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Reactive solute-transport simulation of pre-mining metal concentrations in mine-impacted catchments: Redwell Basin, Colorado, USA

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ABSTRACT

With the increased importance of water resources in the western United States and many areas worldwide, the remediation of impacts from historical mining becomes ever more important. A possible process of making decisions about remediation for a catchment might include identification of principal sources of metals in the catchment, classification of the sources as natural or anthropogenic, and simulations to evaluate different options for removal of anthropogenic sources. The application of this process is based on understanding the pre-mining conditions in the catchment, so that remediation goals appropriately correct for the impacts of mining. A field experiment in Redwell Basin, Colorado, provided a setting to demonstrate this process and to evaluate pre-mining concentrations through reactive solute-transport modeling. The field experiment provided spatially detailed stream and inflow samples that were the basis for model calibration. Only two inflows along the study reach were affected by mining or mine exploration. To simulate pre-mining conditions, these inflows were removed from the model calibration; the result was a simulation of the stream with all the non-mining inputs. At a point downstream from the two mining inflows, the simulated pre-mining pH would have been 5.1, up from the measured 3.8. At the higher pH, the streambed likely would have been coated with Al precipitate. Simulated pre-mining Zn and Cu would have been 1300 μg/L and 18 μg/L, lower than the measured concentrations of 3340 and 93 μg/L. Despite these changes, the pre-mining conditions would not have met aquatic-life standards.

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1. Introduction

With the increased importance of water resources in the western United States and many areas worldwide, the remediation of impacts from historical mining becomes ever more important. Recent studies of the U.S. Geological Survey (Nimick et al., 2004; Church et al., 2007) have illustrated the kinds of geologic, hydrologic, and biologic information that can be used to make science-based decisions for remediation. These studies suggest a possible process of making decisions about the remediation that includes three important steps (Kimball et al., 2006a). First, all the sources of metals in the catchment should be quantified to enable a ranking in terms of their impact on the catchment. Next, those sources should be identified as natural or anthropogenic to put focus only on anthropogenic sources. Finally, an adequate combination of anthropogenic sources must be treated in some way to reduce metal loading and achieve remediation goals. However, the application of this process is based on knowledge of the pre-mining conditions in the catchment, so that remediation goals do not over- or under-correct for the impacts of mining.

These three steps have been illustrated by recent studies. An approach to quantify metal loads affecting catchment streams has been suggested by Kimball et al. (2002, 2007a,b). This approach relies on field experimentation combining a tracer-dilution study to define the hydrologic context and synoptic-sampling study to understand metal sources and the spatial variability of the in-stream profiles. This mass-loading approach results in a ranking of sources in terms of their impact on stream-water quality. Evaluating natural versus anthropogenic sources of metals in a catchment was the focus of a recent study in the Animas River basin (Mast et al., 2007). By sampling sources over a large area, Mast et al. used multivariate techniques to classify them between mined and un-mined drainage, and further distinguished the un-mined sources according to the type of alteration that affected the drainage. Assessing remediation options has been developed as a method using reactive solute-transport modeling by Runkel and Kimball (2002). Given the choices for remediation, the resulting in-stream concentrations can be simulated for each of those choices. This, of course, could provide a cost-saving option for making decisions.

But a key to making those decisions is an understanding of pre-mining conditions in a catchment. Many approaches have been suggested for determining pre-mining conditions. Furniss and Hinman (1998) proposed that natural ferricrete may be a key to

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understanding acidic pre-mining drainage (Nimick et al., 2009). Miller and McHugh (1994) proposed that natural analog catchments might provide adequate assessment for pre-mining conditions. Several other methods have been reviewed by Alpers and Nordstrom (2000). A modeling approach has been suggested by Runkel et al. (2007) that combines field experimentation, the classification of anthropogenic sources, and simulation of pre-mining concentrations by "removing" the mining impacts.

This study presents a detailed field experiment in Redwell Basin, an alpine catchment in central Colorado, USA that has been affected by metals from natural and anthropogenic sources. The basin presents a unique setting where limited mining is combined with un-mined mineral deposits so that mining impacts can be easily identified. Pre-mining concentrations can be evaluated by simulating the removal of these impacts through reactive solute-transport modeling that simulates the effects of geochemical reactions in the context of hydrologic transport.

1.1. Study area

Because of a unique tectonic setting and the combination of mined and un-mined sources of metals to the stream, Redwell Basin, in south, central Colorado, USA provides an example of how geochemical reactions can be understood in this important hydrologic context (Fig. 1). The Redwell Basin is a small, high-gradient catchment and originates at an elevation of over 3350 m. The streambed mostly contains cobble and boulder bed materials along most of the study reach. The stream flows in a hanging glacial valley, and then it cascades from the hanging valley to its confluence with Oh-Be-Joyful Creek.

Redwell Basin contains porphyry-style molybdenum mineralization at a depth of about 750 m below land surface, and near-surface polymetallic vein mineralization. Sulfide minerals in the latter consist primarily of pyrite, galena, and sphalerite. The porphyry systems have been delineated by drilling (Thomas and Galey, 1982). The vein systems have been mined historically for Ag, Cu, Pb, and Zn (Berger et al., 2001) but the mines are inactive now. Overall, the basin is comprised of a thick package of Cretaceous to Tertiary sedimentary rocks of marine (the Mancos Shale), marginal marine, and fluviolacustrine origins (the Mesa Verde, Ohio Creek, and Wasatch Formations) that were intruded by molybdenum-bearing porphyritic granite stocks about 16–18 million years ago. The sedimentary sequence consists of silty sandstone, sandy limestone, and carbonaceous shale overlain by shale, thick bedded and massive sandstone, coal, and carbonaceous shale (Gaskill et al., 1967). Intrusive activity associated with the porphyritic stocks metamorphosed the sedimentary units up to 450 m

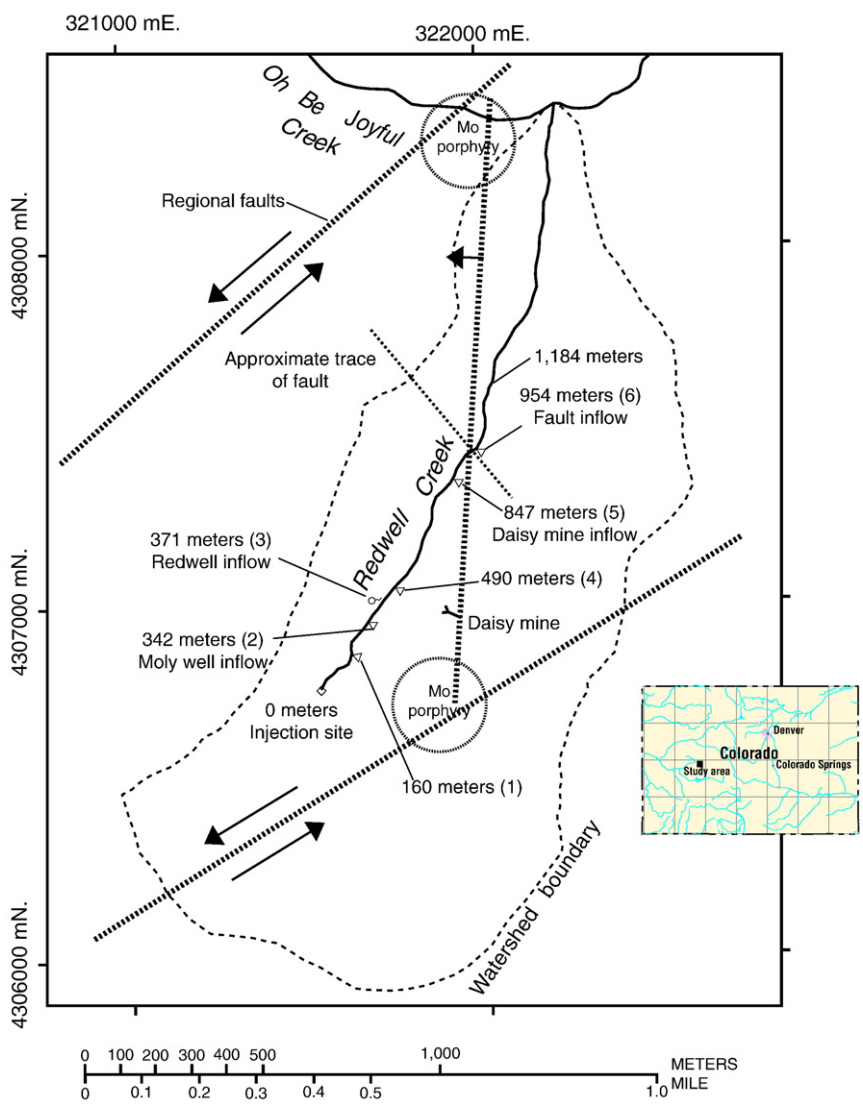

Fig. 1. Location of Redwell Basin study area indicating the injection reach, location of important inflows, generalized fault system, and other important features.

outward (Dowsett et al., 1981). Within the basin the sedimentary rocks vary from albite-epidote hornfels facies to hornblende hornfels facies.

In the upper part of Redwell Basin, a rhyolitic breccia pipe crops out. Gaskill et al. (1967) mapped the pipe as felsite and describe it as altered quartz and feldspar rock rich in pyrite. Subsequent drilling has delineated a subsurface molybdenum deposit. Stockwork molybdenum mineralization is centered around porphyritic stocks (the Mt. Emmons and Redwell deposits), which are believed to be connected at depth. In Redwell Basin, one stock underlies the rhyolitic breccia pipe that formed by the release of magmatic gases and fluids (Sharp, 1977). Geological and geochemical studies of the Mt. Emmons/Redwell Basin area have suggested that the deposit is of the Climax type, which is characterized by highly evolved granite intrusions enriched in trace elements, including Ba, Cs, F, Li, Mo, Nb, Sn, Ta, Ti, Th, U, W, Zr and the light rare earth elements. Outward from the stocks, hydrothermal fluid flowed through principal structures and resulted in base- and precious-metal vein-type mineralization. Hydrothermal alteration, also centered around the stocks, consists of a potassic core, followed by a phyllic zone, and a propylitic zone (Thomas and Galey, 1982).

North-east and north-west trending faults are the dominant structures within the basin (Fig. 1). The intersection of these faults is believed to have localized the Redwell breccia pipe (Sharp, 1977, and re-interpreted by B. Berger, U.S. Geological Survey, written commun., 2001). Base-metal mines in the vicinity exploited sulfide mineralization along these prominent structures. The Daisy Mine, located on the south eastern side of Redwell Basin, occurs along the Daisy fault and contained abundant sphalerite, pyrite, argentiferous galena, chalcopyrite, and bornite (Sharp, 1977). Although presently abandoned, water drains from some of the Daisy lower workings. A natural, ferricrete-depositing spring, the Red Well, also contributes acidic, metal-rich water to the stream in Redwell Basin. Carbon in the ferricrete deposits has been dated as old as 2800 years before the present (Fall, 1997).

1.2. Previous studies

Background on methods for the tracer-injection and synoptic-sampling aspects of this study has been reported for many hydrologic settings affected by acid-rock and acid-mine drainage; the approach has been used to quantify loading to many different streams (Walton-Day et al., 2002; Kimball et al., 2002, 2003; Nimick et al., 2004; Church et al., 2007). Runkel et al. (2007) demonstrated how this approach also can be applied to the question of pre-mining concentrations. This study applies the approach of Runkel et al. to a setting where the identification of mine-related sources is straightforward and the results also indicate potential remediation options. This purpose is supported by a preliminary summary of this field work (Verplanck et al., 2004; Wanty et al., 2004). Wanty et al. (2004) presented an evaluation of natural and anthropogenic sources of metals to Redwell Creek. Their study apportioned inflows to the two kinds of sources by a careful evaluation of sampled inflows in terms of the geology of the catchment.

2. Methods

2.1. Field-scale experiment

Tracer-injection methods have been applied to mine drainage studies as part of the U.S. Geological Survey Toxic Substances Hydrology Program to investigate metal loadings (Kimball et al., 2002, 2004, 2007b). Synoptic sampling is the name given to a spatially detailed sampling that ideally would occur at one instant in time, but practically occurs over a few hours. This approach gives a spatially intensive "snapshot" of chemistry and discharge to quantify in-stream loads. The approach includes a tracer-injection study to quantify discharge and other hydrologic characteristics of the stream, and synoptic sampling to provide a detailed chemical characterization of the stream and inflows to the stream along the study reach. Combined discharge and chemical data provide a profile of mass loading along the study reach, allowing a comparison among metal sources in the catchment. Because a conservative tracer is diluted by any inflow to the stream between each pair of stream sites, this method also can address the quantification of ground-water inflow to a stream.

The tracer-injection study began with a careful evaluation of all visible inflows to the study reach. This was accomplished by walking the entire study reach from the selected injection site to the confluence with Oh-Be-Joyful Creek (Fig. 1). Sampling sites included the visible inflows, stream sites that were upstream and downstream from visible inflows, and other stream locations downstream from where there was likely ground-water inflow. All sites are referenced by their measured distance along the study reach.

A continuously injected chemical tracer provides a way to measure discharge that includes the hyporheic flow of the stream, because the tracer follows the water as it moves in and out of the streambed and areas of transient storage (Bencala and Walters, 1983). During base-flow conditions, tracer dilution allows the detection of relatively small and large increases in streamflow. Once the tracer reaches a steady concentration at each point along the stream, called the plateau condition, discharge can be calculated at any point. Discharge of inflows is calculated as the difference in discharge of stream samples upstream and downstream from the inflow. Thus, that discharge includes all surface- and ground-water inflows within that stream segment (Kimball et al., 2002). To divide the total inflow into surface- and ground-water components would require a secondary discharge measurement of the inflow, which was not done in this study. During the tracer plateau, numerous samples are collected along the stream to provide a synoptic view of the variability of stream chemistry (Bencala and McKnight, 1987). Each synoptic stream sample has a measured discharge because of the tracer concentration it contains, and each inflow has an associated discharge calculated as the difference in discharge between surrounding stream sites.

Lithium chloride was selected for the injection solution because both high and low pH conditions would be encountered along the study reach. The injection began at 13:00 h (MDT) on 8/28/01 and continued until 15:10 h on 8/29/01. The injectate solution had a Li concentration of 27,500 mg/L and a Cl concentration of 141,000 mg/L (essentially equal molar concentrations); the injection rate was 0.00396 L/s. Precision metering pumps were used to inject the tracer, and a Campbell CR-10 data logger controlled the pumps by counting pump revolutions and adjusting the voltage to the pumps to maintain a constant number of revolutions over each two-minute period. This careful control assured that any variations of tracer concentration downstream from the injection resulted from hydrologic change and not from pump variation.

Concentrations of Li in stream environments are typically low, with background concentrations at or near lower detection limits. Spatial variability in background Li concentrations is low, such that background concentrations are nominally uniform. Given the assumption of uniform background concentrations, stream discharge at any location downstream from the injection is given by:

$$Q_D = Q_{INJ} C_{INJ} / (C_D - C_B) \quad (1)$$

where

Q_D	is stream discharge at the downstream site, D, in L/s,
Q_{INJ}	is the injection rate of the pump, in L/s,
C_{INJ}	is the injectate concentration, in mg/L,
C_D	is the tracer concentration at plateau at site D, in mg/L, and
C_B	is the naturally occurring background concentration, in mg/L.

Given the calculated discharge, Q_D, it is possible to use that discharge as a starting point and then use a second conservative tracer for calculations on downstream. Eq. (2) gives the calculation to find

discharge at a site downstream from an inflow, given the discharge upstream from the inflow. For stream segments with no sampled inflow concentration, the general background concentration of the tracer could be used.

$$Q_D = Q_U(C_U - C_L) / (C_D - C_L) \quad (2)$$

where

Q_D is stream discharge at the site, D, downstream from the inflow, in L/s,
Q_U is the discharge calculated for the upstream site, U, in L/s,
C_U is the tracer concentration at U, in mg/L,
C_L is the tracer concentration in the inflow, L, in mg/L, and
C_D is the tracer concentration at the downstream site, D, in mg/L.

Values of C_L are measured for sampled inflows and the value of C_B for Eq. (1) might also come from the sampled inflow concentrations.

In the analysis of this experiment, Cl was used initially as the conservative tracer in the upper part of the stream from 0 to 366 m because the pH of the stream was greater than 7.0; discharge was calculated using Cl concentrations in Eq. (1). Even at the first site downstream from the salt injection, where the Li and Cl concentrations were the highest (Fig. 2), some of the Li had been lost with respect to Cl because of sorption of Li to the streambed at the relatively high pH. The mole ratio of Li to Cl continued to decrease downstream to 366 m because of the loss of Li to the streambed. Starting at 366 m the pH changed abruptly to 4.35 so that Li became the conservative tracer. From that point to 865 m, the mole ratio of Li to Cl increased because Cl, rather than Li, was sorbed to the streambed precipitates. The calculated discharge at 366 m was used as a starting point for calculations using Li in Eq. (2) for each subsequent stream site. From 943 m to 2160 m, the tracer had not reached a plateau condition, and the observed dilution of SO_4 was used to calculate the discharge using Eq. (2).

The presence of Fe and Al colloids in acidic, metal-rich drainage complicates the definition of dissolved metal concentrations (Morel and Gschwend, 1987; Moran and Moore, 1989; Kimball et al., 1995). Two operationally-defined concentrations were used in this study for the synoptic stream samples. A 10,000 Dalton molecular weight membrane was used to obtain a "dissolved" concentration, referred to as the filtered concentration throughout the discussion. This is not a legally defined dissolved concentration (Horowitz et al., 1992), but in the presence of a continuum of colloid sizes, it is much closer to a truly dissolved concentration than a 0.45-µm filtrate. Upon acidification, an unfiltered concentration provided a total-recoverable metal concentration. Colloidal metal concentrations were defined as the difference between the total-recoverable and the 10,000-Dalton filtered metal concentration, similar to the definition of Kimball et al. (1995), although they used a different ultrafiltration membrane size. All metal concentrations were determined by inductively coupled plasma-atomic emission spectrometry or mass spectrometry in a Denver, USGS laboratory (Lamothe et al., 2002).

For quality assurance, samples were evaluated for charge balance, and all samples were within 10%; all but a few samples were within 5%. Analytical precision was determined by repeatedly analyzing reference samples that were collected during the synoptic sampling. These reference samples covered a wide range of concentration, and precision typically varied from greater than 10% at concentrations near 1 µg/L to less than 3% at concentrations near 100 µg/L. This method has been described by Kimball et al. (2007a). Equipment and procedure blanks were analyzed and no contamination was observed. Anion concentrations were determined from 0.45-µm filtered samples using ion chromatography in the Utah Water Science Center laboratory (Kimball et al., 1999). The FeII/FeIII ratio in the ultrafiltrate sample, which was used in the Fe speciation calculations, was fixed in the field by adding strong HCl. The FeII and total Fe concentrations were subsequently measured colorimetrically in the Utah Water Science Center lab, providing the fraction of dissolved FeII (To et al., 1998). For the model input, FeII was set equal to the fraction of FeII from the colorimetric determination multiplied by the filtered ICPAES Fe concentration. FeIII was set equal to the remaining filtered Fe from ICPAES. Total alkalinity was determined by titration in the Utah Water Science Center lab. Temperature, pH, and specific conductance were determined in the field.

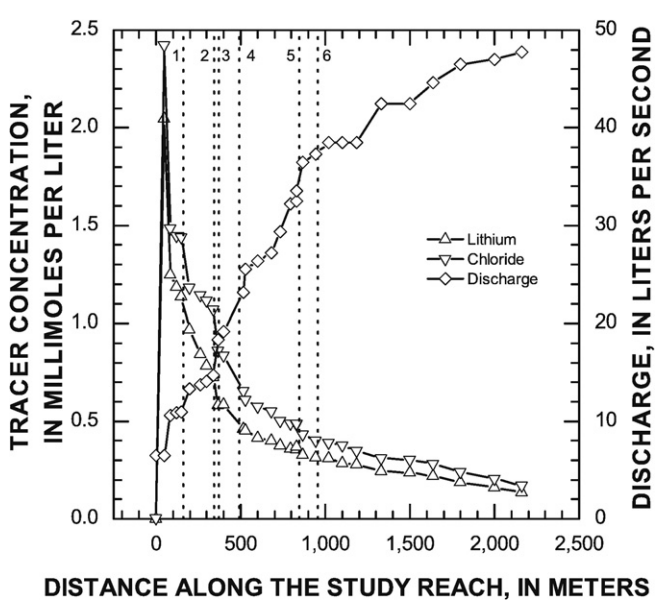

Fig. 2. Variation of lithium and chloride concentrations and calculated discharge with distance along the study reach, Redwell Creek, Colorado, August 2001. The numbered vertical lines indicate important inflow locations: (1) breccia inflow, (2) "Moly Well" inflow, (3) Redwell Spring, (4) talus inflow, (5) Daisy Mine inflow, and (6) fault inflow.

2.2. Reactive solute-transport modeling

Reactive solute-transport modeling for this analysis used OTEQ, a solute-transport model that couples one-dimensional transport with equilibrium chemistry (Runkel et al., 1996a,b, 1999; Runkel, 2009). The resultant model accounts for a variety of physical and chemical processes, including advection, dispersion, transient storage, transport and deposition of water-borne solid phases, acid-base reactions, complexation, precipitation–dissolution, and sorption. Consideration of these processes provides a general modeling framework for the simulation of trace–metal fate and transport.

The purpose of using OTEQ with tracer-injection and synoptic-sampling data from the field experiment in Redwell Basin was to calculate plausible pre-mining concentrations in the stream. The calculation also yields one of the possible remediation options. The approach from Runkel et al. (2007) involves a simulation of existing conditions based on a field experiment. This is followed by making choices as to which sources can be attributed to mining and eliminating those sources. Simulation of in-stream chemistry after selected mining sources are removed indicates possible effects of remediation on the catchment.

Application of the solute-transport model was limited to the reach from 263 to 1184 m, which included the mine-related inflows and the majority of natural inflows. The model reaches are detailed in Table 1, which gives the increase in stream discharge for each reach. Inflow concentrations for most reaches were set equal to the dissolved concentrations from the sampled inflows (Fig. 3). The site at 1184 m will serve as a selected reference point for demonstrating pre-mining concentrations and remediation effects. The first step in evaluating pre-mining conditions is to characterize and quantify the hydrologic

Table 1
Model reaches including discharge and inflow locations.

Reach and distance (meters)	Discharge (liters per second)		Locations of observed inflows	Inflow assignment
	Top of reach	Within reach		
1:263–297	13.76	0.36	266-LBI	266-LBI
2:297–339	14.12	.56	314-RBI	314-RBI
3:339–366	14.68	3.65	342-"Moly Well"	[a]342-"Moly Well"
4:366–400	18.33	.86	370-LBI, 371-Redwell Spring	[b]371-Redwell Spring
5:400–516	19.19	3.96	470-LBI, 490-RBI	490-RBI
6:516–530	23.15	2.39	521-RBI	521-RBI
7:530–600	25.54	.82	537-RBI, 558-RBI	537-RBI
8:600–658	26.36	.87	No sampled inflows	537-RBI
9:658–681	27.23	2.17	662-LBI	662-LBI
10:681–735	29.4	2.81	689-RBI, 699-RBI	699-RBI
11:735–795	32.21	.28	774-RBI	774-RBI
12:795–830	32.49	1.11	No sampled inflows	699-RBI
13:830–865	33.6	2.9	847-Daisy Mine	847-Daisy Mine
14:865–943	36.5	.79	870-RBI, 881-LBI	881-LBI
15:943–1022	37.29	1.22	954-LBI	954-LBI
16:1022–1100	38.51	0	1029-RBI	NC with no increase in streamflow
17:1100–1184	38.51	0	1130-RBI	NC with no increase in streamflow
18:1184–1332	38.51	3.96	1192-RBI, 1221-RBI	1221-RBI

[LBI, left-bank inflow; RBI, right-bank inflow; NC, no chemistry.]
[a] With a reduced concentrations for Al, Cd, Cu, Fe, Mn, Pb, SO4, and Zn, see text.
[b] With a reduced concentration for Fe, see main text.

and geochemical processes that affect metal concentrations under existing conditions by calibrating the reactive solute-transport model to mechanistically describe the relevant processes. The calibrated model can then be modified to remove mining impacts and estimate pre-mining water quality. The OTEQ model couples the OTIS solute transport model (Runkel, 1998) with a chemical equilibrium submodel. The equilibrium submodel is based on MINTEQ (Allison et al., 1991), a model that calculates the distribution of chemical species that exist within a batch reactor at equilibrium. Governing equations are formulated in terms of chemical components, where the total component concentration is the sum of all dissolved, precipitated, and sorbed species. Precipitated and sorbed species may reside within the water column or on the streambed. Total component concentrations are partitioned between dissolved, precipitated, and sorbed phases based on equilibrium submodel calculations for each model segment. Components used in the Redwell application include Al, CO_3 (total inorganic carbon), Ca, Cd, Cu, Fe(II), Fe(III), Mg, Mn, Pb, SO_4, TOTH (total excess hydrogen), and Zn. Development of a calibrated model of existing conditions requires (1) quantification of hydrologic parameters, (2) specification of geochemical reactions and equilibrium constants, and (3) assignment of boundary conditions and inflow chemistry.

2.2.1. Quantification of hydrologic parameters

The parameters needed in OTEQ to specify hydrologic transport are streamflow and main-channel cross-sectional area. Spatial variation in these hydrologic parameters was considered by breaking the study reach into model reaches based on changes in streamflow (Table 1). Estimates of streamflow were developed using the tracer-dilution method (Kilpatrick and Cobb, 1985) and the observed dilution of the Cl and Li tracers. Tracer breakthough curves at 339, 830, and 2160 m were used to estimate conservative transport parameters (channel cross-sectional area, dispersion, and transient storage) for each model reach (Runkel, 1998).

2.2.2. Specification of geochemical reactions and equilibrium constants

In other studies of streams affected by mine drainage, comparisons of the equilibrium calculations for sorption and precipitation reactions in OTEQ to the field data have shown that these geochemical reactions in the stream are sufficiently fast to be considered at equilibrium (Broshears et al., 1996; Runkel and Kimball, 2002). The same comparison applies to this study; are the chemical equilibrium calculations, in the context of hydrologic transport in OTEQ, a good description of the field data? Unless noted otherwise, equilibrium constants for all acid/base, complexation, precipitation, and sorption reactions were set using default values from the equilibrium submodel. These default values are based on a revised version of the MINTEQ database (Dzombak and Morel, 1990; Allison et al., 1991) that is consistent with the WATEQ4F database distributed with PHREEQC (Parkhurst and Appelo, 1999). Equilibrium constants and activity coefficients were adjusted for the effects of temperature (10.5 °C) and ionic strength (0.002 M) within the equilibrium submodel. Precipitation reactions for Al and Fe(III) were defined using microcrystalline gibbsite [$Al(OH)_3$, default log $k = -8.77$] and ferrihydrite [$Fe(OH)_3$, default log $k = -4.89$] as the solid phases.

Sorption of Ca, Cd, Cu, SO_4, TOTH, Pb, and Zn to freshly precipitated Fe oxides was modeled using a surface complexation approach and the database of Dzombak and Morel (1990); see also Allison et al. (1991); Runkel et al. (1999). The mass of sorbent within each model segment was based on the amount of precipitated Fe(III) within the water column, as determined by the equilibrium submodel. Precipitated Fe(III) on the streambed was assumed to be saturated with respect to sorbed species and is therefore not a sink in the steady-state analysis presented here. Sorption parameters (i.e., specific surface area, sorbent molecular weight, and low affinity site density) were set using the best estimates of Dzombak and Morel (1990). High affinity site density was set equal to the upper value reported by Dzombak and Morel (1990), reflecting the high sorptive capacity of freshly precipitated Fe oxides (Runkel et al., 1999).

2.2.3. Assignment of boundary conditions and inflow chemistry

A key part of the calibration process is to specify the component concentrations at the upstream boundary (263 m) of the modeled system and within inflow waters entering each reach. Upstream boundary concentrations for most components were set using the total recoverable concentrations observed from the synoptic sampling at 263 m; boundary concentrations for Al, Fe, and Pb were set using total recoverable concentrations from 297 m. Most reaches include one or more sampled inflows that were used to set component inflow concentrations (Table 1). When more than one inflow was available for a given reach, the largest observed inflow was generally used. Component inflow concentrations for reaches without observed inflows were set using inflow data from a nearby location.

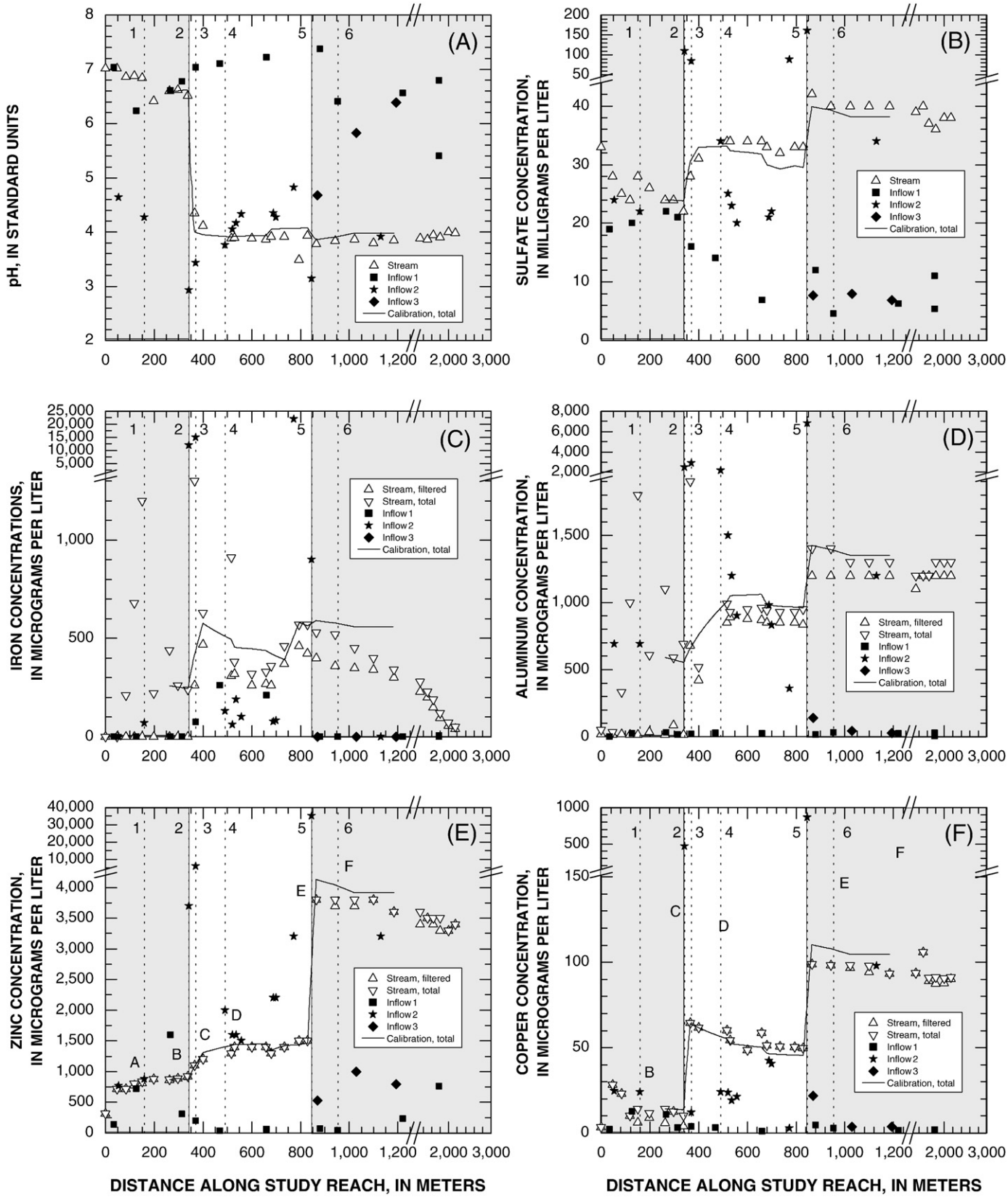

Fig. 3. Variation of observed values of (A) pH, and concentrations of (B) sulfate, (C) iron, (D) aluminum, (E) zinc, and (F) copper with distance along the study reach, Redwell Basin, August 2001. Model calibrations also are indicated for total concentrations because filtered and total concentrations are essentially the same at the low pH of the stream in Redwell Basin. Alternating shaded areas indicate locations of stream groups classified by multivariate cluster analysis. The numbered vertical lines indicate important inflow locations: (1) breccia inflow, (2) "Moly Well" inflow, (3) Redwell Spring, (4) talus inflow, (5) Daisy Mine inflow, and (6) fault inflow.

Inflow concentrations for most reaches were set equal to the dissolved concentrations from the sampled inflows. Two exceptions include the reach from 339 m to 366 m, and the reach from 366 m to 400 m. In the first reach, use of dissolved inflow concentrations from the Moly Well (342 m) resulted in an over prediction of the stream concentration at 366 m for several components (Al, Cd, Cu, Fe, Mn, Pb, SO_4, and Zn). Inflow concentrations for these components were therefore reduced so that the observed stream concentrations at 366 m were reproduced. Similarly, for the second reach, use of the dissolved Fe inflow concentration from the Redwell (371 m) resulted in an over prediction of the stream Fe concentration at 400 m; the Fe inflow concentration for reach 4 was therefore reduced to reproduce the observed stream concentration. These reductions in inflow concentrations reflect the fact that these two reaches are influenced by additional inflow that is more dilute than the selected inflows (e.g. the dilute inflow at 370 m)."

2.2.4. Simulation of pre-mining conditions

Pre-mining conditions were modeled by removing both the discharge and the chemistry for those inflows identified as mine-related. All the other inflows remained in the simulation representing the drainage from weathering natural altered and unaltered rock. For the example of Redwell Basin, this pre-mining scenario also represented a possible example of a remediation option.

Table 2
Descriptions of synoptic sampling sites, including multivariate classification, and field and tracer data, Redwell basin, Colorado, August 29, 2001.

Distance, meters	Source	Site description	Group	Sample time	pH, standard units	Lithium, μg/L	Chloride, mg/L	Discharge, L/s
0	S	T0 site — injection site	1	14:15	7.01	<.01	0.16	6.49
34	LBI	From small pond	1	14:10	7.03	<.01	0.18	.40
48	S	Upstream from right and left bank inflows	1	14:05	7.01	14,200	85.9	6.49
53	RBI	Inflow draining breccia area	2	14:00	4.64	2.6	0.19	4.92
84	S	Upstream from right and left bank dry inflows	1	13:55	6.86	8670	52.6	10.6
119	S	Upstream from right bank inflow	1	13:50	6.88	8230	51.3	10.9
126	RBI	Draining small outcrop in grass	1	13:48	6.23	2.7	0.41	.20
151	S	Upstream from right bank inflow with iron stain	1	13:45	6.84	7880	51.0	10.9
160	RBI	Draining breccia outcrop (1)	2	13:40	4.27	2.9	0.22	3.74
199	S	Downstream from pond after mixing of breccia inflow	1	13:35	6.42	6720	41.9	13.3
263	S	Along cascades above left bank	1	13:25	6.60	5850	40.6	13.8
266	LBI	Small puddle in grass	1	13:25	6.61	5850	41.9	.77
297	S	At base of waterfall	1	13:15	6.62	5440	39.6	14.1
314	RBI	From cascade near pit	1	13:10	6.77	1	0.36	1.11
339	S	T1 site — upstream from Moly well inflow	1	12:50	6.51	5040	38.0	14.7
342	RBI	Drainage from Moly well inflow (2)	2	12:55	2.93	3.4	0.69	3.64
366	S	Stream downstream from Moly Well inflow	2	12:48	4.35	4030	30.5	18.3
370	LBI	Small spring next to Redwell	1	12:40	7.03	3.3	0.23	<.1
371	LBI	Redwell natural spring (3)	2	12:38	3.43	5.4	0.43	.86
400	S	Downstream from Redwell spring	2	12:30	4.12	4070	29.7	19.2
470	LBI	Pond in marsh	1	12:20	7.10	2.8	0.14	3.09
490	RBI	Draining talus slope (4)	2	12:18	3.76	3.5	0.25	3.09
516	S	Downstream from marsh area	2	12:14	3.88	3200	23.2	23.1
521	RBI	Small stream after marsh	2	12:12	4.05	2.9	0.24	2.77
530	S	Between right bank inflows	2	12:10	3.89	3160	21.7	25.5
537	RBI	Inflow with iron stain	2	12:05	4.16	2.9	0.26	.85
558	RBI	Above road to Redwell spring	2	12:00	4.33	2.3	0.25	.85
600	S	Downstream from inflows from rock glacier	2	11:55	3.88	2890	20.4	26.4
662	LBI	Draining our of area with small pines	1	11:32	7.22	1.4	0.16	1.24
681	S	Downstream from left bank at plugged drill hole	2	11:30	3.91	2780	19.5	29.4
689	RBI	Near drill hole	2	11:25	4.35	2.6	0.22	1.99
699	RBI	From marsh with sedges	2	11:15	4.27	2.8	0.23	1.99
735	S	Downstream from two right bank inflows at cascade	2	11:10	3.91	2600	17.8	32.2
774	RBI	Seep from mossy area	2	11:00	4.82	9.5	0.44	.28
795	S	At Mesa Verde Formation upstream from prospect pit	2	11:00	3.49	2490	17.3	32.5
830	S	T2 site — downstream from prospect pit	2	10:50	3.93	2480	17.1	33.5
830	S	T2 site — replicate	2	10:55	3.94	2570	17.3	33.5
847	RBI	Daisy Mine inflow (5)	2	10:45	3.14	18	0.83	2.98
865	S	Downstream from Daisy Mine inflow	3	10:30	3.78	2280	15.4	36.5
870	RBI	Small inflow in muddy area	3	10:35	4.68	1.6	0.27	1.33
881	LBI	Drainage among pines	1	10:20	7.37	1.2	0.17	1.33
943	S	Downstream from right bank Mesa Verde Formation ledge	3	10:15	3.84	2170	14.3	37.3
954	LBI	Drainage along North–South fault zone (6)	1	10:10	6.41	<.01	0.23	1.21
1022	S	Along North–South fault zone before ledge	3	10:05	3.86	2160	13.8	38.5
1029	RBI	Flow from fractures	3	10:00	5.83	1.5	0.30	<.1
1100	S	Downstream from Mesa Verde Formation "gates"	3	9:50	3.80	1990	13.4	38.5
1130	RBI	At start of talus slope inflows	2	9:40	3.91	480	1.76	<.1
1184	S	At bottom of cascade reach	3	9:35	3.85	1930	12.4	38.5
1192	RBI	Draining talus on right bank	3	9:30	6.39	1.3	0.21	3.94
1221	RBI	Spring from under outcrop of Mesa Verde Formation	1	9:20	6.56	<.01	0.24	3.94
1332	S	Start of steep drop	3	9:15	3.88	1690	11.0	42.5
1500	S	Downstream from waterfall	3	8:55	3.86	1640	10.8	42.5
1639	S	Farther downstream from waterfall	3	8:40	3.94	1530	10.0	44.6
1767	RBI	Two springs from rocks on hillslope	1	8:30	6.79	2.2	0.18	1.91
1800	S	Upstream from large waterfall	3	8:25	3.90	1320	8.59	46.5
2000	S	Among avalanche debris	3	8:10	4.00	1120	7.29	47.0
2160	S	T3 site — stream near mouth	3	8:00	3.98	950	6.05	47.8

[Source: S, stream; LBI, left-bank inflow; RBI, right-bank inflow; Group, stream or inflow group from cluster analysis; mg/L, milligrams per liter; μg/L, micrograms per liter; numbers in parentheses correspond to locations in Fig. 1 and vertical lines in Figs. 2–4 and 6.]

3. Results and discussion

Descriptions of synoptic sampling sites, tracer concentrations, and calculated discharge are listed in Table 2. Stream samples along the study reach defined 30 stream segments, and those segments included in the OTEQ modeling are indicated in Table 1. Stream segments bracketed 28 sampled inflows, but some stream segments had no sampled inflows. These segments still provide information about possible dispersed, subsurface inflow to the stream if there was dilution of the tracer in that segment.

3.1. Hydrologic context

For the purposes of setting the hydrologic context, which allows the calculation of loads, the tracer-dilution method provided a discharge for each stream sample and for each inflow by the difference between the surrounding stream sites. Using those values, discharge increased from 6.5 to 48 L/s along the study reach; discharge increased in 25 of the 30 stream segments, but no single segment accounted for more than 10% of the increase. Some of the inflows that were important with respect to metal loading are indicated by vertical lines in Fig. 2, and a few of them were among the larger inflow discharges. An artesian well from prospecting activity, called the "Moly Well" (342 m) accounted for almost 9% of the increase, the talus inflow (490 m) drained much of the eastern side of the basin, and accounted for almost 10%, and the "Daisy Mine" inflow (847 m) accounted for just over 7%. The Redwell Spring (371 m) accounted for 2% of the increase. Discharge from the fault trace that crosses the stream, the fault inflow (954 m) accounted only for 3% of the increase in flow.

3.2. Synoptic chemistry

Spatially detailed synoptic sampling of stream and inflow sites gives a context for understanding sources of loadings and how particular inflows affect in-stream chemical reactions and chemical character. Detailed results of chemical analyses of the synoptic samples are listed in the electronic Supplementary data.

3.2.1. Inflow chemistry

In a watershed affected by many natural processes and anthropogenic activities, inflow chemistry can range from acidic and metal-rich to alkaline and dilute. Classification of inflow chemistry, by the cluster-analysis method of "partitioning among medoids" (Kaufman and Rousseeuw, 1990; Kimball et al., 2006b), suggested three distinct groups of inflow samples. The principal distinctions among the inflow groups are evident by differences in pH, SO_4, Fe, Al, Zn, and Cu (Fig. 3). Inflows along the study reach that had near-neutral pH with relatively low concentrations of SO_4, Zn, and other metals were classified into inflow group 1. These inflows reflect little influence from the Mo mineralization, vein deposits, or mining. Instead they reflect the weathering of the unmineralized sedimentary strata. Many samples were affected by mineralization and were classified into inflow group 2 that was characterized by low pH and high concentrations of SO_4, Zn, and other metals. This group included the drainage from the breccia intrusions (53 and 160 m), drainage from the flowing "Moly Well" (342 m), Redwell Spring (371 m), drainage from right-bank talus slopes (490 m), and drainage from the Daisy Mine (847 m). These inflows include anthropogenic and naturally acidic drainage. Inflow group 3 generally had a chemical character that was intermediate between the unaffected and affected inflow groups.

3.2.2. Stream chemistry

Stream samples also were classified into groups by cluster analysis. Unlike the inflow groups, however, the grouping of stream samples represents the significant chemical changes along the study reach, not sources. Thus, the chemical differences among stream samples distinguish the samples spatially. The spatial groups are indicated by shading of three different sections of the study reach in Fig. 3. The first group of stream samples occurred upstream from the inflow of the "Moly Well" (342 m). A substantial change in chemical character occurred downstream from the well inflow. Variations in pH (Fig. 3A) and concentrations of SO_4 (Fig. 3B), and particularly Cu (Fig. 3F) show substantial changes that represent the stream groups. The "Moly Well" inflow caused an in-stream decrease of pH from 6.51 to 4.35; an increase of SO_4 concentration from 21.7 to 28.0 mg/L; and an increase of Cu concentration from 3.9 to 58 µg/L. Downstream from the "Moly Well" inflow to the Daisy Mine inflow (847 m), pH remained low and most metal concentrations increased from additional inflows; these samples represent the second stream group. With the Daisy Mine inflow, concentrations of SO_4, Zn, and most other metals increased considerably, but pH remained essentially the same. Samples downstream from the

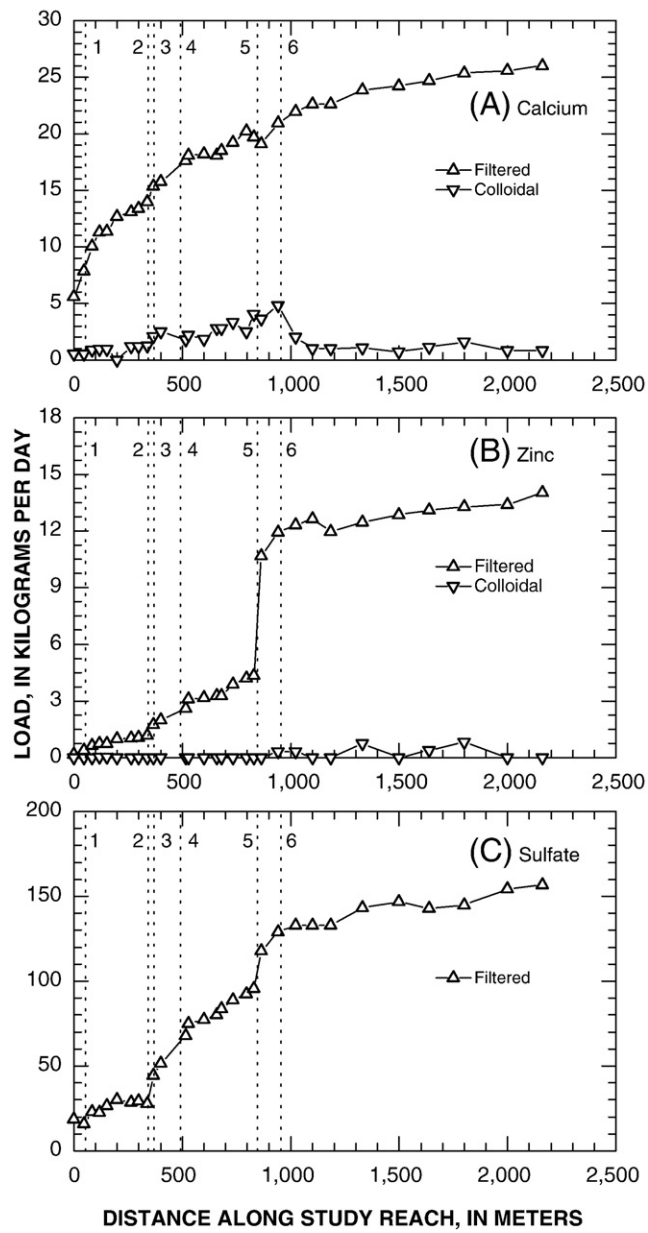

Fig. 4. Variation of loads of (A) calcium, (B) zinc, and (C) sulfate with distance along the study reach, Redwell Basin, Colorado, August 2001. The numbered vertical lines indicate important inflow locations: (1) breccia inflow, (2) "Moly Well" inflow, (3) Redwell Spring, (4) talus inflow, (5) Daisy Mine inflow, and (6) fault inflow.

Daisy Mine inflow were classified as stream group 3. Perhaps the longitudinal profile of Cu concentration shows the changes the best, with a substantial increase in concentration at both locations (Fig. 3F).

3.2.3. Patterns of loading

The changes in chemical composition of the stream samples must be evaluated in the context of solute loading to be able to determine which inflows — sampled or unsampled — had the greatest effect on stream chemistry. Three general patterns of loading occurred among these solutes, and are illustrated by the patterns of Ca, Zn, and SO_4 in Fig. 4. The pattern of Ca load (Fig. 4A) is typical of all the major elements, including Mg, Na, SO_4, and Si. The "Moly Well" (342 m) and the fault (954 m) inflows contributed a relatively larger portion of the Ca load, but the load consistently increased all along the study reach. This pattern likely represents the weathering of the sedimentary strata, all of which would be sources of the major elements. In contrast to that pattern of consistent increase along the entire study reach, Zn load (Fig. 4B) increased mostly at one point, the Daisy Mine inflow (847 m). This second pattern also is similar to the loading profiles of Cd and Mn, and a variation on this pattern was typical for Al, Cu, Fe, and Pb, which all had a substantial load from the "Moly Well" inflow (342 m). Finally, the load profile of SO_4 (Fig. 4C) was a combination of both patterns, and had a gradual increase in load in most stream segments, but also increase substantially at the "Moly Well" inflow (342 m) and the Daisy Mine inflow (847 m).

The mass loading can be summarized by comparing the total loading of major elements and metals at the principal locations of loading (Fig. 5). For major elements, the contribution from weathering upstream from the study reach is evident in that the upstream sum is the second greatest input to the study reach (Fig. 5A). In contrast, almost none of the metal loading comes from upstream of the study reach (Fig. 5B). The "Moly Well" inflow (342 m) and the Daisy Mine inflow (847 m) are the two greatest sources of metals, accounting for over half of the Cu and Zn loads to the stream (at this scale, Cu load is difficult to see in Fig. 5B). Loading from two of these locations, the Breccia inflow (160 m) and the fault inflow (954 m), was nearly as great as that from the "Moly Well." Neither the breccia nor the fault inflows were particularly noteworthy for large contributions to discharge (vertical lines 1 and 6 in Fig. 2) or for high concentrations of metals (Fig. 3), yet in the context of the hydrology of the catchment, both had substantial contributions to loading. This result points out that both the hydrology and chemistry of sources must be evaluated to understand the significance of an inflow.

3.3. Simulating existing conditions

Profiles of mass load are the result of inflow contributions of load and the subsequent reactive chemistry in the stream. Reactive solute-transport modeling with OTEQ, quantifies the profiles and provides in-stream concentrations. Existing conditions that are plotted in Fig. 3 were used to calibrate OTEQ. Comparing the results of the calibration with the observed data indicates that the simulation of pH matches the variation of sampled pH along the study reach, with the major change that occurred downstream from the inflow of the "Moly Well" (at 2 in Fig. 3A). The simulation indicates a slight increase in pH downstream from the inflow at 662 m and a decrease downstream from the Daisy Mine inflow at 847 m. The concentration profile of SO_4 was reasonably simulated (Fig. 3B), and especially indicates the importance of the "Moly Well" inflow (342 m) and the Daisy Mine inflow (at 5 in Fig. 3B) as sources of SO_4.

Although the observed data indicated the presence of Fe colloids downstream from the "Moly Well" inflow (total Fe was greater than filtered Fe, downstream from line 2, Fig. 3C), the calibration simulation did not. Upstream from the "Moly Well" inflow, filtered Fe was less than detection. But with the decrease in pH downstream from the "Moly Well" inflow, the simulation of existing conditions showed the filtered and total Fe were equal. This result suggests that the log K for ferrihydrite in the MINTEQ submodel did not agree with the mineral precipitation in the stream. For example, at 516 m, the log of the ion activity product (IAP) for the ferrihydrite precipitation reaction (the log of the ratio of the activity of hydrogen ion cubed over the activity of ferric iron), was 2.38, while the log equilibrium constant was 4.89; indicating more than two orders of magnitude under-saturation with the precipitating mineral. At pH 3.88, the precipitating mineral might actually resemble schwertmannite, $Fe_8O_8(OH)_6(SO_4)$. An IAP for this mineral form can be calculated for the stream samples and has a reasonably constant value at most stream sites downstream from the "Moly Well" inflow.

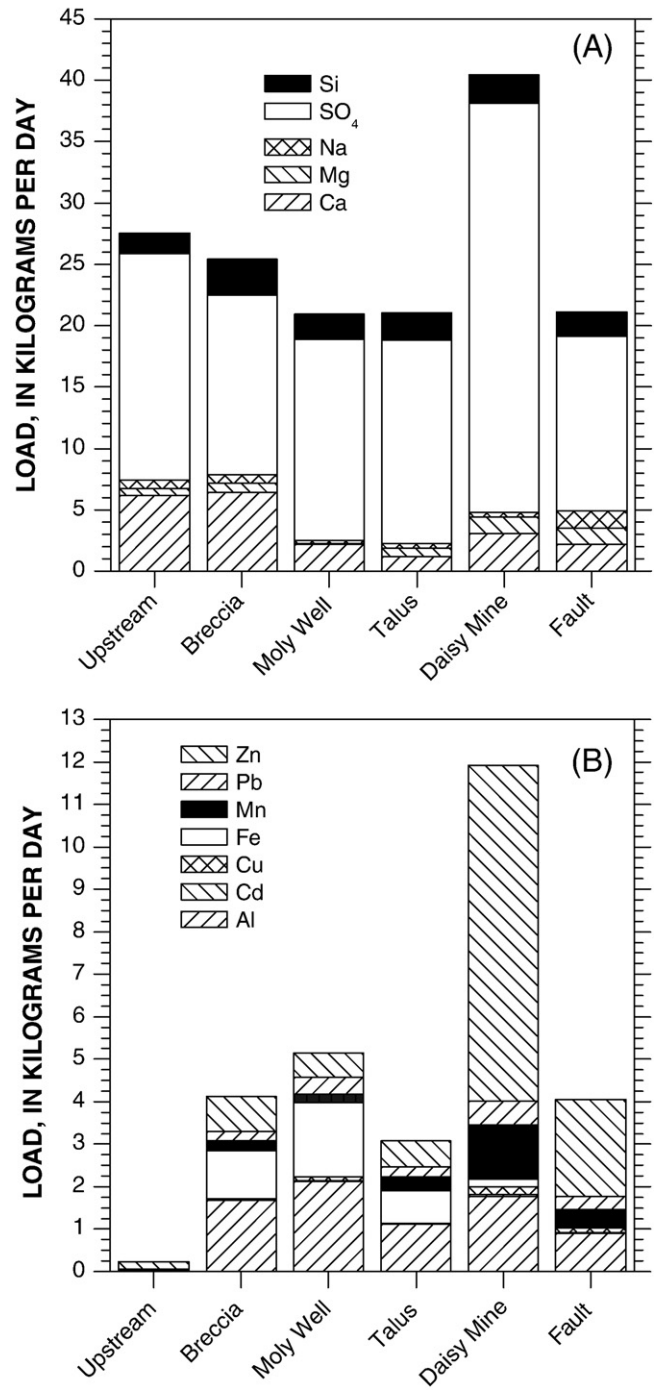

Fig. 5. Sum of load for (A) major elements and (B) metals at principal locations of inflows, Redwell Basin, Colorado, August 2001.

Table 3
Comparison of observed, calibration, and simulated pre-mining concentrations at the end of simulations downstream from mining inflows (1184 m).

Constituent	Measured	Calibration	Simulated pre-mining
pH, in standard units	3.85	3.98	5.12
Ca, in mg/L	6.3	7.3	7.7
Mg, in mg/L	.98	1.53	1.23
SO4, in mg/L	31	38	25
Al, in µg/L	1100	1352	140
Cd, in µg/L	27	30	8.5
Cu, in µg/L	93	105	18
Fe, in µg/L	310	560	361
Mn, in µg/L	681	750	383
Pb, in µg/L	459	459	207
Zn, in µg/L	3440	3920	1320

[Observed: filtered sample; mg/L, milligrams per liter; µg/L, micrograms per liter.]

Simulation results for Fe are important for the simulation of Cu and Zn sorption because of possible sorption to Fe colloids in the water column. Partitioning to the colloidal phase by sorption onto precipitated Fe was simulated for both Cu and Zn (Fig. 3E and F). Total recoverable concentrations of both metals were slightly over-estimated by the model downstream from the Daisy Mine inflow (at 5, Fig. 3E and F), and the filtered concentrations were essentially equal to the total concentrations. Thus, at a pH near 4, the simulation did not predict sorption that may have occurred for Zn because the total and filtered concentrations of observed data were slightly different (Fig. 3E). Concentrations of Ca and Mg (not shown) also were simulated to provide two components used to determine hardness-based water-quality standards. Their simulated patterns reproduced the general features of the observed concentration profiles.

Calibration results of existing conditions can be compared to the observed concentrations for the site at the end of the simulation reach, 1184 m (Table 3). After the inflow of the "Moly Well," calibrated total and filtered concentrations were equal for Fe, Al, and Zn. The majority of calibration values are reasonable, but the calibrated concentrations for Fe, Al, and Zn were high. At a pH near 4, the simulation did not produce colloidal Fe or Al, and so the observed filtered concentrations were lower (Fig. 3C and D). Likewise, the simulation did not produce the sorption that likely caused a difference for Cu and Zn (Fig. 3E and F) in the filtered and total concentrations downstream from the "Moly Well" inflow (342 m). Webster et al. (1998) have suggested that SO_4 may increase the sorption capacity of hydrous Fe oxides, and that may explain the difference between observed and simulated results. Upstream from that point, where the pH was closer to 6.5, a distinct difference between total and filtered Cu concentrations, for a few samples, indicating sorption to the Fe colloidal mater (Fig. 3F).

3.4. Simulating pre-mining conditions

Simulation of pre-mining conditions requires a selection of the inflows that represent mining. For Redwell Basin, the choice of mine-related inflows is straight forward because mining was limited to the Daisy Mine and the artesian "Moly Well." These two inflows, both their discharge and chemistry (i.e., their loads), were eliminated from the model simulation to estimate pre-mining conditions. The two inflows represented 48% of the total loads of Cu and Zn. Pre-mining calculations start at 263 m and end at 1184 m, downstream from the Daisy Mine and fault inflows (Table 2). Simulated pre-mining values are compared to the calibration values in Fig. 6.

Despite removal of the mining inflows, several inflows of acid-rock drainage still resulted in a pre-mining pH near 5. A low pH is consistent with the natural ferricrete, dated as pre-mining, near the Redwell Spring and at other locations along the stream. The pre-mining concentration of SO_4 was substantially lower than under existing conditions (Fig. 3B; Table 2). Pre-mining concentrations of Ca and Mg were slightly higher than observed concentrations with the pre-mining simulation (Table 2).

At the higher pre-mining pH, the simulated results for pre-mining metal concentrations were substantially different from the results of the calibration simulation. Both Fe (Fig. 6C) and Al (Fig. 6D) concentrations were lower than concentrations from the calibration simulation. In the case of Fe, the pre-mining simulation calculated a substantial difference between total and filtered Fe concentration, indicating the presence of colloidal Fe at a pH of 5.1 (Fig. 6C). The pattern of filtered and total Al concentrations suggests that Al would have been present mostly as colloidal Al for the pre-mining condition (Fig. 6D). An excess of colloidal Al can lead to limiting conditions for benthic invertebrates (Niyogi et al., 1999). Simulated Cu and Zn concentrations for pre-mining conditions are much lower than current conditions; the decrease from observed Cu concentration was 80%, and the decrease from observed Zn concentration was 62%. At both the pre-mining and the calibration pH, filtered and total Zn and Cu were equal in each simulation, and thus appear as one line (Fig. 6E and F). Despite lower pre-mining concentrations, Cu, Zn, and other metals occurred at concentrations higher than acute and chronic toxicity criteria for aquatic life, based on a calculated hardness of 22 mg/L as $CaCO_3$.

4. Conclusions

Redwell Basin, in central Colorado presents an opportunity to consider pre-mining metal concentrations because of its geology and limited mining history. Field-scale experiments, combined with reactive solute-transport modeling, provide a means to calculate pre-mining water quality in the catchment. Results indicate substantially lower concentrations of SO_4 and metals without the influence of drainage from mine- and exploration -related inflows to the stream. Even without the effects of mining, however, the pH of the stream in Redwell Basin would have been acidic because of the acid- rock drainage from mineral alteration in the catchment. The lower pre-mining concentrations of Zn and Cu would have been an impairment to aquatic life, because the concentrations exceed the hardness- based criteria for acute and chronic toxicity.

Simulations of existing conditions did not always match observed data. As noted (Section 3.3), the simulations did not predict the formation of colloidal Fe and Al (Fig. 3C and D). This result suggests that the Fe and Al solids actually forming in the stream have a different solubility than the ideal solids in the OTEQ data base. Also the simulations over predicted Zn and Cu concentrations downstream from the Daisy Mine inflow (at E in Fig. 3E and F). Again, this is likely because colloidal Fe was not predicted. In- stream geochemical reaction rates were faster than the time of transport (seconds to minutes) between sites. This is consistent with other stream- scale studies that have evaluated reaction rates (Kimball et al., 1994; Broshears et al., 1996).

These simulation results also suggest that even if remediation removed all the impacts of mining on the catchment, the result would not be sufficient to bring the stream to meet water- quality criteria. In this sense, the exercise of field experimentation and reactive solute-transport modeling provides a means to weigh the cost of remediation against the possible results. Interpretation of the model results presented here must be conducted in light of model and system uncertainty. But the result for pre- mining concentrations, and by extension remediation options, that exceed water- quality criteria is well within model uncertainty for the Redwell Basin. Reactive transport modeling is a useful tool for the evaluation of pre- mining conditions and subsequent evaluation of remedial alternatives in complex natural systems, where multiple hydrologic and geochemical processes determine metal fate.

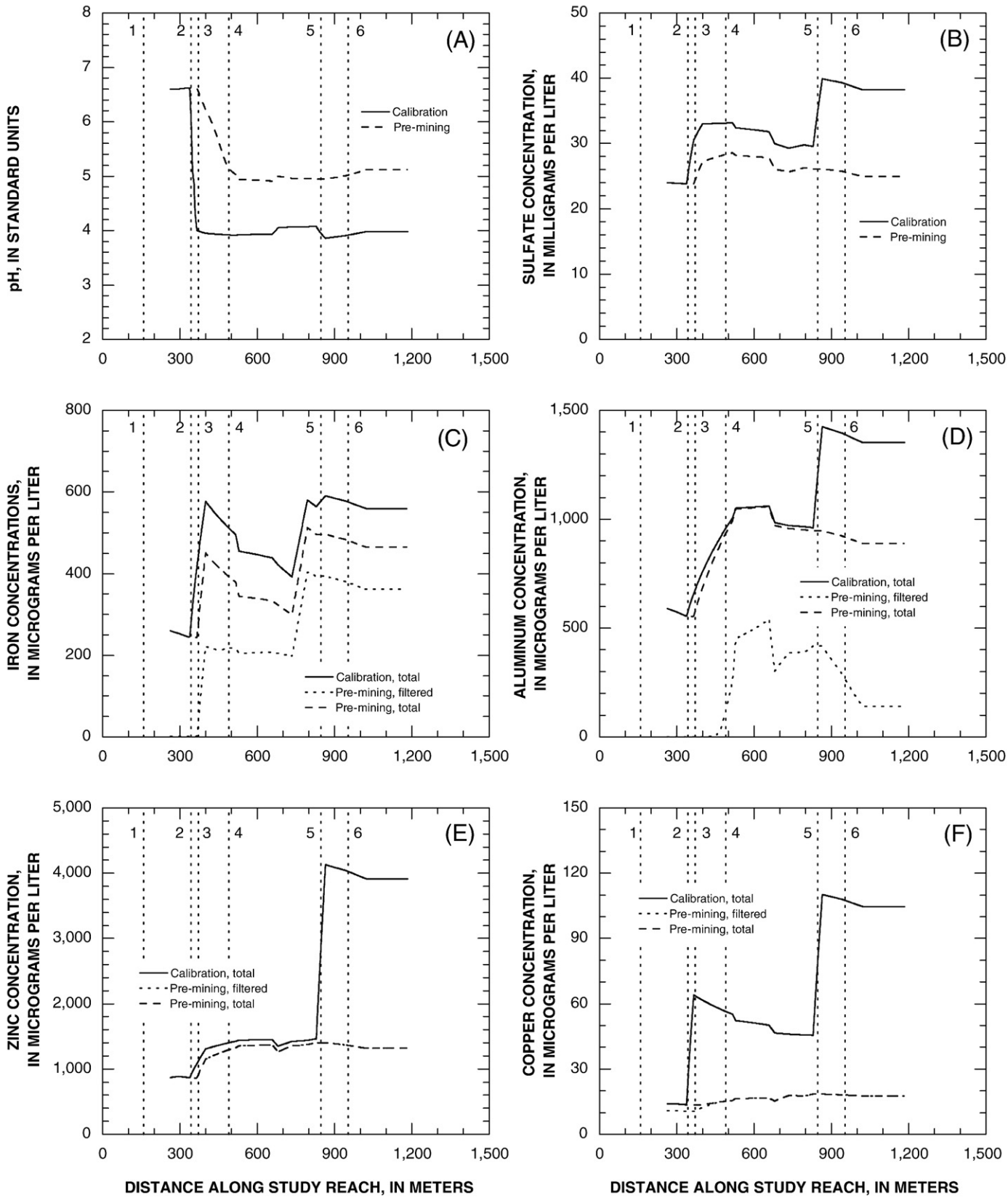

Fig. 6. Calibration and pre-mining simulation results for (A) pH, and concentrations of (B) sulfate, (C) iron, (D) aluminum, (E) zinc, and (F) copper with distance along the study reach, Redwell Basin, August 2001. The numbered vertical lines indicate important inflow locations: (1) breccia inflow, (2) "Moly Well" inflow, (3) Redwell Spring, (4) talus inflow, (5) Daisy Mine inflow, and (6) fault inflow.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.chemgeo.2009.05.024.

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