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Review

Hydrogeochemical processes governing the origin, transport and fate of major and trace elements from mine wastes and mineralized rock to surface waters

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ABSTRACT

The formation of acid mine drainage from metals extraction or natural acid rock drainage and its mixing with surface waters is a complex process that depends on petrology and mineralogy, structural geology, geomorphology, surface-water hydrology, hydrogeology, climatology, microbiology, chemistry, and mining and mineral processing history. The concentrations of metals, metalloids, acidity, alkalinity, Cl^-, F^- and SO_4^{2-} found in receiving streams, rivers, and lakes are affected by all of these factors and their interactions. Remediation of mine sites is an engineering concern but to design a remediation plan without understanding the hydrogeochemical processes of contaminant mobilization can lead to ineffective and excessively costly remediation. Furthermore, remediation needs a goal commensurate with natural background conditions rather than water-quality standards that might bear little relation to conditions of a highly mineralized terrain. This paper reviews hydrogeochemical generalizations, primarily from US Geological Survey research, that enhance our understanding of the origin, transport, and fate of contaminants released from mined and mineralized areas.

Mobility of potential or actual contaminants from mining and mineral processing activities depends on (1) *occurrence*: is the mineral source of the contaminant actually present? (2) *abundance*: is the mineral present in sufficient quantity to make a difference? (3) *reactivity*: what are the energetics, rates, and mechanisms of sorption and mineral dissolution and precipitation relative to the flow rate of the water? and (4) *hydrology*: what are the main flow paths for contaminated water? Estimates of relative proportions of minerals dissolved and precipitated can be made with mass-balance calculations if minerals and water compositions along a flow path are known. Combined with discharge, these mass-balance estimates quantify the actual weathering rate of pyrite mineralization in the environment and compare reasonably well with laboratory rates of pyrite oxidation except when large quantities of soluble salts and evaporated mine waters have accumulated underground. Quantitative mineralogy with trace-element compositions can substantially improve the identification of source minerals for specific trace elements through mass balances. Post-dissolution sorption and precipitation (attenuation) reactions depend on the chemical behavior of each element, solution composition and pH, aqueous speciation, temperature, and contact-time with mineral surfaces. For example, little metal attenuation occurs in waters of low pH (<3.5) and metals tend to maintain element ratios indicative of the main mineral or group of minerals from which they dissolved, except Fe, SiO_2, and redox-sensitive oxyanions (As, Sb, Se, Mo, Cr, V). Once dissolved, metal and metalloid concentrations are strongly affected by redox conditions and pH. Iron is the most reactive because it is rapidly oxidized by bacteria and archaea and Fe(III) hydrolyzes and precipitates at low pH (1–3) which is related directly to its first hydrolysis constant, $pK_1 = 2.2$. Several insoluble sulfate minerals precipitate at low pH including anglesite, barite, jarosite, alunite and basaluminite. Aluminum hydrolyzes near pH 5 ($pK_1 = 5.0$) and provides buffering and removal of Al by mineral precipitation from pH 4–5.5. Dissolved sulfate behaves conservatively because the amount removed from solution by precipitation is usually too small relative to the high concentrations in the water column and relative to the flow rate of the water.

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1. Introduction

The processes governing the production and transport of acid mine drainage (AMD) and drainage from unmined but mineralized areas are numerous and complex (Nordstrom, 1982; Nordstrom and Alpers, 1999a; Blowes et al., 2003; Jambor et al., 2003). Acid mine drainage is understood to be acidic drainage coming from mining and mineral processing activities and acid rock drainage is more general and refers to both acid mine drainage and natural acid drainage. Although there have been many laboratory studies on the oxidation of sulfide minerals during the last four decades, fewer field studies have been done examining the behavior of major and trace elements during downstream transport in fluvial systems. Of greater concern is the limited transfer of hydrogeochemical research knowledge to remediation teams attempting to alleviate trace-element contamination of water supplies. This paper reviews and outlines some generalizations regarding controls on the geochemistry of trace elements mobilized from mineralized areas into surface waters and attenuation processes that occur during down-gradient transport from the author's research and that of others in the US Geological Survey (USGS). There is much more work on this topic from the USGS than can be covered in this review, such as the coal mine drainage investigations by Cravotta (2008a,b,c), the effects of metals from mine drainage on aquatic biota (Luoma and Carter, 1990; Besser et al., 2001, 2007; Luoma and Rainbow, 2005, 2008), metals transport in major rivers (Alpers et al., 2000a,b), and geochemistry of passive treatment, especially wetlands (Walton-Day, 2003).

Mobility of potential or actual contaminants from mining and mineral processing activities depends on (1) *occurrence*: is the mineral source of the contaminant actually present? (2) *abundance*: is the mineral present in sufficient quantity to make a difference? (3) *reactivity*: what are the energetics, rates and mechanisms of mineral dissolution and precipitation relative to the flow rate of the water? and (4) *hydrology*: what are the water flow paths for contaminated water? Concentrations of constituents in natural waters depend to a large extent on the *rate of dissolution relative to the flow rate of the water* (Berner, 1978; Maher, 2010). A simple generalization is that for a trace element to be mobile in aquatic environments at least these four characteristics must be met, it must be present in the source rocks, it must be present in sufficient quantities, it must be soluble, and it must be in the water flow path. Hence, this paper begins with geologic considerations.

To illustrate hydrogeochemical processes, examples will be given for five mine sites: (1) the Questa mine along the Red River Valley, New Mexico (NM), (2) the Summitville mine, southwestern Colorado (CO), (3) the Leviathan mine, southeastern California (CA), (4) the Richmond portal of the Iron Mountain mines, northern California (CA), and (5) the Osamu Utsumi mine, Poços de Caldas, Brazil.

2. Geologic considerations

Element mobility begins with the abundance and availability of rock, mineral, and processed mineral materials. Source rocks and host rocks can have a wide range of composition and mineralogy from silicic to ultramafic igneous rocks and from limestone to black shale sedimentary rocks. Metamorphic rocks are formed from either igneous or sedimentary rocks. Known element associations with major rock types are helpful (Clarke, 1924; Rankama and Sahama, 1950); e.g., concentrations of Co, Ni, Cr, Mg and Fe are higher in mafic to ultramafic rocks whereas Mo, Be, F, Sn and W are higher in granitic (silicic) rocks. When acid waters dissolve granitoids or intermediate composition volcanics, the higher concentration of Al in the rock will produce higher dissolved Al concentrations than in mafic terrains.

Hydrothermal alteration can further concentrate these elements in sulfide minerals to form ore deposits. Arsenic concentrations are usually quite high in rocks that have Au mineralization because of the similarity in geochemistry during hydrothermal processes. Certain elements such as Au and As are more strongly associated with hydrothermal alteration and the source of ore-forming fluids than the particular lithology in which these elements are found. Understanding these associations is an important foundation for predicting which metals might occur at a given site (Plumlee et al., 1999).

Hydrothermal alteration also changes the chemistry and mineralogy of the host rocks depending on the temperature and chemistry of the fluids interacting with the rock. Propylitic alteration is characterized by an epidote–chlorite–albite mineral assemblage but carbonates are commonly present to offer neutralization capacity that counteracts the acidity produced from pyrite oxidation. Argillic alteration, however, is characterized by kaolinite, montmorillonite and pyrophyllite and usually lacks any carbonate to buffer acidity. Sericitic alteration is characterized by sericite, quartz and pyrite and may contain carbonates but often creates acid waters because the pyrite is present in greater quantities than carbonate minerals. More details on alteration zones and their mineralogy can be found in Guilbert and Park (1986) and Pirajno (2009).

The geology not only provides the petrologic source for trace-elements but it also provides the physical framework for water flow paths. The structural properties of the rocks, the porosity and permeable fractures, provide pathways for water–mineral reactions and element mobility.

Structural and geomorphological studies can contribute to the understanding of water-table levels and potentiometric surfaces, aquifer permeability, surface-water travel times, and time periods for erosion and sediment transport. Examples of these can be found in the Questa baseline results (Nordstrom, 2008). Caine (2006) mapped pervasive joint networks and fault zones in volcanic rocks

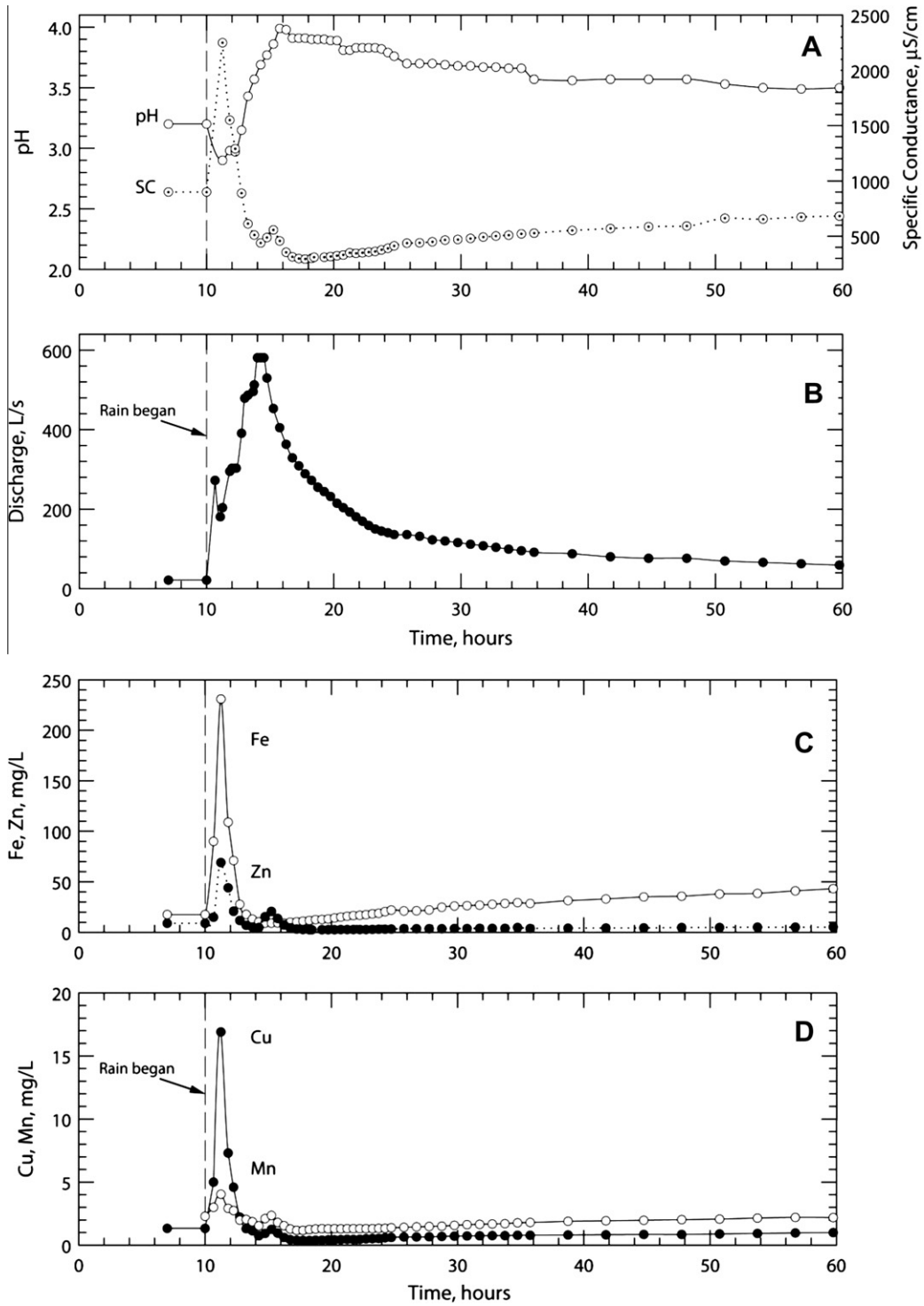

Fig. 1. Response of pH and specific conductance (A) to a rainstorm event and changing discharge of Contrary Creek, Virginia, USA (B) with consequent changes in Fe, Zn (C), and Cu, Mn (D) concentrations (modified from Dagenhart, 1980; Nordstrom, 2009).

of the Red River Valley that might increase the bedrock permeability. He then estimated the likelihood that groundwater could be contributed to the Red River from the volcanic rocks in a limited area where these fractured rocks occurred using a constrained range of gradients and hydraulic conductivities. His conclusion was that some groundwater contributions from bedrock aquifers to the Red River are certainly possible, contrary to conventional wisdom. Vincent (2008), also working in the Red River Valley, described how the combination of alluvial fans that had pushed across the river and some narrowing of low permeability bedrock had the effect of forcing groundwater to emerge into the river at several specific points along a the reach. These locations did not

align adjacent to where the catchment mouth entered the main river drainage but often kilometers downstream. His study explained the results of changing river-water chemistry along the Red River and provided key insights needed for regulatory and remediation planning.

A very important aspect of contaminant mobility from mine sites is knowledge of the approximate amounts, mineralogic and lithologic composition, and weathering potential of waste materials. Characterization of a mine site needs to, and usually does, include this information but examples occur where characterization was not adequately completed (including evaluation of remediation scenarios) and the ultimate cost of cleanup was doubled or tripled from the initial estimate.

3. Hydrologic and climatic considerations

Dissolved constituents in natural waters are released through geochemical weathering processes, transported through the hydrologic cycle, and often facilitated by microbial processes. Water flow paths are particularly difficult to quantify in mountainous, hard rock terrains typical of many mineralized areas but they are essential for identifying natural sources of contaminants (Nordstrom, 2008). Streams, lakes and rivers are the receiving water bodies for acidic drainage, and their water compositions depend on the composition and flow of surface and ground waters into them as well as the in-stream reactions (Kimball et al., 1994). In settings where a long-term flow of acidic groundwater continues into a river that experiences increasing droughts, the river-water quality will decline because of decreasing dilution from meteoric recharge (Nordstrom, 2009). The groundwater/surface-water interactions are particularly important in these terrains.

Another hydrogeochemical phenomenon that causes episodic discharges of acidic metal-rich fluids into surface waters is sometimes known as the "first flush." During the dry season, and more pronounced during extended droughts, soluble salts build up on the surface of mine wastes and soils. Soluble salt formation can occur in soils and sediments unaffected by mining activities as well. When the first major rainstorms appear, these salts are quickly dissolved and flushed into receiving surface waters in areas unaffected by mining (Durum, 1953; Hendrickson and Krieger, 1960, 1964; Edwards, 1973; Walling, 1974; Walling and Foster, 1975; Kennedy and Malcolm, 1978) and areas affected by mining (Dagenhart, 1980; Hart et al., 1982; Younger, 2000; Younger and Blanchere, 2004; Gyzl and Banks, 2007; MacCausland and McTammany, 2007; Cánovas et al., 2010). Most commonly a spike (rapid-response increase followed by a decrease) in metal concentrations occurs during the rising limb of the stream or river discharge. This phenomenon was best demonstrated by Dagenhart (1980) for mine wastes from the Sulphur, Boyd Smith and Arminius mines located along Contrary Creek, Virginia, USA. Efflorescent salts that appeared during the summer on these three mine tailings were collected and identified by X-ray diffraction and elemental analysis. The main salts consisted of melanterite, rozenite, copiapite group, halotrichite–pickeringite, alunogen and gypsum. Water samples were collected from Contrary Creek with an autosampler at a gauge site before and during rainstorm events. The results from a rainstorm of September 12–14, 1978 are shown in Fig. 1. During the rising limb of the discharge there is a spiked decrease in pH and similar increase in specific conductance and metal concentrations. This spike indicates the rapid "first flush" of soluble salts dissolving from the waste piles. Following the spike there is dilution of the water composition to concentrations lower than those that existed before the storm. Clean water runoff eventually dilutes both the solubilized salts and the continual seepage of acid mine water. As the rainstorm ends, the metal concentrations will gradually increase to a level representing a steady state between clean groundwater discharge and acid seepage from the mine piles.

This pattern changes and becomes much more complex for a large river system such as the Rio Tinto in southern Spain. The Rio Tinto discharge is about an order of magnitude greater than Contrary Creek but increases much more during rainstorm events because of its much greater drainage area. It also contributes AMD from one very large area where mining has transpired since Roman times and numerous smaller mines. Rainfall varies considerably throughout the drainage, tributary catchments within the drainage basin respond according to area and elevational gradient as well as storm intensity and duration. Nevertheless, the large masses of mine wastes and their associated acid efflorescent salts and evaporatively concentrated mine waters can cause considerable spiked decreases in pH and increases in metal concentrations associated with major runoff after the dry season as reported by Cánovas et al. (2010) for the Rio Tinto. These rainstorm events can transport considerably more metals, SO_4^{2-} and acidity than the loads transported during low flow for a similar period of time. For example, Cánovas et al. (2010) estimated that during October of 2005 when three rainstorms came through the basin, the increased load from those events contributed 22–35% of the annual pollution load whereas the monthly discharge for October only contributed 8.3% of the annual discharge.

4. Chemical considerations: conservative and non-conservative elements

Elements can be grouped according to whether they react substantially (non-conservative) or react little (conservative) during downstream or downgradient transport. This simple division can be a very helpful one but it must be remembered that (1) it is partially an inherent property of the element, (2) partially a function of the pH, solution composition, redox chemistry, temperature, water flow rates, and microbiology, and (3) no element is entirely conservative or non-conservative. In acidic waters (pH < 4), metal cations generally stay dissolved except Fe(III) and the more insoluble metals such as Au, Ag, Pb, and Ba. Gold and silver, as the metallic elements, have inherently low solubilities in most acidic solutions. Lead and Ba form the very insoluble sulfate minerals,

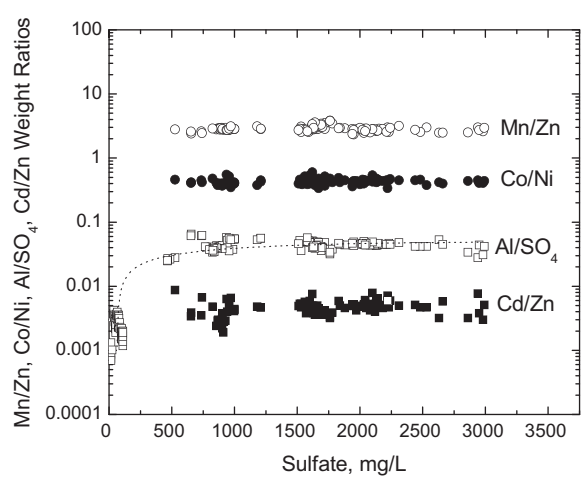

Fig. 2. Plot of Mn/Zn, Co/Ni, Al/SO_4, and Cd/Zn weight ratios for the Straight Creek aquifer. The pH ranges from 3 (with SO_4^{2-} concentration about 2500–3000 mg/L) at the headwaters to 4 (with SO_4^{2-} concentrations about 500–1000 mg/L) at the downgradient end of the aquifer (data from Naus et al., 2005). Dotted line represents Al/SO_4 ratios for the Red River downstream from the Straight Creek catchment, northern New Mexico, USA.

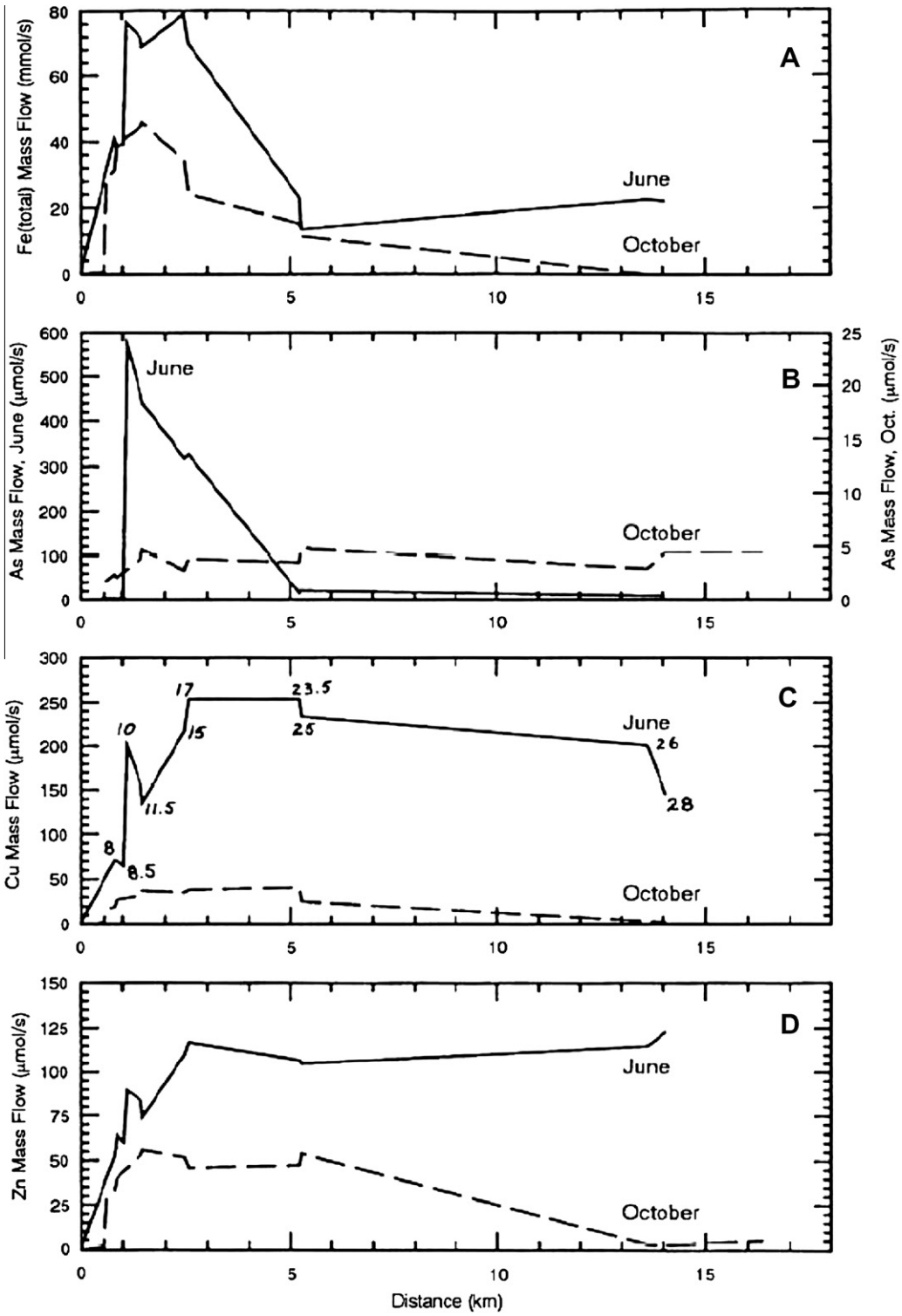

Fig. 3. Mass flow for Fe (a), As (b), Cu (c) and Zn (d) under two different flow regimes for the Leviathan Creek/Bryant Creek, southeastern California, drainage system (from Webster et al., 1994). Most of the acid mine drainage from the Leviathan mine enters the main drainage within the first kilometer downstream from the mine.

anglesite and barite, respectively, in acid-sulfate waters (Nordstrom and Alpers, 1999a).

Most major and trace elements in naturally acidic groundwaters of the Straight Creek debris-fan aquifer near Red River, NM, decrease in concentration with downgradient transport but their metal/sulfate ratios are constant (Nordstrom, 2008). These groundwaters are slowly diluted by seepage of water from the sides of the canyon. Analyses of the headwater creek flowing into the debris fan and several wells placed downgradient were monitored for 12–18 months. Most of the water compositions were constant over time and showed decreasing SO_4^{2-} concentrations from the most upgradient well (median of 2000 mg/L) to the most downgradient well (median of 1000 mg/L). The decrease in SO_4^{2-} concentration could be explained by additional dilute water coming into the

fan from the side canyon bedrock aquifer (McAda and Naus, 2008). The pH increases from 3 to 4 over this range of decreasing SO_4^{2-} concentrations. Constant weight ratios for Mn/Zn, Cd/Zn and Co/Ni relative to decreasing SO_4^{2-} concentrations were observed as shown in Fig. 2. Constant ratios indicate there is no significant attenuation of metals during downgradient flow while the SO_4^{2-} concentrations become diluted through mixing. It also suggests one mineral might be the major source for these elements, e.g. Cd/Zn is in the range of sphalerite compositions and Co/Ni is in the range of that found in pyrite compositions. The exception is shown by the data for Al/SO_4 ratios. Included with the Straight Creek data for Al/SO_4 ratios are ratios for the Red River (pH = 7.5–8.5) downstream from Straight Creek catchment with a dotted line showing the trend of decreasing ratios with decreasing SO_4^{2-} concentrations. Once the acid water seeps into the river, Al is precipitated as demonstrated by greatly decreased Al/SO_4 ratios at low SO_4^{2-} concentrations. Here is an example of an element that behaves conservatively over a range of low pH and non-conservatively for higher pH values. A more detailed summary of the behavior of Al is given in Section 4.3.

In surface waters, Fe and As are attenuated most rapidly (Wakao et al., 1988; Webster et al., 1994; Williams, 2001). Both elements are rapidly oxidized and Fe forms insoluble colloidal precipitates on which As readily sorbs. In some instances actual Fe–As mineral precipitation, such as tooeleite, has been identified (Morin et al., 2003, 2007). Arsenic is rapidly oxidized in geothermal waters as well as in acid-mine drainage (Wilkie and Hering, 1998; Gihring et al., 2001) and it is thought to be catalyzed by microbes. However, Fe(III) also rapidly oxidizes As so that it may depend on the Fe(III)/As(III) ratio. As soon as dissolved Fe(II) starts oxidizing and precipitating the As rapidly oxidizes and sorbs onto the precipitating hydrous ferric oxides (HFO).

In Fig. 3 the mass flux of four elements from the Leviathan mine, Fe, As, Cu and Zn in Leviathan–Bryant Creek are compared for two different seasons, June and October of 1982 (Webster et al., 1994). The flows are lower in June and less diluted with lower pH values than in October which causes a change in the metal profiles. The source of the AMD contains high concentrations of Fe(II) (over 1000 mg/L), accounting for the high concentrations in Leviathan Creek (the name applies to the upper 5 km of the creek and below 5 km it is named Bryant Creek). The rapid decrease of Fe is caused by rapid oxidation of Fe(II) and precipitation of the resulting Fe(III) (Fig. 3a). As rapidly as the Fe is precipitated, As is also removed through sorption and co-precipitation in the June profile (Fig. 3b), a good example of simultaneous removal of As with Fe. In the October sampling the mine effluent As and Cu concentrations were much lower than in June. Copper flux for June shows a small amount of removal (Fig. 3c) and Zn flux for June (Fig. 3d) is unaffected by the Fe precipitation processes but shows removal in October. This removal of Zn in October would be related to the higher pH values of 6–8 for Bryant Creek compared to 4–5.9 in June. Hence, natural attenuation depends on pH and Fe concentrations which will fluctuate depending on seasonal flow patterns. Rough estimates of attenuation could be predicted using the generalized double-layer model in the MINTEQ code (Webster et al., 1994).

4.1. Mass balances

When characterizing a site for actual or potential hydrologic contaminants, the core concept is that of the law of conservation of mass, or simply mass balances. Mass balances are commonly applied to loading calculations and have become a regulatory feature with the application of total maximum daily loads, or TMDL (e.g. National Research Council, 2001). A "load" is a mass-flux calculation usually in units of mass per unit time. There are other types of mass balances. One is the mass balance on ions in solution required for electroneutrality known as charge balance, a quality-control check on a chemical analysis for major ions. The charge-balance equation can be combined with a mass-balance equation on species of the same element in solution (or combined solid and aqueous species) to solve simultaneous equations for solving chemical problems in aqueous solution. Another mass balance is that required during the dissolution of precipitation of minerals in geochemical reactions. A simulation of pyrite oxidation with PHREEQC (Parkhurst and Appelo, 1999) under three equilibrium conditions: (1) oxidation to an acid ferrous sulfate solution, (2) oxidation to an acid ferric sulfate solution, and (3) oxidation to an acid solution with precipitation of ferrihydrite found in Nordstrom (2004).

Another is the mass-balance approach, or inverse modeling, for converting groundwater analyses along a flow path to masses of minerals dissolved and precipitated (Plummer et al., 1983; Parkhurst and Plummer, 1993; Glynn and Plummer, 2005). Four different examples of mass balances for acid-rock drainage will demonstrate characteristic trends for the weathering of sulfide-mineralized rock.

The first example is for effluent water from the Richmond portal at Iron Mountain, California, a major superfund site still undergoing remediation after 28 a of site characterization and remedial action. The Richmond mine consists of underground tunnels and excavations that entered a large massive sulfide deposit consisting of 95% pyrite and smaller percentages of chalcopyrite and sphalerite. The host rock is a rhyolite that has undergone keratophyric alteration (thermal alteration in seawater). The mass balance was calculated as an output–input type with the assumption that input water (rainwater) was so pure compared to the composition of the output water that its composition could be neglected. It was further assumed that although soluble salts formed and dissolved inside the mine workings all but melanterite could be ignored in the mass balances and the overall difference in water chemistry could be attributed to the dissolution of primary minerals based on mineral chemistry data from Kinkel et al. (1956). Melanterite is the first soluble salt to form from evaporating acid mine water still in contact with pyrite (Nordstrom and Alpers, 1999a). Iron oxyhydroxides were not considered to precipitate because of the known large abundance of soluble Fe-sulfate salts (Nordstrom and Alpers, 1999b; Jamieson et al., 2005). The effluent water chemistry is given in Table 1. The mass balance results are shown in Table 2 where millimolality refers to the molality of the respective minerals or gases dissolved (positive number) or minerals precipitated or gases degassed (negative number). From this calculation it is clear that the main reaction is the oxidation of pyrite and sphalerite and the precipitation of melanterite and silica. This site is an extreme example of pyrite oxidation because the mine workings are located

Table 1
Major solute composition of Richmond mine portal, Iron Mountain mines, northern California, USA, effluent water (1990-09-11; Alpers et al., 1992).

Constituent	Millimolality
Fe	390.4
Cu	5.35
Zn	3.69
Na	13.0
K	8.42
Ca	5.35
Mg	41.0
Al	100.8
SiO_2	3.22
SO_4	1486
pH	0.4

Table 2
Mass balance results for Richmond mine portal effluent assuming the composition of the water composition could be derived from the precipitation (negative amount) and dissolution (positive amount) of the listed minerals (from Alpers et al., 1992).

Mineral phase	Model 1, millimolality	Model 2, millimolality
Pyrite	1068	1066
Sphalerite	39.5	39.5
Chlorite	13.6	13.7
Albite	12.0	12.0
Sericite	12.0	12.0
Chalcopyrite	5.2	5.2
Kaolinite	4.3	6.8
Epidote	2.4	–
Calcite	–	4.7
Melanterite	−699	−695
SiO_2	−124	−122
O_2	3830	3830
CO_2	–	−4.7

within a massive sulfide body. However, as shown in the next two examples, the precipitation of an Fe phase and a silica phase is always a necessary process in the weathering of pyritic rock.

For the Iron Mountain water one could write the overall reaction in moles as:

$$\begin{aligned}
&1.07\text{pyrite} + 0.04\text{sphalerite} + 0.005\text{chalcopyrite} + 3.8O_2 \\
&\quad + 0.014\text{chlorite} + 0.012\text{albite} + 0.012\text{sericite} + 0.004\text{kaolinite} \\
&\quad + 0.002\text{epidote} + H_2O \\
&\quad \rightarrow 0.7\text{melanterite} + 0.39Fe^{2+}_{(aq)} + 0.1SiO_{2(s)} + 0.003SiO_{2(aq)} \\
&\qquad + 0.004Zn^{2+} + 0.005Cu^{2+}_{(aq)} + 0.013Na^{+}_{(aq)} + 0.008K^{+}_{(aq)} \\
&\qquad + 0.468H^{+} + 0.005Ca^{2+}_{(aq)} + 0.04Mg^{2+}_{(aq)} + 0.1Al^{3+}_{(aq)} \\
&\qquad + 1.49HSO^{-}_{4(aq)}
\end{aligned}$$

Quantitative assessments of weathering rates in groundwaters require age-dating. Age dating may be possible with chlorofluorocarbons, $^2H/He$, or other isotopes (Coplen, 1993; Plummer et al., 1993; Bethke and Johnson, 2008) and field weathering rates can be derived from mass balances and age dates (e.g. Burns et al., 2003). When underground mining draws down the water table and water is drained to a single portal, the weathering can be simply calculated from the measured discharge and the water composition. Based on decades of monitoring and an average discharge of about 265 L (70 gallons)/min, the average weathering rate from the Richmond portal is about 17,100 mol of pyrite/h (Alpers et al., 1992). This is an extreme rate that can be compared to a natural rate (unaffected by mining) described in the third example for Straight Creek.

The second example is mine drainage from the Leviathan mine, California (Ball and Nordstrom, 1989; Webster et al., 1994). The mineralogy at this site is not so well characterized but the description fits that of a near-surface hot spring environment with a large layer of pure S lying on top of and adjacent to an andesitic tuff (Evans, 1966). It was primarily mined for S that was used to make H_2SO_4. Assuming pyrite, silica sinter, kaolinite, K-feldspar, andesine and chlorite to be present, and that silica and goethite can precipitate, a mass-balance calculation was done for major ions in the effluent water of the number five tunnel collected in 1982 (Ball and Nordstrom, 1989). It was shown by trace-element determinations and by S isotopes that nearly all the H_2SO_4 was produced from pyrite oxidation, not from S oxidation (Ball and Nordstrom, 1985). At the time the water sample was collected the discharge was about 1 L/s which is about 40 mmol of pyrite weathering/h (Table 3).

Table 3
Mass-balance results for Leviathan mine, southeastern California USA, portal drainage.

Mineral phase	Model, millimolality
Pyrite	39.25
Kaolinite	6.78
Calcite	2.87
K-spar	0.353
Andesine	1.005
Chlorite	0.442
NaCl	0.240
Goethite	−11.25
Silica	−14.7
pH	1.80

Table 4
Mass-balance results for Straight Creek (New Mexico, USA) water composition, from Nordstrom (2008).

Mineral phase	Model, millimolality
Pyrite	8.66
Dolomite	4.64
Gypsum	3.78
Kaolinite	1.40
Oligoclase	0.44
Fluorite	0.20
Sphalerite	0.11
Illite/ Sericite	0.032
Chalcopyrite	0.029
Goethite	−7.40
Silica	−2.89
pH	2.98

The third example is from Straight Creek, Red River Valley, NM. The valley hosts Precambrian metamorphic rocks, quartz latite porphyry, and andesitic and rhyolitic volcanic rocks (Ludington et al., 2005). Hydrothermal alteration is apparent in many locations and it ranges from propylitic to quartz–sericite–pyrite. Where abundant pyritized rock encounters the weathering zone, natural acid-rock drainage occurs. The Straight Creek drainage was studied in some detail to elucidate the hydrogeochemical processes of acid drainage and groundwater chemistry in the downgradient debris fan. A mass balance was calculated (Nordstrom, 2008) for natural acid water occurring near the headwaters of Straight Creek using mineralogical results from Plumlee et al. (2005). The results are shown in Table 4.

Note that in this example there are two sources of SO_4^{2-} in the water, gypsum and pyrite. Most hydrothermal mineral deposits formed anhydrite or gypsum in their alteration zones. In the Red River, calcite and pyrite coprecipitated in fractures during hydrothermal alteration and reacted during weathering to form secondary gypsum. Abundant gypsum can be found in mineralized areas and on debris fans. The mass balance suggests that almost twice as much aqueous SO_4^{2-} comes from pyrite oxidation than from gypsum dissolution. Again Fe and silica minerals are precipitated. These are the dominant reactions.

Discharge from Straight Creek averaged about 37.85 L (10 gallons)/min, for the period 2001–2003. Hence the weathering rate is approximately 5.46 mmol of pyrite/h, six orders of magnitude less than that at Iron Mountain. An estimate of natural weathering rates for sulfides at Iron Mountain came to a similar conclusion – that mining could enhance weathering rates up to three orders of

magnitude more than natural weathering rates (Alpers et al., 2007).

These pyrite weathering rates can be compared to laboratory rates of pyrite oxidation in batch experiments with or without microbial Fe oxidation. Microbial pyrite oxidation rates were standardized in an interlaboratory comparison with the same monoculture (*Acidithiobacillus ferrooxidans*, Olson, 1991) and the results were quite consistent at 0.22 mmol of Fe/L/h with a relative standard deviation of 32%. If this is converted to 0.22 mmol of pyrite/h by assuming that the rate is independent of the solid/solution ratio, it is substantially less than field rates. A faster laboratory rate occurs when high concentrations of dissolved Fe(III) are mixed with pyrite, which is typical of abiotic oxidation rate studies (Garrels and Thompson, 1960). Again the abiotic oxidation rates with Fe(III) as the oxidant are fairly consistent among different investigators (Nordstrom and Alpers, 1999a) and are in the range of 0.2–20 mmol pyrite/h for pH < 3 (assuming aqueous Fe(III) concentrations are in equilibrium with freshly precipitated hydrous ferric oxide (HFO) such as ferrihydrite or schwertmannite, Mckibben, 1984; McKibben and Barnes, 1986). The pyrite oxidation rate estimate for Straight Creek is greater than the biotic rate but very comparable to the abiotic rate. The pH values for Straight Creek water are typically about 2.5 and may be lower at the actual sites of oxidation. For pH of 2–2.5 McKibben (1984) estimates rates of 1–3 mmol/h which is comparable to the field rate. The rate for Leviathan, however, is higher than the abiotic rate and the rate at Iron Mountain is more than six orders of magnitude higher. For Leviathan the grain size of the pyrite is extraordinarily small, called "cryptocrystalline" by Pabst (1940). The small grain size could easily account for the higher oxidation rate at Leviathan. At Iron Mountain, especially the Richmond mine, the high heat flux has caused substantial evaporation of waters underground and huge quantities of soluble salts have formed. At this site the weathering rate actually reflects the transport of evaporated mine pools and dissolution of soluble salts more than the oxidation of pyrite. I would suggest that the laboratory oxidation rates, especially the abiotic rates, provide an upper limit to pyrite weathering and when field rates are substantially higher than these rates it likely reflects the dominance of acid water concentrated by evaporation and dissolution of efflorescent salts moving through the system. In spite of the numerous variables that might affect any comparison between field and laboratory rates, these initial findings are encouraging.

The last example is from a study of weathering at Osamu Utsumi mine near Poços de Caldas, Brazil (Nordstrom et al., 1992). The site was studied as one of several natural analogs to a radioactive waste repository (Miller et al., 1994). The Osamu Utsumi mine was a U deposit consisting of an alkali intrusive complex of phonolite and nepheline syenite that had been hydrothermally altered and then exposed to about 75 Ma of supergene weathering (Holmes et al., 1992; Schorscher and Shea, 1992). Detailed mineralogical investigations revealed important information about mineral chemistry and the characteristics of the ore deposit (Waber et al., 1992). Pyrite mineralization was one of the signatures of the hydrothermal alteration and acid-mine drainage was produced during open-pit mining. The groundwaters beneath the open pit were sampled from boreholes and a mass-balance calculation was done on a groundwater from a relatively shallow borehole (SW01; Nordstrom et al., 1992) as shown in Table 5. This aquifer contains calcite and siderite but not enough to neutralize the effects of pyrite oxidation in the shallow subsurface. Hence, the amount of pyrite dissolved is slightly less than that found at the Straight Creek site. Other aspects are much the same, most of the Fe dissolved from pyrite is precipitated as secondary HFO and more silica is precipitated than in the previous example. It should be noted that to achieve a more quantitative mass balance result, dissolved Al values are needed for the groundwater samples. They play an important role in the mass transfer for breakdown of feldspars and phyllosilicates. In these examples the pH is too low for clay minerals to be stable and they dissolve. Without dissolution of kaolinite, for example, a mass balance could not always be achieved.

Table 5
Minerals dissolved and precipitated to form a shallow acidified groundwater below the Osamu Utsumi open pit, Poços de Caldas, Minas Gerais, Brazil (from Nordstrom et al., 1992).

Mineral phase	Millimolality
Pyrite	6.152
Calcite	2.777
Kaolinite	1.22
Potassium feldspar	0.966
Manganese oxyhydroxide	0.839
Fluorite	0.393
Sphalerite	0.196
Albite	0.087
Chlorite	0.0762
Ferrihydrite	−5.192
Silica	−4.622
CO_2	−2.777
pH	3.37

4.2. Fe(III) precipitation

Oxidation of Fe(II) occurs rapidly at low pH but at measureable rates of about 1–5 mmol/L/h in surface waters by chemoautotrophic bacteria and archaea (Nordstrom, 2003). During the oxidation of dissolved Fe and down-drainage neutralization of the acid water, HFO minerals precipitate, such as micro- to nano-crystalline goethite, schwertmannite and ferrihydrite. The precipitate is usually a mixture of phases of uncertain composition and crystallinity. Using $Fe(OH)_3$, or "ferrihydrite", as a proxy for HFOs, more than 1500 samples of acid-rock drainage and receiving streams from locations in the western USA were selected to calculate ferrihydrite saturation indices using WATEQ4F (Ball and Nordstrom, 1991). The samples were screened for charge balance and they had to contain both Fe(II/III) determinations and electrometric measurements of redox potential. The results are shown in Fig. 4.

Supersaturation of up to nearly four orders of magnitude is indicated relative to a log K = 4.9 (freshly precipitated HFO). The range

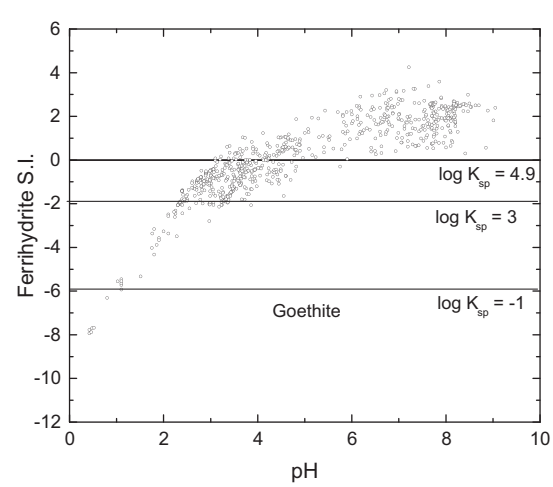

Fig. 4. Ferrihydrite [$Fe(OH)_3$] saturation indices relative to pH for 1510 screened analyses from western USA mine sites.

of log K from 3 to 4.9 reflects the range of reported values (Nordstrom et al., 1990). This amount of supersaturation is not reasonable and the possibility of it being caused by colloids of HFOs getting through the filter equipment had to be considered. One approach to this problem was to consider the effect of introducing detection limits for Fe(III) and for the redox potential measurements. The comparison of Eh calculated from Fe(II/III) determinations to Eh from electrode measurements is shown in Fig. 5. Most of the values at high potential (>0.550 V) agree quite well but far fewer values agree well at lower potentials. Values that were below the detection limits for Fe(III), which were estimated to be anything <Fe(III)/(Fe(II) + Fe(III)) = 3%, were eliminated. Values of redox measurement that were made on samples with Fe < $10^{-5.5}$ molar were also eliminated (Morris and Stumm, 1967; Naus et al., 2005). The result for the comparison of Eh values is shown in Fig. 6. Now most of the values fall within a ±0.050 V range.

After elimination of all data points which are below the detection limits for Fe(III) and for electrode measurements, the revised ferrihydrite saturation index diagram has virtually eliminated the effect of gross supersaturation (Fig. 7). Saturation with respect to HFO is now seen to be maintained and the supersaturation seen previously is likely an artifact of HFO colloids passing through the filter apparatus.

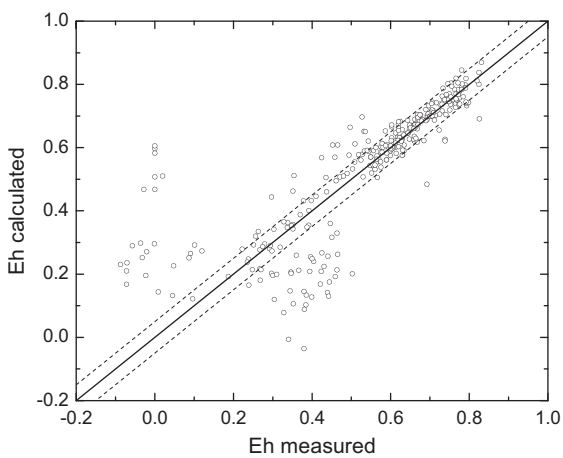

Fig. 5. Eh calculated from Fe(II/III) determinations and speciation from the WATEQ4F code substituted into the Nernst equation compared to the measured redox potential corrected for the half-cell reference potential. All values in volts. Samples are the same as those used in Fig. 4.

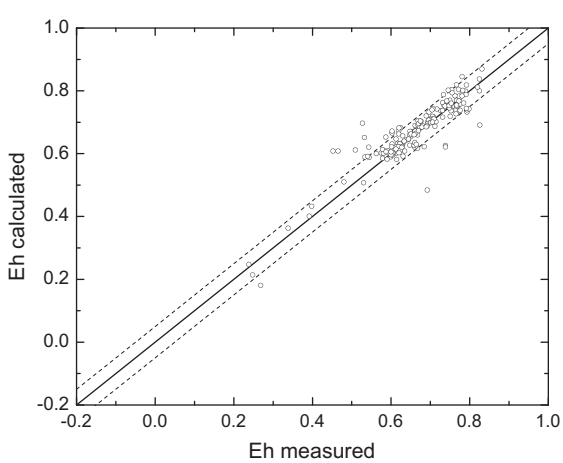

Fig. 6. Same plot as Fig. 5 with all points removed for which Fe determinations were less than $10^{-5.5}$ m and Fe(III) determinations were less than 3% of the total dissolved Fe concentration.

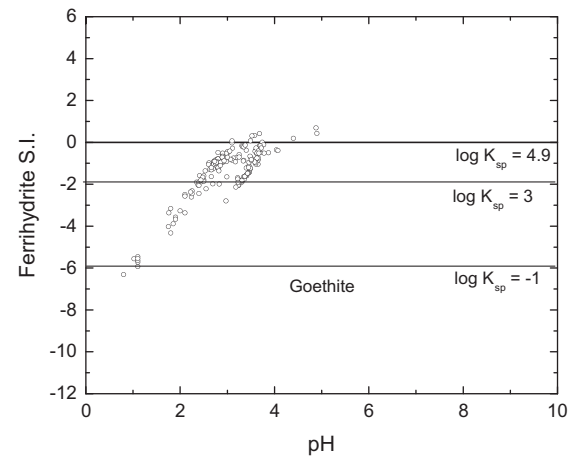

Fig. 7. Same plot as Fig. 4 after removing all points below detection limits of Fe(III) and of redox electrode measurements.

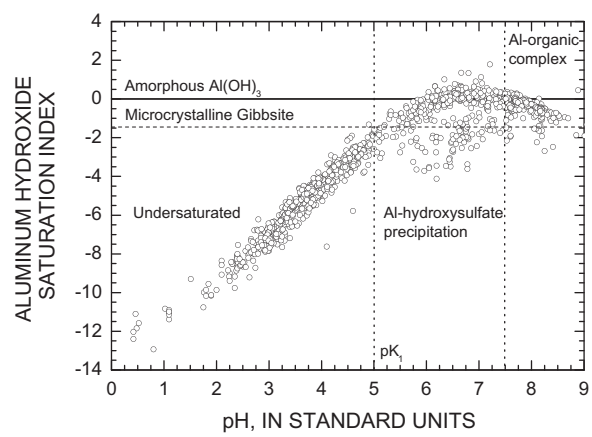

Fig. 8. $Al(OH)_3$ saturation indices relative to pH for the same samples shown in Fig. 4.

4.3. Al precipitation

Aluminum also precipitates from acid surface waters when they are diluted or neutralized to a pH of ⩾4.5–5 (Nordstrom and Ball, 1986) because $pK_1 = 5$ for Al^{3+} hydrolysis, a necessary condition for onset of precipitation. This hydrolysis would also provide some pH buffering. For groundwaters, there appears to be a buffering and precipitation of Al closer to a pH of 4 and co-precipitation of silica may be important (Blowes et al., 2003; Naus et al., 2005). Using the same data set of 1510 samples, saturation indices are plotted for $Al(OH)_3$ in Fig. 8. Three ranges of pH can be identified that describe Al geochemistry. For pH values < 5, Al is conservative in surface waters; for pH values of 5–7.5 a solubility limit is reached which corresponds to "amorphous" $Al(OH)_3$ (or microcrystalline basaluminite, Bigham and Nordstrom, 2000). For pH values > 7.5 the Al concentrations are typically low and organic complexing likely dominates (Ball et al., 2005). Relatively constant concentrations of dissolved Al have been observed for this pH range and it is difficult to interpret without organic complexing. For the Red River, NM, the dissolved Al concentrations cluster tightly around 0.16 mg/L whereas the dissolved organic C is 1–2 mg/L. The

downturn trend in the data for pH > 7.5 is an artefact of the speciation code when it applies hydrolysis to form $Al(OH)_4^-$ species instead of applying organic complexes.

Water analyses plotted in Fig. 8 that are substantially below the general trend for pH > 5 are dilute surface waters that have not mixed with acid Al-rich waters. The main trend is to be expected for waters that begin as acid rock drainage with pH < 4 and high dissolved Al concentrations that become diluted as they mix with cleaner, circumneutral pH, mountain streams during downstream transport. A good example of the solubility control comes from the Red River where acid seeps enter the carbonate-buffered river at several points along banks yet the dissolved Al concentration remains constant while the unfiltered, acidified samples continually increase in Al because of the buildup of colloidal Al in the surface water (Fig. 9).

The Al concentration profile in Fig. 9 is quite striking because the dissolved Al is fairly constant in spite of the loadings of Al-rich acid seeps but the total Al (unfiltered, acidified samples) concentration continually increases downstream. This result would be caused by a solubility control with some particles of the Al precipitate remaining in the water column without depositing as suggested by Fig. 8. Although the exact nature of the precipitate is not well-characterized, other studies have shown that it is a fine-grained form of basaluminite and often amorphous to standard X-ray diffraction (Clayton, 1980; Bigham and Nordstrom, 2000). White precipitates consistent with a basaluminite composition have been found in many places where Al-rich acid waters mix with neutral waters giving a buffered pH near 5 after mixing (Nordstrom and Ball, 1986; Minikawa et al., 1996; Bigham and Nordstrom, 2000).

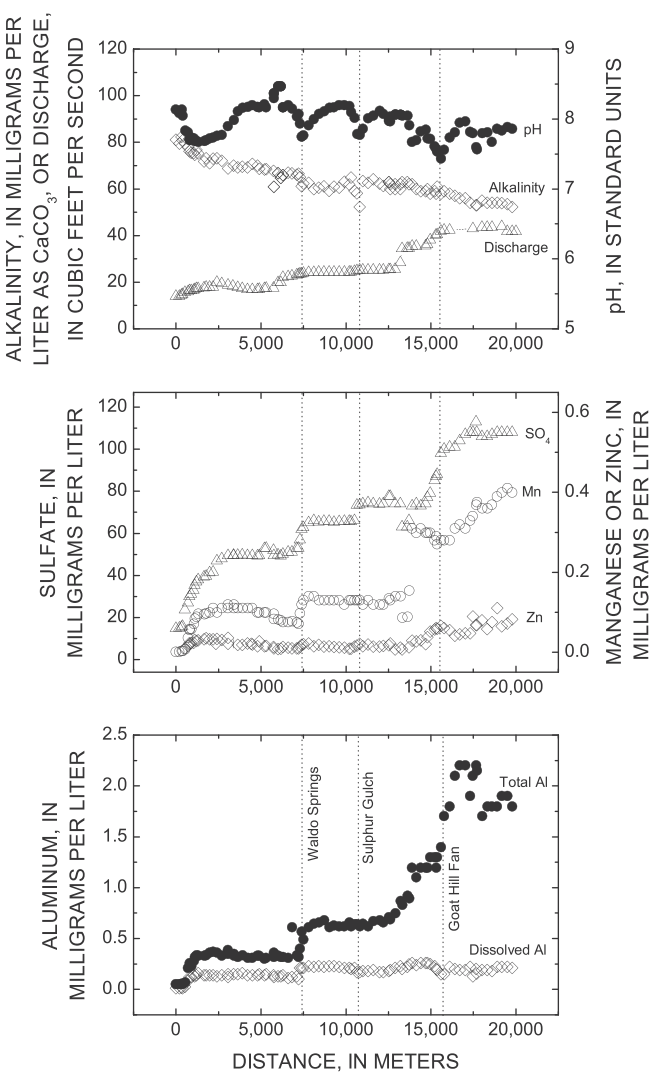

Fig. 9. Profile of pH, alkalinity, discharge, and Mn, Zn, SO_4, total Al, and dissolved Al concentrations along the central portion of the Red River, northern New Mexico, USA (from Nordstrom, 2005, 2008). (N.B. – 1 Cubic foot = 0.0283 m^3).

4.4. Mn mobility

Points of mixing of natural and mining acid seeps into the Red River can be seen in Fig. 9 where the pH of the river decreases at four distinct locations, near the beginning of the profile and then at the three other locations labeled Waldo Springs, Sulphur Gulch and Goat Hill fan (Kimball et al., 2006; Nordstrom, 2008). The continued mixing of acid causes the gradual decline of alkalinity from about 80 to 50 mg/L and SO_4^{2-} concentrations can be seen to increase at the same points where the pH decreases. The Mn concentration profile is more complicated because of its redox properties. Reduced Mn, Mn(II), occurs in many groundwaters and is much more soluble than oxidized Mn, Mn(IV), which would be the stable form in oxygenated surface waters. Hence, dissolved Mn(II) from groundwater seeps (derived from dissolution of rhodocrosite and manganiferous calcite) contributes Mn to the river but this gradually decreases in concentration from oxidation and precipitation. The flux profile for Mn and additional elements for the Red River can be found in Kimball et al. (2006). Further interpretations of element geochemistry over a range of pH in the mineralized and mined area of the Red River can be found in Nordstrom (2008).

4.5. Diel variations in metal concentrations and iron photoreduction

In addition to seasonal variations, metal concentrations can vary in the course of a 24-h (diel) period for a single location on a stream or river reach. The amount of variation can range from undetectable to several-fold but the pattern is unmistakenly related to the solar cycle. This phenomenon has been observed in several streams affected by acid mine drainage (McKnight and Bencala, 1988; Fuller and Davis, 1989; Nimick et al., 2003, 2005, 2011; Gammons et al., 2005, 2007a,b; Nimick and Gammons, 2011). Interpreting the cause of these cycles has been challenging. Temperature and pH changes play a role and can affect sorption equilibria on short time scales; Fe photoreduction is important and has a clear diel trend, and algal growth and uptake cannot be ruled out but seems less important. Regardless of the mechanism, it is imperative that diel cycles of trace metals be observed and identified when characterizing trace metal transport in streams and rivers. An additional complexity is that one diel cycle may only tell you how concentrations vary on that day/night cycle. Diel cycles also vary with seasons and flow regimes (Nimick et al., 2005).

An important aspect of the diel variations in metal concentrations is the phenomenon of Fe photoreduction. Dissolved Fe is photosensitive and solar radiation can convert aqueous Fe(III) and Fe(III) colloids to Fe(II) (McKnight et al., 1988) which can then fuel Fe-oxidizing chemoautotrophic bacteria (Gammons et al., 2008). Iron photoreduction will reverse the sorption process by dissolving colloids. Solar-driven reduction of colloids increases the complexity of sorption modeling because the rate of photoreduction now depends on unpredictable weather conditions such as cloud cover.

4.6. Sorption

It is not the intention of this paper to review sorption processes in connection with other processes but a few generalizations with

regard to partitioning of trace metals between dissolved and suspended particulates should be made.

The two elements that are removed from solution most rapidly with Fe oxidation and HFO precipitation are As and Tl (Fig. 3, Webster et al., 1994, and unpublished data on Tl). Common metal contaminants from mine drainage show sorption isotherm edges that vary with pH and typically sorb from most strongly to less strongly as Pb > Cu > Zn > Cd. The sorption isotherms, however, are very sensitive to the substrate. For example, Webster et al. (1998) found that schwertmannite had greater sorption than ferrihydrite at a given pH and AMD precipitates had markedly greater sorption than schwertmannite for the same pH. They also showed the presence of sulfate affected sorption.

Paulson and Balistrieri (1999) have shown the greater ability of HFO and particulate organic C to sorb trace metals compared to the other common precipitate in AMD, hydrous Al oxides, though adjustment of the complexation constants was necessary to obtain a good fit to experimental data. Some progress has been made on developing a database for cation sorption modeling on hydrous manganese oxide (Tonkin et al., 2004). Using the HFO database from Dzombak and Morel (1990), Tonkin et al. (2002) were able to simulate the sorption of Pb, Cu, and As for field precipitates from mixing of acid drainage with ambient surface water. By modifying the complexation constants, Balistrieri et al. (2003) were able to model the sorption of a wider range of metal cations and metal oxyanions.

5. Reactive-transport modeling based on synoptic sampling with tracer-injection

Although this paper cannot cover comprehensively the field of surface-water reactive-transport modeling for mineralized areas, it would be remiss not to summarize and review some of the major contributions that USGS personnel have made to this important topic. Further, several of the previously cited studies would not have been possible without synoptic sampling and discharges with tracer-injection, techniques that were developed and refined over several decades. The importance of this subject cannot be emphasized too much (Caruso et al., 2008).

Early studies on solute transport in streams and rivers (Kennedy, 1971; Kennedy and Malcolm, 1978; Kennedy et al., 1984; Jackman et al., 1984) led to the concept of transient storage (Bencala and Walters, 1983) and simulations of reactive interactions of ions with the bed sediment (Bencala, 1983; Bencala et al., 1984). During transport along a study reach, as much as 68% of the travel time may be spent in transient storage but most frequently it is 1–20% (Runkel, 2002). Tracer injections of conservative and non-conservative constituents have been used to develop mathematical models for simulating reactive transport (Zand et al., 1976; Jackman et al., 1984). Although fluorescent dyes are the most sensitive of tracers, they have been found to be unstable under some chemical conditions such as acidic and Fe-rich waters (Bencala et al., 1986). Solutions of LiCl are best for acid waters (more conservative behavior and cost-effective) and solutions of NaBr are best for neutral to basic waters (Bencala et al., 1990) with some exceptions (R.L. Runkel, USGS, pers. comm., 2011). Generally Br^- is the best inorganic tracer.

Synoptic sampling with tracer-injection was critical to the Questa study where groundwater–surface water interactions and downstream changes in river-water chemistry could not be interpreted without this information (Ball et al., 2005; Kimball et al., 2006). This study was of particular importance to a mining company and the regulatory authorities which needed to know the extent to which natural background was contributing contaminants to the surface waters. Numerous other synoptic/tracer-injection studies have been completed by the USGS for catchments affected by acid mine drainage in mined areas of the US (Kimball et al., 2003, 2006 and references therein).

A major step forward in the development of reactive-transport modeling of acid rock drainage was developing computer codes. Based partly on previous work already cited above, an equilibrium-based solute-transport code (Runkel et al., 1996a) was developed from a one-dimensional transport code with inflow and storage (OTIS; Runkel, 1998) combined with the geochemical code MINTEQ (Allison et al., 1991). The combined code, known as OTEQ (Runkel, 2010), has been used for several objectives including simulation of field-based pH modification experiments (Broshears et al., 1996; Runkel et al., 1996b), sorption (Runkel et al., 1999), and evaluating remedial alternatives for acid mine drainage (Runkel and Kimball, 2002; Ball et al., 2004; Walton-Day et al., 2007; Kimball and Runkel, 2010; Kimball et al., 2010).

6. Some comments on natural background

"Natural background" conditions, better framed as pre-mining conditions, should be the cleanup goal for any mine-site remediation (Runnells et al., 1992). Unfortunately, there is little quantitative information on pre-mining water, rock, soil and biota conditions, other than new mining operations, so inferences guided by analogs and modeling must be resorted to (Alpers and Nordstrom, 2000). Quantitative studies on mineralized but unmined areas can be very helpful to document natural weathering rates of rocks with sulfide mineralization contrasted with weathering rates from mined materials. The USGS has studied natural weathering in several mineralized, unmined areas that include the upper Alamosa River basin near Summitville, CO (see papers in Posey et al., 1995), the Silverton area in the San Juan Mountains, CO, (Church et al., 2007), and the Red River Valley, NM (Nordstrom, 2008).

Well before the Summitville mine was most recently mined (1984–1992), it was recognized that naturally high concentrations of acidity occurred in the upper Alamosa River (Pendleton et al., 1995) where no mining had taken place and was located above the confluence of mine drainage (Wightman Fork) with the main stem of the Alamosa River. Characterization of the upper Alamosa confirmed that weathering of sulfides had caused natural acidity to develop (Miller and McHugh, 1994; Walton-Day et al., 1995) and would place a limit on the effects of remediation. Further monitoring at key locations in the Alamosa River basin detailed the natural chemical variations in the composition of upper Alamosa River water (Ortiz and Ferguson, 2001; Ortiz and Stogner, 2001; Rupert, 2001) and provided important information for synoptic sampling, tracer-injection studies, and evaluation of remedial alternatives based on reactive-transport modeling (Ball et al., 2004).

A major USGS initiative on abandoned mine lands with field studies in the San Juan Mountains, Colorado and Boulder Creek, Montana contains abundant information on how geology, hydrology, and biology of these field sites can be integrated to provide a firm foundation for characterizing and remediating mine-contaminated sites (Nimick et al., 2004; Church et al., 2007). The 50 research papers contained in these volumes not only cover a broad range of hydrogeochemical and biological characterization but they also demonstrate how a wide diversity of scientific methods and techniques can contribute solutions to the complex nature of AMD. Because the San Juan Mountains contain a mixture of mined areas and unmined, mineralized basins it was an excellent area to compare and contrast natural processes relative to those affected by mining.

Other important work on pre-mining water quality that includes solute-transport modeling are USGS investigations in

Redwell Basin, CO (Kimball et al., 2010) and Red Mountain Creek, CO (Runkel et al., 2007). Verplanck et al. (2009) give several examples of naturally acidic surface and ground waters in the southern Rocky Mountains for mineralized porphyries. These are good analogies of what water compositions would be like before mining in areas that have been mined. Nimick et al. (2009) examined Cu concentrations in ferricrete and could relate these to the pH and Cu concentration in the water from which the ferricrete formed, providing valuable insight into pre-mining water-chemistry conditions.

During 2001–2005, the USGS gathered data to determine the pre-mining groundwater quality for an active mine site, the Questa molybdenum mine in the Red River Valley, NM. The approach used was to study in detail a proximal natural analog site with very similar geology and hydrology as the actual mine site. The conclusions are set out in 27 USGS reports that cover geology, mineralogy and mineral chemistry, hydrology (surface water and groundwater), airborne-visible imaging spectroscopy, sediment chemistry of two lakes, and aqueous geochemistry (interpretation of geochemical reactions that account for observed water chemistries) for both surface water and groundwater. The results are summarized in Nordstrom (2008) and an important conclusion was that it was not possible to derive a single concentration for each constituent of concern because the groundwater chemistry changed dramatically over relatively short distances because of rapid changes in rock mineralization.

7. Conclusions

This paper reviews and summarizes selected USGS research on hydrogeochemical processes governing trace-element mobilization and attenuation from mineralized areas during transport in surface waters. The main conclusions are:

(1) Geology forms the physical and chemical framework for solid sources of water-quality contaminants in mineralized settings.
(2) Hydrology forms the physical and chemical framework for contaminant mobility.
(3) Mass balances can connect the partitioning of trace elements from mineral sources to the water. By combining mass balances with water flow rates, a field-based mineral weathering rate can be obtained. Rates for pyrite weathering vary from 17,100 mol/h for an extreme example of portal discharge from a massive sulfide mineral deposit to 5.5 mmol/h in an unmined, naturally mineralized, pyritized rock undergoing natural weathering. Rates of more than about 20 mmol/h may be indicative of efflorescent salt dissolution and evaporated mine water transport rather than a field rate of pyrite oxidation.
(4) Equilibrium solubilities provide an upper limit to dissolved concentrations of trace elements but formation of colloids and organic complexing complicates the interpretation. Speciation of Fe geochemistry is confounded by precipitating colloids passing through most filters and contributing solid-phase particulates to the operational definition of dissolved Fe. Aluminum geochemistry is better behaved and tends to reach a solubility-equilibrium control by an Al hydroxysulfate phase in the pH range 4–5.5. At pH values of 7.5 and higher, dissolved organic C may complex Al to produce spurious speciation results.
(5) Diel cycles, which affect temperature and photosynthesis, can change metal concentrations of streams and rivers and need to be monitored to constrain the actual range of concentration for a given time of year. Iron photoreduction also follows diel cycles and changes the dissolved Fe(II/III) ratio and the proportion of Fe(III) colloids which affects sorbed trace metals.
(6) Modeling reactive transport based on synoptic sampling with tracer-injection can offer practical approaches to understanding contaminant transport and to the evaluation of remediation scenarios.

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