Reactive solute transport in streams

2. Simulation of a pH modification experiment

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Abstract. We present an application of an equilibrium-based solute transport model to a pH-modification experiment conducted on the Snake River, an acidic, metal-rich stream located in the Rocky Mountains of Colorado. During the experiment, instream pH decreased from 4.2 to 3.2, causing a marked increase in dissolved iron concentrations. Model application requires specification of several parameters that are estimated using tracer techniques, mass balance calculations, and geochemical data. Two basic questions are addressed through model application: (1) What are the processes responsible for the observed increase in dissolved iron concentrations? (2) Can the identified processes be represented within the equilibrium-based transport model? Simulation results indicate that the increase in iron was due to the dissolution of hydrous iron oxides and the photoreduction of ferric iron. Dissolution from the streambed is represented by considering a trace compartment consisting of freshly precipitated hydrous iron oxide and an abundant compartment consisting of aged precipitates that are less soluble. Spatial variability in the solubility of hydrous iron oxide is attributed to heterogeneity in the streambed sediments, temperature effects, and/or variability in the effects of photoreduction. Solubility products estimated via simulation fall within a narrow range (pK_{sp} from 40.2 to 40.8) relative to the 6 order of magnitude variation reported for laboratory experiments (pK_{sp} from 37.3 to 43.5). Results also support the use of an equilibrium-based transport model as the predominate features of the iron and pH profiles are reproduced. The model provides a valuable tool for quantifying the nature and extent of pH-dependent processes within the context of hydrologic transport.

Introduction

In part 1 of this manuscript [Runkel et al., this issue] an equilibrium-based solute transport model is developed for the simulation of trace-metal fate and transport in streams. In this paper, we present an application of the model to a field-scale experiment in which the pH of a small stream was temporarily altered. Application of the model to this pH modification experiment serves two purposes. Our primary goal is to demonstrate some practical aspects of model application. Emphasis is placed on the process of parameter estimation and the modeling of pH. A secondary purpose is to show how the model may be used to address several research issues related to trace-metal fate and transport in streams. With these goals in mind, we describe the pH modification experiment and present several hypotheses that may be tested through model application. We then discuss model formulation and the process of parameter estimation. The paper concludes with a discussion of model results as they relate to the study hypotheses.

Model Application

Although laboratory studies provide insight into the nature of geochemical reactions, field-scale studies are required to link the theoretical aspects of geochemistry with the more complex interactions that occur in natural settings. The pH modification experiments are designed to study the effects of pH variation on biological and geochemical processes. Data obtained from these experiments are used to assess system behavior in response to natural pH variation and the variation due to anthropogenic influences (e.g., acid rain and acid mine drainage). In this section we apply the equilibrium-based solute transport model to a pH modification experiment conducted on the Snake River, a small stream in the Rocky Mountains of Colorado.

Snake River pH Modification

The Snake River is a naturally acidic, metal-rich stream near Montezuma, Colorado. The stream is representative of other naturally acidic streams in Colorado and is hydrologically and chemically similar to many mountain streams contaminated by acid mine drainage. Pyrite is disseminated in the older rocks within the watershed, covering the area north of Landslide Peak to Webster Pass (Figure 1) [Theobald et al., 1963]. Because of the weathering of pyrite, the headwaters of the Snake River have an annual pH range of 3.2–4.5 [McKnight and Bencala, 1989]. Amorphous iron oxides coat the streambed, and elevated levels of aluminum, iron, manganese, and zinc are common throughout the year. The geology of the area is described by Theobald et al. [1963]. In this paper, we are concerned with the headwater region of the Snake River, that area

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above the confluence of the Snake River and Deer Creek, another small mountain stream. This headwater region has a drainage area of 11.7 km², a slope of 50 m/km, and is located above 3,200 m in elevation. Flows near the confluence range from 0.1 to 0.5 m³/s under low flow conditions, and peak at about 2.0 m³/s during spring runoff [McKnight and Bencala, 1989].

On August 30, 1983, a pH modification experiment was conducted to ascertain the effects of pH variation on trace-metal chemistry in the Snake River [McKnight and Bencala, 1989; Bencala et al., 1990]. Beginning at 0900 a 10.49-M solution of lithium chloride was injected at a rate of 86.6 mL/min. This injection continued for 6 hours, until 1500. Lithium chloride is a nominally conservative tracer in acidic streams, such that data obtained from downstream sites may be used to estimate hydraulic transport parameters [Bencala et al., 1990]. Also, beginning at 0900, a 7.25-M solution of sulfuric acid (H₂SO₄) was injected at a rate of 950 mL/min, terminating at 1200.

Sampling protocols and analytical procedures were as described by McKnight and Bencala [1989]; a brief summary is given here. Water samples were filtered through 0.2-μm filters; pH was measured in unfiltered samples. Aliquots from the filtered samples were acidified with HNO₃ for cation and trace metal analysis. Iron redox states for selected samples were determined using the 2,2'-bipyridine colorimetric method. Anions were analyzed using ion chromatography; iron and aluminum were analyzed using a graphite furnace atomic absorption spectrophotometer; sodium and lithium were analyzed using a flame atomic absorption spectrophotometer. Additional cations and trace metals were analyzed using an inductively coupled plasma spectrophotometer.

Sampling locations are shown in Figure 1. All distances are in terms of the injection point, SN0, located at 0 m, approximately 25 m upstream of a small culvert. Sampling sites U0 and D0 are located approximately 5 m upstream and 10 m downstream from SN0, respectively. Site SN1 is located at 628 m. The stream reach between SN0 and SN1 is a fairly uniform reach in which the stream is several meters wide and less than one-half meters deep. Site P1, at 1365 m, is above the first of two large beaver ponds. Site P2, at 1487 m, is located on a short, free-flowing length of stream that connects the beaver ponds. Downstream from the second pond is site P3, at 1605 m. A final site is SN2, at 2845 m, immediately above the confluence with Deer Creek.

As shown in Figure 2, injection of H₂SO₄ into the Snake River caused a significant decrease in pH that produced a dynamic iron response. Figure 2a depicts sulfate (SO₄) concentrations at sites SN1 and SN2, where SO₄ is a measure of the acid added to the system. After a short travel time, a distinct SO₄ front arrives at site SN1, and concentrations re-

**Figure 1.** Sampling locations within the headwater region of the Snake River watershed.

**Figure 2.** Instream concentrations of (a) sulfate, (b) pH, and (c) total dissolved iron at two sampling locations in response to the sulfuric acid injection.
main elevated over the 3-hour injection period. The rise in SO$_4$ is accompanied by a sharp drop in pH, as shown in Figure 2b. The decline in pH results in an increase in dissolved iron, as shown in Figure 2c. Plots of SO$_4$, pH, and iron at the intermediate sites exhibit features similar to those shown for SN1 and SN2.

The pH modification described above had a dramatic effect on dissolved iron concentrations in the Snake River. Several chemical and biologically mediated reactions influence the speciation of iron in acidic waters, including hydrolysis, precipitation/dissolution, microbial oxidation, and photo reduction. Precipitation/dissolution reactions are of importance as abundant quantities of hydrous iron oxides coat the bed of the Snake River and other metal-rich streams. These hydroxide coatings are often mixtures of amorphous materials and goethite [Langmuir and Whittemore, 1971]. Precipitation/dissolution of hydrous iron oxide [Fe(OH)$_3$(s)] is governed by

$$\{\text{Fe}^{3+}\} \cdot \{\text{OH}\}^{3} = K_{sp}$$

where (1) is a mass action equation for the reaction at equilibrium. $K_{sp}$ is the solubility product for hydrous iron oxide, and (Fe$^{3+}$) and (OH$^-$) are the activities of the free ferric iron and hydroxide species, respectively. In (1) the free ferric iron activity is related to the hydroxide activity to the third power; small changes in pH therefore cause relatively large changes in dissolved ferric iron. As given by $K_{sp}$, the solubility of Fe(OH)$_3$(s) is a function of the solid's composition. Newly precipitated oxides are often amorphous in form and are generally more soluble than aged precipitates. Langmuir and Whittemore [1971] report $pK_{sp}$ values ranging from 37.3 to 43.3, with lower values (higher solubilities) corresponding to freshly precipitated amorphous material and higher values corresponding to aged mixtures of goethite and lepidocrocite. This 6 order of magnitude variation in $K_{sp}$ poses a problem when modeling precipitation/dissolution, as incorrect specification of $K_{sp}$ may result in substantial under or over prediction of dissolved iron concentrations.

Microbial oxidation and photo reduction control the distribution of iron between the ferrous [Fe(II)] and ferric [Fe(III)] oxidation states. The oxidation of ferrous iron into ferric iron in acidic streams is described by several authors [Nordstrom, 1985; McKnight et al., 1988; McKnight and Bengala, 1988]. In most oxic, high pH waters, oxidation of ferrous iron is rapid. In water with pH levels below 5, however, the abiotic oxidation rate is extremely slow. Oxidation rates in acidic waters increase in the presence of microbes that catalyze the reaction [Lacey and Lawson, 1970]. Photo reduction of ferric iron has been noted in surfactants [Collienne, 1983, Madsen et al., 1986; McKnight et al., 1988; Kirnball et al., 1992], including the Snake River [McKnight and Bengala, 1988]. Photo reduction occurs when incident solar radiation in the range of 250–425 nm provides the chemical energy necessary to reduce ferric iron to ferrous iron. Photo reduction and oxidation transfer of mass between the ferrous and ferric oxidation states and may be viewed as competing processes. During daytime hours, photo reduction dominates over oxidation. At night, photo reduction ceases and oxidation becomes the dominant process. This interplay between photo reduction and oxidation causes a diurnal variation in ferrous and ferric iron [McKnight et al., 1988; McKnight and Bengala, 1988].

![Figure 3. Two-tiered iron response at site SN1. The initial increase in iron is attributable to dissolution from a trace compartment (zone I). The sustained plateau is attributable to dissolution from a less soluble, abundant compartment (zone II).](image)

Study Hypotheses

**Hypothesis 1: Dynamic equilibrium.** Examination of experimental data indicates that the response of iron to the decrease in pH was immediate. This is seen by comparing Figures 2b and 2c and noting the correspondence between the arrival time of the pH pulse and the maximum dissolved iron concentration. As discussed by McKnight and Bengala [1989], the primary purpose of the experiment was to determine the rates of chemical processes relative to those of hydrodynamic transport. Their goal was to determine the applicability of an equilibrium-based transport model. If the rates were sufficiently fast, local equilibrium could be assumed, and use of such a model would be appropriate. They concluded that the rapidity of the iron response supported the equilibrium-based approach. This issue is revisited herein, where we examine the ability of the equilibrium-based transport model to simulate pH and dissolved iron.

**Hypothesis 2: Sources of dissolved iron.** McKnight and Bengala [1989] concluded that the increase in dissolved iron was due to the dissolution of hydrous iron oxides and the photoreduction of ferric iron. They hypothesized that the dissolved iron originated from two compartments of hydrous iron oxide on the streambed. Their hypothesis is based on the general shape of the dissolved iron profile at SN1. At 9.4 hour, dissolved iron concentrations rose sharply to 30 μM as the pH front arrived. This initial peak was followed by a gradual decrease in concentration to 25 μM. At 10.1 hour the concentration stabilized and remained steady until the cessation of the injection. This two-tiered iron response is depicted in Figure 3. McKnight and Bengala hypothesized that the initial increase in iron (zone I) resulted from the dissolution of a "trace" compartment that was present in a limited quantity, and that the eventual plateau (zone II) occurred when the trace compartment was depleted and the source of iron was an "abundant" compartment, present in an unlimited quantity during the injection.

Several potential processes may be responsible for the observed differences between the effective solubilities of the two compartments. First, the initial peak attributed to the trace compartment may have been due to the dissolution of suspended hydroxide particles in the water column. This explanation is unlikely as iron concentrations in filtered and unfiltered samples are similar in the Snake River [McKnight and Bengala, 1989]. Second, the trace compartment may have contained
freshly precipitated hydroxides that were amorphous in form and more soluble than older precipitates contained in the abundant compartment. Finally, the trace compartment may have contained smaller particles with higher relative surface areas; these particles would have been more soluble than larger particles found in the abundant compartment. The actual mechanism responsible for the observed profile may be some combination of the latter two explanations given above. In this work, we investigate the two-compartment hypothesis and assess the role of photoreduction in controlling dissolved iron concentrations. In addition, the effective solubility of the hydrous iron oxides coating the streambed is determined.

**Hypothesis 3: Effect of storage zone chemistry.** Several authors have hypothesized that the transient storage zone is an area of heightened chemisorbed and biological transformation due to the intimate contact between solutes and solid surfaces and longer travel times [e.g., Castro and Hornberger, 1991]. The equilibrium-based transport model is therefore formulated to allow for the consideration of equilibrium chemistry within both the transient storage zone and the main channel [Runkel et al., this issue]. We investigate the importance of storage zone chemistry for the specific reactions affecting iron during the Snake River pH modification. To this end, simulations with and without storage zone chemistry are examined.

**Model Formulation**

The simulations presented herein are developed using the model presented by Runkel et al. [this issue]. Three issues relating to model formulation remain unaddressed: (1) consideration of two compartments containing hydrous iron oxide, (2) consideration of photoreduction and oxidation, and (3) simulation of pH. The two compartments of hydrous iron oxide are modeled by defining a single single phase with a solubility product that is dependent on the mass of immobile precipitate. For each computational segment, an initial concentration of immobile precipitate, \( P_{b}^{sun} \), is specified. This concentration represents the total concentration in the trace and abundant compartments prior to the pH modification. Also specified for each segment is the initial quantity in the abundant compartment, \( P_{b}^{abund} \). The difference between these two concentrations defines the initial concentration in the trace compartment, \( P_{b}^{trace} \). While the amount of immobile precipitate, \( P_{b} \), exceeds \( P_{b}^{abund} \), the solubility product of the trace compartment, \( K_{scr,1} \), is in effect. When the trace compartment is depleted in a given segment, \( P_{b} \) falls below \( P_{b}^{abund} \) and the solubility product for the abundant compartment, \( K_{scr,2} \), is used. Under this formulation, the trace compartment represents freshly precipitated hydrous iron oxide while the abundant compartment represents aged precipitates that are less soluble. Although dissolution from the trace compartment provides the components needed to form the solid phase for the abundant compartment, precipitation is precluded as the solubility product for freshly precipitated iron hydroxide \( (K_{scr,1}) \) is in effect.

The processes of photoreduction and oxidation are considered by specifying a single parameter to dictate the percentage of total water-borne iron that is ferrous. (Total water-borne iron is defined as the sum of all ferric and ferrous iron species present in the water column, including both dissolved and particulate forms.) Although this formulation is empirical, it does provide a simple mechanism wherein simulation results reflect the proper ferrous/ferric ratios. To implement the fixed percentage approach, an additional loop is placed around the sequential iteration procedure described by Runkel et al. [this issue]. Within each time step, this loop provides an iterative procedure for fixing the percentage of ferrous iron. As each iteration begins, the sequential iteration procedure is used to determine component concentrations as a function of transport and chemistry. After convergence of the sequential iteration technique the total water-borne iron concentration is computed as well as the percentage of the total that is ferrous. These percentages are then compared with those from the previous iteration to test for convergence of the outer loop. This convergence test is given by

\[
|\theta^{n+1} - \theta^n| < 0.0005
\]  

(2)

where \( \theta \) is the percentage of total water-borne iron that is ferrous and \( n \) denotes the iteration. If Equation (2) holds for all segments, the outer loop has converged and a new time step is initiated. If the solution has not converged, total component concentrations for Fe(II) and Fe(III), \( T_{Fe(II)}^{tot} \) and \( T_{Fe(III)}^{tot} \), are set using

\[
T_{Fe(II)}^{tot} = \rho^{init} \rho^{Fe(II)} + P_{b}^{Fe(II)}
\]  

(3)

\[
T_{Fe(III)}^{tot} = (1 - \rho^{target}) T_{Fe(II)}^{tot} + P_{b}^{Fe(III)}
\]  

(4)

where \( \rho^{target} \) is the desired or "target" percentage of ferrous iron, \( T_{Fe(II)}^{tot} \) is the total water-borne iron concentration, and \( P_{b}^{Fe(III)} \) is the concentration of immobile precipitate of Fe(III). External source sink terms [Runkel et al., this issue] for Fe(II) and Fe(III) are computed by comparing the quantities given by (3) and (4) with values from the previous iteration. A new iteration of the Fe(II)/Fe(III) loop then begins.

One of the goals of model application is to determine the ability of the equilibrium-based model to simulate pH. Models of chemical equilibria generally use one of two methods for the calculation of pH, namely the electron-neutrality and proton condition methods [Morel and Morgan, 1972]. Using the electron-neutrality approach, the mass balance equation for hydrogen species is replaced by the charge balance or electroneutrality equation. This approach to pH modeling is implemented in the PHREEQE equilibrium model [Parkhurst et al., 1980]. A second method for modeling pH is based on the specification of the proton condition. Under this method, a mass balance equation is written for the "excess" hydrogen ions in the system. This equation, known as the proton condition, is given by:

\[
H_T = \sum H^+ \text{species} - \sum OH^- \text{species}
\]  

(5)

where \( H_T \) is the excess hydrogen concentration.

The choice of a computational method for pH is dictated in part by the formulation of the equilibrium submodel. The model presented in part I of this manuscript utilizes the numerical framework of MINTEQ [Wessell et al., 1976; Allison et al., 1991], a chemical equilibrium model that uses the proton condition. Simulations of pH presented herein are therefore based on the proton condition method. In contrast, models based on PHREEQE rely on the electroneutrality approach for the computation of pH. In reviewing the literature, there appears to be some confusion regarding the two methods and their use in solute transport models. Engesgaard and Kipp [1992, p. 2832], for example, dismiss the use of the proton condition, because "the presence of hydrogen in the water molecule makes it difficult to transport numerically." As a practical matter, the presence of hydrogen in the water molecule does not preclude the use of the proton condition. This is
due to the fact that the proton condition does not represent hydrogen per se but rather the excess hydrogen in the system. It is therefore possible to transport this excess quantity without confounding it with that of the water molecule. This fact is reiterated by Yeh and Tripati [1991] and confirmed by the simulations provided herein.

### Parameter Estimation

Model application requires estimates of the parameters, variables, and rate constants describing the relevant physical and chemical processes. This section presents a summary of the estimation procedure for several quantities. Additional information on chemical parameters is provided in the simulation section.

### Geochemical data, thermodynamic data, and discretization

The complete data set for the pH modification experiment includes measurements for 11 dissolved constituents: aluminum (Al), calcium, chloride (Cl), fluoride, total iron (Fe(II) + Fe(III)), magnesium, manganese, sodium (Na), sulfate, zinc, and lithium (Li). Data obtained from each sampling location indicate that the primary effect of the pH modification was an increase in total dissolved iron concentrations; the remaining constituents are relatively unaffected by the change in pH. Simulation of the iron dynamics is therefore the primary emphasis. The equilibrium-based solute transport model is formulated such that each chemical component is transported as a separate solute. Given the complete data set, 13 components are possible. This component set is developed by considering the 11 constituents enumerated above (where total iron is divided into two oxidation states, Fe(II) and Fe(III)), and introducing excess hydrogen (H) to model pH. Consideration of the complete component set therefore results in a set of 13 partial differential equations describing transport and 13 nonlinear algebraic equations describing chemical equilibrium. (For a development of the nonlinear algebraic equation associated with each component, see Allison et al. [1991].)

The number of species formed by the 13 components is quite large. To lower simulation run times, the component set is reduced by noting that some of the components behave conservatively at the ambient pH levels considered for the Snake River problem. Chemical equilibrium simulations, for example, indicate that the components Li, Na, and Cl exist entirely as free ions in solution (e.g., the concentration of the uncomplexed species Li⁺ accounts for 100% of the component Li). Furthermore, many of the components have little or no interaction with ferrous or ferric iron and do not significantly affect pH. On the basis of these observations the component set used for the remainder of this work consists of five components: Al, Fe(II), Fe(III), SO₄, and H. Simulations based on this reduced component set are in general agreement with those using the complete component set.

Equilibrium computations within the equilibrium submodel are based on the thermodynamic database provided with MINTEQ [Allison et al., 1991]; equilibrium constants for all aqueous-phase reactions are set to the default values provided in the database. Solubility products for the precipitation/solution of hydrous iron oxide are set via simulation. The ionic strength of the solution is fixed at 0.003 M, and the temperature of the stream is spatially and temporally fixed at 10°C. Activity coefficients for ionic strength corrections are computed using the modified Debye-Hückel and Davies equations. Equilibrium constants are corrected for temperature using the van’t Hoff equation. Both of the corrections are described by Allison et al. [1991]. Finally, the computational segments are 3 m in length and a time step of 10 s is used.

### Transport parameters and hydraulic state variables

Tracer injection experiments provide the data needed to compute the volumetric flow rate Q and the lateral inflow rate q_{L_{in}} associated with each stream reach. In addition, application of a conservative solute transport model [e.g., Runkell and Broshears, 1991] allows for the determination of cross-sectional areas (A), dispersion coefficients (D), and the transient storage parameters (α and A s). For the Snake River experiment, these parameters were determined by Bencala et al. [1990], based on data from the lithium chloride injection. From this work, the volumetric flow rate at the upstream boundary is 0.224 m³/s. The remaining quantities are summarized in Table 1, where the modeled network is composed of five stream reaches. Each reach is considered a homogeneous unit over which the specified parameters apply. The terms of each reach correspond to a sampling location.

### Upstream boundary conditions

Solution of the transport equations requires the specification of an upstream boundary concentration. The boundary conditions are in terms of the lower-borne component concentration T₀ at the upstream boundary (at x = 0 m). During daytime hours, however, concentrations of mobile solids in the Snake River are relatively low, such that T₀ is adequately approximated by the dissolved component concentration C. In general, the upstream boundary concentrations for the components are developed by considering the dissolved concentrations at site U0, the sampling location immediately upstream of the injection point. Additional conditions come into play for components that are part of the injected solution (H and SO₄).

**Aluminum (Al):** The upstream boundary condition for Al is set at 59 µM based on data from U0.

**Ferrous (Fe(II)) and ferric iron (Fe(III)):** For the Snake River experiment, total dissolved iron concentrations were determined for each sample, as opposed to separate measurements of ferrous and ferric iron. Three exceptions to this sampling regimen occurred at SN2, where ferrous/ferric determinations were made for samples obtained prior to, during, and after the injection experiment. Ferrous iron concentrations in the three water samples account for the majority of the total iron in solution, as shown in Table 2. The percentages shown in the table are combined with additional information to partition the total iron between the Fe(II) and Fe(III) components at the upstream boundary. A typical value of the total dissolved iron concentration at site U0 is 21.6 µM. Specific percentages

### Table 1. Hydraulic and Transient Storage Parameters

<table>
<thead>
<tr>
<th>Reach</th>
<th>A_s m²</th>
<th>D, m²/s</th>
<th>q_{L_{in}} m³/s/m</th>
<th>A_s m²</th>
<th>α, s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 0–628 m (SN0–SN1)</td>
<td>0.61</td>
<td>0.75</td>
<td>6.2E⁻⁵</td>
<td>0.10</td>
<td>2.5E⁻⁵</td>
</tr>
<tr>
<td>2: 628–1365 m (SN1–P1)</td>
<td>0.55</td>
<td>0.60</td>
<td>8.3E⁻⁵</td>
<td>0.02</td>
<td>5.0E⁻⁵</td>
</tr>
<tr>
<td>3: 1365–1487 m (P1–P2)</td>
<td>1.90</td>
<td>0.50</td>
<td>13.1E⁻⁵</td>
<td>1.50</td>
<td>50.0E⁻⁵</td>
</tr>
<tr>
<td>4: 1487–1605 m (P2–P3)</td>
<td>1.80</td>
<td>0.20</td>
<td>16.1E⁻⁵</td>
<td>0.50</td>
<td>10.0E⁻⁵</td>
</tr>
<tr>
<td>5: 1605–2845 m (P3–SN2)</td>
<td>0.70</td>
<td>0.20</td>
<td>2.8E⁻⁵</td>
<td>0.12</td>
<td>20.0E⁻⁵</td>
</tr>
</tbody>
</table>

Adapted from Bencala et al. [1990]. Read 6.2E⁻⁵ as 6.2 × 10⁻⁵.
Table 2. Dissolved Ferrous and Ferric Iron Concentrations at SN2

<table>
<thead>
<tr>
<th>Time, hour</th>
<th>Ferrous Iron, (\mu M)</th>
<th>Ferric Iron, (\mu M)</th>
<th>Percent Ferrous, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0927 (preinjection)</td>
<td>12.9</td>
<td>0.2</td>
<td>98.5</td>
</tr>
<tr>
<td>1234 (injection)</td>
<td>24.9</td>
<td>2.1</td>
<td>92.2</td>
</tr>
<tr>
<td>1438 (postinjection)</td>
<td>11.5</td>
<td>0.1</td>
<td>99.1</td>
</tr>
</tbody>
</table>

Adapted from McKnight and Bencala [1989].

used to divide this quantity between Fe(II) and Fe(III) are given in the simulation section.

**Sulfate (SO\(_4\))**: The upstream boundary condition for SO\(_4\) is determined by considering the background SO\(_4\) concentrations at U0 and the amount of SO\(_4\) added via the \(\text{H}_2\text{SO}_4\) injection. At U0, dissolved SO\(_4\) concentrations are approximately 385 \(\mu M\). The amount of SO\(_4\) added by the injection (512 \(\mu M\)) is determined by considering the SO\(_4\) concentration of the injectate, the injection rate, and volumetric flow rate. The time-varying upstream boundary concentration for SO\(_4\) is given by

\[
T_{w_0} = 385 \, \mu M \quad \text{for} \quad -\infty < t < 0900 \, \text{hours}
\]

\[
T_{w_0} = 897 \, \mu M \quad 0900 \, \text{hours} < t < 1200 \, \text{hours}
\]

\[
T_{w_0} = 385 \, \mu M \quad 1200 \, \text{hours} < t < \infty
\]

**The proton condition (H)**: The final component \(H\) differs from the other components in that direct measurements of the component concentration are not available, as the proton condition has “no direct experimental meaning” [Morel and Morgan, 1972]. The total excess hydrogen concentration \((H_T)\) is therefore not provided by standard chemical analyses. A procedure for determining \(H_T\) is illustrated by two of the example input files distributed with MINTEQ. In general, the \(pH\) of a perturbed system may be computed if the background \(pH\) is known. The general procedure is as follows:

Step 1: Begin with an unperturbed system for which the \(pH\) is known. Perform chemical equilibrium computations for a batch system with \(pH\) fixed at the known value.

Step 2: The background \(H_T\) is calculated by applying (5) to the results from the equilibrium calculations.

Step 3: The \(H_T\) corresponding to a perturbed system is determined by adding the \(H\) associated with the perturbation to the background \(H_T\) value. The \(H_T\) so provided allows for the computation of \(pH\) for the perturbed system.

The procedure for determining the hydrogen boundary condition generally follows that given above. The background \(H_T\) is determined by completing equilibrium calculations for U0 where \(pH\) is fixed using observed values. These runs are examined to determine the excess \(H\) in the unperturbed stream. Background \(H_T\) values range between 50 and 60 \(\mu M\), and the preinjections and postinjection boundary conditions for \(H\) are set accordingly. For the injection period the \(H\) added by the injectate is twice the added SO\(_4\), as there are two hydrogen ions in \(\text{H}_2\text{SO}_4\). The excess hydrogen added by the injection is therefore 1025 \(\mu M\), a quantity that is added to the background concentration to set the injection period boundary concentration at 1085 \(\mu M\).

**Lateral inflow concentrations.** Downstream from the injection point, the stream gains flow through lateral inflows. The solute concentrations associated with these lateral inflows are difficult to quantify due to the heterogeneous nature of the Snake River watershed. Although sampling of individual inflows is possible, work by Bencala and McKnight [1987] indicates that inflow concentrations vary substantially over short spatial scales. Iron inflows, for example, are reported to range from 1.25 to 24 \(\mu M\), for samples collected between SN1 and P3. A dense sampling network is therefore required to determine accurate reach-averaged values of the inflow concentrations. An additional complication is the need to consider the relative contributions of groundwater inflow and the associated concentrations. In any event, inflow samples were not obtained during the 1983 experiment, and other methods for computing the inflow concentrations are required.

Lateral inflow concentrations specified for each component represent total water-borne concentrations. For the Snake River it is reasonable to assume that solutes entering through lateral inflow are primarily in dissolved form, as some of the water enters from the subsurface (where solid transport is negligible) and the surface water contributions are known to contain little mobile precipitate. The task is to estimate the dissolved concentrations in the inflow for each component on a reach-specific basis. For conservative components, lateral inflow concentrations for each reach may be back calculated based on instream values, as described by Bencala et al. [1990]. This is accomplished by considering the instream concentrations at the beginning and end of each reach and performing a mass balance. The reach-averaged lateral inflow concentration \(C_L\) \([\text{ML}^{-1}]\) is given by

\[
C_L = \frac{Q_1C_1 - Q_2C_2}{q_{\text{LIN}}\Delta l}
\]

where \(Q_1\) and \(Q_2\) are the volumetric flow rates at the upstream and downstream ends of the reach, respectively \([\text{L}^3\text{T}^{-1}]\). \(C_1\) and \(C_2\) are the instream concentrations at the upstream and downstream ends \([\text{ML}^{-3}]\). \(q_{\text{LIN}}\) is the lateral inflow rate \([\text{L}^3\text{T}^{-1}]\). \(\Delta l\) is the reach length \([\text{L}].\)

Application of (7) for conservative components is justified as the concentration of a strictly conservative solute increases or decreases only in response to dilution or concentration through lateral inflows. For the component set considered here, (7) is used for SO\(_4\) and Al. SO\(_4\) has been found to be approximately conservative in the Snake River [Bencala et al., 1990], while Al has also been found to behave conservatively at low \(pH\) in another metal-enriched stream [Nordstrom and Ball, 1986]. Preinjection data at the initial and terminal ends of each reach are used to compute the inflow concentrations for SO\(_4\) and Al. With minor modification, the same approach is used to compute the excess hydrogen \((H)\) entering via lateral inflow. Instream concentrations of \(H\) are determined using preinjection data and \(pH\) as input to the equilibrium computations. Equation (7) is then used to compute the lateral inflow concentrations for \(H\).

For iron the assumption of conservative behavior is not appropriate, and use of (7) is not warranted. Lateral inflow concentrations for total iron are therefore set at 5.6 \(\mu M\), the median observed inflow concentration reported by Bencala and McKnight [1987]. Because of the magnitude of the iron response during the injection period, selection of the inflow concentrations is not of great importance, as instream processes overwhelm the effects of lateral inflow. Given the total iron inflow concentration, the task of determining individual concentrations for Fe(II) and Fe(III) still remains. Selection of
Table 3. Estimated Lateral Inflow Concentrations

<table>
<thead>
<tr>
<th>Reach</th>
<th>SO$_4^-$</th>
<th>Al$^+$</th>
<th>H$^+$</th>
<th>Total Fe$^{\dagger}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>736.</td>
<td>86.</td>
<td>195.</td>
<td>5.6</td>
</tr>
<tr>
<td>2</td>
<td>792.</td>
<td>169.</td>
<td>16.</td>
<td>5.6</td>
</tr>
<tr>
<td>3</td>
<td>596.</td>
<td>114.</td>
<td>420.</td>
<td>5.6</td>
</tr>
<tr>
<td>4</td>
<td>596.</td>
<td>114.</td>
<td>420.</td>
<td>5.6</td>
</tr>
<tr>
<td>5</td>
<td>218.</td>
<td>7.</td>
<td>100.</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Concentrations are in μM.
*Estimated via (7).
$^{\dagger}$Median value from 1984 data set.

the percentages used for this determination is discussed in the simulation section.

Lateral inflow concentrations for each reach are summarized in Table 3. Estimated inflow concentrations generally lie within the range of observed inflow data collected in 1984 [Bencala and McKnight, 1987].

Simulations

Given the parameters estimated above, an application of the equilibrium-based transport model to the Snake River experiment is presented. Because of model complexity, uncertain parameter estimates, and natural variability, use of any model to "predict" the response of a natural system is a questionable undertaking [Konikow and Bredehoeft, 1992; Oreskes et al., 1994]. Here we have taken an alternate approach wherein the model is used to quantify important processes and to support or refute existing theories. Our specific purpose here is to investigate the hypotheses formulated for the Snake River pH modification.

Simulation of pH. Simulation of pH is an important task because pH is a master variable that affects the chemical composition of natural systems. Precipitation and dissolution reactions for metal hydroxides, for example, are pH dependent. Failure to adequately simulate pH will therefore overestimate or underestimate the concentrations of dissolved metals. During the Snake River experiment, pH decreases as H$_2$SO$_4$ dissociates and donates protons to the system. As pH decreases, Fe(OH)$_3$ dissolves from the streambed, releasing three moles of OH$^-$. Dissolution has the counter effect of increasing pH, due to the liberation of OH$^-$. These processes are represented within the framework of the model. The addition of protons by H$_2$SO$_4$ is reflected in higher H$^+$ concentrations at the upstream boundary. The increase in excess hydrogen is transported downstream, and equilibrium calculations are completed for each stream segment. This allows for the computation of pH at each point in space.

Results from this simulation are shown in Figure 4. Chemical reactions considered in the simulation include acid-base reactions, complexation, dissolution of Fe(OH)$_3$(s), photoreduction, and oxidation. Simulation results for pH are encouraging as predicted values are consistently within 0.2 pH units of the observed values. The general agreement between simulated and observed pH suggests a lack of significant sources or sinks affecting protons in the modeled system. This is in contrast to the work of Chapman [1982] and Broshears et al. [1995], where difficulties arise in modeling pH. Chapman [1982] introduces several surface reactions to represent a reservoir of sorbed protons on the streambed. This reservoir provides the base-neutralizing capacity necessary to reconcile differences between simulated and observed pH. Without the addition of the surface reactions, simulated values are in excess of observed data. Recent work by Broshears et al. [1995] also suggests a source of protons that may be attributable to surface reactions. Both of these works involve base injections that result in pH levels that are in excess of those observed for the present case.

Simulation of ferricydrildissolution and photoreduction. The observed increase in dissolved iron is attributable to the dissolution of hydrous iron oxides. At the two sites immediately downstream from the injection (SN1 and P1), total dissolved iron profiles exhibit a two-tiered response that led McKnight and Bencala [1989] to hypothesize that two compartments of hydrous iron oxide contribute to the dissolved iron pulse. To test this hypothesis, a two-compartment model is formulated as described above. Each compartment contains ferricydrild, the mineral defined in the chemical submodel to represent the amorphous form of Fe(OH)$_2$(s). Application of the two-compartment model requires specification of the solubility products for the two compartments ($K_{sp,1}$ and $K_{sp,2}$) and the amount of ferricydrild in the trace compartment ($P_{b,1}$). Simulation of photoreduction and oxidation requires the specification of an additional parameter, $\theta_{net}$. In addition, lateral inflow concentrations and upstream boundary conditions are for total iron; these totals must be partitioned between Fe(II) and Fe(III).

Because of the heterogeneous nature of the stream environment, difficulties in transferring the results of laboratory studies to the field, and the extreme variability in laboratory-determined solubility products, the parameters controlling dissolution may not be specified a priori. Parameter estimates are therefore obtained via simulation. Data at the upstream sites exhibit a well-defined peak immediately following the $pH$
Table 4. Chemical Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Preinjection and Postinjection</th>
<th>Injection Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_{\text{target}}$</td>
<td>98%</td>
<td>92%</td>
</tr>
<tr>
<td>Percent Fe(II), boundary</td>
<td>98%</td>
<td>92%</td>
</tr>
<tr>
<td>Percent Fe(II), inflows</td>
<td>93%</td>
<td>93%</td>
</tr>
</tbody>
</table>

decrease, as well as a sustained plateau after the initial peak. The solubility product for the trace compartment ($K_{sp1}$) controls the magnitude of the initial peak, whereas the solubility product for the second compartment ($K_{sp2}$) controls the level of the plateau. The amount of ferricydrite in the trace compartment ($P_{F}^{\text{trace}}$) controls the time at which the iron profile drops down to the plateau, i.e., when the trace compartment is depleted, $K_{sp2}$ takes effect and lower iron concentrations result.

Estimates of $\theta_{\text{target}}$ are based on observed values of percent ferrous (Table 2). The percentages used to partition total iron between Fe(II) and Fe(III) at the upstream boundary and in the inflows are also based on observed values of percent ferrous, as well as simulations of the preinjection period. During daylight hours, particulate iron is generally not present in the water column and precipitation is therefore precluded. Under the assumption that dissolution is not occurring, the preinjection period may be viewed as a time during which the stream is in equilibrium with the solid phase on the streambed. Simulations of the pre-injection period should therefore result in little or no precipitation or dissolution. If the specified percent ferrous is too high (for a given $K_{sp}$), simulations will indicate dissolution from the bed; conversely, if the specified percentage is too low, simulations will indicate precipitation. Using trial and error, the percent ferrous is adjusted such that simulations of the preinjection period result in the equilibrium condition. These percentages and estimates of $\theta_{\text{target}}$ are summarized in Table 4.

Simulation results are presented in Figure 5, where simulated results are for the total water-borne iron concentration. The total water-borne iron concentration represents all ferrous and ferric iron in dissolved form and a small amount of particulate ferric iron. Observed data are for the total concentration of ferrous and ferric iron passing through a 0.2-μm filter. Mass passing through this filter size generally consists of dissolved species, but may include solid phases, as hydrous iron oxides are known to pass through a 0.1-μm pore size membrane [Kimball et al., 1992]. Inspection of Figure 5 indicates a close correspondence between observed and simulated concentrations at the three most upstream sites. At these sites the two-compartment approach reproduces the dominant features of the observed iron profiles. For example, simulated iron concentrations at SN1 increase rapidly at 9.4 hour, such that the peak matches the maximum observed value. From 9.4 to 10.0 hours this peak is maintained and the solution is in equilibrium with the trace compartment. At 10.0 hour this initial peak drops down to the plateau level due to depletion of the trace compartment. At this time, the trace compartment is absent and the waters are in equilibrium with the abundant compartment throughout the remainder of the simulation. At 12.5 hour the pulse of low-pH water passes, and iron concentrations drop from the plateau to preinjection levels.

Correspondence between observed and simulated concentrations is less satisfactory at the final two sites (P3 and SN2). The two-compartment approach is problematic at these sites due to differences in the arrival of the pH front (Figure 4). At the upper sites the pH front arrives as a square wave; pH drops sharply and immediately reaches a minimum value that is maintained throughout the passage of the front. This characteristic allows for a clear distinction between the two compartments. In contrast to the upper sites, arrival of the pH front at P3 and SN2 is more gradual due to the effects of dispersion and transient storage. Because pH continues to decrease throughout the injection period, it is difficult to distinguish between the two compartments. Simulations using the two compartment approach result in a bimodal iron profile that is not justified given the relatively flat profile observed during the pH depression. The reaches ending at P3 and SN2 are therefore modeled using a single compartment of ferricydrite.

The simulation presented in Figure 5 relies on the specification of spatially variable solubility products. An alternate approach, presented by Runkel [1993], uses observed data at SN1 to estimate spatially constant values for $K_{sp1}$ and $K_{sp2}$. The resultant simulations underestimate iron concentrations at the downstream sites. This underestimation may be due to spatial variability in the processes of dissolution and ph oreduction. This variability may be represented by considering spatially variable properties of the solid phase, as we have done here, or by considering spatial variability in the rates of ph oreduction. Use of higher ph oreduction rates in the lower reaches (i.e., higher $\theta_{\text{target}}$) would result in higher iron concentrations. Higher ph oreduction rates in the lower reaches would be justified if the lower reaches received more incoming
Table 5. Properties of the Solid Phase Ferrihydrite

<table>
<thead>
<tr>
<th>Reach</th>
<th>( p_{\text{trace}} ) ( \mu M )</th>
<th>( pK_{sp1} ) Estimated*</th>
<th>( pK_{sp1} ) Adjusted†</th>
<th>( pK_{sp2} ) Estimated</th>
<th>( pK_{sp2} ) Adjusted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.38</td>
<td>41.05</td>
<td>40.57</td>
<td>41.19</td>
<td>40.71</td>
</tr>
<tr>
<td>2</td>
<td>18.37</td>
<td>40.93</td>
<td>40.45</td>
<td>41.19</td>
<td>40.71</td>
</tr>
<tr>
<td>3</td>
<td>12.00</td>
<td>40.93</td>
<td>40.21</td>
<td>41.19</td>
<td>40.47</td>
</tr>
<tr>
<td>4</td>
<td>NA†</td>
<td>40.83</td>
<td>40.80</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>5</td>
<td>NA†</td>
<td>40.74</td>
<td>40.59</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

*Value used in simulation.
†Estimated value adjusted for error in simulated pH.
‡Not applicable. Only a single compartment is considered.

Solar radiation than the upper reaches. Site inspection of the watershed indicates that the converse is true because of the effects of shading, however, and higher rates are not justified.

Reach-specific solubility products and trace compartment quantities used within the simulation are summarized in Table 5. In general, solubilities of the two compartments increase in the downstream direction. Estimated solubility products should not be directly compared, however, as they are dependent on the simulated pH values. For a given \( K_{sp} \), underestimation of pH results in higher iron concentrations than would be realized under observed conditions. Because the ferrihydrite solubility product is the product of \((Fe^{3+})\) and \((OH^-)^3\) (equation (1)), small changes in pH cause large changes in the estimated solubility product, given a fixed concentration of \(Fe^{3+}\). Solubility products adjusted for errors in the simulation of pH are given in Table 5.

Spatial variability in the solid phase is examined by plotting the adjusted solubility products as a function of distance (Figure 6). Three parameter groups are plotted: (1) trace compartment solubility products for SN1, P1, and P2, (2) abundant compartment solubility products for SN1, P1, and P2, and (3) solubility products used in the single compartment formulation for P3 and SN2. All three groups suggest a general trend in which solubility increases in the downstream direction. This spatial variability is relatively minor when compared to the solubility products reported by Langmuir and Whittemore [1971] (Figure 6). The increase in solubility with distance may be attributed to variable properties of the solid phase and/or temperature effects. Reach-to-reach variability in the properties of the solid phase may be related to spatial variability in photoreduction. The amount of tree cover generally increases in the downstream direction, such that the role of oxidation relative to photoreduction is increased. The net result is the production of ferric iron that may precipitate if waters become oversaturated. This interaction between photoreduction and oxidation produces a continual supply of freshly precipitated iron that may be more soluble than that on the streambed in upstream reaches.

Discussion

The hypotheses put forth at the beginning of this paper may now be considered in light of the simulation results presented above.

Hypothesis I: Dynamic equilibrium. The rapid response of iron to the pH decrease suggests a system in which chemical reactions are fast relative to hydrologic processes. Our results support the use of an equilibrium-based model, as the predominant features of the iron response are reproduced by the simulation. In addition, the close agreement between simulated and observed pH supports the proton condition approach for the modeling of pH. Despite these observations, a closer look at the assumption of equilibrium is warranted as part of the simulation exercise involved the adjustment of \(K_{sp}\) to obtain an adequate representation of the iron profile. Although equilibrium approach is justified for many reactions, it comes into question when dissolution from the streambed is considered. Chapman [1982], for example, argues for a pseudokinetic approach due to the lack of prolonged contact between the flowing waters and the streambed.

For the case of ferrihydrite dissolution the suitability of a strictly equilibrium approach is difficult to assess, given the high variability in the solubility product governing dissolution. In general, it is possible to argue for both equilibrium controlled and kinetically controlled dissolution. This is shown in Figure 7, where simulation results at SN1 are shown for two

Figure 6. Spatial variability in \(K_{sp}\). Solubility increases with downstream distance.

Figure 7. Effect of variation in \(K_{sp1}\) on the simulated iron peak. Uncertainty in \(K_{sp1}\) makes it possible to argue for either kinetically controlled or equilibrium-controlled dissolution.
model runs. In the first simulation, \( pK_{sp1} \) is set equal to 41.00, resulting in an overestimation of the initial peak. Thus if the \( pK_{sp1} \) specified is the "true" solubility of the trace compartment, a kinetic approach to dissolution is required, as a mechanism is needed to prevent the rapid depletion of iron in the trace compartment. For the second run, \( pK_{sp1} \) equals 41.05, and the peak is properly simulated. If 41.05 represents the true solubility of the trace compartment, the equilibrium approach is adequate and no consideration of kinetics is required.

**Hypothesis 2: Sources of dissolved iron.** The solubility of hydrous iron oxides is a function of many factors including age ("freshly precipitated" versus "aged"), particle size, and surface area. The propensity of a given source of iron to dissolve may therefore be viewed as a continuum in which certain fractions or "compartments" more readily dissolve. This continuum is represented using two compartments of ferrimagnetic iron oxides. Simulation results indicate that (1) effective solubilities of the two compartments lie within a narrow range (Figure 6), and (2) the two-compartment framework is a reasonable representation for the upper reaches of the Snake River during the \( pH \) modification experiment. The two compartments of ferrimagnetic iron oxides in these reaches appear to have similar characteristics, given by the closeness of the solubility products.

The two-compartment representation is less satisfactory in the lower reaches, where a single compartment approach is used to model the iron profiles at F3 and SN2. The failure of the two-compartment approach appears to be related to the hydraulic properties of the stream; both of these sites are below two large beaver ponds, such that in-stream mixing is enhanced. This mixing results in a more gradual \( pH \) decrease that produces a bimodal iron profile under the two-compartment approach. Another potential explanation is related to the shading that occurs in the reaches ending at F3 and SN2. Uneven distributions of solar radiation may affect the rate of photoreduction thereby resulting in less uniform solid phases that are not aptly modeled using two compartments. Further work is needed to develop a more robust representation of hydrous iron oxides with variable properties.

McKnight and Bencala [1988] also hypothesized that photoreduction reactions were a major source contributing to the iron pulse. The importance of photoreduction may be seen by considering simulation results with and without photoreduction. This is shown in Figure 8 where simulation results at SN1 are presented. Results from a simulation that considers only dissolution are shown in Figure 8a; results from the previous simulation in which both dissolution and photoreduction/oxidation are considered are shown in Figure 8b. Because photoreduction is not considered, the simulation shown in Figure 8a requires the specification of a more soluble solid phase (\( pK_{sp1} = 40.35, pK_{sp2} = 40.7 \)) than that used in the previous simulation (Table 5); that is, use of solubility products from Table 5 results in an underprediction of iron concentration when photoreduction is not considered. Three features of the simulations underscore the importance of photoreduction. First, without photoreduction, the decline in the initial peak is much slower than is indicated by the four data points defining the peak. With photoreduction, the rate of decrease in the initial peak is very similar to that of the observed data. Second, consideration of photoreduction produces results that are consistent with observed values of ferrous and ferric iron; that is, the relative concentrations of ferrous and ferric iron are in agreement with those given in Table 2. When photoreduction is not considered, all of the mass associated with the iron pulse (Figure 8a) is from the dissolution of ferrimagnetic iron and is therefore entirely ferric iron. As a result, the percentage of total iron that is ferrous ranges from 60 to 75%. These figures are in direct conflict with observed data, which indicate a ferrous iron percentage of 92% (Table 2). Finally, simulations without photoreduction suggest the presence of particulate iron in the water column. In Figure 8 the difference between the total water-borne and total dissolved iron concentrations corresponds to the amount of particulate iron present in the water column. This amount of particulate iron was not observed during the \( pH \) modification. When photoreduction is considered, very little particulate iron is present, and the dissolved and water-borne concentrations are roughly equivalent (Figure 8b).

**Hypothesis 3: Effect of storage zone chemistry.** The equilibrium-based solute transport model is formulated such that equilibrium chemical reactions take place in both the main channel and the transient storage zone. In the foregoing simulation, equilibrium chemistry is considered for only the main channel. Although the physical effects of transient storage are considered, chemical reactions are not modeled within the storage zone. This approach is used to eliminate the additional calls to the equilibrium submodel required for the storage zone. The approach is based on the assumption that storage zone chemistry has a negligible effect on total iron concentrations in the main channel.

A simulation that includes storage zone chemistry was conducted in order to verify the above assumption. Results indicate that total iron concentrations are virtually unaffected by the addition of storage zone chemistry. The additional computational expense of including storage zone chemistry is therefore not justified for the particular problem considered here. The negligible effect of including chemistry in the storage zone is explained by noting that the primary effect of adding storage zone chemistry is to increase the mass of the trace compartment. This additional mass is inconsequential, however, due to the assumption of chemical equilibrium. Prior to depletion of the trace compartment in the main channel, waters entering the storage zone will be in equilibrium with the trace compartment such that dissolution will not occur in the storage zone. Upon depletion of the trace compartment in the main channel,
iron concentrations are controlled by the solubility of the abundant compartment and any additional mass introduced by dissolution of the trace compartment in the storage zone is lost to precipitation.

In general, the importance of storage zone chemistry is determined on a problem-specific basis. Here we have only considered the processes of precipitation/dissolution, photoreduction and oxidation; the importance of storage zone chemistry may become apparent for more complex systems in which additional processes, such as sorption, are considered. The effects of chemical reactions within the storage zone ultimately depend on the chemistry of the problem, the physical importance of the storage zone, and the rate of hydrologic transport.

Conclusion

The pH-dependent reactions such as precipitation/dissolution and oxidation/reduction are important processes affecting the fate and transport of iron and other trace metals in streams. Quantitative analysis of both hydrologic transport mechanisms and geochemical processes is essential for the correct interpretation of data obtained from natural systems. In this paper we have presented an application of an integrated modeling framework that considers hydrologic transport and geochemical processes. Our basic approach was to use the model in "descriptive" mode, wherein the dominant chemical and physical processes were identified, as opposed to using the model to predict environmental conditions. The complex nature of the natural system generally precludes the use of such models for predictive purposes [Konikow and Bredehoef, 1992; Oreskes et al., 1994]. Simulations were performed to investigate the processes responsible for the observed increase in dissolved iron concentrations and to determine if the identified processes are aptly modeled within an equilibrium-based model. From this work we present the following conclusions:

1. Results support the use of an equilibrium-based transport model, as well as the proton condition approach for modeling pH. Kinetically limited dissolution can not be ruled out, however, due to uncertainty in the solubility product for hydrous iron oxide.

2. The increase in iron observed during the Snake River experiment is attributable to the dissolution of hydrous iron oxides and the photoreduction of ferric iron. Because of extreme variability in the solubility product for hydrous iron oxide, it is difficult to specify $K_{sp}$ a priori; $pK_{sp}$ values estimated via simulation range from 40.2 to 40.8.

3. For the Snake River experiment, equilibrium reactions within transient storage zones have a negligible effect on total iron concentrations in the main channel.

The model provides a valuable tool for quantifying the nature and extent of pH-dependent processes within the context of hydrologic transport. The application presented here concerns the study of geochemical processes based on data from a pH modification experiment. We envision additional applications, such as the evaluation of treatment systems for acid mine drainage, the analysis of episodic acidification, and other applications wherein pH-dependent processes are of interest.

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References


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