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A simulation-based approach for estimating premining water quality: Red Mountain Creek, Colorado

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Abstract

Regulatory agencies are often charged with the task of setting site-specific numeric water quality standards for impaired streams. This task is particularly difficult for streams draining highly mineralized watersheds with past mining activity. Baseline water quality data obtained prior to mining are often non-existent and application of generic water quality standards developed for unmineralized watersheds is suspect given the geology of most watersheds affected by mining. Various approaches have been used to estimate premining conditions, but none of the existing approaches rigorously consider the physical and geochemical processes that ultimately determine instream water quality. An approach based on simulation modeling is therefore proposed herein. The approach utilizes synoptic data that provide spatially-detailed profiles of concentration, streamflow, and constituent load along the study reach. This field data set is used to calibrate a reactive stream transport model that considers the suite of physical and geochemical processes that affect constituent concentrations during instream transport. A key input to the model is the quality and quantity of waters entering the study reach. This input is based on chemical analyses available from synoptic sampling and observed increases in streamflow along the study reach. Given the calibrated model, additional simulations are conducted to estimate premining conditions. In these simulations, the chemistry of mining-affected sources is replaced with the chemistry of waters that are thought to be unaffected by mining (proximal, premining analogues). The resultant simulations provide estimates of premining water quality that reflect both the reduced loads that were present prior to mining and the processes that affect these loads as they are transported downstream. This simulation-based approach is demonstrated using data from Red Mountain Creek, Colorado, a small stream draining a heavily-mined watershed. Model application to the premining problem for Red Mountain Creek is based on limited field reconnaissance and chemical analyses; additional field work and analyses may be needed to develop definitive, quantitative estimates of premining water quality.
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1. Introduction

Hard-rock mining activities in the western United States have left a landscape that is littered with

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adits, shafts, mine dumps and tailing impoundments. Although these artefacts of our mining legacy are of historical significance, they also pose a threat to water quality by introducing metals and acidity into streams and groundwaters. Effective remediation of abandoned mine lands requires considerable site-specific information including information on the sources of contamination, the processes controlling instream concentrations, and the likely condition of the watershed prior to mining. Information on the sources of contamination is needed due to the number and diversity of potential sources in a given watershed. Land management agencies have limited resources with which to implement remedial actions such that only a small fraction of potential sources are subject to clean up. In an effort to efficiently use available resources, an objective approach for characterizing sources of contamination has been developed for small watersheds. The approach is based on synoptic studies that provide spatially-detailed profiles of concentration, streamflow, and constituent load along the stream reach of interest (Kimball et al., 2002). This spatially-detailed information may be used to rank potential sources by identifying sources that contribute the highest metal loads. Sources contributing the highest metal loads may thus be targeted for future remedial actions. In addition to providing the basis for source characterization, data from synoptic studies may be used to study instream processes through the application of reactive stream transport models (Runkel and Kimball, 2002). Information on instream processes is also needed for effective remediation as physical and geochemical processes determine the degree to which constituent concentrations are attenuated as water moves downstream. This attenuation of instream concentrations is an important aspect of the problem when remedial actions are designed to meet water quality standards at a downstream point of compliance.

Information on the likely condition of the watershed prior to mining is perhaps the most difficult aspect of the remediation problem, as baseline, premining water quality data are usually unavailable. This information is needed to set realistic cleanup goals, due to the fact that some streams draining mined watersheds were acidic and metal rich prior to mining (Runnells et al., 1992). As a result, premining concentrations in some streams may have exceeded generic water quality standards that were developed for unmineralized watersheds. Use of generic water quality standards to set remediation goals may therefore be an inefficient use of the limited resources available for cleanup. In consideration of this inefficiency, regulatory agencies have the option of formulating site-specific numeric standards when the use of existing generic standards is unrealistic. These site-specific standards may be based on estimates of premining water quality. Various approaches have been used to estimate premining water quality, including the use of historical data, geochemical analogues, geochemical modeling, and mass balance (Runnells et al., 1992; Alpers and Nordstrom, 2000). In this paper, an approach for reconstructing premining water quality based on reactive stream transport modeling is demonstrated. This demonstration uses synoptic data from Red Mountain Creek, Colorado, a headwater stream draining a watershed that contains numerous abandoned mine dumps, mill tailing impoundments, and large areas of unconfined tailings (Nash, 2002). This application of reactive transport modeling differs from other approaches of determining premining water quality in that the effects of instream reactions and downstream transport are explicitly considered. In addition, use of reactive stream transport modeling provides a framework for implementing existing approaches, such as the use of geochemical analogues. As such, the modeling approach is intended to complement, rather than replace, existing approaches. Application of reactive transport modeling to the premining problem for Red Mountain Creek is based on limited field reconnaissance and chemical analyses, such that the results presented are for demonstration purposes only. Development of definitive, quantitative estimates of premining water quality requires additional data collection and analysis efforts that are beyond the scope of the present work (see Section 4.2.2); estimates of premining water quality presented herein are therefore preliminary and qualitative.

2. Methods

2.1. Overview of approach

Estimation of premining water quality using synoptic data and reactive transport modeling may be viewed as a 3-step process as described in the subsections that follow. Step 1 involves documenting the water quality of Red Mountain Creek under existing conditions (Sections 2.2–2.4). The primary activity within Step 1 is the collection of synoptic

data that provide spatially-detailed profiles of concentration, streamflow and constituent load. These synoptic data provide the information needed to assess loading from individual sources. Sources having the highest contributions to instream load may be subject to further investigation. Field reconnaissance, for example, may be used to qualitatively determine the degree to which individual sources are affected by mining. In Step 2, synoptic data are used to calibrate a reactive stream transport model that describes the physical and geochemical processes that influence instream concentrations under existing conditions (Sections 2.5.1 and 2.5.2). A key input to the model is the quantity and quality of sources entering the study reach through lateral inflow (seeps, springs and tributaries entering the main stem) and at the upstream boundary (Red Mountain Creek waters entering at the top of the study reach). During model calibration, simulation results are compared with instream data, and model inputs are adjusted to obtain a close correspondence between simulated and observed concentrations. Following calibration, the simulation reproduces the general features of the data by considering the loading attributed to source waters and the geochemical processes that act to attenuate concentrations. In Step 3, the calibrated model is used to perform an additional simulation that provides estimates of premining water quality (Section 2.5.3). In this simulation, the chemistry of each mining-affected source is replaced with the chemistry of a source thought to be unaffected by mining (a proximal analogue; Alpers and Nordstrom, 2000). The resultant simulations provide estimates of premining water quality that reflect the reduced loads present prior to mining and the geochemical processes that affect loads as they are transported downstream.

Implementation of Steps 1–3 requires numerous assumptions related to data collection, data interpretation, model specification, and model calibration. Although these assumptions are introduced in the subsections that follow (Sections 2.2–2.5), many additional details are provided as part of the discussion (Section 4).

2.2. Study location

The San Juan Mountains of southwestern Colorado contain numerous headwater streams that are contaminated by acid mine drainage. Red Mountain Creek originates at the top of Red Mountain Pass, south of Ouray, CO and flows ~12 km before merging with the Uncompahgre River. The subject of this paper is the upper 5.4 km of Red Mountain Creek (Fig. 1), a free-flowing section of the stream that is within a steep canyon (stream slope ~220 m/km). Stream depth during low-flow periods is generally <0.5 m, and stream width ranges from 1 to 4 m. Numerous inflows along the study reach introduce metals and acidic waters. These inflows consist of mine drainage and natural sources of water (Runnells et al., 1992). Elevated concentrations of Fe, Al, Cu and Zn are observed, and pH remains below 3.4 throughout the study reach. Under these conditions, precipitated hydrous Fe oxides coat the streambed and the stream is virtually devoid of typical montane aquatic life (Moran and Wentz, 1974; Mize and Deacon, 2002).

Red Mountain Creek drains water from Red Mountains #1, #2, and #3, which lie on the east side of the watershed (Fig. 1). The rocks in these mountains are hydrothermally altered and consist of acid-sulfate and quartz–sericite–pyrite assemblages. In these assemblages, original feldspar and other silicate minerals have been replaced by fine-grained minerals predominated by quartz, illite (sericite), alunite, other clay minerals, and 10–15% finely disseminated and fracture-filling pyrite (D. Bove, USGS, personal communication, 2004). In contrast, bedrock along the west side of the watershed is primarily overprinted by propylitic alteration, which consists of calcite, chlorite, epidote and, in places, fine-grained disseminated pyrite. Nash (2002) notes that these different alteration assemblages have a striking effect on water quality. Waters draining the west side of the watershed tend to have circumneutral pH values and relatively low metal concentrations, whereas waters draining the east side tend to be acidic with high metal concentrations (Neubert, 2000).

The 5.4-km study reach flows through the heart of the Red Mountain mining district, the United States' second largest Ag producer during the 1880 s. The most famous deposits are termed breccia pipe or chimney deposits that are associated with the acid sulfate alteration along the east side of the watershed. In general, these deposits were nearly vertical, cylindrical to elliptical ore bodies that ranged from 100 to 600 m in width and length. In addition to Ag, mined deposits were rich in Cu, Pb and Au (Nash, 2002). Vein deposits lie along the west side of the watershed and were mined in the 1900 s for Pb, Zn, Cu and Ag. Tunnels were driven on the west side of the watershed to reach ore deposits

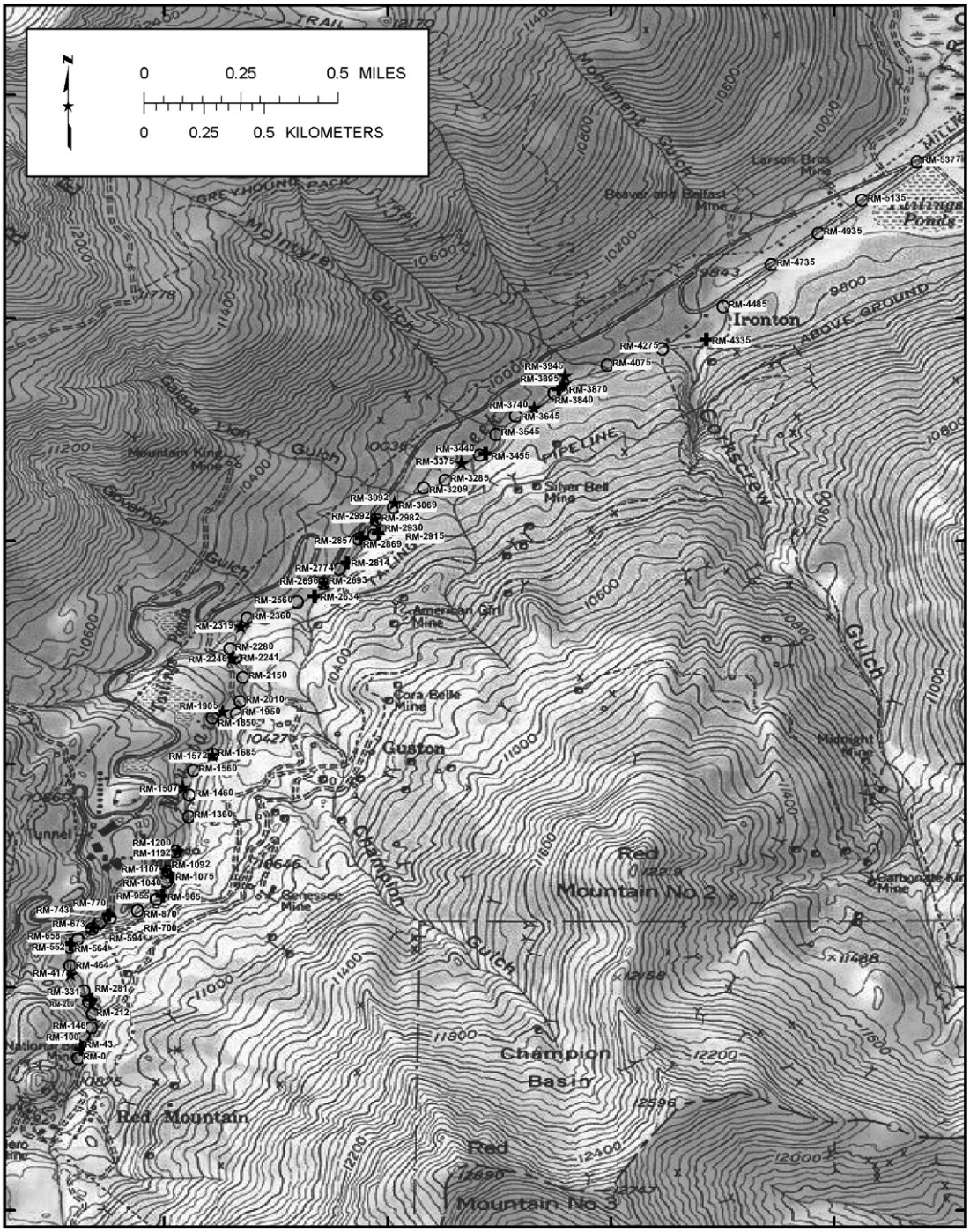

Fig. 1. Map of Red Mountain Creek including instream samples (circles), right bank inflows (plus signs), and left bank inflows (stars).

that had previously been accessed from the Telluride mining district. In addition, the Treasury tunnel was driven to access the Idarado mine workings and provide ore for the Idarado mill complex located along Red Mountain Creek (Nash, 2002).

2.3. Tracer injection and synoptic sampling

Quantification of constituent sources and loads requires estimates of streamflow and constituent concentration. An approach used in small water-

sheds is to combine the tracer-dilution method (Kilpatrick and Cobb, 1985) with synoptic sampling (Bencala and McKnight, 1987; Kimball et al., 1994, 2002). The tracer-dilution method provides estimates of streamflow, and synoptic sampling provides a description of stream and inflow chemistry. Use of the tracer-dilution method is generally preferred over conventional stream gaging techniques when conducting synoptic studies in small, mountain watersheds. Two primary reasons for this preference are (1) small, mountain streams are often shallow systems with irregular streambeds; these features may cause considerable error in streamflow estimates obtained by conventional gaging; and (2) synoptic studies require the estimation of streamflow at numerous (20–60) instream sites; obtaining numerous estimates of streamflow using conventional gaging is often not possible due to personnel and time constraints. Implementation of the tracer-dilution method typically involves the continuous injection of a conservative tracer at a constant rate. Because the tracer is conservative, downstream decreases in tracer concentration are attributed solely to dilution. Potential tracers include LiCl, NaBr and NaCl. Lithium chloride is typically the tracer used in acidic streams due the conservative behavior of Li at low pH and the low background concentration of Li in most fresh waters. Although the tracer-dilution method is theoretically straightforward, practical application is often confounded by laboratory and field sampling errors (e.g., Runkel et al., 2005). Despite these errors, streamflow estimates obtained using the tracer-dilution method are generally considered more accurate than estimates from conventional stream gaging in small mountain streams.

On August 25, 2002, a continuous injection of a LiCl solution was initiated at the upstream end of the study reach (5 m downstream of RM-100, Fig. 1). Synoptic samples were collected at 48 stream sites and 29 inflow locations (Fig. 1) on the following two days; all stream samples were collected on August 27 after instream Li concentrations had reached a steady-state plateau. Collection of stream samples proceeded in the downstream-to-upstream direction, to avoid contaminating samples with resuspended streambed materials. Stream samples were collected as rapidly as possible to minimize effects of diel metal fluctuations (Nimick et al., 2003; elapsed time between adjacent stream samples was ~5 min). Sampled inflows ranged from small springs to well defined tributaries such as Champion Gulch (Fig. 1). Stream and inflow sampling sites are identified herein using an 'RM' prefix followed by a numeric value indicating the distance (in m) from the top of the study reach to the sampling location, as measured along Red Mountain Creek. Inflow samples are further classified as being right- or left-bank inflows, where 'right' and 'left' are from the perspective of an observer who is walking downstream.

Samples were transported to a central processing area where aliquots were prepared for cation and anion analyses. Onsite processing included filtration, measurement of pH and specific conductance, and preservation of samples for cation analysis. Filtration was completed using tangential flow units equipped with 0.45-μm and 10,000-D membranes. Two filtrates were prepared for each stream sample, resulting in filtered (0.45 μm) and ultrafiltered (10,000 D) aliquots; a single 0.45-μm filtrate was prepared for each inflow sample. Unfiltered ('total recoverable'), filtered ('dissolved'), and ultrafiltered aliquots were thus available for cation and anion analyses. Use of filtered aliquots to represent the dissolved constituent concentration is based on a comparison of filtered and ultrafiltered results; this comparison indicates filtered and ultrafiltered concentrations of reactive constituents (Fe and As) are comparable. Use of the 0.45 μm filtrate provides consistency between stream and inflow samples, and with existing water quality standards. Aliquots for cation analysis were acidified to pH <2.0 with ultrapure HNO_3, and cation concentrations were determined using inductively coupled Ar plasma–mass spectrometry (ICP–MS). ICP–MS analyses were performed at the University of Southern Mississippi, under the direction of Dr. Alan Shiller (Dr. Shiller's laboratory has been approved by the USGS Branch of Quality Assurance). Dissolved anion concentrations were determined from filtered, unacidified samples by ion chromatography (IC). IC analyses were performed at the USGS in Salt Lake City, UT, using the quality-assurance procedures described by Kimball et al. (1999). Aliquots for Fe speciation were placed in amber bottles and preserved with concentrated HCl to fix the ratio of Fe(II) to Fe(III) in filtered samples (To et al., 1999). Ferrous and total dissolved Fe were determined colorimetrically (Brown et al., 1970). Alkalinity was determined from filtered, unacidified samples. Concentrations of Li tracer were determined by atomic absorption spectroscopy.

Synoptic samples collected in August 2002 are thought to be representative of Red Mountain

Creek water quality under low-flow conditions. Streamflow estimates ranged from 6.23 L/s (0.22 cubic feet/s) at the injection site to ~28 L/s (3 cfs) at the end of the study reach (Runkel et al., 2005). Additional details on sampling locations and sample processing are provided by Runkel et al. (2005; available at http://infotrek.er.usgs.gov/pubs/).

2.4. Loading analysis

Estimates of instream constituent load provide an objective means of determining the sources that have the greatest effect on instream water quality. To this end, the study reach was divided into 47 stream segments that are demarcated by the 48 stream samples. The 48 stream sampling locations were placed so as to bracket known surface inflows (surface springs and tributaries); when surface inflows were not observed, sampling locations were spaced to provide a minimum resolution of 300 m. An increase in mass load from one stream site to the next indicates that the stream segment brackets a source of constituent mass. Potential sources include surface inflow waters sampled during the synoptic, unsampled inflows (e.g., groundwater inflow), and contaminated bed sediments.

Mass load is generally defined as the product of streamflow and constituent concentration. Three specific load calculations are used to quantify the sources of loading to Red Mountain Creek. Raw instream load is defined as the simple product of estimated streamflow and observed constituent concentration. Spatial profiles of raw instream load show increases and decreases in load over the length of the study reach. Some of the raw load increases are easily explained as they appear in stream segments that bracket observed inflows that add a substantial amount of flow and/or have elevated metal concentrations. Other load increases occur in segments without observed inflows, suggesting possible ground-water sources. Decreases in raw instream load, in contrast, are not expected in Red Mountain Creek for many constituents, as the depressed instream pH inhibits geochemical reactions that would result in decreased load. Further, decreases in load caused by loss of streamflow to the underlying ground-water system are unlikely to occur given the continuous dilution of the Li tracer (and associated increases in streamflow) along the entire study reach (Appendix 1 of Runkel et al., 2005). Most of the decreases in load are therefore attributable to errors in the estimation of streamflow and the observed constituent concentration. Three types of error are considered here: (1) error in the observed constituent concentration that arises due to uncertainty in laboratory analyses, (2) error in the observed Li concentration that arises due to uncertainty in laboratory analyses (this type of error causes uncertainty in the streamflow estimate obtained by tracer-dilution), and (3) sampling error due to variability in constituent and tracer concentrations over the channel cross section. Sampling error is of particular concern for Red Mountain Creek where shallow depths precluded the collection of width and depth integrated samples.

An estimate of the potential errors in raw load is obtained by considering the errors associated with replicate sampling. Replicate samples were collected at two stream sites, where two samples were collected in sequence over a short time period (<2 min). Given the stable hydrologic conditions observed during sampling and the short time interval between sample collection, the replicate samples are treated as if they were collected concurrently. In the absence of error, load estimates based on concurrent replicate samples would be identical. Load estimates from replicate sampling differ in practice, however, due to the types of error discussed above. At a given replicate site, the % relative error in load may be calculated (Runkel et al., 2005). The % relative error may be used to develop the corrected instream load as follows. First, the maximum % relative error for each constituent is determined using data from the two stream sites at which replicate samples were collected. Starting at the top of the study reach, each decrease in the raw instream load is compared with the maximum relative error. If the decrease exceeds the maximum error, the decrease is considered valid and the corrected load is simply equal to the raw load. If the decrease is less than the maximum error, the decrease is assumed to result from laboratory and/or field error. The corrected instream load in this case is set equal to the load at the previous stream site, such that the observed decrease in raw instream load is not included in the corrected instream load. Cumulative instream load is developed by summing all the increases in corrected instream load. For a given stream segment, the cumulative instream load is increased if the corrected instream load exhibits an increase and is held constant if the corrected load exhibits a decrease. The cumulative instream load thus represents the total amount of loading within

the study reach (whereas the corrected instream load represents the net amount of loading that results after both increases and decreases in load; i.e., the net loading after chemical reaction).

Raw, corrected, and cumulative instream loads are calculated using total recoverable concentrations. An increase in corrected instream load for a given stream segment indicates that the segment includes a source of constituent mass. The % contribution of a source is determined by dividing the within segment load increase by the cumulative instream load at the end of the study reach (5377 m). Given this definition, each of the potential sources is ranked by considering the stream segment's contribution to the corrected loads for Al, As, Cd, Pb, Cu and Zn (Runkel et al., 2005).

2.5. Simulation of geochemical reactions and downstream transport

2.5.1. Reactive transport model

The reactive transport model used here is known as OTEQ (one-dimensional transport with equilibrium chemistry; Runkel et al., 1996a, 1999). OTEQ is formed by coupling a solute transport model (Runkel, 1998) with a chemical equilibrium submodel. The submodel is based on MINTEQ (Allison et al., 1991), a model that calculates the distribution of inorganic species under the assumption of chemical equilibrium. The coupled model considers a variety of processes including advection, dispersion, transient storage, transport and deposition of water-borne solid phases, acid/base reactions, complexation, precipitation/dissolution, and sorption. Governing equations 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; precipitated and sorbed species residing in the water column are subject to transport and settling. Total component concentrations are partitioned between dissolved, precipitated and sorbed phases based on equilibrium calculations for each computational stream segment (this application uses a 1 m segment length).

Components used in this application include Al, As [H_3AsO_4 for As(V)], Cd, Cu, Fe(II), Fe(III), F, Pb, SO_4, total excess H (TOTH), total inorganic $C(CO_3)$, and Zn (Arsenic species in Red Mountain Creek are assumed to be in the As(V) oxidation state, as arsenate is the dominant form of As in oxygenated surface waters, Hem, 1985). Precipitation reactions for Al and Fe(III) are defined using microcrystalline gibbsite [$Al(OH)_3$, $\log k = -8.77$] and ferrihydrite [$Fe(OH)_3$] as the solid phases, respectively. Ferrihydrite was chosen over SO_4-containing Fe solids such as Schwertmannite (Bigham et al., 1996) due to an observed lack of colloidal SO_4 in the water column of Red Mountain Creek. Sorption of As, Cd, Cu, Pb, SO_4, TOTH and Zn to freshly precipitated Fe oxides is modeled using a surface complexation approach and the database of Dzombak and Morel (Dzombak and Morel, 1990; Allison et al., 1991; Runkel et al., 1999). The mass of sorbent within each computational stream segment is based on the amount of precipitated Fe(III) within the water column, as determined by the equilibrium submodel. Precipitated Fe(III) on the streambed is assumed to be saturated with respect to sorbed species and is therefore not a sink in the steady-state analysis presented herein (similarly, dissolution and/or desorption from the streambed is not a source in the steady-state analysis as the amount of mass on the streambed is finite). This assumption is based on the relatively steady meteorological and hydrological conditions observed in the days prior to synoptic sampling; under these steady conditions, constituent loading should be steady, such that equilibrium (steady-state) between the streambed and water column is obtained. Transfer of mass between Fe(II) and Fe(III) due to microbial oxidation and photoreduction (Nordstrom, 1985; McKnight et al., 1988) is modeled by specifying the percentage of total dissolved Fe [Fe(II) + dissolved Fe(III)] that is Fe(II). Under this approach, mass is transferred between Fe(II) and Fe(III) to maintain the specified percentage (Runkel et al., 1996b) (e.g., mass is transferred from Fe(II) to Fe(III) following precipitation of Fe(III)).

Unless noted otherwise, equilibrium constants for acid/base, complexation, precipitation and sorption reactions are set using default values from the equilibrium submodel. These default values are based on a version of the MINTEQ database (Allison et al., 1991) that has been revised to be consistent with the wateq4f.dat, a database distributed with PHREEQC (Parkhurst and Appelo, 1999). Sorption parameters (i.e., specific surface area, sorbent molecular weight, low affinity site density) are set using the best estimates of Dzombak and Morel (1990). High affinity site density is 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). Equilibrium constants and activity coefficients are adjusted for the effects of temperature (11 °C) and ionic strength (0.02 M).

2.5.2. Existing conditions

An important part of the simulation-based approach is the development of a calibrated model that considers the physical and geochemical processes that influence existing conditions. During model calibration, model inputs are set to values which reflect the modeler's best estimate of a given input. Simulation results based on these best estimates are then compared to instream data, and model inputs are adjusted to improve the correspondence between simulated and observed concentrations. Adjustment of model inputs is generally restricted to process information that is highly uncertain. Streamflow estimates, for example, are not typically part of the calibration process, as the estimates obtained by tracer-dilution are considered sufficiently accurate. The constituent concentrations associated with inflowing waters (component inflow concentrations), in contrast, are often subject to adjustment due to spatial variability in inflow concentration (e.g., Bencala and McKnight, 1987). The modeler's best estimate of inflow concentration is frequently based on observed data from a sampled inflow, but this best estimate may be subsequently modified if the sampled inflow is not considered representative of all inflowing waters (e.g., the concentration of diffuse groundwater inflow may differ from that of the sampled surface inflow). Another common adjustment during the calibration process is the modification of equilibrium constants controlling mineral solubility; these constants are known to be highly variable (e.g., Langmuir and Whittemore, 1971).

To begin the calibration process, best estimates of streamflow, hydrologic parameters and chemical data that describe constituent loading along the study reach were developed. The study reach was first divided into 39 reaches based on changes in streamflow and water chemistry (Table 1). Streamflow estimates (Table 1) were obtained by tracer-dilution (Runkel et al., 2005). Hydrologic parameters (main channel cross-sectional area, longitudinal dispersion coefficient) were determined by fitting an advection–dispersion model (Runkel, 1998) to the time series of Li concentration at the ends of reaches 6, 26, 35, and 38. Estimates of main channel cross-sectional area ranged from 0.09 to 0.38 m^2; estimates of the longitudinal dispersion coefficient ranged from 0.15 to 3.3 m^2/s. Chemical data from sampled inflows were used to specify component inflow concentrations (Table 1). The upstream boundary condition was set using component concentrations of the stream sample collected upstream of the injection site (RM-100). Percentages of Fe(II) used to model photoreduction and oxidation were based on observed data (Table 1).

Component concentrations at the upstream boundary and within the inflows were set equal to observed concentrations for most components. Two exceptions are TOTH and CO_3, components that were assigned concentrations based on stand-alone MINTEQ computations. In these computations, pH and alkalinity were fixed at observed values and TOTH and CO_3 were determined from the speciated output. For samples without alkalinity, CO_3 concentrations were based on equilibrium with atmospheric CO_2.

Assignment of inflow chemistry based on sampled inflows (Table 1) and the use of default equilibrium constants results in a generic description of the study reach that has not been calibrated to match observed stream data. This description reproduces the general features of the observed concentration profiles but is lacking in some respects. Several modifications were therefore made to improve correspondence between the simulation and observed data: (1) the upstream boundary concentration for As was set equal to the observed concentration at RM-146, (2) ferrihydrite solubility was increased by changing the equilibrium constant from the default value ($\log k = -4.89$) to -4.29, (3) the surface complexation constant for sorption of $H_2AsO_4^-$ was changed from the default value (8.2) to 8.8, (4) reach 11 inflow concentrations for As, Fe(II), Fe(III) and SO_4 were decreased by 60%, 23%, 23% and 20%, respectively, and (5) settling of precipitated and sorbed species was simulated by specifying a settling velocity (2×10^{-5} m/s) and effective settling depth (0.45 m). Modifications (1) and (4) were made after changes to equilibrium constants failed to improve the correspondence between the simulation and observed data. Modification (1) was made after a review of the data indicated that the total recoverable As concentration at the upstream boundary (RM-100) was anomalously high; modification (4) was made under the assumption that the sampled inflow (Table 1) was not representative of all the inflow water entering the reach.

Table 1
Model reaches including streamflow, inflow locations, and Fe(II) percentages

Reach and distance (m)[a]	Stream flow (L/s)		Locations of observed inflows (m)[b]	Fe(II) %
	Top of reach	*w/i* reach increase		
1:105–269	6.10	0.00	None	70
2:269–331	6.10	1.59	**281D**	70
3:331–464	7.69	0.35	**417D**	70
4:464–552	8.04	0.45	None (**417D**)	70
5:552–594	8.49	0.93	**564D-'natural' inflow**	70
6:594–658	9.43	0.04	None (**564D**)	70
7:658–700	9.47	2.06	**673T-West Branch, Red Mountain Creek**	70
8:700–743	11.52	0.39	None (**673T**)	70
9:743–870	11.92	3.14	**770D**	70
10:870–955	15.06	0.00	None	60
11:955–1040	15.06	5.97	**965D-manhole inflow**	60
12:1040–1092	21.03	0.95	**1075D**	60
13:1092–1192	21.98	1.16	**1107T**	60
14:1192–1460	23.13	0.15	**1200T**	60
15:1460–1560	23.29	0.22	**1507T**	60
16:1560–1685	23.51	1.23	**1572T**	60
17:1685–1850	24.74	0.43	None (**1572T**)	60
18:1850–2010	25.16	0.00	1905	60
19:2010–2150	25.16	0.12	None (**1905D**)	60
20:2150–2241	25.28	0.00	None	60
21:2241–2280	25.28	0.03	**2246D**	60
22:2280–2360	25.31	6.59	**2319T-Commodore Spirit Gulches**	60
23:2360–2560	31.90	0.00	None	60
24:2560–2693	31.90	3.66	**2634D-Champion Gulch**	60
25:2693–2774	35.56	1.75	**2721T**	60
26:2774–2857	37.31	0.36	**2814D**	60
27:2857–2915	37.67	0.25	**2869T**	60
28:2915–2982	37.92	4.92	**2930D**	60
29:2982–3069	42.84	21.39	**2992T**	80
30:3069–3209	64.23	5.14	**3092T**	80
31:3209–3285	69.36	0.00	None	80
32:3285–3440	69.36	7.73	**3375T**	80
33:3440–3645	77.10	0.00	3455	80
34:3645–4075	77.10	2.89	**3740D**, 3870, 3895, 3945	80
35:4075–4275	79.99	0.63	None (**3740D**)	80
36:4275–4485	80.62	5.56	**4335D-Corkscrew Gulch**	80
37:4485–5135	86.18	0.00	None	80
38:5135–5377	86.18	0.44	None (**4335D**)	80

[a] Reach 39 is a 'dummy' reach used to implement the downstream boundary condition (Runkel, 1998).
[b] Inflow used to represent reach inflow chemistry shown in bold; inflow used in calibration is shown parenthetically if it is not within reach boundaries. Suffix 'D' indicates that component inflow concentrations are based on dissolved concentrations; suffix 'T' indicates that component inflow concentrations are based on total recoverable concentrations.

The remaining modifications are discussed in Section 4.1.1.

2.5.3. Premining

Given the calibrated model of existing conditions, estimates of premining water quality may be obtained by simulation. To conduct a premining simulation, the chemistry of mining-affected sources is replaced with the chemistry of sources that are thought to be unaffected by mining (as used here, 'source' refers to inflow waters entering a stream segment, or waters entering at the upstream boundary of the study reach). Accurate simulation of premining conditions therefore requires detailed information on the degree to which individual sources are affected by mining. Mining-affected sources are subject to replacement, whereas unaffected sources are potential analogues for premining source waters. Under this approach, each of the sources used as input to the calibrated model should be the subject of a thorough investigation in which a variety of techniques are used to quantify the effect

of mining, or lack thereof (Section 4.2.2). Such an analysis for the 30 stream reaches with non-zero inflow (Table 1) is beyond the scope of the present work, where the primary objective is to demonstrate the simulation-based approach. For the premining simulations shown here, the four largest mining-affected sources (Section 3.1.2) were replaced with a single source thought to be unaffected by mining. Determination of mining effects is based on simple field reconnaissance in which individual sources were tracked from their point of entry into Red Mountain Creek to their origin higher up in the watershed. Reconnaissance of the four largest sources (Sections 2.4 and 3.1.2) provided qualitative evidence of mining effects. Similar reconnaissance of a nearby source (RM-564, Table 1) did not reveal any obvious signs of mining, with inflow waters discharging from a marshy area with abundant vegetation. Like the mining-affected sources, RM-564 drains a mineralized area on the east side of the watershed and the water is acidic and metal rich (pH = 3.1, dissolved Al = 29 mg/L). As such, RM-564 is a good candidate for use as a proximal, premining analogue (Alpers and Nordstrom, 2000). Using this rudimentary analysis, a premining simulation was conducted in which the calibration chemistry in three reaches (11, 24 and 28; Table 1) and at the upstream boundary was replaced with the chemistry from reach 5 (RM-564, Table 1). Waters entering at the upstream boundary and the inflows entering reaches 11, 24 and 28 represent the four sources that contribute the highest constituent loads (Section 3.1.2).

3. Results

The complete data set for the Red Mountain Creek study includes chemical analyses for 24 different constituents (Runkel et al., 2005). The discussion that follows is limited to pH and eight of the constituents used as components within the reactive transport model (Al, As, Cd, Cu, Fe, Pb, SO_4, Zn). Although Cu, SO_4 and Zn are discussed below, study results are not shown for these constituents in the associated figures; interested readers are referred to Runkel et al. (2005).

3.1. Existing conditions

3.1.1. Constituent concentration and pH

Spatial profiles of pH and concentration (Al, As, Cd, Fe and Pb) for sampled inflows and stream sites are depicted in Fig. 2a–l. Values of instream pH are less than 3.0 at the top of the study reach, and exhibit a gradual increase over the first 900 m (Fig. 2g). This increase is negated further downstream, as acidic waters are introduced by two right-bank inflows (RM-965, pH = 2.9, and RM-1075, pH = 2.8; Fig. 2a). Another gradual pH increase occurs from RM-1092 to RM-2982, as pH climbs from 2.9 to 3.1. A relatively sharp increase in pH is observed downstream of RM-2982, following the addition of circumneutral waters from a left-bank inflow (RM-2992, pH = 8.2; Fig. 2a). Values of pH downstream of RM-2992 remain above 3.25 through the end of the study reach.

Concentration profiles for As, Al, Cu, Cd, Fe and Zn exhibit features that are generally consistent with the changes in pH noted above. Instream concentrations for these constituents decrease over the first 900 m, then increase sharply at RM-1040 following the addition of metal-rich waters from a right-bank inflow (RM-965; Fig. 2b–e, h–k). Gradual decreases are observed over the next ~1900 m, followed by sharp declines in concentration as a left-bank inflow (RM-2992) provides dilution. In addition to this dilution effect, the pH increase downstream of RM-2992 results in the formation of Fe precipitates and the sorption of As, as indicated by the marked difference between dissolved and total recoverable concentrations (Fig. 2h–i). The remaining constituents (Al, Cu, Cd, Zn) are transported conservatively through the study reach (dissolved and total recoverable are approximately equal; Fig. 2j–k). The spatial concentration profile for Pb differs slightly from the other constituents, in that instream concentrations increase over the first 660 m, due to Pb-rich inflow waters draining a right-bank mine dump (RM-281; Fig. 2f and l). Lead concentration then decreases at RM-700, following the introduction of dilute inflow waters from the West branch of Red Mountain Creek (left-bank inflow RM-673; Fig. 2f). A final increase in instream Pb occurs downstream of RM-700, after the addition of a right-bank inflow (RM-770). Dissolved concentrations of Al, Cd, Cu, Pb and Zn exceed chronic aquatic life standards (generic, 'table value standards'; Colorado Department of Public Health and Environment, 2000) along the entire study reach, whereas dissolved concentrations of As exceed the chronic standard along parts of the study reach (Fig. 2i–l).

Simulations of pH, Al, As, Cd, Cu, Fe, Pb, SO_4 and Zn under existing conditions reproduce the

dominant features of the observed spatial profiles (Fig. 2g–l). Notable discrepancies between simulated and observed conditions include (1) failure to model small changes in pH, including the gradual decrease in pH from RM-3069 to the end of the study reach (Fig. 2g), (2) overestimation of dissolved As and Fe from RM-3069 to the end of the study reach (Fig. 2h–i), and (3) overestimation of Pb concentrations from RM-955 to the end of the study reach (Fig. 2l).

3.1.2. Mass loads

As discussed above, right-bank inflow RM-965 appears to have a large effect on instream concentrations. This effect and the effects of other source waters are formally quantified using mass loading profiles. Spatial profiles of load are depicted in Fig. 2 (Al, As, Cd, Fe, Pb) and in Runkel et al. (2005). Panels S–W of Fig. 2 show the corrected and cumulative instream load for specific constituents, while panels X–Z, AA, and BB depict the % contribution of each stream segment to the cumulative instream load (for profiles of raw instream load, see Runkel et al., 2005). Corrected instream loads of Al, Cd, Cu, Pb and Zn exhibit a generally continuous increase in response to loading from various sources and the acidic pH. These constituents do not form solid phases at low pH, such that they are transported conservatively and any loss of instream load is negligible. Corrected and cumulative instream loads for these constituents are therefore similar. Corrected instream loads for Fe and As, in contrast, exhibit a gradual decrease over parts of the study reach. This decrease is caused by the formation of solid phase material that settles to the streambed. The loss of mass is reflected in a divergence between cumulative and corrected instream loads (Fig. 2s–t). Increases in corrected instream load result from sources of constituent mass; these sources are further quantified as the % contribution (Fig. 2x–z, aa, bb).

The eight largest sources of constituent load to Red Mountain Creek are discussed in Runkel et al. (2005); the four largest sources are summarized here. Although source identification is based on increases in load for specific stream segments, most of the sources discussed below are in terms of the sampled inflow that enters a given stream segment. Presentation of sources is thus based on the assumption that observed increases in load are attributable to sampled inflows, rather than unsampled inflow or contaminated bed sediments. This assumption is supported by an inflow loading analysis (Runkel et al., 2005) and model simulations in which sampled inflows are used to assign reach inflow chemistry (Table 1; Fig. 2a–l).

Source 1 is RM-965, the largest contributor of Al, As, Cd, Cu, Fe and Zn to the study reach (Fig. 2x–z, aa). RM-965 is an acidic, metal-rich right-bank inflow (pH = 2.9; Fig. 2a–f) that enters Red Mountain Creek after discharging from an overflowing manhole; the manhole is part of a sewer system that drains the Genessee Mine. Source 2 includes all of the Red Mountain Creek headwaters above the injection site (constituent loads at RM-100, a stream site near the top of the study reach, indicate substantial headwater loading; Fig. 2s–w). This headwater source is the largest contributor of Pb and the second largest contributor of As and Cu (Fig. 2y, bb). The observed loading is likely due to a mine adit known as right-bank inflow RM-43, the Red Mountain Adit, streamside waste rock, and contributions from the Hero, National Belle, Hudson and Enterprise mines (Fig. 2 in Hardy et al., 1999). Source 3 is Champion Gulch (right-bank inflow RM-2634), a tributary whose watershed includes numerous mine shafts and adits in the Guston area (Fig. 1). Champion Gulch is the second largest contributor of Al, Cd and Fe (Fig. 2x, z, aa). Source 4 is RM-2930, a right-bank inflow that emanates from a concrete channel fed by the Joker Tunnel and two pipes. RM-2930 is the largest contributor of SO_4 and the second largest contributor of Zn.

3.2. Premining conditions

Premining results are shown in Fig. 2m–r, along with existing data. Depicted simulation results include pH and dissolved constituent concentrations from the primary premining simulation, and pH and constituent concentration from a second premining simulation in which conservative transport is assumed (total recoverable concentrations from the primary premining simulation are not shown as they are similar to the results from the second premining simulation). Results for these two simulations are nearly identical in the upper part of the study reach, such that they are visually indistinguishable (Cd results are identical for the entire study reach; only the primary simulation is shown). Results for the two simulations generally diverge downstream of RM-2982, due to precipitation and sorption reactions included within the primary

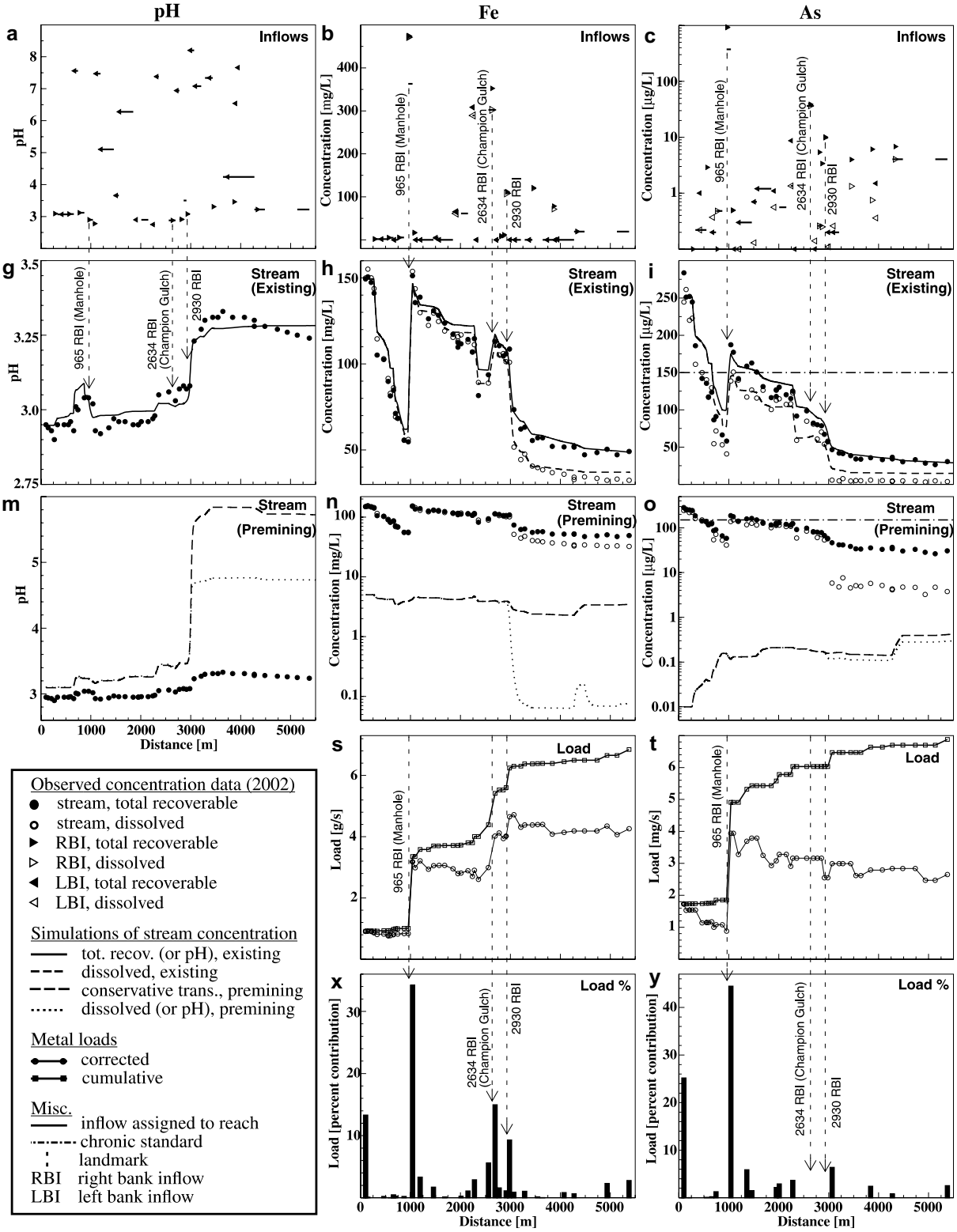

Fig. 2. Observed inflow data (panels a–f), observed stream data and simulations for existing conditions (panels g–l), simulations for premining conditions (panels m–r), profiles of load (panels s–w), and percent load contribution by segment (panels x–z, aa, bb), for Red Mountain Creek, Colorado.

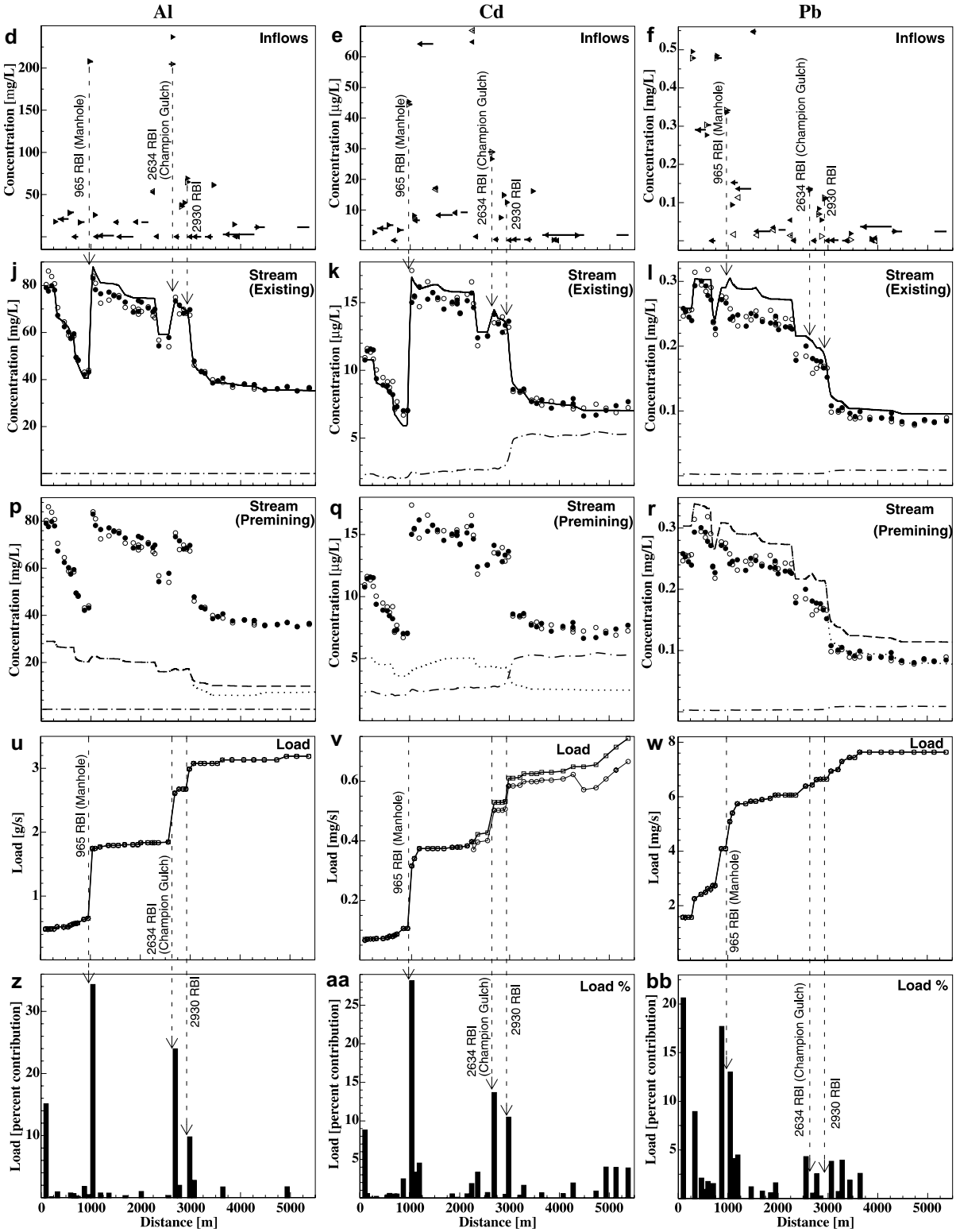

Fig. 2 (*continued*)

premining simulation. Results from the primary simulation are discussed here; results from the conservative simulation are discussed in Section 4.2.3.

Values of premining pH are generally higher than existing conditions, whereas dissolved constituent concentrations are generally lower (Fig. 2m–r). Estimates of premining pH are 0.2–0.4 pH units higher than existing conditions upstream of RM-2982, remaining below pH 3.6. Premining pH values downstream of RM-2982 increase to ~4.7 after the addition of the circumneutral left-bank inflow (RM-2992). Premining results for Fe follow a similar pattern, with a ~1 order of magnitude reduction in concentration relative to existing conditions upstream of RM-2982, and a ~2 order of magnitude reduction downstream of RM-2982 (Fig. 2n). Estimates of premining conditions for As, Al, Cd, Cu and Zn indicate large reductions in concentrations relative to existing conditions (Fig. 2o–q). Despite these reductions, premining concentrations of dissolved Al, Cu and Zn remain above the chronic aquatic life standard over the length of the study reach. In contrast, premining As concentrations are ~2 orders of magnitude below the chronic standard along the entire study reach, and premining Cd concentrations are below the chronic standard downstream of RM-2992 (Fig. 2o and q). The simulation for Cd illustrates the importance of left-bank inflow RM-2992, as the inflow acts to dilute Cd concentration while increasing water hardness, a quantity used to determine the chronic standard. Premining Pb concentrations are very similar to those observed under existing conditions, such that premining concentrations exceed the chronic standard over the length of the study reach (Fig. 2r).

4. Discussion

4.1. Existing conditions

4.1.1. Constituent concentration and pH

Detailed characterization of existing conditions in the 5.4-km study reach was made possible by the combined tracer-dilution and synoptic sampling approach. This combined approach has the advantage of providing concentration data for instream and inflow sites, while providing a spatially-detailed profile of streamflow for the analysis of constituent loading and geochemical reactions. Potential analyses range from simple, qualitative examination of the data, to complex analyses such as reactive transport modeling. Simple examination of the collected inflow data, for example, provides qualitative information on the sources of acidic water and constituents to Red Mountain Creek. Constituent concentrations associated with right-bank inflows (east side of watershed) generally exceed concentrations of left-bank inflows (west side) (Fig. 2b–f). Similarly, right-bank inflows are acidic (pH < 3.5), whereas most left-bank inflows are circumneutral (Fig. 2a). These differences between the eastern and western portions of the watershed are consistent with the observations of Nash (2002) and an alteration map that shows a highly mineralized area on the east side (D. Bove, USGS, personal communication, 2004). Sources entering from the east side of the watershed appear to be the most detrimental to Red Mountain Creek, an observation that is formally quantified by the loading analysis (Section 3.1.2).

In addition to the inflow analysis presented above, inflow data are a key input to the reactive transport model, as they are used to represent the chemistry of sources entering the study reach through lateral inflow. Component inflow concentrations for each reach were based on observed inflow concentrations (Fig. 2a–f), and this assignment of inflow chemistry resulted in a good reproduction of observed stream data (Fig. 2g–l). One exception to the use of observed inflow chemistry occurred in reach 11, where the use of observed As, Fe, and SO_4 inflow concentrations from RM-965 resulted in an over estimation of instream concentrations at RM-1040. Inflow concentrations were therefore adjusted downward during the calibration process to provide a closer correspondence between simulated and observed concentrations (Fig. 2b–c and h–i).

Additional changes were made during the calibration process to more accurately simulate the reactive processes affecting Fe and As. Precipitation of Fe oxides was modeled using a ferrihydrite equilibrium constant of −4.29, a value that produced close correspondence between simulated and observed concentrations of dissolved Fe (Fig. 2h). This calibrated constant falls within the range of values used in previous model applications (Broshears et al., 1996; Runkel et al., 1996b; Runkel and Kimball, 2002; $\log k = -2.85$ to -5.29), and is well within the reported range (Langmuir and Whittemore, 1971). Reproduction of dissolved As concentration was improved by specifying a surface complexation constant for H_2AsO_4 of 8.8, a value

that is within the 95% confidence level (Dzombak and Morel, 1990). Despite this calibration, As sorption is underestimated downstream of RM-2992 (Fig. 2i). Settling of precipitated (Fe) and sorbed (As) mass was simulated using a settling velocity based on mean particle radius (2 μm; Broshears et al., 1996) and an effective settling depth of 0.45 m. The specified settling depth was adjusted during calibration to improve the simulation of total recoverable Fe and As. The calibrated value likely exceeds the mean depth of Red Mountain Creek, possibly reflecting the fact that some particles were too small to settle to the streambed.

In summary, simulation results reproduce features of pH and concentration profiles under existing conditions after relatively minor adjustments to observed inflow chemistry and default equilibrium constants. Simulations of conservative constituents (Al, Cd, Cu, Pb, SO_4, Zn; Fig. 2j–l) are remarkably good considering the fact that they are based on observed inflow concentrations. This reproduction of observed profiles lends credence to the calculated streamflow estimates and supports the idea that sampled inflows are representative of the waters entering Red Mountain Creek (i.e., groundwater inflow concentrations are comparable to those of the sampled surface inflows, and/or the amount of groundwater inflow is minimal). Simulations of pH and reactive constituents (As, Fe) are also very good given the relatively small changes in the equilibrium constants during calibration (Fig. 2g–i). The reproduction of dissolved As and Fe concentrations by simulating well-known processes supports earlier conclusions that these constituents are reactive within Red Mountain Creek (Sections 3.1.1 and 3.1.2). Simulation of pH and reactive constituents is a difficult task due to constituent interactions (e.g., pH affects Fe precipitation, Fe precipitation affects pH, and As sorption is affected by pH and the amount of precipitated Fe). Explicit consideration of these interactions provides an important constraint on the modeling approach, such that unrealistic simulations are unlikely. The general success in reproducing existing conditions using observed inflow chemistry and reasonable equilibrium constants indicates that the calibrated model is a suitable starting point for the consideration of premining conditions.

4.1.2. Mass loads

Results of the loading analysis (Section 3.1.2) have implications for the remediation of Red Mountain Creek. Remedial actions to date include the revegetation of tailing impoundments and hydrologic controls to divert water away from mine waste (Hardy et al., 1999). Although these remedial actions may improve the water quality associated with snowmelt and rainfall–runoff, they may do little to address sources that contribute metals and acidity over the entire hydrologic year (e.g., flowing adits). Additional remedial actions that address sources of contamination active during low-flow periods may therefore be needed. The potential for effective remediation may be enhanced by two factors. First, most major sources appear to be surface inflows rather than diffuse groundwater inflow. Collection of source water may therefore be relatively straightforward. Second, the four largest sources account for most of the loading, such that the number of sources requiring treatment may be small (sources 1–4 account for 83%, 72%, 70%, 69%, 64% and 61% of the Al, Fe, As, Zn, Cu and Cd loading, respectively; Fig. 2x–z, aa).

4.2. Premining conditions

4.2.1. Premining water quality of Red Mountain Creek

The simplistic nature of the application presented here in which only a handful of sources were qualitatively investigated precludes the use of these results to make definitive, quantitative estimates of premining water quality for Red Mountain Creek. Despite this caveat, the premining simulations are in general agreement with other findings. Runnells et al. (1992) note that Red Mountain Creek was historically known simply as 'Red Creek', presumably due to red Fe oxide coatings that were present on the streambed prior to mining. Using early geologic publications, they conclude that it is 'obvious that Red Mountain Creek was naturally contaminated by acid rock drainage' (Runnells et al., 1992). Further, Nash (2002) concludes that much of the loading is attributable to natural, unmined sources, a conclusion based in part on the presence of abundant ferricrete deposits within the watershed.

4.2.2. Identification of mining-affected sources and proximal analogues

Successful implementation of the simulation-based approach requires accurate identification of mining-affected sources and sources representing proximal analogues. In the demonstration presented here, simple field reconnaissance is used

to qualitatively determine the degree to which individual sources are affected by mining. Actual applications of the approach should employ additional techniques that quantitatively determine the history and origin of source waters. Potential techniques include the use of geographic information systems, chemical analyses of stable isotopes and rare earth elements (Verplanck et al., 1999; Davis et al., 2000), use of factor and cluster analyses to characterize source chemistry (Davis et al., 2000; Kimball et al., 2002), and the use dendrochemistry (Witte et al., 2004). Geographic information systems, for example, may be used to depict the spatial relationships between water quality conditions and watershed features, such as hydrothermal alteration zones, mine locations, geologic structures, and surficial deposits (Yager et al., 2000). Consideration of these spatial relationships may aid in the identification of sources by elucidating the main factors affecting water chemistry, including the extent of deposit exposure, grade of mineralization, presence of carbonate rocks, and the proportion of Fe-sulfides (Kelley and Taylor, 1997).

Use of the techniques noted above may help determine if the proximal analogue used in the present application is an appropriate choice for Red Mountain Creek. Although proximal analogue concentrations for most constituents are well below the concentrations of the four mining-affected sources, Pb concentrations of the proximal analogue exceed concentrations for sources 2–4 (Table 2). As a result, the simulation-based estimate of premining Pb concentrations is approximately equal to the concentrations observed under existing conditions (Fig. 2r). This result indicates that the proximal analogue is not representative of premining conditions, or that premining Pb concentrations were actually similar to the observed postmining concentrations. The task of differentiating between these two possibilities could be aided by the techniques noted above.

The simulation-based approach does not address previously identified problems with the analogue approach. Alpers and Nordstrom (2000) note that mined areas tend to have a high degree of mineralization and hydrothermal alteration, such that mined areas would have had greater contributions than unmined analogue areas. As a result, proximal analogues may provide an underestimate of premining concentrations. In addition, mining activities affect groundwater flow paths and water table elevations, resulting in changes to ground and surface water flow regimes (Alpers and Nordstrom, 2000). The potential mining-related change in flow regime is noteworthy for the present application, in which the distribution of flow under existing conditions is assumed to be unchanged relative to premining conditions. This assumption may be unrealistic, given the extensive mining activities in the Red Mountain Creek watershed. Note, however, that changes in flow regime could be addressed within the simulation-based approach (e.g., use of groundwater flow modeling to redistribute inflow waters along study reach). A related complication is the potential for changes in physical and/or biological states (e.g., amount and nature of substrate and biota) that result from changes to the hydrologic regime. These potential changes should be thoroughly evaluated and appropriate modifications should be made to the premining simulation if conditions warrant (i.e., if it is thought that existing and premining conditions are substantially different with respect to physical and/or biological states).

Table 2
Source and proximal analogue water quality

Constituent	Dissolved concentration (or pH)				
	Source 1: RM-965 (manhole)	Source 2: RM-100 (headwaters)	Source 3: RM-2634 (Champion G.)	Source 4: RM-2930 (right-bank inflow)	Proximal analogue: RM-564 (right-bank inflow)
pH	2.90	2.95	2.88	3.08	3.08
Al (mg/L)	207	80	205	65	29
As (μg/L)	936	244	36	10	0.01
Cd (μg/L)	44	11	29	12	5
Cu (mg/L)	10.4	4.6	3.0	0.3	1.6
Fe (mg/L)	471	150	302	108	5
Pb (μg/L)	342	247	136	113	303
SO_4 (mg/L)	2895	980	2616	1446	315
Zn (mg/L)	11.8	2.6	5.5	6.2	1.2

4.2.3. Simulation of geochemical processes during downstream transport

The reactive transport model rigorously considers the physical and geochemical processes that affect concentrations as water moves downstream. For the case of premining, replacement of mining-affected sources with proximal analogues affects instream concentrations in three ways: (1) mass balance calculations account for the reduction in loads and acidity; (2) instream, geochemical processing changes in response to reduced loads and acidity; and (3) reduced loads and acidity are transported downstream. The model thus provides estimates of premining water quality that reflect both the reduced loads and acidity that were present prior to mining, and the geochemical processes active during downstream transport.

Consideration of geochemical processes is an important part of the simulation exercise, as is evident from a comparison of the primary, reactive premining simulation and a second simulation in which conservative transport is assumed (Fig. 2m–r). Premining concentrations are lower when geochemical processes are considered, such that premining analyses based on the assumption of conservative transport will tend to overestimate premining concentration. This overestimation may lead to the formulation of water quality standards that are too high relative to premining conditions. Similarly, the conservative premining simulation overestimates pH, as it does not consider the precipitation of Fe oxides, a reaction that dampens the pH increase downstream of inflow RM-2992 (Fig. 2m). With the exception of Fe, differences in premining concentration for the reactive and conservative simulations are relatively small (Fig. 2n–r). This observation is somewhat misleading, however, as large differences between reactive and conservative simulations for pH and Fe could lead to large differences in Cu and Zn concentrations further downstream. These large differences would arise if additional premining inflow waters produced further increases in pH that promote sorption of Cu and Zn onto Fe oxides.

Another aspect of the reactive transport model is the ability to produce results that would not be anticipated using other methods of analysis. Runkel and Kimball (2002), for example, simulated a remedial option that led to an increase in dissolved Pb concentrations. For the present case, the pH of the proximal analogue is only slightly higher than the pH of mining-affected sources (Table 2). Despite this small change in pH, the premining simulation results in a substantial pH change relative to existing conditions downstream of RM-2992 (Fig. 2m).

4.2.4. Relationship to previous approaches for determining premining water quality

The simulation-based approach shares three common features with other approaches: (1) use of synoptic data and constituent mass balance, (2) use of geochemical modeling, and (3) consideration of downstream transport. With respect to use of synoptic data and mass balance, several investigators employ a similar approach, in which streamflow and concentration data are used to determine mass loads (Mast et al., 2000; Bird, 2003; Wanty et al., 2004). Although these studies determine the percentage of loading attributable to natural and mining-affected waters, no attempt is made to estimate instream, premining concentration. Miller and McHugh (1999), in contrast, use geochemical modeling to determine premining concentrations at three instream sites. These calculations consider the mixing of waters from unmineralized parts of the watershed and waters from unmined, mineralized parts of neighboring watersheds (geochemical analogues). Their approach differs from the simulation-based approach in that sorption reactions and the effects of downstream transport are not considered. In addition, no attempt is made to constrain the geochemical and mixing calculations by calibrating to existing conditions. With respect to downstream transport, Helgen and Moore (1996) determine premining bed sediment concentrations using equations that consider the physical processes that move sediment downstream. Their approach is primarily applicable to circumneutral-pH streams in which instream concentrations are low relative to contaminated bed sediments, such that the effects of instream transport and reaction can be ignored.

In contrast to previous approaches, the simulation-based approach includes all of the features discussed above, in a single, unified framework. Changes in constituent loading due to replacement of mining-affected sources with premining analogues are reflected within mass balance calculations. These changes are in turn routed downstream by model equations that rigorously consider physical transport and geochemical processes. The simulation-based approach thus complements and extends various features of previous approaches to the premining problem.

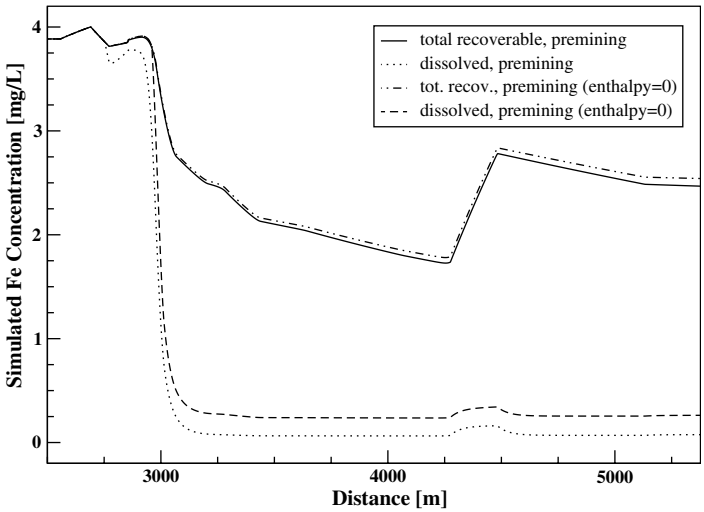

Fig. 3. Fe concentrations from the primary premining simulation and a third premining simulation in which the enthalpy of reaction for ferric dihydroxide has been set to 0.

4.2.5. Reactive transport modeling and uncertainty

Although the approach presented here holds promise for the evaluation of premining conditions, the effects of uncertainty on model estimates should be thoroughly considered. First and foremost, simulation results are highly dependent on accurate identification of mining-affected sources and proximal analogues (Section 4.2.2). In addition to this consideration, model applications should employ a formal sensitivity analysis in which a range of model parameter values are investigated. Results from such an analysis would allow for the development of upper and lower bounds on premining concentrations. Potential model parameters for inclusion in a formal sensitivity analysis include equilibrium constants for precipitation and sorption reactions, reaction enthalpy values, settling depths and velocities, and oxidation/reduction percentages. When considering the effects of these parameters, geochemical differences between existing (low pH) and premining (elevated pH) conditions should be taken into account. For example, Runkel and Kimball (2002) discuss potential differences in Fe oxide formation when considering systems with low versus elevated pH. The simulated processes at low pH (model calibration) may not correspond to processes active at elevated pH (e.g., the stoichiometry of the Fe oxide phase and the associated sorption reactions may be pH dependent). Further, some constituents may be conservative under existing conditions and reactive at elevated pH, such that the relevant reactions are not part of the calibration procedure. Such is the case for Al in the analysis presented here, where premining simulations assume an equilibrium constant for Al precipitation based on microcrystalline gibbsite. Other equilibrium constants could be equally valid (e.g., amorphous $Al(OH)_3$).

One important difference between the present application and that of Runkel and Kimball (2002) is the use of a revised thermodynamic database (Section 2.5.1). As noted by Ball et al. (2004), the revised database includes a non-zero enthalpy value for ferric dihydroxide (17.1 kcal/mole) that affects ferrihydrite precipitation (enthalpy values are used to calculate temperature-corrected equilibrium constants). To quantify the effect of this revision, a third premining simulation was conducted in which the enthalpy for ferric dihydroxide was deleted (i.e., set to 0.0, as in the original, unrevised database). Deletion of the enthalpy value results in an increase in ferrihydrite solubility (Fig. 3). This difference in solubility may have important implications for applications in which the amount of sorbent (precipitated Fe oxide) is limiting. This sensitivity of simulation results to changes in a single model parameter illustrates the need for careful selection of thermodynamic data (Parkhurst and Appelo, 1999).

5. Conclusions

A simulation-based approach for the estimation of premining water quality is presented herein. The approach is primarily applicable to acidic,

metal-rich streams in which drainage from mineralized areas may have resulted in elevated concentrations prior to the advent of mining. Such streams are complex systems in which a suite of physical and geochemical processes determine instream water quality. By rigorously considering these processes, the approach provides a unified framework for the estimation of premining conditions. Successful implementation of the approach requires spatially-detailed profiles of concentration, streamflow, and constituent load along the study reach. In addition, mining-affected sources of constituent load and sources representing premining analogues must be accurately identified. Failure to meet these requirements may result in estimates of premining water quality that are highly uncertain.

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