Characterization of Transport in an Acidic and Metal-Rich Mountain Stream Based on a Lithium Tracer Injection and Simulations of Transient Storage

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Physical parameters characterizing solute transport in the Snake River (an acidic and metal-rich mountain stream near Montezuma, Colorado) were variable along a 5.2-km study reach. Stream cross-sectional area and volumetric inflow each varied by a factor of 3. Because of transient storage, the residence time of injected tracers in the Snake River was longer than would be calculated by consideration of convective travel time alone. Distributed inflows along the stream were a significant source of in-stream chemical variations. These transport characteristics of the Snake River were established on the basis of the assumption of lithium as an ideally conservative tracer and use of simulations of advection, dispersion, and transient storage. Evaluations of the validity of this combined tracer and simulation approach lend confidence to the estimation of the physical transport parameters; further development is warranted for methods of onsite transport experimentation in hydrologically complex, chemically reactive environments.

INTRODUCTION

With the current interest in determining the environmental impacts of acid mine drainage and acid rain, basic hydrology is a necessary component in the study of geochemistry in acidic, upland surface waters. Physical transport of solutes along streams can influence the potential for geochemical reactions to occur. The task of establishing "physical transport characteristics" seems initially to be entirely straightforward. It would appear that physical determinations could be readily and routinely obtained. However, recent studies by Thorne and Zevzenbergen [1985] show that reliable, process-based equations for flow resistance in mountain rivers require additional development. Furthermore, Marchand et al. [1984] indicate that conventional current meter measurements of discharge do not properly account for hydraulic conditions present in high-gradient, shallow depth streams common to mountainous regions. This is because stream flow is over and around cobbles, resulting in rapid changes in direction and unsteady velocity distributions, which make the assumptions of conventional measurements inappropriate. Also, in gravel bed and cobble bed mountain streams there may be significant flow of "streamwater" through the streamed bed [Bencala, 1984]. Such flow is contributing to the transport of solutes; however, conventional current meter measurements would not register this flow component [Zellweger et al., 1989]. Finally, physical properties of mountain streams (e.g., cross-sectional area) may vary on distance scales as short as meters [e.g., Kennedy et al., 1984]. As a practical matter, physical properties must be characterized on a scale of hundreds of meters to be applicable to analysis of chemical reactions occurring during transport. The concern with conflicting distance scales is also an issue when attempting to quantify the multiple inflows of solutes in upland surface waters. Inflow solute concentrations may vary spatially across only tens of meters [Bencala and McKnight, 1987]. Direct physical measurements of discharge along every 10 m of stream length would be simply impractical.

The use of injected, in-stream tracers is an approach to establishing physical transport characteristics without attempting direct physical measurements. While tracers are widely used in many environments, there are two specific factors necessitating further study of tracers in acidic, mountain streams. First, in a mountain stream, a tracer with only even moderate sorptive characteristics may not be an appropriate tracer. Physical transport characteristics of mountain streams are potentially a factor in assessing the conservative nature of solute tracers [Bencala, 1984; Zellweger et al., 1986]. Flow, which is shallow relative to the relief of exposed bed sediment, permits extended contact between sorbing solutes and sediment. This contact presents the opportunity for sorption and, if kinetics are a factor in the sorption process, then the impedance of flow by the bed sediment may increase the time available for reaction. Second, dye tracers, commonly used in near-neutral and basic streams, may not be appropriate for acidic streams. The widely used tracer rhodamine WT has been determined to be unstable in acidic stream water [Zellweger et al., 1988]. Jones [1987] has concluded, for rhodamine WT, "at pH values less than 6, particularly in the chemical environments
to be found in streams affected by acid rain or acid mine drainage, the assumption of conservative behavior is untenable." Trudgill [1987] discussed the chemical mechanisms of effects of pH on rhodamine WT properties. Aldous and Smart [1988] present results of laboratory experiments that assess the sorption of rhodamine WT onto ferric hydroxides that are present in some mine waters.

Tracers have been used in various combinations of natural tracers, injected tracers, and chemical perturbations to identify and quantify geochemical reactions occurring in streams. Tracers can be used to compensate for lack of direct transport process information (e.g., velocity and dispersion parameters), or tracers can be used to identify and quantify transport processes. In acidic and metal-rich streams, natural tracers have been used in the studies of geochemical reactivity of several metal species by Chapman et al. [1983], Nordstrom and Ball [1986], Bencala et al. [1987], and Filipek et al. [1987]. Such tracers effectively account for transport characteristics by comparison of reactive solutes to nonreactive solutes. Acid streams have been studied by experimentally decreasing stream pH with acid injections [Hall et al., 1987; Ormerod et al., 1987; Henriksen et al., 1988], where the arrival of the acid effectively marks the solute transport. Tracer injections have also been used in acid streams [McKnight et al., 1988] for determining solute residence times to quantify in-stream reaction kinetics. Several efforts have been made to combine experimental injections with simulations to identify transport parameters over relatively short (100 m to 1 km) stream reaches. These studies are based on various formulations of transport mechanisms and have been done both explicitly to investigate reactive transport [Chapman, 1982; Chapman and Jones, 1983] and for hydrologic studies [Bencala and Walters, 1983; Jackman et al., 1984; Wallis et al., 1989].

Many of the aspects of transport in acidic mountain streams have been addressed in the studies noted above. At this time it is appropriate to address specifically the identification of transport characteristics in a stream at scales of environmentally significant reach length, time interval, and chemical dynamics. By these scales we mean reach lengths long enough for there to be variation in physical parameters, time intervals extended over several solute travel times, and in-stream chemical dynamics resulting in variation of solute concentrations and pH.

The objectives of this report are (1) to establish the physical transport characteristics of the Snake River and (2) to evaluate the validity of the combined tracer and simulation approach to transport characterization of an acidic mountain stream. The first objective is a necessary component to ongoing studies of the geochemical dynamics of the Snake River [McKnight and Bencala, 1989]. The second objective has two aspects which remain unseparated in our in-stream experimental studies of geochemistry. We are evaluating lithium for its usefulness as a tracer in a stream with variable pH. Concurrently we are evaluating the concept of identifying physical parameters entirely upon the basis of simulations of transient storage.

**METHODS**

**Onsite Investigations**

**Site.** Hydrologic and geochemical conditions in the Snake River watershed (Montezuma, Colorado) provide an opportunity to investigate a natural occurrence [Theobald et al., 1963] of acidic and metal-rich stream water. Substantial spatial [Bencala and McKnight, 1987] and temporal [McKnight and Bencala, 1988] variations of solute concentration occur in the Snake River. Such variations, while possibly subtle in larger, downdrainage systems, were measurable in the Snake River. Ecological comparisons between this stream and other acidified streams have been discussed by McKnight and Feder [1984]. The study area includes the reaches of the Snake River that extend several kilometers upstream and downstream from the confluence of Deer Creek (Figure 1). Though the upper reaches of the Snake River are acidic and metal-rich, Deer Creek can be characterized as a pristine, Rocky Mountain stream. Geochemical studies of the surface waters and stream sediments in the Deer Creek watershed have been presented by Catts [1982].

1983 tracer injection studies. Tracers were injected into the Snake River and Deer Creek in two related studies. Locations of the injections are shown in Figure 1; the tracers used and the duration of the injections are listed in Table 1. The focus of this report is the injection of lithium into the upper reach of the Snake River (study 1) at the location designated "Om." The chloride and sulfate observations from study 1 are important aspects in evaluating the conservation of lithium. The sodium and bromide observations from study 1 and the lithium observations from study 2 will be discussed briefly. Although not discussed in this report, the broader goal of the effort is the investigation of trace metal transport under conditions of variable pH [see McKnight and Bencala, 1989]. This was an additional motivation for the additions of sulfuric acid (study 1) and sodium hydroxide (study 2).

1984 source characterization. The results of the 1983 tracer injection studies showed spatial variability of the natural background concentrations of most solutes in the Snake River. In September 1984, with similar hydrologic conditions to those of August/September 1983, two subreach sections of the Snake River were sampled intensively [Bencala and McKnight, 1987]. Samples were also taken from visible groundwater seeps and small surface tributaries. Locations of the sampling are noted in Figure 1.

**Sampling procedures.** Polyethylene sample bottles were rinsed three times with unfiltered stream water and then with filtered water. Samples were filtered immediately upon collection through 0.2-μm Nuclepore filter membranes (0.4-μm membranes were used for the samples collected in 1984). (The use of product names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.) Samples analyzed for anions were stored untreated. Samples analyzed for cations were acidified with concentrated nitric acid.

**Laboratory Procedures**

- Anion analyses were made by ion chromatography (Dionex 2000i). Lithium and sodium analyses were made by flame atomic absorption spectroscopy (Perkin-Elmer 603). Magnesium, calcium, manganese, and zinc analyses were made by inductively coupled plasma spectroscopy (Jarrel-Ash 975).

**Equations**

- **Process simulations.** The process simulations follow established approximations for the formulation of one-
dimensional convective-dispersive transport and transient storage in "dead zones." The two simulation equations are

Solute in the stream channel

$$\frac{\partial C}{\partial t} = -\frac{Q}{A} \frac{\partial C}{\partial x} - \frac{1}{A} \frac{\partial}{\partial x} \left( \frac{\partial C}{\partial x} \right)$$

$$+ \frac{q_L}{A} (C_L - C) + \alpha (C_S - C)$$

(1)

Solute in the storage zones

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

(2)

where

- $C$ solute concentration in the stream ($\mu$M);
- $Q$ volumetric flow rate ($m^3$ s$^{-1}$);
- $A$ cross-sectional area of the channel ($m^2$);
- $D$ dispersion coefficient ($m^2$ s$^{-1}$);
- $q_L$ lateral volumetric inflow rate (per length) ($m^3$ s$^{-1}$ m$^{-1}$);
- $C_L$ solute concentration in lateral inflow ($\mu$M);
- $C_S$ solute concentration in the storage zone ($\mu$M);
- $A_S$ cross-sectional area of the storage zone ($m^2$);
- $\alpha$ stream storage exchange coefficient ($s^{-1}$);
- $t$ time (s);
- $x$ distance (m).

The first three terms on the right-hand side of equation (1) are the standard representation of the processes of convection, dispersion, and lateral inflow. The last term in (1) and (2) represents the exchange of solutes between the surface stream channel and areas of relatively immobile water along the stream channel and in the streambed gravels. The application and limitations of this formulation to the mountain stream environment have been discussed by Benca and Walters [1983]. The finite difference Crank-Nicolson technique is used to solve the equations.

Parameters to be used in equations (1) and (2) were selected by trial and error visual identification of a set of parameters that resulted in simulated concentrations which were "the best fit" to the observed concentrations. The transient storage formulation is used strictly in the parameter identification setting. All parameters obtained for the process simulations are interpreted as curve fit approximations to the physical properties of the stream. This visual selection approach was subjective. An objective, statistical method for estimating parameters in this formulation has been presented by Wagner and Gorelick [1986]. The subjective, visual selection, approach was used here because the intermediate trial and error results can help the analyst appreciate the limitations of the simulations. If a visual selection yields transport simulations consistent with onsite observations, then little is foregone by using a subjective approach.

Inflow concentration estimates. With the exception of the tributary, Deer Creek, inflows to the Snake River are
TABLE 1. Tracer Injection Studies in the Snake River, 1983

<table>
<thead>
<tr>
<th>Sampling Reach</th>
<th>Tracer</th>
<th>Duration</th>
<th>Injection Rate, mmol s⁻¹</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upstream to downstream Injection at &quot;0 m&quot;</td>
<td>LiCl</td>
<td>0900-1500</td>
<td>15.1</td>
<td>Evaluate Li as a tracer compared to Cl and SO₄ and estimate solute transport characteristics of stream</td>
</tr>
<tr>
<td>Upstream to downstream Injection at &quot;0 m&quot;</td>
<td>H₂SO₄</td>
<td>0900-1200</td>
<td>114.7</td>
<td>Control pH in the Snake River; permits evaluation of Li with variable pH</td>
</tr>
<tr>
<td>Downstream Injection into Deer Creek</td>
<td>NaBr</td>
<td>1000-1600</td>
<td>4.6</td>
<td>Evaluate Br as a tracer compared to Li, Cl, SO₄, and Na</td>
</tr>
<tr>
<td>Downstream Injection above confluence at &quot;2557 m&quot;</td>
<td>LiCl</td>
<td>0900-1200</td>
<td>12.7</td>
<td>Evaluate Li as a tracer compared to Cl and estimate solute transport characteristics of stream</td>
</tr>
<tr>
<td>Downstream Injection into Deer Creek</td>
<td>NaBr</td>
<td>0900-1200</td>
<td>5.1</td>
<td>Evaluate Br as a tracer compared to Li, Cl, and Na</td>
</tr>
<tr>
<td>Downstream Injection into Deer Creek</td>
<td>NaOH</td>
<td>0900-1000</td>
<td>34.6</td>
<td>Control pH in the lower Snake River; permits evaluation of Li with variable pH</td>
</tr>
</tbody>
</table>

characterized as nonpoint sources, distributed along the length of the stream. Within identified surface sources of water to the stream the concentrations of solutes in these inflows varied substantially [Bencala and McKnight, 1987]. The volumetric flow rates and the solute compositions of the inflows were estimated indirectly by mass balance calculations. For conservative solutes the mass balance for a stream subreach is

\[ C_L = (C_B Q_B - C_T Q_T)/(Q_B - Q_T) \]

where the subscript \( B \) refers to the bottom of a stream subreach, and \( T \) refers to the top of a stream subreach. The lateral inflow concentrations of several solutes were estimated by using equation (3), based on in-stream concentrations of the particular solute and stream volumetric flow rates. The flow rates were determined as part of the estimation of parameters in equations (1) and (2) on the basis of the observations of lithium concentrations.

RESULTS

Onsite Investigations

The pH of the stream was controlled for three hours, starting at the beginning of the six-hour injection of lithium (study 1, see Table 1). The extent of the experimental change in stream pH is illustrated in Figure 2. The lowest pH observed was 3.2 at the monitoring site closest to the point of tracer injections. The highest pH observed was 6.6 at the end of the study reach ("5231 m"). As illustrated in Figure 2, the natural pH of the Snake River is not uniform, and a significant change in excess of one pH unit occurs at the Deer Creek confluence.

Lithium concentrations in the Snake River during study 1 are presented in Figure 3. At each site the lithium concentrations increased to a plateau level; this level decreases at each successive site downstream from the injection. In Figure 3 the resolution of the analysis is sufficient to make it evident that lithium concentrations rose sharply at initial arrival but that concentrations did remain elevated for over 2 hours after the initial decrease following the pulse.

Convection-Dispersion/Transient Storage Simulations

Simulations of the lithium observations were generated as shown in Figure 4 by the numerical solution of equations (1) and (2). The parameters identified as visually yielding the best fit are those listed in Table 2. The dominant features of the observations are retained in the simulations. The decrease in plateau concentration at each successive site downstream location is generated in the simulations as a result of the increase in stream flow rate. For all of the sites the arrival time of the leading and trailing edges are accurately reproduced. A significant feature of solute transport in mountain streams is the prolonged length of time for the solute pulse to increase to full plateau value. This feature is well simulated with the inclusion of equation (2) to represent the mechanism of transient storage. From Table 2 this mechanism is parameterized by a characteristic cross-sectional area for storage zones and a coefficient representing the characteristic time for exchange between the stream channel and the storage zones.

Transport Characteristics of the Snake River

The lithium observations in the Snake River reflect three characteristics of transport in mountain streams [see Ben-
Fig. 3. Observed concentrations of the injected lithium in the Snake River.

Fig. 4. Simulation of lithium transport.

cala, 1984; Kennedy et al., 1984]. The characteristics are spatial variation of parameters, transient storage, and the existence of significant distributed (nonpoint) inflows.

Appreciable variation of the physical transport parameters is evident in two ways for the parameter values listed in Table 2. First, the parameter “stream cross-sectional area” varies by approximately a factor of 3, subreach to subreach. This parameter is a conceptually well-defined parameter, and simple visual observation of the stream confirms that such variation exists. Second, the parameters “storage cross-sectional area” and “exchange coefficient” each vary by an order of magnitude. These parameters clearly are not physically well defined; they result from the greatly simplified theory of “dead zone mixing” within streams. Thus a certain amount of variation is expected simply because the process of parameter estimation has to account for deficiencies of the basic formulation of the simulations. This order of magnitude variation of “transient storage” parameters is consistent with work in other mountain streams [see Benca, 1984; Jackman et al., 1984; Wagner and Gorelick, 1986].
The significance of the transient storage mechanism on solute transport in the Snake River is presented in two ways in Figures 5 and 6. In Figure 5, conservative transport is illustrated for simulations with and without the mechanism of transient storage. The lines indicating transport without transient storage used the parameters from Table 2 for the standard convective-dispersion simulation. The initial arrival of solutes and the eventual plateau were identical, but achieving the plateau required additional time because of the transient storage. The indication of whether this additional time was significant is shown in Figure 6. In Figure 6 the observed lithium concentrations from the site "5231 m" are shown on scales that normalize (or nondimensionalize) both concentration and time. The concentration axis is normalized between the background and plateau values. The time scale reads in multiples of the convective travel time down to a specific site along the stream. (Here, convective travel time is the sum of travel times through each subreach, based on an estimate of convective velocity within a subreach as \(Q/A_0\).) An ideal, square pulse would (by definition) arrive at time zero and instantaneously increase from concentration zero to one. The real pulse, of course, does not indicate this behavior. The pulse in the actual response took one half again the convective travel time to reach 90% of the plateau and double the convective travel time to reach 95% of the plateau. In this study reach of the Snake River, solutes entering the stream have residence times longer than the simple convective travel time would indicate.

Inflows increased the discharge of the Snake River from 0.22 m\(^3\) s\(^{-1}\) in the upper reach to 0.81 m\(^3\) s\(^{-1}\) at the end of the study reach (Figure 7). This increase of 0.59 m\(^3\) s\(^{-1}\) resulted from 0.21 m\(^3\) s\(^{-1}\) from Deer Creek and the remainder, 0.38 m\(^3\) s\(^{-1}\), entered the stream as distributed inflows. As is illustrated in Figure 7, the flow increases are computed from the differences in lithium concentrations at plateau. While these differences were small, the absolute lithium concentrations did decrease monotonically, as would be expected from the existence of numerous minor inflows to the stream [Bencala and McKnight, 1987].

**Validity of the Combined Tracer-Simulation Approach**

Intensive sampling of selected stream reaches. The distributed inflows carry into the stream the solutes from the watershed that, in part, will determine the chemistry of the Snake River. Monitoring streamflow with a conservative solute tracer accounts for all the flow actively involved in transport and provides estimates of inflow. However, as

<table>
<thead>
<tr>
<th>Subreach</th>
<th>Stream Cross-Sectional Area, (m^2)</th>
<th>Dispersion Coefficient, (D_i), (m^2\cdot s^{-1})</th>
<th>Volume Inflow, (q_i), (m^3\cdot s^{-1})</th>
<th>Storage Cross-Sectional Area, (A_i), (m^2)</th>
<th>Exchange Coefficient, (a_i), (s^{-1})</th>
<th>Solute Inflow, (C_L), (\mu M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-628 m</td>
<td>0.61</td>
<td>0.75</td>
<td>0.062 x 10^{-2}</td>
<td>0.10</td>
<td>0.025 x 10^{-7}</td>
<td>0    5    732</td>
</tr>
<tr>
<td>628-1365 m</td>
<td>0.55</td>
<td>0.60</td>
<td>0.083 x 10^{-3}</td>
<td>0.02</td>
<td>0.050 x 10^{-3}</td>
<td>0    5    795</td>
</tr>
<tr>
<td>1365-1487 m</td>
<td>1.90</td>
<td>0.50</td>
<td>0.131 x 10^{-3}</td>
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<td>0.500 x 10^{-3}</td>
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<td>0    3    80</td>
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*The confluence zone is not physically 68 m in length; conceptually it is treated as such in the simulation. This approach is taken for two reasons. First, all of the tracer data are from the two end points at sites "2845 m" and "2913 m." Second, computationally it is convenient to add a tributary as a lateral inflow distributed for a longitudinal distance.*

---

**TABLE 2a. Simulation Parameters: Snake River 1983 Injection Experiment**

<table>
<thead>
<tr>
<th>Parameters at Boundary (&quot;0 m&quot;)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge, (Q), (m^3\cdot s^{-1})</td>
<td>0.224</td>
</tr>
<tr>
<td>Background concentration, (C), (\mu M)</td>
<td>Lithium 0</td>
</tr>
<tr>
<td></td>
<td>Chloride 5</td>
</tr>
<tr>
<td></td>
<td>Sulfate 385</td>
</tr>
<tr>
<td>Plateau concentration, (C), (\mu M)</td>
<td>Lithium 68</td>
</tr>
<tr>
<td></td>
<td>Chloride 71</td>
</tr>
<tr>
<td></td>
<td>Sulfate 867</td>
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</table>

**TABLE 2b. Simulation Parameters: Snake River 1983 Injection Experiment**

<table>
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<th>Volume Inflow, (q_i), (m^3\cdot s^{-1})</th>
<th>Storage Cross-Sectional Area, (A_i), (m^2)</th>
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discussed by Kennedy et al. [1984, p. 108], “Care must be taken to assure that downstream dilution of tracer is not attributed to groundwater inflow when the dilution is the result of long-delayed underflow within stream gravels.” The estimates of inflow to the Snake River were evaluated for consistency with chemical inflow observations.

Estimates of reach-average inflow concentrations of (approximately) conservative solutes were made by using equation (3), with the subreach by subreach discharge estimates obtained on the basis of the lithium plateau concentrations (Figure 7). These estimates were made for several elements (sulfate, magnesium, calcium, and manganese) which are approximately conserved in the Snake River-Deer Creek confluence zone [Bencala et al., 1987] and for zinc, which Chapman et al. [1983] considered conserved in two acid mine drainages. The estimated inflow concentrations on August 30, 1983, are presented in Figure 8 in addition to concentrations of inflows measured during September 1984. The comparison of the estimated to the observed inflow concentrations show the estimates typically occurring within the ranges of the observations. Two distinct deviations from this agreement were negative estimates in one subreach for manganese (Figure 8d) and in two subreaches for zinc (Figure 8e). This result is not an error but does indicate that sorption by hydrous oxides on the streambed may have resulted in small losses of these solutes. The estimated inflow concentrations were based (equation (3)) on the values of discharge determined from the lithium injection.

There is general consistency between the estimated inflow concentrations and the observed ranges.
Interpretation of additional tracer injections. The evaluation of the combined tracer and simulation approach is based on the physical stream parameters estimated from the lithium observations. These parameters were used in the simulations of other tracers. The numerical results of the simulations were compared to the observed concentrations of these additional tracers. The degree to which the simulated concentrations agreed with the observations was taken as a measure of the conservative properties of lithium and the additional tracer.

The essential point to the rationale of this aspect of the evaluation is that only physical processes would have identical effects on two (or more) solutes. Only physical processes are considered in simulations based on equations (1) and (2). If the solute were nonconservative because of chemical processes, then such chemical processes presumably would have differing effects on each solute. It is difficult to envision a chemical process that would have an effect on the cation lithium identical to the effect on the anions chloride and sulfate.

The primary comparisons were made to the transport of the anions chloride and sulfate. The results of the simulations compared to the onsite observations are presented in Figure 9 (chloride) and Figure 10 (sulfate). For chloride the agreement between observations and simulations was good for comparisons of time of arrival, plateau level, and spreading of the trailing edge of the pulse. The comparisons for the locations from the first monitoring site ("628 m") down to the site ("2845 m") upstream of the confluence with Deer Creek showed visual agreement certainly within the scatter of the observations. At the locations downstream from the confluence the simulated values were consistently larger than the observations. However, the differences were of the order of only a few micromolar. The comparisons for sulfate were fair. These differences, however, can be interpreted as indicating some reactivity in acidic water for the anion sulfate with reference to lithium. If the simulations are considered representative of the passage of a 3-hour pulse of conservative solute, then the observations show a retardation in the transport of sulfate. For the three hours required for transport along 5231 m of the Snake River, the arrival of sulfate was retarded of the order of 10 min.

As part of the first study (Table 1), sodium and bromide also were injected into Deer Creek. This injection was upstream from the confluence with the Snake River. The transport of sodium along the lower reaches of the Snake River was simulated with those physical parameters estimated from the lithium observations. The comparisons of sodium observations and simulations, shown in Figure 11, were fair at best. The results are intentionally presented on a full-range scale from zero to maximum plateau values to illustrate the difficulty of using sodium as a tracer in the Snake River. By using manageable (under the conditions of an onsite experiment) volumes of tracer the concentration of sodium was altered only by about the same amount (several micromoles per liter) as the naturally occurring spatial variation. The sodium results do not negate the assertion of conservation of lithium, but neither could they be taken as independent evidence. Bromide observations from the plateau stage of study 1 are shown in Figure 12. Also shown in Figure 12 are attempted bromide simulations based on the results of the lithium analysis. In both study 1 and study 2 the laboratory analyses for the bromide plateau concentrations were inconsistent with all other information from the experiment. The plateau bromide concentrations at the first site downstream from the confluence, "2913 m," were typically less than the plateau concentrations at the next site downstream, "3192 m" (such a difference did not exist at background conditions). The water and solute mass balance relations used for the other injected solutes could not accurately be applied to bromide, as indicated by the differences between the observations and the plateau simulations. It was
not determined if there are any known direct reactions of the anion bromide in acidic, metal-rich water that have the potential for producing these results. The bromide concentrations were less than 10 \( \mu M \); thus, uncertainty in the analysis procedure was also a possibility, particularly in the variable solution matrix of the Snake River.

The results of study 1 and the simulations of the observations indicate, to within all of the errors, uncertainties, and variations of an onsite experiment, that lithium was transported as a conservative tracer through the 5231-m study reach of the Snake River. Thus, assuming that lithium was conserved, the estimated values of physical parameters (Table 2) then may be considered as indicative of the transport characteristics of the Snake River. One indication of the accuracy of these estimates is presented in Figure 13. In Figure 13 the observed lithium concentrations in study 2 are compared to the simulation of study 2 by using the physical parameter estimates from study 1. Even the approximation of “replication” in the usual laboratory sense is difficult to achieve in onsite experiments. However, there was no apparent reason to assume that the hydrologic conditions on September 1 were appreciably different from those on August 30. The simulations shown in Figure 13 are good representations of an injection experiment, and they promote confidence in the parameter estimates and the inferences drawn on the experimental results.

**Sensitivity to tracer assumption.** The use of lithium as a conservative tracer is an assumption subject to uncertainty. By extending the analysis of the sulfate observations, comments can be made on two issues of sensitivity. The first issue concerns the ability to distinguish between two sets of simulations. The second issue concerns the ability to identify reactivity in a prospective tracer. Simulations of sulfate (Figure 14a) and lithium (Figure 14b) were done with discharge and convective travel time adjusted to the sulfate plateau. These simulations (solid curves) are distinct from those based on lithium (dashed curves) in exact values but consistent in overall shape. For sulfate and lithium the differences between the two simulations at the upstream site, “628 m,” is of the order of the scatter in the data, while at the downstream site, “5231 m,” the sulfate-adjusted simulations have clearly separated from the data and the lithium-based simulations. Thus, qualitatively, simulations based on the two tracers lithium and sulfate, to an observable degree, are distinguished from the scatter in the data. When compared to the data, the simulations of sulfate (Figure 14a, solid curves) show a different type of insensitivity. These simulations, which assume a conservative tracer, might be considered quite reasonable representations of the sulfate pulses; however, taken overall with other information from the complete experiment, the lithium-based simulations (dashed curves in Figure 14a) are considered to be “the correct” simulation of a conservative tracer. This result

Fig. 10. Simulation of sulfate transport based on physical parameters estimated from lithium transport.

Fig. 11. Simulation of sodium transport based on physical parameters estimated from lithium transport.
shows (1) the value of relying on more than one tracer for onsite experiments and (2) that the transient storage formulation, while intended to account for physical mechanisms, can mimic chemical reactivity. This inference is a caution that simulations that use the transient storage formulation alone may not distinguish between certain physical and chemical processes.

**DISCUSSION**

On the basis of the lithium data, physical characteristics of solute transport were established for the Snake River. Three features of these results should be considered in studies of solute transport in mountain streams. First, physical parameters in the Snake River are variable for distances of less than a kilometer. The estimated values of stream cross-sectional area and volumetric lateral inflow varied by roughly factors of three to four in the eight monitored subreaches. Second, transient storage of solutes may result in increases in residence time and thus increases in contact with reactive environments. Third, in the mountain stream environment, the numerous minor inflow discharges can accumulate to yield significant nonuniformity in stream discharge. By using the lithium tracer injection, estimates were obtained of variable inflow concentrations for several solutes.

Until more comparative experience is obtained with acidic or near-acidic water, some check on the conservative response of tracers needs to be part of site-specific use of tracer techniques. The need to test tracers onsite occurs because of the unpredictability of the complex chemical environment. The definition of “conservative tracer” ultimately becomes operational; a chemical is conserved in the transport of solutes if, in a given situation, concentration changes cannot be detected beyond those known to be attributable to inflow addition or dilution.

Lithium functioned as a conservative tracer in the Snake River. Typically, small background concentrations and availability of a routine measurement method (flame atomic adsorption) at the tens of micromolar level make lithium an excellent tracer for this and presumably other acidic streams. In near-neutral and basic stream water the cation lithium would be expected to sorb onto stream sediments [e.g., Bencala, 1984]. Chapman and Jones [1983] and Jones [1987] also have work in progress to evaluate tracer properties of the cation lithium and the anion bromide for use in acidic streams. Lithium has previously been used in industrial [Olenik, 1974] and environmental [Gospodaric and Habbic, 1976] water-tracing applications.

In this study, lithium was evaluated against the response of the solutes chloride, sulfate, and sodium. The anion chloride was not the most effective tracer in the Snake River. Kennedy et al. [1984] and Fish [1981] suggested the possibility of sorptive losses of chloride in acidic waters. When compared to the more precisely determined lithium, chloride was essentially conservative. Thus the lack of effectiveness was presumably the result of background concentration being near the level of reliable detection (3 μM) and a tendency for sample contamination at this level by contact with ubiquitous common salt during handling. The simulation analysis indicates a slight retardation (minutes) of sulfate transport. However, for some applications sulfate would be an effective tracer [Bencala et al., 1987]. Chapman [1982, p. 164] successfully treated sodium as conservative in water with acid mine drainage; however, he adds that its “comparison suggests that a slight attenuation (of sodium) might be occurring (within the experimental reach).” In a low pH system the hydrogen ion is a major cation occupying exchange sites on the streambed sediment therefore changes in pH may change the quantity of other cations sorbed on the sediment by a cation exchange mechanism.

Although chloride, sulfate, and sodium are commonly thought to have nominally conservative characteristics, they are more likely to be naturally present in moderate background concentrations. This presence has the practical disadvantage of limiting analytical resolution of the tracer concentration in excess of background concentrations. The possible difficulty with relying on a proportionally large increase in an otherwise trace constituent is that sorption or other chemical processes may temporarily dominate the response when the solute is first introduced into the stream system.

The concept of identifying physical parameters entirely upon the basis of simulations of transient storage was evaluated concurrently with the evaluation of lithium. The simulations of chloride and of a second lithium injection were consistent with the identified parameters. Simulations of sulfate suggested mild retardation and attenuation. Simulations were made in which parameters were adjusted to
use in industries and processes.

When the leachate from the uranium mine in the mountain pool-and-riffle stream is discharged, it can modify the pH of the water, which in turn affects the solubility of uranium. The diagrams show the concentration of sulfate and lithium in the stream over time, indicating the movement and reaction of these elements.

For example, the sulfate concentration increases significantly at certain times of the day, reflecting the dynamics of the hydrological processes. Similarly, the lithium concentration shows fluctuation, which could be attributed to the release of these ions from the mine's discharges.

These simulations provided results distinct from those considered to be 'the correct simulations.'

It remains impractical to consider the study of every stream potentially affected by man's activity. Studies of a given stream are intended first to document specific characteristics of that stream and second to provide general information about the spatial and temporal scales of instream processes. The evaluation of tracers was done for several tracers with comparisons of lithium-based transport simulations to observed concentrations. This approach allows for evaluations of several tracers injected at multiple locations, at different times, and for different time intervals.

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