INTERPRETING SPATIAL PROFILES OF CONCENTRATION IN ACID MINE DRAINAGE STREAMS

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ABSTRACT

Spatial profiles of pH and concentrations of toxic metals in streams affected by acid mine drainage are the result of the interplay of hydrologic and geochemical processes. This paper describes the use of a reactive solute transport model to provide a physically and thermodynamically quantitative interpretation of these profiles. The model combines an advection-dispersion module that includes transient storage with a geochemical speciation module based on MINTEQA2. Input to the model includes stream hydrologic properties derived from tracer-dilution experiments, headwater and lateral inflow concentrations analyzed in field samples, and a thermodynamic database. Simulations reproduced the general steady-state patterns of observed pH and concentrations of aluminum, iron, and sulfate in St. Kevin Gulch, an acid mine drainage stream near Leadville, Colorado.

Key words: Acid mine drainage; reactive transport modeling; geochemical modeling

INTRODUCTION

Acid mine drainage degrades water quality in many of our nation's streams. Effective remediation at these sites requires an understanding of the diverse physical, chemical, and biological processes that control spatial profiles of concentrations of metals and other acid constituents. This paper presents an approach to site characterization that includes tracer-dilution experiments, synoptic sampling, and steady-state reactive transport modeling. Tracer experiments quantify physical transport, and synoptic sampling defines the spatial distribution of constituent concentration in inflow and instream waters. The primary interpretive tool is a reactive solute transport model that characterizes the interplay of transport and chemical reactions that produce the observed spatial profiles of concentration.

SITE AND METHODS

We applied our site characterization methods to a 1497-meter reach of St. Kevin Gulch, a mountain stream receiving acid mine drainage near Leadville, Colorado (figure 1). The stream receives water that flows from a collapsed adit of an abandoned silver and zinc mine contributing metal-rich, acidic inflow in a series of springs that discharge at the base of a mine dump. Pools, riffles, and cascades in this small ($Q < 20$ L/s), shallow stream caused a rapid mixing of inflows. The 1497-meter reach was divided into 10 subreaches (figure 2a). Water samples were collected at many stream sites, both upstream and downstream from eight sampled inflows. Upstream from the acid inflows (0-363 m), streamwater was affected by mine drainage, but loads of metals were relatively small. Between 363 and 484 m, the stream became much more acidic, and pH decreased (figure 2b). Downstream from the acidic inflows, Shingle Mill Gulch entered St. Kevin Gulch (at 501 m). This confluence doubled the discharge (figure 2c) and increased the pH. Additional loading of some acidic constituents from ground-water seepage occurred in the next downstream reach (526-781 m). In the remaining subreaches, additional loading was minimal.

Tracer Injection and Synoptic Sampling

A tracer solution of 7.4 M LiCl was injected into St. Kevin Gulch at a rate of 27 mL/min for 36 hours. Sampling sites and inflow locations are referenced by their distance downstream from the injection. The arrival of the LiCl pulse and the development of a plateau concentration were observed at seven sites, ranging from 26 to 1804 m downstream from the injection (figure 1). During the plateau period, additional samples were collected from these six sites, from seven visible inflows, from St. Kevin Gulch upstream and downstream from each inflow, and from a pit dug in an area of ground-water seepage. Pressure filtration, using 0.1 µm nitrocellulose membrane filters, defined an operational dissolved sample. Analysis of acidified samples for metals was by ICP-AES. Ferrous iron was measured in filtered, unacidified samples using the 2,2'-bipyridine colorimetric method. Filtered, unacidified samples were analyzed for chloride and sulfate by ion chromatography. Specific methods were reported by Kimball and others (1994).

Reactive Transport Equations

Physical transport and mixing was simulated by a module that includes advection-dispersion and transient storage (Bencala and Walters, 1983; Runkel and Broshears, 1991). These processes are described by the following equations:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{\partial}{\partial x}\left(DA\frac{\partial C}{\partial x}\right) + \frac{q_L}{A}(C_L - C) + \alpha(C_S - C)$$

where C = solute concentration in the stream $\{ML^{-3}\}$
t = time $\{T\}$

$$\frac{\partial C_S}{\partial t} = -\alpha \frac{A}{A_S} (C_S - C)$$

Q = volumetric flow rate $\{L^3T^{-1}\}$
A = cross-sectional area of the stream $\{L^2\}$
x = distance $\{L\}$
D = dispersion coefficient $\{L^2T^{-1}\}$
q_L= inflow rate per unit stream length $\{L^3T^{-1}L^{-1}\}$
C_L= solute concentration in lateral inflow $\{ML^{-3}\}$
α = stream-storage exchange coefficient $\{T^{-1}\}$
C_S= solute concentration in the storage zone $\{ML^{-3}\}$
A_S = cross-sectional area of the storage zone $\{L^2\}$

In Kimball and others (1994), empirical rate constants were presented as a means of site characterization. In this manuscript we explore the use of equilibrium thermodynamic concepts in site characterization. Chemical reactions were simulated by a module based on the geochemical speciation model MINTEQA2 (Allison and others, 1991). This module was coupled with the physical transport module by a sequential iteration method (Runkel, 1993). The geochemical module applies equilibrium thermodynamic concepts in calculations of chemical speciation, including sorption reactions and the formation of aqueous complexes and solid species.

RESULTS

Tracer Experiment and Synoptic Sampling

Transient profiles of chloride concentration at two sites are shown in figure 3a. Discharge at these and other sites of transient sampling was calculated by the dilution required to match the measured plateau concentration of the chloride tracer. The downstream increase in discharge was from 3.4 to 14 L/s. Travel time for the conservative tracer through the study reach was about 8 hours. Stream cross-sectional areas were adjusted to reproduce tracer behavior consistent with observed arrival and departure times. The cross-sectional areas of the storage zones and stream-storage exchange coefficients were adjusted to accommodate deviations from traditional advective-dispersive behavior in the observed concentration profiles. A summary of fitted parameters is presented in table 1. The steady state profile of chloride indicates the spatial distribution of dilution by inflows along the study reach (figure 3b). Simulated chloride concentrations are slightly higher than observed chloride concentrations because the synoptic sampling occurred a day before the plateau concentrations were fully developed at downstream sites. The chemical character of inflows is shown in table 2.

Reactive Transport Simulations

Three simulations were conducted to interpret the observed profiles of pH, aluminum, iron, and sulfate. In the first simulation, no solids were specified. In the latter two simulations, iron and aluminum hydroxides or hydroxysulfate and oxyhydroxysulfate solids were permitted to precipitate.

Figure 4 depicts observed and simulated pH and concentrations of aluminum, iron, and sulfate when no solid-phase controls are defined. Simulated concentration profiles reflect loading near the mine dump and dilution by Shingle Mill Gulch, but remain higher than observed profiles at downstream sites. This discrepancy is a clear indication of chemical reactions that remove these constituents from the dissolved phase.

Common controls on metal solubility include the formation of insoluble metal hydroxides. Al and Fe, for example, are known to undergo the following reactions:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$$

Reported formation constants for $Fe(OH)_3$, $K_f = \{H^+\}^3\{Fe^{3+}\}^{-1}$, range from 10^{-8} to 10^{-0} (Langmuir and Whittemore, 1971; Davis and Runnels, 1987), but most values are in the range of 10^{-5} to 10^{-3} (Nordstrom and others, 1990). The formation constant for amorphous $Al(OH)_3$, $K_f = \{H^+\}^3\{Al^{3+}\}^{-1}$, has been reported at $10^{-10.8}$ (Nordstrom and others, 1990); the formation constants of more crystalline forms of $Al(OH)_3$ (gibbsite) range from $10^{-9.35}$ to $10^{-8.11}$ (Nordstrom and others, 1990). Figure 5a shows that the iron profile in the more downstream subreaches can be simulated with an iron hydroxide formation constant of 10^{-3}, which is within the reported range. Simulated iron in the subreaches near the dump are less than observed values, perhaps reflecting occurrence of kinetic limits on chemical precipitation and/or on the aggregation of <0.1μm precipitates in these subreaches. In the downstream subreaches simulated aluminum concentration was higher than observed concentration even when the least soluble solid phase of gibbsite ($K_f = 10^{-8.11}$) was specified (figure 5b). This result may reflect use of an unrepresentatively large value for aluminum concentration in inflow seepage in the subreach between 526 and 781 m, or a different solid phase may control aluminum concentration.

Neither of the simulations shown in figure 5 provides an explanation for the observed decrease in sulfate concentration in the downstream reaches (figure 4d). This decrease may be explained by the formation of aluminum and iron hydroxysulfate or oxyhydroxysulfate solids. Sulfur is a component of streambed sediment in St. Kevin Gulch, where it has been measured at a Fe/S ratio varying from 4.5 to 7.1 (Smith, 1991). This range is comparable to the range in Fe/S ratio in oxyhydroxysulfates of iron identified in acid mine waters by Bigham and others (1990), who described the formation of a poorly crystallized solid (schwertmannite) with the stoichiometry, $Fe_{16}O_{16}(OH)_{12}(SO_4)_2$. Formation of schwertmannite was simulated by specifying the following reaction:

$$16Fe^{3+} + 2SO_4^{2-} + 28H_2O \rightarrow Fe_{16}O_{16}(OH)_{12}(SO_4)_2 + 44H^+$$

No reported values for the formation constant of schwertmannite were available. A formation constant, $K_f = \{H^+\}^{44}\{Fe^{3+}\}^{-16}\{SO_4{}^{2-}\}^{-2} = 10^{-27.33}$, was used and represents a fitted value equal to the ion activity product calculated for average instream concentrations in the downstream half of the study reach.

Nordstrom (1982) described solid phase controls on aluminum concentration in waters of high sulfate concentration and low pH. A variety of aluminum hydroxysulfate minerals may regulate aluminum concentration, including jurbanite [$Al(SO_4)OH$], alunite [$KAl_3(SO_4)_2(OH)_6$], and basaluminite [$Al_4(SO_4)(OH)_{10}$]. Based on solubility diagrams presented by Nordstrom (1982), we selected jurbanite as the most likely solid phase control within the observed range of pH and aluminum and sulfate concentration in St. Kevin Gulch. Nordstrom (1982) cited a solubility product, $K_{sp} = \{Al^{3+}\}\{OH^-\}^3 = 10^{-17.8}$ for jurbanite, which at 10 °C is equivalent to a formation constant of $10^{3.23}$.

Figure 6 presents the results of simulations conducted with schwertmannite specified as the iron solid phase control and jurbanite specified as the solid phase control for aluminum. Most of the observed iron profile is reproduced by the simulation (figure 6a); simulation of smaller iron concentration in the subreaches near the mine dump may be attributable to kinetic limits on precipitation and aggregation. The aluminum (figure 6b) profile was not reproduced unless the formation constant for jurbanite was approximately $10^{4.25}$, which is somewhat higher than the reported value. Even with this less soluble value for jurbanite, the simulated sulfate concentration remained higher than the observed profile (figure 6c).

CONCLUSIONS

We have presented an approach to site characterization in streams affected by acid mine drainage. Because interactive processes control the behavior of acid constituents at these sites, a rigorous definition of site hydrology and spatial patterns of contaminant loading is necessary. A reactive solute transport model is offered as an internally consistent means of integrating our knowledge about a site and for testing hypotheses about physical and chemical processes that determine contaminant profiles.

An application at St. Kevin Gulch, a mountain stream receiving acid mine drainage near Leadville, Colorado, has demonstrated the reactive nature of aluminum, iron, and sulfate in the stream. Observed profiles of these constituents were reproduced by specifying hydroxide, hydroxysulfate, or oxyhydroxysulfate controls on metal solubility. For iron, either iron hydroxide [$Fe(OH)_3$] or schwertmannite [$Fe_{16}O_{16}(OH)_{12}(SO_4)_2$] may serve as solid phase controls. Simulation of lower concentrations of iron in the subreaches of acid loading suggested kinetic limits on precipitation and aggregation. The aluminum profile could not be produced by simulations using the reported range in solubility for $Al(OH)_3$. The aluminum profile could be reproduced only when the formation constant for jurbanite [$Al(SO_4)OH$] was somewhat higher than a reported value. Lack of fit between observed and simulated concentrations of aluminum and sulfate may also be attributable to an unrepresentative value for inflow concentrations in a subreach of major ground-water seepage.

REFERENCES

Allison, J.D., D.S. Brown, and K.J. Novo-Gradac, 1991, MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: Version 3.0 User's Manual, Rep. EPA/600/3-91/021, U.S. Environmental Protection Agency, Washington, D.C.

Bencala, K.E. and R.A. Walters, 1983, Simulation of solute transport in a mountain pool-and-riffle stream: A transient storage model, Water Resources Research, 19(3):718-724.

Bigham, J.M., U. Schwertmann, L. Carlson, and E. Murad, 1990, A poorly crystallized oxyhydroxysulfate of iron formed by bacterial oxidation of Fe(II) in acid mine waters, Geochimica et Cosmochimica Acta 54:2743-2758.

Davis, A. and D.D. Runnels, 1987, Geochemical interactions between acidic tailings fluid and bedrock: Use of the computer model MINTEQ, Applied Geochemistry, 2:231-241.

Kimball, B.A., R.E. Broshears, K.E. Bencala, and D.M. McKnight, 1994, Coupling of hydrologic transport and chemical reactions in a stream affected by acid mine drainage, Environmental Science and Technology, 28:2065-2073.

Langmuir, D. and D.O. Whittemore, 1971, Variations in the stability of precipitated ferric oxyhydroxides, Adv. Chem. Ser., 106:209-234.

Nordstrom, D.K., 1982, The effect of sulfate on aluminum concentrations in natural waters: Some stability relations in the system Al_2O_3-SO_3-H_2O at 298 K, Geochimica et Cosmochimica Acta 46:681-692.

Nordstrom, D.K., L.N. Plummer, D. Langmuir, E. Busenberg, H.M. May, B.F. Jones, and D.L. Parkhurst, 1990, Revised chemical equilibrium data for major water-mineral reactions and their limitations, in Chemical Modeling of Aqueous Systems II, D.C. Melchior and R.L. Bassett, eds., American Chemical Society, Washington D.C., p. 398-413.

Runkel, R.L., 1993, *Development and application of an equilibrium-based simulation model for* reactive transport in small streams, Ph.D. dissertation, Department of Civil, Environmental, and Architectural Engineering, University of Colorado, Boulder, 202 p.

Runkel, R.L. and R.E. Broshears, 1991, One dimensional transport with inflow and storage (OTIS): A solute transport model for small streams, Technical Report 91-01, Center for Advanced Decision Support for Water and Environmental Systems, University of Colorado, Boulder, 85 p.

Smith, K.S., 1991, Factors influencing metal sorption onto iron-rich sediment in acid-mine drainage, Ph.D. dissertation, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, 239 p.

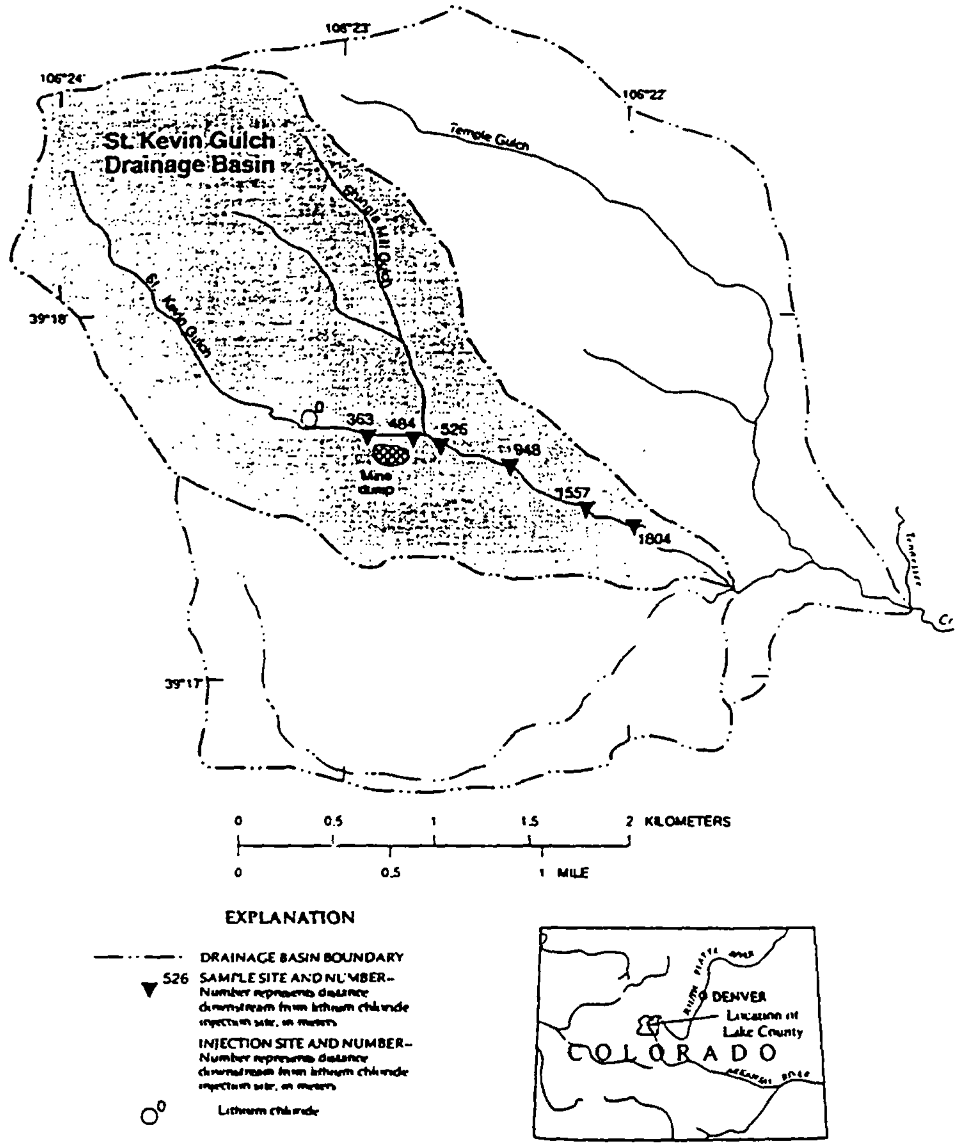

Figure 1. Location of St. Kevin Gulch drainage basin, indicating injection point for LiCl tracer and sampling sites for transient simulation (from Kimball and others, 1994).

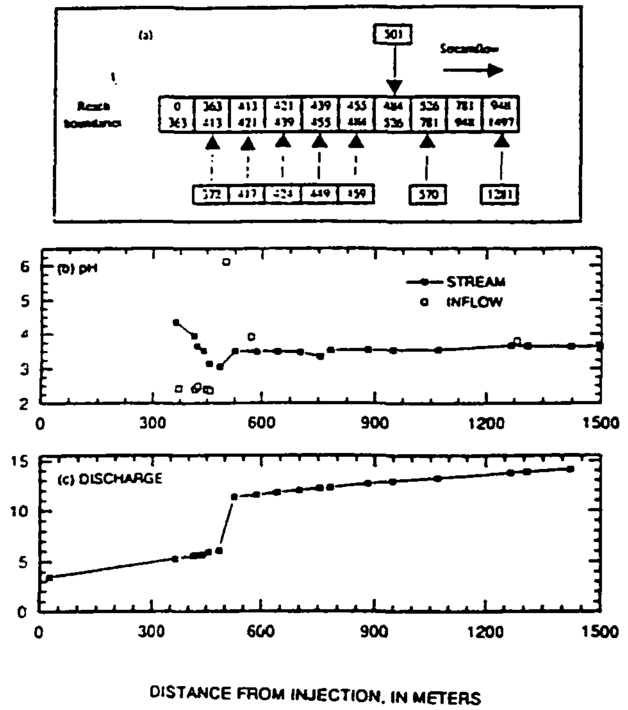

Figure 2. (a) Schematic representation of subreaches used for simulating reactive solute transport at St. Kevin Gulch, indicating inflows corresponding to table 2. Variation of (b) pH and (c) discharge with distance downstream (from Kimball and others, 1994).

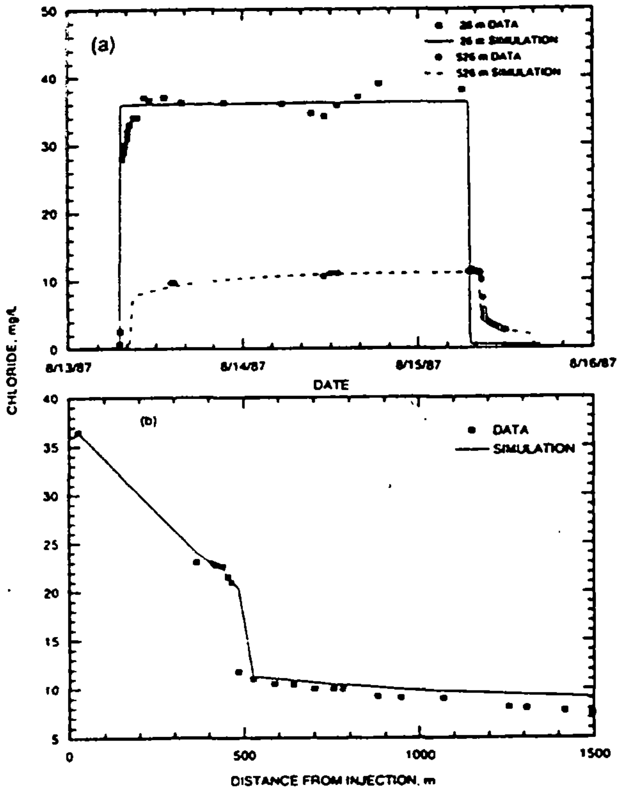

Figure 3. (a) Transient simulation of chloride concentration at 26 and 526 m, indicating the use of simulation curves to determine discharge and residence time. (b) Steady-state simulation of chloride, indicating spatial aspects of discharge (from Kimball and others, 1994).

Figure 4

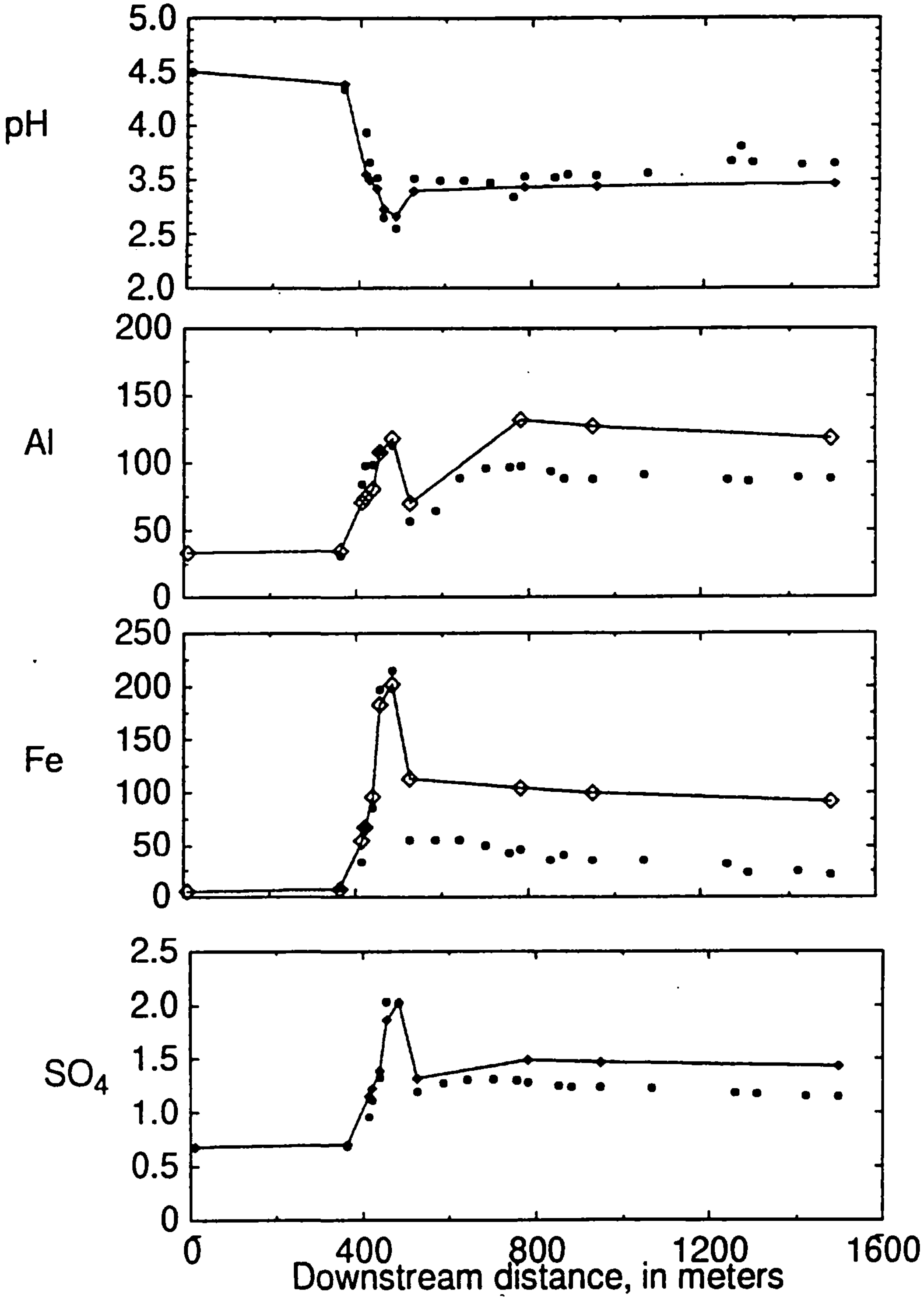

Figure 4. (a) Simulated (lines) and observed (solid circles) pH and concentrations of aluminum (μM/L), iron (μM/L), and sulfate (mM/L) at St. Kevin Gulch with no controlling solids specified.

Figure 5

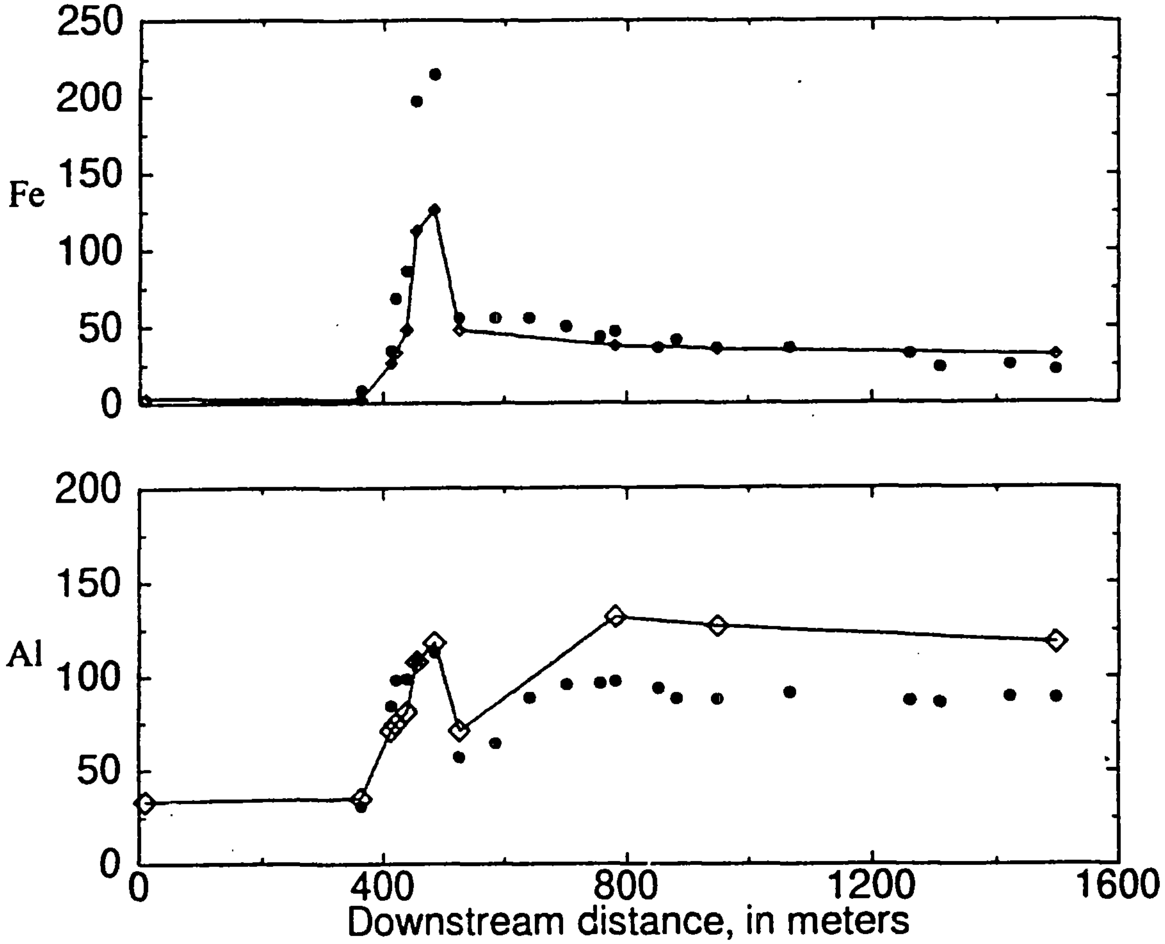

Figure 5. (a) Simulated (lines) and observed (solid circles) pH concentrations of aluminum (μM/L) and iron (μM/L) at St. Kevin Gulch with $K_f = 10^{-3.0}$ for $Fe(OH)_3$ and $K_f = 10^{-8.11}$ for $Al(OH)_3$.

Figure 6

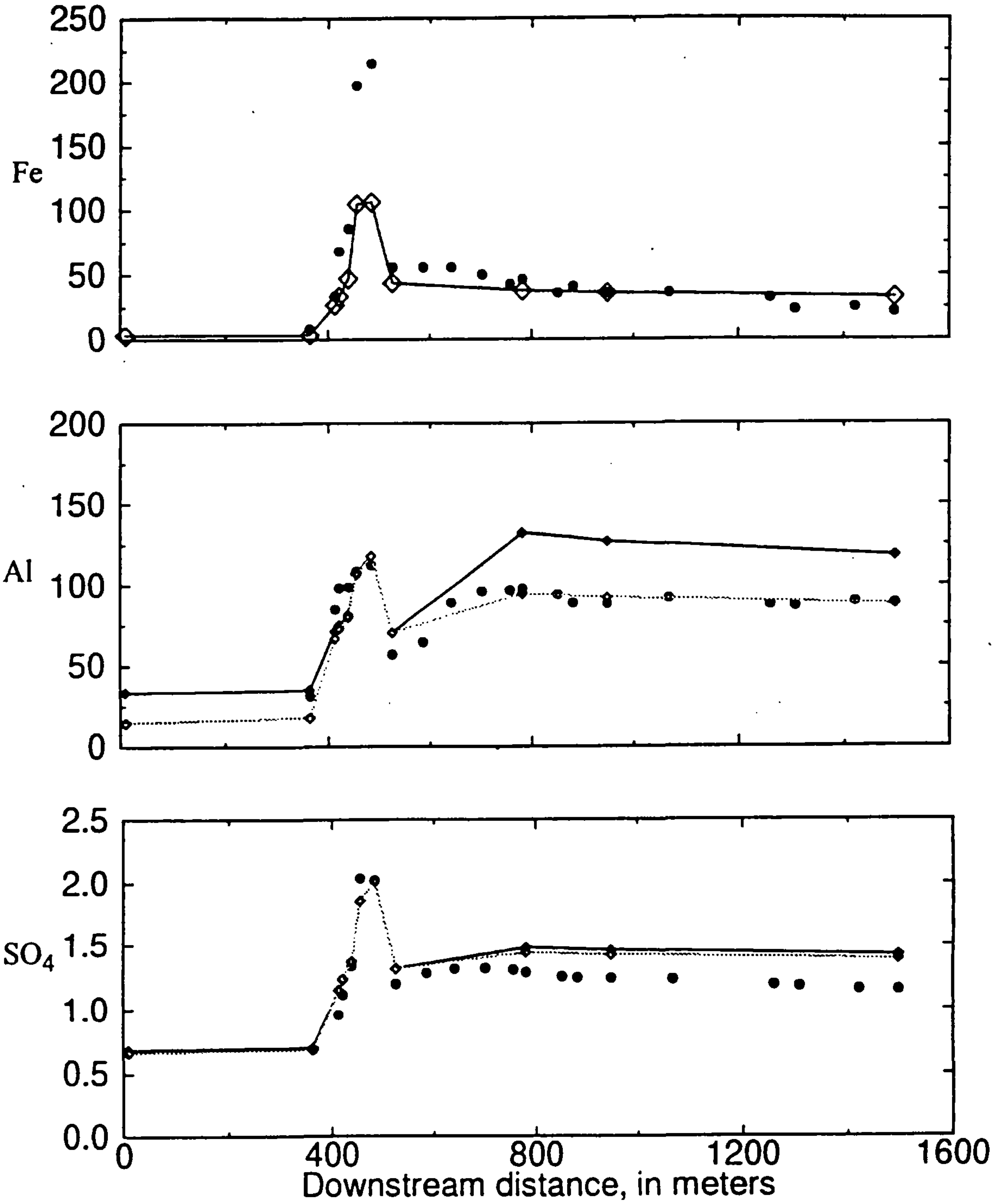

Figure 6. (a) Simulated (lines) and observed (solid circles) concentrations of aluminum (μM/L), iron (μM/L), and sulfate (mM/L) at St. Kevin Gulch with $K_f = 10^{-27.33}$ for schwertmannite and $K_f = 10^{3.23}$ (solid line) or $K_f = 10^{4.25}$ (dashed line) for jurbanite.

Table 1. Fitted parameters for simulation of hydrologic transport at St. Kevin Gulch (after Kimball and others, 1994)

Reach boundaries (m)	Maximum discharge in reach (x 10^3 m^3s^{-1})	Stream cross-sectional area (m^2)	Storage zone cross-sectional area (m^2)	Stream-storage cross-sectional area (x 10^4 m^2)	Dispersion coefficient (m^2s^{-1})
0-363	5.25	0.05	0.10	0.70	0.20
363-413	5.52	.05	.10	.70	.20
413-421	5.57	.05	.10	.70	.20
421-439	5.61	.05	.10	.70	.20
439-455	5.90	.05	.10	.70	.20
455-484	6.07	.05	.10	.70	.20
484-526	11.3	.07	.50	.70	.20
526-781	12.3	.20	.20	.30	.20
781-948	12.9	.20	.20	.30	.20
948-1497	14.1	.20	.20	.30	.20

Table 2. Chemical character of inflows to St. Kevin Gulch (after Kimball and others, 1994).

Reach boundaries (m)	Location of sampled inflow (m)	Lateral inflow of subreach (x 10^6 $m^3s^{-1}m^{-1}$)	pH	Sulfate (mgL^{-1})	Aluminum (mgL^{-1})	Iron (mgL^{-1})
0-363	none	5.40				
363-413	372	5.50	2.42	974	21.1	53.5
413-421	417	6.25	2.40	1050	15.6	86.6
421-439	424	2.22	2.48	1330	14.5	159
439-455	449	18.1	2.40	1190	18.0	114
455-484	459,469[a]	5.86	2.35	993	18.5	68.3
484-526	501	125	6.11	40.1	.19	0.06
526-781	570[b]	3.76	3.91	330	22.7	0.33
781-948	none	3.77				
948-1497	1281	2.17	3.81	96	.60	0.30

[a] Average values for two inflows

[b] Sampled from a shallow pit rather than a visible inflow.