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Is iron redox cycling in a high altitude watershed photochemically or thermally driven?

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ABSTRACT

Many studies have shown that the concentration of aqueous Fe^{2+} increases in surface waters during exposure to sunlight and attribute this phenomenon either to photoreductive dissolution of ferric minerals/colloids or to ligand-to-metal charge transfer within organic complexes of Fe^{3+}. In a multi-summer study of iron redox cycling in a relatively high pH stream (Middle Crow Creek, MCC) that drains a mostly-granitic watershed at an altitude of 2400 m, aqueous Fe^{3+} (not Fe^{2+}) concentrations were correlated with both sunlight and temperature. A steady state model fails to explain the $[Fe^{2+}]$ and $[Fe^{3+}]$ data from this stream. However, Fe^{2+} concentrations can be explained using a simple kinetic model in which rate constants for oxidation and reduction were obtained by fitting data from in situ oxidation experiments, including first-order thermal (nonphotochemical) reduction of Fe^{3+}. Rate constants obtained from experiments in the dark result in too much Fe^{2+} to match the data from illuminated experiments, requiring a net photooxidation process to explain $[Fe^{3+}]$ measured in MCC. The organic content of MCC results in high concentrations of Fe–DOM complexes that not only act as a reservoir contributing to daily changes in $[Fe_{tot}]$ as measured by our methods, but whose photochemistry may contribute highly oxidizing reactive oxygen species to the stream. In situ studies suggest that photochemical reduction of organically bound Fe^{3+} occurs, followed by thermal release of Fe^{2+} to the water column and subsequent rapid re-oxidation.

1. Iron biogeochemistry in natural waters

In recent decades, much attention has been given to iron cycling in natural waters. The fate, transport, and mobility of iron in the environment are directly related to its bioavailability and key role in global biological productivity. Most iron-containing enzymes catalyze biologically mediated redox reactions and are components of electron transport chains that operate during both photosynthesis and respiration (Harrison and Hoare, 1980). Iron can be a limiting nutrient for phytoplankton in several aquatic systems, and processes that affect its distribution and availability may influence global climate (Martin et al., 1990; Watson et al., 2000). Iron redox cycling also affects the bioavailability of other metals and chemical species; for example, dissolution of iron oxides to which other metals or organic contaminants are sorbed can remobilize the sorbed species (Markwiese and Colberg, 2000).

Studies of iron redox cycling in natural waters have highlighted photo- and microbially-induced reactions as well as the importance of coordination chemistry involving a multitude of naturally occurring ligands. Photo-induced reduction of Fe^{3+}-containing minerals/colloids and organic complexes has been linked to increases in ferrous iron concentrations in natural waters (McKnight et al., 1988; Emmenegger et al., 2001; Meunier et al., 2005). When inorganic iron complexes or mineral/colloid iron (hydr)oxides take part in photoredox reactions, reductive dissolution/dissociation produces the more soluble Fe^{2+} (Koenings, 1976; Collienne, 1983; Waite and Morel, 1984). Iron also reacts photolytically through ligand-to-metal charge transfer in aqueous Fe^{3+}–organic complexes, which simultaneously oxidizes the organic component and reduces Fe^{3+} to Fe^{2+} (Miles and Brezonik, 1981; Collienne, 1983; Voelker et al., 1997; Gao and Zepp, 1998). Photochemical iron redox cycling, in conjunction with such organic species, contributes to the pool of reactive oxygen species found in surface waters through processes such as the Fenton reaction (Goldstone et al., 2002; Rose and Waite, 2005).

In high altitude streams and lakes where solar intensity is high, $[Fe^{2+}]$ might be expected to reach high levels relative to less intensely illuminated oxic waters (McKnight et al., 1988; Scott et al., 2003). On

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Abbreviations: MCC, Middle Crow Creek; DOM, dissolved organic matter; dsbphen, colorimetric reagent (4,7-diphenyl-1,10-phenanthroline disulfonate); TOC, total organic carbon; ICP-MS, inductively coupled plasma-mass spectroscopy.

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the other hand, the Fe^{2+} oxidation rate can also be correspondingly high depending on a complex interplay between low temperature (which leads to high $[O_2]$ levels), pH, and iron complexation (e.g., Meunier et al., 2005). Several researchers (Millero et al., 1987; Stumm and Morgan, 1996) provide a simple expression for the Fe^{2+} oxidation rate as a function of pH:

$$-\frac{d[Fe^{2+}]}{dt} = k[Fe^{2+}][O_2][OH^-]^2 \qquad (1)$$

where *k* is the rate constant and [x] indicates molar concentration of x. The temperature dependence of Fe^{2+} oxidation has been discussed in Sung and Morgan (1980), Millero et al. (1987), Santana-Casiano et al. (2005) and elsewhere. Millero et al. (1987) report an activation energy of 29 ± 2 kJ mol^{-1}. The low activation energy indicates relatively weak temperature dependence overall — as temperature rises, the rate constant rises but the solubility of O_2 in water decreases. Because we are working in fresh water, the ionic strength dependence reported in Millero et al. (1987) was less important.

Oxidation of Fe^{2+} by O_2 results in the production of the superoxide radical ($O_2^{-\bullet}$), which can itself oxidize Fe^{2+} resulting in a continuing cascade of iron oxidation reactions similar to the Haber–Weiss mechanism (e.g., Koppenol et al., 2008). Rose and Waite (2005) showed that the presence of strong Fe(III) binding ligands increases the rate of Fe(II) oxidation. Net photooxidation of iron may occur when illumination of dissolved organic matter (DOM) produces hydroxyl ($OH^{\bullet}$) or alkylperoxy ($ROO^{\bullet}$) radicals or other oxidants such as singlet oxygen, which then react with Fe(II) species (Zepp et al., 1977; Mill et al., 1980).

Here, using the example of a moderately high altitude stream in Wyoming that is characterized by relatively high pH, we address a simple question: does iron photoreduction contribute significantly to daytime aqueous Fe^{2+} concentrations in this system? To answer this question, we follow diurnal Fe^{2+} and Fe^{3+} concentrations at two sites along Middle Crow Creek (MCC), Wyoming, over a 4-year period. Because of the many unknowns with regard to the rates of reactions involving a variety of reactive oxygen species in our compositionally complex and unconstrained natural system (e.g., Meunier et al., 2005), we have taken a simplified approach (such as the use of Eq. (1)) together with isolation experiments in which separate water samples from MCC were held in isolation chambers in the dark and in the light.

2. Materials and methods

2.1. Field sites

Middle Crow Creek is a mountain stream located at an altitude (of the two sampling sites) of 2450 ± 30 m in a primarily granitic watershed in southeastern Wyoming, USA. MCC is characterized by fast-moving reaches between areas of beaver-ponding. MCC has relatively high aqueous iron concentrations (0.1 to 30.0 μM), possibly because of weathering of mafic xenoliths in the granitic bedrock. Animal grazing in this area causes substantial sediment disturbance and introduces animal waste to the stream. MCC exhibits relatively high primary productivity during the summer, and relatively high levels (5–20 mg C L^{-1}) of organic matter (total) in the water column.

Two locations on MCC were sampled over a four-year period. The sun directly irradiates the water in both sites, and insolation is limited solely by cloud cover and time of day. These sites thus allow photochemical reactions to take place in the water column and presumably on sediments in shallow waters. MCC is approximately 1 m deep at the sample locations (small beaver ponds). MCC is a small turbulent stream system in a windy environment. It is well mixed, even in the small beaver ponds. Mixing was confirmed by a lack of temperature difference between surface and bottom waters. Also, conductivity measurements over time were invariant in previous work at the same locations (Warner, 1999). Total iron concentrations varied somewhat (10-fold) between the sites, but $[Fe^{3+}]/[Fe^{2+}]$ ratios varied much less that this between the two sites. Temperature, pH, and dissolved organic matter (DOM) concentrations were also very similar between the two sites.

Samples of MCC water were characterized for total organic carbon (TOC), temperature, pH, and aqueous iron speciation. Water samples were taken at 1 or 2 h intervals over periods of 5 to >24 h. On several occasions, stream samples were also isolated from stream and sunlight, while remaining bathed in the MCC to maintain constant temperature.

2.2. Experimental procedures

All chemicals were reagent grade, and all were used as received. Disulfonated bathophenanthroline (4,7-diphenyl-1,10-phenanthroline disulfonate: dsbphen) was purchased from Fluka, (Buchs, Switzerland). Nitric acid, OPTIMA, was purchased from Fisher Scientific (Fair Lawn, NJ), and hydrazine dihydrochloride from Sigma Aldrich Chemical Company (St. Louis, MO).

All water samples were acidified to approximately pH 1 with HNO_3 to maintain iron ratios (Lee and Stumm, 1960). TOC was determined by a Shimadzu TOC-5000A Total Organic Carbon Analyzer (Columbia, MD). Samples were analyzed for aqueous iron (Fe^{2+} and Fe_{tot}) on site using a portable Ocean Optics S2000 spectrophotometer (Dunedin, FL) using either 1 or 10 cm sample cells with fiber optic light transmission. $[Fe^{2+}]$ was determined by measuring the absorbance of the aqueous tris-disulfonated bathophenanthroline iron(II) complex at 532 nm (dsbphen method) (Trinder, 1956; Blair and Diehl, 1961; Barry and Sherlock, 1971).

Calibration curves of Fe(II) standards were used to calculate extinction coefficients valid for the instrumental setup ($\varepsilon_{1\ cm} = 21{,}470$ L mol^{-1} cm^{-1}; $\varepsilon_{10\ cm} = 21{,}714$ L mol^{-1} cm^{-1}); the differences in extinction coefficients are due to cell geometry. Total aqueous iron concentrations $[Fe_{tot}]$ were determined by reduction of ferric iron using hydrazine hydrochloride followed by the use of the dsbphen method for $[Fe^{2+}]$. Ferric iron $[Fe^{3+}]$ was calculated as the difference between $[Fe_{tot}]$ and $[Fe^{2+}]$, which can result in increased uncertainty relative to direct measurement of Fe^{3+}. Detection limits and quantification limits – 3× and 10× the standard deviation of the blank, respectively – were determined from the standard deviation of 20 blank measurements for each system. Limits of detection and quantification for the 10 and 1 cm pathlengths were 0.03 and 0.003, and 0.1 and 0.01 μM, respectively.

Temperature and pH were determined with an Orion model 1230 meter and probe, and pocket Orion QuiKcheK temperature and pH meters (Thermo Electron Corp., Waltham, MA). The pH meters have automatic temperature correction and were regularly calibrated with pH reference standards.

The effects of light on iron redox partitioning in MCC were determined by isolating stream water in two large evaporation dishes — one shielded with aluminum foil (dark) and the other unshielded (light). These in-stream isolation experiments also confirmed whether or not changes in iron concentration were influenced by upstream or sediment inputs. The containers were bathed in the stream to maintain a constant temperature. Water from the containers was sampled and compared with stream samples taken at the same time. Oxidation rate studies were performed on the MCC water shielded from sunlight by measuring $[Fe^{2+}]$ and $[Fe_{tot}]$ at ten-minute intervals.

3. Results

3.1. Water characteristics and diurnal iron speciation

Middle Crow Creek is “tea-colored” due to high concentrations of DOM, probably of humic origin. Total organic carbon ranged from 5.21