper precipitates is unlikely given the observed pH. Second, total water-borne copper concentrations exceed dissolved concentrations, indicating the presence of particulate copper in the water column. The concurrent presence of particulate iron indicates the possibility of sorption to iron oxides. Finally, the decrease in total copper indicates sorption by the iron-oxide coated streambed.

Given these observations, OTEQ was used to simulate the sorption of copper onto freshly precipitated hydrous ferric oxide (HFO) in the water column and aged HFO on the streambed. In the simulation, sorption reactions between dissolved copper and HFO were governed by the generalized two layer model (Dzombak and Morel, 1990) as implemented within the equilibrium submodel. Simulation of copper sorption requires the specification of several parameters to characterize the sorptive surfaces and sorption reactions. Except where noted below, parameters were set to the recommended values given by Dzombak and Morel (1990). Exceptions included the site density associated with freshly precipitated HFO (set at the maximum value reported by Dzombak and Morel, 1990), the surface complexation constant for copper sorption onto fresh HFO (set at the reported maximum), and the surface complexation constant for sorption onto aged HFO (set below the reported minimum). These deviations from the recommended values were made so that copper was preferentially sorbed to freshly precipitated HFO.

Simulation results are shown in figure 6. Simulated and observed concentrations of dissolved copper are in close agreement immediately following the second pH step. Simulated values generally exceed observed concentrations during the latter part of the pH modification. As the pH modification was discontinued, desorption of copper produced a spike that was in excess of pre-injection copper levels. This spike is accurately reproduced by the simulation. The simulation's failure to reproduce the copper loss during the latter part of the pH modification is attributable to errors in modeling pH. As noted by Broshears and others (1996), a number of issues make concurrent simulation of iron and aluminum precipitation and pH a difficult task. In the work presented here we have made no attempt to improve the simulations of Broshears and others (1996). Simulation of pH therefore underestimates observed pH by 0.1-0.4 units. Given this increment in pH, closer agreement between observed and simulated copper would be obtained. Despite this shortcoming, the OTEQ simulation reproduces the general features of the observed data. OTEQ's ability to consider pH-dependent processes such as precipitation and sorption provides a process-based approach for the study of trace metal fate and transport

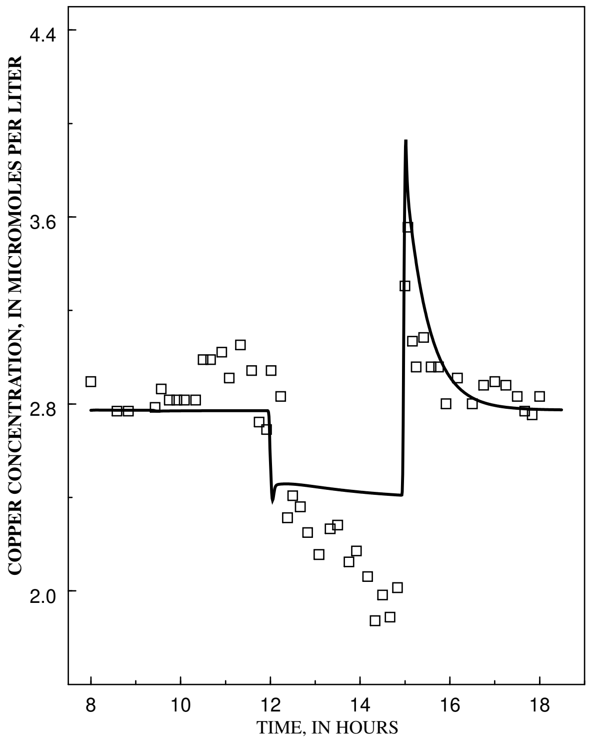

Figure 6. Observed (symbols) and simulated (solid line) copper concentrations in Saint Kevin Gulch, Colorado, 24 m from the injection point.

SOFTWARE AVAILABILITY

The OTIS solute transport model has been documented by Runkel (1998) and is available for public use. Executable versions of the model, source code and sample input files are available at `http://webserver.cr.usgs.gov/otis`. A similar software package for OTEQ will be made available after development of user documentation.

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