

Biogeochemical processes controlling midday ferrous iron maxima in stream waters affected by acid rock drainage

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Abstract

The biogeochemical cycling of Fe in acid rock drainage (ARD) streams has presented ongoing challenges to reactive solute transport modeling. Previous studies have relied on the pH-dependent solubility of Fe oxides as the main control of the mid-day Fe(II) maxima concentration in ARD streams. In this study, the authors assess the potential for Fe(II)-oxidizing reactions, including the Fenton and microbial oxidation reactions, to constrain the mid-day Fe(II) maxima concentration. At mid-day, pseudo-equilibrium between Fe(II) oxidizing reactions and photoreduction was assumed in order to evaluate the observed Fe(II) maxima and develop an equation to represent this steady state scenario. This steady state condition is assumed only while light intensity, reactivity of oxides and dissolved organic matter (DOM), and microbial populations remain approximately constant. Three Rocky Mountain ARD streams with known values for Fe(II) were evaluated and average photoreduction rates ranging from 5.56×10^{-4} to 1.39×10^{-3} $\mu\text{M/s}$ were found during mid-day steady state Fe(II) maxima. Application of Fe redox biogeochemistry to reactive solute transport modeling may improve predictive capabilities of various trace metal and solute interactions incorporated with the cycling of Fe within ARD streams. Further, model improvement of Fe cycling may enable more accurate remediation predictions for ARD streams.

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1. Introduction

In freshwater and marine ecosystems the biogeochemistry of dissolved organic material and Fe are coupled through many abiotic and biotic reactions (Waite and Morel, 1984; Waite et al., 1995; Voelker et al., 1997; Emmenegger et al., 2001; McKnight et al., 2001b). In addition to pH-dependent precipitation reactions, two important reactions are complexation of Fe by dissolved organic compounds, including humic substances, siderophores and other organic acids, and sorption of humic substances by Fe oxides through surface complexation reactions (Evanko and Dzombak, 1998). Other dissolved organic material (DOM) and Fe reactions control energy transfer through photo-

chemical or microbial pathways (McKnight et al., 2001b). For all these reactions, pH can be considered a master variable, influencing the solubility of Fe(III), the ionization of fulvic acid and many reaction rates (Gundersen and Steinnes, 2003). The importance of certain reactions depends upon the sources and concentration of DOM and dissolved Fe, the reactivity of DOM and Fe oxides, and the photochemical or microbial energy flux in the system.

The interplay of precipitation/dissolution, photochemical, and microbial reactions can be readily observed in the diel variation of Fe, DOM, and their photoproducts in acidic streams with abundant Fe oxides. In these streams, increasing light intensity during the morning causes increasing rates of photoreduction of dissolved Fe(III) and colloidal Fe oxides as well as concomitant increases in Fe(II) concentration (McKnight et al., 1988; Kimball et al., 1992). Similarly, photolysis of DOM is a daytime source of both superoxide and H_2O_2 . Daytime peaks in H_2O_2 concentration have been

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observed in these acidic streams (Scott et al., *in press*). Superoxide can reduce Fe(III), whereas H_2O_2 can oxidize Fe(II) through the Fenton reaction. At midday the Fe(II) and H_2O_2 peroxide concentrations typically reach a maximum and then decrease in the afternoon (McKnight et al., 1988; McKnight and Bencala, 1988). At night, microbial oxidation of Fe(II) becomes the dominant process causing decreases in Fe(II) concentration (McKnight et al., 1988).

Acidic metal-enriched streams are common in many regions of the world in association with the weathering of pyrite, which is referred to as acid rock drainage (ARD). In addition to low pH and high dissolved Fe concentrations, ARD systems are characterized by accumulation of Fe oxides on streambeds and in wetland and lacustrine sediments. In Rocky Mountain watersheds, ARD commonly occurs as a result of both natural biogeochemical processes and exposure of pyrite to O_2 through mining activities. In ARD systems, Fe and DOM concentrations are controlled by precipitation of Fe oxides and sorption of DOM by these oxides (McKnight et al., 1992, 2002). Past research has quantified many of these reactions at the stream scale (Kimball et al., 1994) and has led to the development of a reactive solute transport model, OTEQ (Runkel et al., 1996a,b, 1999; Broshears et al., 1996). The OTEQ model has been used to evaluate possible water quality outcomes for remediation scenarios for abandoned mine sites (Runkel and Kimball, 2002).

The predictive capability of OTEQ and other solute transport models depends upon inclusion of the dominant reactions and successful representation of their dependence on environmental conditions, such as pH, light intensity, reactivity of Fe oxides and dissolved organic material. In this context, photoreduction and sorption of DOM by Fe oxides are particularly challenging processes to model. Runkel et al. (1996b) and Broshears et al. (1996) assumed that these processes were controlled by pH. In their models, the percentage of the total dissolved Fe that was Fe(III) was specified in order to simulate the photoreduction of dissolved Fe(II) and the photoreductive dissolution of Fe oxides. Furthermore, the variability in reactivity of Fe oxides and DOM can be significant. Hrnčir and McKnight (1998) showed that the photoreactivity of streambed Fe oxides decreased 2-fold over an 1800 m stream reach below the mine drainage inflow in the stream. The decrease in photoreactivity was associated with increased crystallinity with aging of the oxides. McKnight et al. (2002) found that the rate of sorption of fulvic acid added to an ARD stream was an order of magnitude faster in the initial 140 m reach because the more aromatic and “sorbable” fraction of the fulvic acid was removed from solution first. Variability in DOM and oxide reactivity can have a major influence on the predicted concentrations of dissolved Fe and

DOM in model simulations. For this reason, it can be difficult to ascertain from comparison of model simulations with field data that the important reactions have indeed been included in the model. From a modeling perspective, once the dominant reactions have been included, parameter variability can be addressed by adjusting parameters between stream reaches based upon some criteria or field or laboratory measurements.

The pH-dependent solubility of Fe oxides may not actually be the process that controls the maximum daytime Fe(II) concentration in ARD streams, as assumed by Runkel et al. (1996b) and Broshears et al. (1996). Rather, the controlling processes may be processes through which Fe(II) is oxidized to Fe(III). McKnight et al. (1988) modeled microbial oxidation as a first order rate process, i.e. as proceeding at a rate that increases with Fe(II) concentration. Another process with a first order rate dependence that has not been included in current reactive transport models for ARD streams is the reaction of Fe(II) with H_2O_2 to produce Fe(III) and water, which is referred to as the Fenton reaction. Hrnčir and McKnight (1998) concluded that the Fenton reaction was responsible for the decrease in H_2O_2 concentration in a stream reach where DOM concentrations were very low because of sorption by large quantities of precipitating Fe oxide. Scott et al. (*in press*) calculated that the Fenton reaction constrained H_2O_2 concentrations, but had only a minor effect on Fe(II) concentrations because of the rapid rate of Fe oxide photoreduction.

In this study, the authors evaluate the potential for Fe(II)-oxidizing reactions to control the maximum concentration of Fe(II) observed at mid-day in acidic, Fe oxide-rich streams. An equation was first developed for the steady state concentration of Fe(II) as a function of the rate of photoreduction, the rate of production of H_2O_2 by photolysis of DOM, and the rate of microbial oxidation of Fe(II). This steady state corresponds to a “pseudo equilibrium” that would change with a change in any of these rates, which are determined by the conditions in the stream (light intensity, reactivity of oxides and DOM, and microbial populations). Previous field results are used to quantify the rates of the processes which oxidize Fe(II) in several streams receiving ARD in the Rocky Mountains. Then the observed range of mid-day Fe(II) concentrations are used to calculate a range of Fe oxide photoreduction rates. Finally, this range is compared to photoreduction rates of Fe oxides that have been observed in field and laboratory studies. Based on this analysis, an approach for formulating Fe oxide photochemistry in reactive solute transport models is proposed.

1.1. Site description

As a result of the mineralogy of the region and mining activities during the late 1800s and early 1900s, ARD-

impacted streams are common in the Colorado Rocky Mountains and represent significant local water quality problems (Moran and Wentz, 1974). At stream confluences where acidic, metal-enriched water from areas of pyrite weathering come in contact with stream water having a higher pH, precipitation of Fe and Al oxides typically occurs. Because Fe precipitates at a relatively low pH, approximately pH 3.5, Fe oxides are ubiquitous in stream reaches below ARD inflows. Precipitation of Fe and Al oxides can cause the removal of other metals and DOM through sorption reactions (McKnight et al., 1992). In the Rocky Mountains, streams affected by ARD not only have similar chemistry, but also comparable geomorphology (Moran and Wentz, 1974). Typically ARD-impacted streams are located in mountainous areas where stream gradients are steep, and they typically have boulder and cobble streambeds. During summer, the water column typically has a depth of 0.5–0.2 m or less, allowing significant penetration of solar radiation to the streambed. This penetration of ultraviolet light to the streambed surface allows photoreduction of Fe oxides to occur in these mountain streams.

This study relies upon results from previous studies of several small mountain streams that are representative of the Fe chemistry of ARD streams. St. Kevin Gulch is part of the upper Arkansas River watershed located approximately 10 km NW of Leadville, Colorado. St. Kevin Gulch receives drainage from many seeps originating from waste rock and tailings piles at the Griffin mine site, located near the confluence of the stream with Shingle Mill Gulch. In the upper reaches of the stream, freshly precipitated Fe oxides coat the streambed causing the characteristic orange discoloration of the rocks. The upper reach is partially shaded by riparian forest. Field data from a previous study in St. Kevin Gulch conducted on 15 September 1995 (Hrncir and McKnight, 1998) were analyzed in this study. In total, 13 sites were sampled, spanning a stream reach of approximately 2 km. The discharge was approximately 0.5 m³/s over this reach, and the travel time from site 580 m to site 1800 m was 40 min, corresponding to an average stream velocity of 0.51 m/s for the 1220 m distance.

The other field results used in this study are from studies of the Snake River and its tributary Peru Creek located in Summit County, Colorado. Above the confluence with Deer Creek, the water quality of the Snake River is affected by natural weathering of disseminated pyrite in the country rock (Theobald et al., 1963). The willows in the riparian area provide minimal shading of the stream in the upper reach. There are numerous abandoned Ag mines throughout the Peru Creek watershed and Fe oxide deposition is extensive below the inflows from these mines (McKnight and Bencala, 1990; Sullivan and Drever, 2001). Peru Creek flows through a steep reach with riparian forest and through several

large wetland areas in the lower reaches above the confluence with the Snake River.

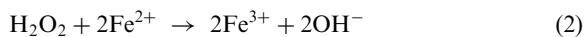
In these streams, photoreduction of dissolved Fe(III) and colloidal Fe oxides in the stream water and Fe oxides on the streambed causes Fe(II) concentrations to increase during the day (McKnight et al., 1988; McKnight and Bencala, 1988; Sullivan et al., 1998). At mid-day the Fe(II) concentrations typically reach a maximum and then decrease in the early afternoon (Fig. 1). At night microbial oxidation of Fe(II) causes the Fe(II) concentrations to decrease downstream (McKnight et al., 1988).

1.2. Biogeochemical processes influencing Fe and DOM in ARD streams

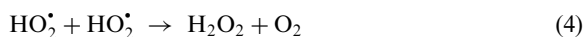
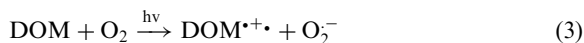
Fig. 2 presents a schematic diagram of the important processes involved in determining the Fe speciation in ARD-impacted streams. The direct photoreduction of Fe(III)OH²⁺, the dominant dissolved Fe(III) species at low pH (pH 3.0–4.5), is as follows:



The photoreductive dissolution of Fe oxides similarly produces dissolved Fe(II). While Fe(II) is produced by photoreduction, it is also consumed in the Fenton reaction (Fukushima and Tatsumi, 2001). Hydrogen peroxide oxidizes Fe(II), producing Fe(III) and a hydroxyl radical. In turn, the hydroxyl radical reacts with Fe(II) resulting in the following overall reaction:



Hydrogen peroxide is produced through photolysis of DOM in the presence of ultraviolet light and O₂ (Scully et al., 1996). The reaction intermediate is a superoxide radical (O₂^{•−}), which can reduce Fe(II). Superoxide radical becomes protonated at the low pH values of acid rock drainage streams to form a peroxy radical (HO₂[•]). Peroxy radical rapidly converts to H₂O₂. The dominant reactions are:



The rate of superoxide radical and H₂O₂ formation is a function of DOM concentration and ultraviolet light intensity. In streams affected by ARD, DOM is limited by sorption onto freshly precipitated Fe oxides and possibly by enhanced degradation by photo-Fenton processes at high Fe(III) concentrations (Fukushima and Tatsumi, 2001). The low DOM concentrations limit the production of superoxide radical and H₂O₂.

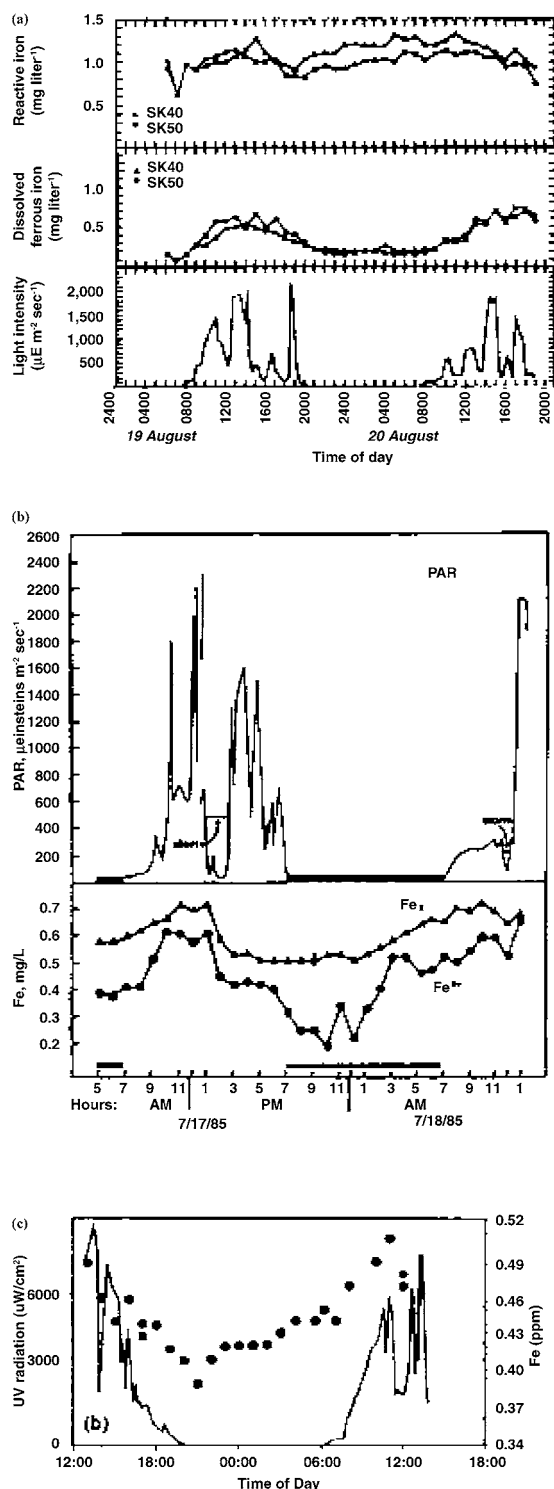


Fig. 1. Diel change in Fe(II) and total dissolved Fe concentrations in acidic, metal-enriched streams in the Colorado Rocky Mountains; A. St. Kevin Gulch (adapted from McKnight et al., 1988), B. Snake River (adapted from McKnight and Bencala, 1988), and C. Peru Creek (adapted from Sullivan et al., 1998).

Under acidic conditions, the abiotic oxidation of Fe(II) is very slow (Singer and Stumm, 1970; Nordstrom, 1985). However, microbial oxidation of Fe(II) proceeds at an observable rate. Fe-oxidizing bacteria, *Thiobacillus ferrooxidans*, oxidize Fe(II) to Fe(III) to acquire energy to fix CO₂ for cell growth in the following process:



The rate at which microbial populations oxidize Fe is faster at higher Fe(II) concentrations, corresponding to a first order dependence on Fe(II) at environmental concentrations. The first order rate dependence of microbial oxidation is represented by the following equation:

$$d[\text{Fe}^{2+}]/dt = k_m[\text{Fe}^{2+}] \quad (6)$$

where k_m is the rate constant for microbial oxidation of Fe(II).

2. Results and discussion

2.1. Rate processes determining midday "pseudo-equilibrium" Fe(II) concentrations in acidic, metal-enriched streams

Consideration of the reactions above provides the framework necessary to evaluate the Fe(II) maxima observed at mid-day in ARD-impacted streams. These maxima correspond to a steady state condition maintained until light intensity decreases, changing the rates of photoreduction of Fe oxides and DOM photolysis. At steady state, photoreduction (production of Fe(II)) is equal to the loss of Fe(II) caused by the Fenton reaction and the microbial oxidation reaction. Mathematically, this steady state corresponds to:

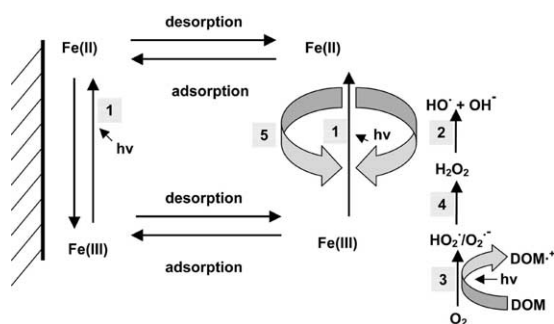


Fig. 2. Schematic diagram showing the processes influencing the chemistry of Fe in the presence of Fe oxide solid phases and photoproducts of DOM; the numbers refer to reactions discussed in the text. (Adapted from Voelker et al., 1997).

$$d[\text{Fe}^{2+}]/dt = 0 = f_1 - k_p[\text{H}_2\text{O}_2][\text{Fe}^{2+}] - k_m[\text{Fe}^{2+}] \quad (7)$$

where f_1 is the production rate of Fe(II) by photo-reduction of Fe oxides ($\mu\text{M s}^{-1}$), k_p is the rate constant for the Fenton reaction at a given pH ($\mu\text{M}^{-1}\text{s}^{-1}$), and k_m is the rate constant for first order microbial oxidation of Fe(II) (s^{-1}). In this approach, the reduction of Fe(III) by superoxide is included in f_1 and is assumed to be small compared to the direct photoreduction of the abundant Fe oxides.

At steady state, the H_2O_2 concentration is also constant and the rate of production by photolysis of DOM is equal to the rate of the Fenton reaction.

$$d[\text{H}_2\text{O}_2]/dt = 0 = f_2 - k_p[\text{H}_2\text{O}_2][\text{Fe}^{2+}] \quad (8)$$

where f_2 is the rate of H_2O_2 production by DOM photolysis.

Rearranging terms in Eq. (8) gives:

$$[\text{H}_2\text{O}_2] = f_2 / (k_p[\text{Fe}^{2+}]) \quad (9)$$

Applying Eq. (9) to Eq. (7) results in the equation:

$$\begin{aligned} 0 &= f_1 - k_p(f_2 / ([\text{Fe}^{2+}]))[\text{Fe}^{2+}] - k_m[\text{Fe}^{2+}] \\ &= f_1 - f_2 - k_m[\text{Fe}^{2+}] \end{aligned} \quad (10)$$

Eq. (10) can be rearranged to obtain an expression for the concentration of Fe(II) at steady state in stream waters affected by ARD as follows:

$$[\text{Fe}^{2+}] = (f_1 - f_2) / k_m \quad (11)$$

This steady state corresponds to a “pseudo-equilibrium” that would change with a change in the rates of the light-driven processes, which are determined by the conditions in the stream (light intensity, reactivity of oxides and DOM, and in the activity of microbial populations).

2.2. Stream-scale estimates of Fe(II) oxidation rates

The downstream changes in the concentrations of Fe(II), Fe_{total} , DOC, and H_2O_2 in St. Kevin Gulch are presented in Fig. 3. The rate of the H_2O_2 consumption by the Fenton reaction was determined by utilizing the data for the decrease in H_2O_2 observed in the upper reach directly below the ARD inflow (580–781 m) assuming no new production of H_2O_2 occurred in this reach. This assumption is based on the substantial reduction in total dissolved Fe and DOC concentrations associated with the abundant freshly precipitated Fe oxides found on the streambed. These freshly precipitated Fe oxides would provide an abundance of available sites for DOM sorption. The authors interpret

this DOM decrease as having caused the cessation of new production of H_2O_2 through DOM photolysis.

The rate of consumption of H_2O_2 is calculated through the Fenton reaction using the change in H_2O_2 concentration between the upstream and downstream concentration and the travel time between sites. The travel time was estimated to have been 395 s between

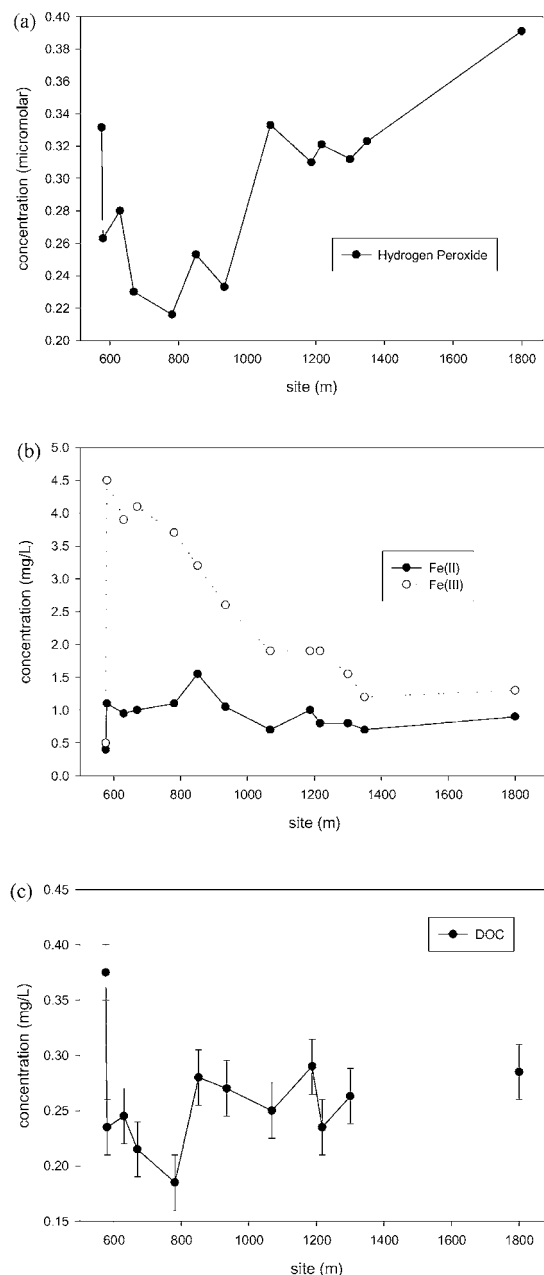


Fig. 3. Downstream changes in the concentrations of Fe(II), Fe_{total} , DOC, and H_2O_2 in St. Kevin Gulch (Adapted from Hrnir and McKnight, 1998).

580 and 781 m based on measured discharge and previous tracer experiments in the stream (McKnight et al., 2001a). The calculated rate of H_2O_2 consumption between 580 m and 781 m is $1.19 \times 10^{-4} \mu\text{M/s}$.

Taking advantage of the Fe(II) concentration being effectively constant in this reach (580 and 781 m), the effective rate constant, k_{obs} , for the Fenton reaction was determined assuming the reaction is first order with respect to H_2O_2 . The effective k_{obs} was determined as follows:

$$-d[\text{H}_2\text{O}_2]/dt = k_p[\text{H}_2\text{O}_2] = k[\text{Fe}^{2+}][\text{H}_2\text{O}_2] \quad (12)$$

The integrated form of the above equation is:

$$\begin{aligned} \ln[\text{H}_2\text{O}_2]_t/[\text{H}_2\text{O}_2]_i &= \ln[\text{H}_2\text{O}_2]_i - x/[\text{H}_2\text{O}_2]_i \\ &= -k_{\text{obs}}t \end{aligned} \quad (13)$$

where $[\text{H}_2\text{O}_2]_i$ is the initial H_2O_2 concentration, $[\text{H}_2\text{O}_2]_t$ is the H_2O_2 concentration at time t , x is the amount of H_2O_2 reacted at time t , and k_{obs} is the rate constant (k_p) multiplied by the Fe(II) concentration, $[\text{Fe}^{2+}]$.

It is important to note that reactive Fe(III) was available at large concentrations in this reach to drive the process of photoreduction, and the Fe(II) concentration was relatively stable at 1.0 mg/l (17.91 μM). The calculated effective rate constant representing the Fenton reaction was $2.78 \times 10^{-5} \mu\text{M}^{-1} \text{s}^{-1}$.

In the downstream reach, the DOM and H_2O_2 concentrations increased to stable values as the precipitation of Fe oxides diminished and new DOM was brought to the stream in lateral inflows from the hyporheic zone and surrounding watershed. In this downstream reach, the production of new H_2O_2 through DOM photolysis compensates for the consumption of H_2O_2 due to the Fenton reaction. By assuming that the rate of consumption in the upstream reach is maintained in the downstream reach, that rate can be used as an estimate of the daytime rate of production of H_2O_2 by photolysis (f_2). This is mathematically represented in Eq. (8).

To determine the rate constant for microbial oxidation McKnight et al. (1988) used night-time measurements of Fe(II) consumption in St. Kevin Gulch. During the night, photoreduction and Fenton reactions do not occur, causing microbial oxidation to dominate the cycling of Fe within stream waters. The resultant rate constant, k_m , for the experiment was $7.22 \times 10^{-5} \text{s}^{-1}$.

Determination of the photoreduction rate for Fe(III)OH^{2+} using field measurements presented a challenge because during the day the rates of change of Fe(III)OH^{2+} and Fe^{2+} are due to photoreduction, Fenton, and microbial oxidation. In order to determine the percentage of change caused solely by photoreduction (f_1), Eq. (11) was applied. Therefore,

$$f_1 = f_2 + k_m[\text{Fe}^{2+}] \quad (14)$$

Using values mentioned above for f_2 and k_m , the calculated value for f_1 is $1.41 \times 10^{-3} \mu\text{M/s}$. Fe(II) concentrations range between 0.7 and 1.0 mg/l at the sites further downstream (1068–1800 m), corresponding to a range for f_1 of $1.0 \times 10^{-3} \mu\text{M s}^{-1}$ to $1.4 \times 10^{-3} \mu\text{M s}^{-1}$.

2.3. Evaluation of mid-day photoreduction rates

Table 1 presents the range in mid-day Fe(II) and total dissolved Fe observed in other diel studies of Fe chemistry in ARD-impacted mountain streams in Colorado (Fig. 1). For the diel studies conducted during low-flow conditions after snowmelt in July and August the range in Fe(II) concentrations is from 0.49 to 1.35 mg/l, less than a 3-fold range. The limited extent of this range in mid-day Fe(II) concentrations provides support for some control on the maximum instream Fe(II) concentrations by oxidative processes associated with DOM inflow and with microbial oxidation. The DOM in these mountain watersheds is strongly controlled by flushing during snowmelt and sorption of DOM by Fe oxides. DOC concentrations are generally about 1 mgC/l or less during low flow conditions (McKnight et al., 1992, 2002; Hornberger et al., 1994; Boyer et al., 1996; Brooks et al., 1999). Thus, variations in DOM chemistry and concentration in summer are not large and would not contribute much to variation in maximum Fe(II) concentrations. It is more difficult to evaluate the factors controlling the rates at which the microbial populations oxidize Fe(II).

Within this result of only a 3-fold variation in range, it is informative to examine the outliers in the data set. The total dissolved Fe concentrations in Peru Creek during the early July sampling date were much lower than the concentrations on later dates, reflecting the greater dilution of Fe(II) released from the streambed under the 5-fold greater streamflow during the late snowmelt period compared with the low flow conditions of late July and August. Another factor which could have limited the steady state Fe(II) concentration could have been a greater DOM concentration associated with snowmelt and subsequently greater H_2O_2 production rates, which would have related to a greater Fenton rate.

It is also interesting to note that the alpine sites in the upper Snake River had the highest Fe(II) concentrations. Three factors that could account for this are: (1) greater exposure of the streambed to sunlight because of the absence of riparian trees that shade the stream, (2) lower input of DOM from the alpine areas compared to the sub-alpine areas, and (3) possibly lower rates of microbial oxidation. Greater irradiation of the streambed could have accelerated photoreduction of Fe oxides from the streambed relative to photolytic production of H_2O_2 , shifting the “pseudo-equilibrium”

Table 1
Fe(II) mid-day maxima concentration and photoreduction rates in 3 Colorado Rocky Mountain streams affects by acid rock drainage

Stream	Site	Date	Time of Maxima	Fe(II) mg/l	Total dissolved Fe, mg/l	Estimated photoreduction rate, $\mu\text{M s}^{-1}$
St. Kevin Gulch ^a	SK40	8/19/86	1100–1500	0.49	1.08	7.52×10^{-4}
		8/20/86	1300–1600	0.61	1.11	9.08×10^{-4}
	SK50	8/19/86	1000–1600	0.57	1.08	8.56×10^{-4}
		8/20/86	1200–1600	0.62	1.02	9.21×10^{-4}
St. Kevin Gulch ^b	SK 40	8/23/88	1050–1450	0.62		9.23×10^{-4}
		8/24/88	0950–1330	0.58		8.73×10^{-4}
	SK 50	8/23/88	1050–1450	0.79	0.82	1.14×10^{-3}
		8/24/88	0950–1330	0.72	0.82	1.05×10^{-3}
St. Kevin Gulch-average						9.28×10^{-4}
Snake River ^c	SN2	7/17/85	1000–1300	0.60	0.69	8.95×10^{-4}
		7/18/85	1000–1300	0.58	0.68	8.69×10^{-4}
Snake River ^d	Alpine-4 sites	7/28/98	~1300	1.25–1.35		1.74×10^{-3}
						1.86×10^{-3}
	Subalpine-5 sites	7/28/98	~1300	1.0–1.1		1.41×10^{-3}
						1.54×10^{-3}
Snake R. average						1.39×10^{-3}
Peru Creek ^e	24-h site	7/1/96	0900–1400		0.094	2.41×10^{-4}
		8/12/96	1300–1600		0.46	7.14×10^{-4}
		8/13/96	0800–1200		0.48	7.40×10^{-4}
Peru Creek average						5.65×10^{-4}

^a McKnight et al., 1988.

^b Kimball et al., 1992.

^c McKnight and Bencala, 1988.

^d Belanger, et al., 2004.

^e Sullivan et al., 1998.

Fe(II) concentrations to higher values. Measurement of DOM and H_2O_2 concentrations would provide useful data for resolving these possible factors.

These rates of photoreduction of streambed Fe oxides can be compared with rates determined in St. Kevin Gulch during the early morning period when Fe(II) concentrations increase in the downstream direction. Kimball et al. (1992) found that for 3 different studies the variation in the rate was less than a factor of two, with the average corresponding to $0.11 \mu\text{mol m}^{-2} \text{s}^{-1}$. This rate is expressed as a flux from the streambed. To convert this value from a flux into a volume of streamwater overlying the streambed, we can divide by the average stream depth of about 0.3 m during low flow, which yields a value of $0.37 \mu\text{M s}^{-1}$. This value is approximately two orders of magnitude greater than the photoreduction rates calculated at steady state.

This large difference in rates is consistent with different Fe(III) substrates being photoreduced over the day-time period. In the early morning, dissolved Fe(III) species are the dominant Fe species and are depleted as the morning progresses (McKnight et al., 1988). Once these Fe species are depleted, the much lower

photoreduction rate of streambed oxides compared with dissolved Fe(III) species and recently precipitated colloidal Fe oxides causes the Fe(II) concentration to plateau.

This large difference in photoreduction rates is consistent with laboratory experiments of Fe photochemistry. Waite and Morel (1984) showed that crystalline Fe oxides had quantum yields for photoreduction that are several orders of magnitude less than those for dissolved Fe(III) species. The results of the laboratory experiments of Hrcir and McKnight (1998) using Fe oxides from the streambed at different sites in St. Kevin Gulch were in the range of $130\text{--}50 \mu\text{mol g}^{-1} \text{h}^{-1}$. The experimental conditions involved the irradiation of a suspension of 15 mg of Fe oxide in 50 ml of stream water. Using these conditions to convert to a photoreduction rate per volume of irradiated stream water yields a range of $1.1\text{--}0.4 \times 10^{-2} \mu\text{M s}^{-1}$. This range is an order of magnitude greater than the range estimated based on the steady state Fe(II) concentrations. Given that the conditions in the experiment optimized photoreduction by maintaining the oxides in suspension by stirring, the effective rates of streambed oxide photoreduction at mid-day appear to be reasonable.

2.4. Application for reactive solute transport models for ARD streams

Runkel et al. (1996b) and Broshears et al. (1996) represented the dynamic processes involved in Fe speciation in their simulations of the changes in Fe concentrations in response to experimental pH shifts in two ARD streams. Their models considered the dissolved Fe(III) concentration to be determined by equilibrium with an Fe oxide solid phase. The solubility of the Fe oxide solid phase changed with pH as controlled by the solubility product specified for the Fe oxide phase. Photoreduction was represented in the models by specifying the percent of the total dissolved Fe that was Fe(II). Runkel et al. (1996b) simulated the results of an experimental addition of acid to the Snake River which caused the Fe(II) concentration to increase substantially. Based on observations during the experiment, this percentage of Fe(II) was set to be lower (93%) for more acidic conditions than before and after the experiment (98%).

Mechanistically, Fe oxides dissolved under the decreased pH and a large portion of this was converted to Fe(II) until an equilibrium Fe(III) concentration was reached. This approach successfully simulated the downstream changes in dissolved Fe during the experiment. Broshears et al. (1996) simulated the changes in Fe and Al concentrations in response to an experimental addition of NaCO₃ to St. Kevin Gulch, which raised the pH from 3.5 to about 5.8. They used the same approach of specifying the percentage of dissolved total Fe as Fe(II), but used a lower value of 80% based on an observed range of 70–90% prior to the experiment. In the model, Fe(II) concentrations were decreased “instantaneously” when the Fe(III) concentration in equilibrium with the Fe oxide decreased in response to the increase in pH. The changes in Al concentrations were successfully simulated; whereas, this approach simulated total Fe concentrations that were much lower than those observed during the experiment, especially at the most upstream sites. The difficulty in simulating Fe behavior was attributed to uncertainty in the relative rates of Fe redox processes during the experiment.

In the equation for the mid-day Fe(II) maxima developed here, the solubility of Fe oxide is not considered. Rather, the Fe(II) concentration is represented as being controlled by a “pseudo-equilibrium”, determined by rates of photoreduction and Fe(II) oxidation. Use of the approach developed here in a reactive solute transport model would require specification of the rate constants for the 3 redox processes represented in the equation. The inclusion of the Fenton reaction involving Fe(II) and H₂O₂ requires one more parameter than in the approach used by Runkel et al. (1996b) and Broshears et al. (1996), which required two parameters

to represent the solubility product for the Fe oxide and the percent of the total Fe that is Fe(II). As represented here, oxidation rates are controlled by first order microbial oxidation of Fe(II) and by the photolytic supply of H₂O₂ for the Fenton reaction. In a given stream, these oxidation rates would be expected to be dependent on the abundance of Fe-oxidizing bacteria and the sources and reactivity of DOM, respectively. At the stream-scale, the range in the effective rate constants may not be large because the variability among patches in the streambed and in DOM in lateral inflow to the stream would be averaged out. However, in order to simulate Fe(II) concentration over a diel cycle or in response to a change in pH would probably involve the introduction of more parameters for characterizing the dependence of photoreduction of Fe oxides on pH and light intensity. Further, to successfully capture the response in the stream, it may be necessary to include two or more oxide phases with differing photoreactivity. For example, successful simulation of the mid-day maximum of Fe(II) observed in St. Kevin Gulch could be achieved by assuming a limited quantity of a highly reactive phase, which would be photoreduced through the morning until depletion. Then at mid-day, photoreduction of a less reactive abundant phase would result in a steady state Fe(II) concentration that did not increase downstream. Such an approach would be similar to the trace and abundant phases used by Runkel et al. (1996b) in their model in simulating a stream-scale experiment in which the pH was lowered (McKnight and Bencala, 1989).

Runkel and Kimball (2002) have used the OTEQ model to predict the changes in water quality in an ARD-impacted stream under different scenarios for remediation of the abandoned mines that drain into the stream. The limitation of the representation of Fe oxide photoreduction in OTEQ results in uncertainty in the predictions for the mobility of Fe below mine inflows and the downstream extent of the streambed affected by Fe oxide deposition. The deposition of Fe oxide on the streambed has a deleterious effect on aquatic organisms at many trophic levels, such as algae, fungi and benthic invertebrates (Niyogi et al., 2002). The photoreduction of Fe oxides also mobilizes other solutes, such as trace metals and phosphate, that are sorbed by Fe oxides (Tate et al., 1995; Munk et al., 2002; Gundersen and Steinnes, 2003). It would be useful to couple the release and sorption of these trace constituents to the processes controlling Fe biogeochemistry in a model framework similar to the surface-complexation model incorporated into OTEQ by Runkel et al. (1999). These trace constituents can be important to ecosystem function, acting as either toxicants or nutrients. Thus, improvement in the representation of Fe redox processes has the potential to improve the predictive capability for ecosystem recovery following remediation.

3. Summary

Based on analysis of results from studies of Colorado Rocky Mountain ARD streams, the authors have shown that Fe(II)-oxidizing reactions, including the Fenton and microbial oxidation reactions, can constrain the nominally steady-state, mid-day Fe(II) maxima concentrations. At mid-day, pseudo-equilibrium was assumed between Fe(II) oxidizing reactions and photoreduction and an equation developed to represent this steady state scenario corresponding to approximately constant light intensity, reactivity of oxides and dissolved organic matter (DOM), and rates of microbial activity. It was found that the average photoreduction rates for 3 ARD streams ranged from 5.56×10^{-4} to 1.39×10^{-3} $\mu\text{M/s}$ during the mid-day steady state Fe(II) maxima. Inclusion of Fe redox biogeochemistry in reactive solute transport models for ARD streams may improve their predictive capabilities for Fe and associated trace metals therefore facilitating remediation of these streams.

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