Wetland Photochemistry as a Major Control on the Transport of Metals in an Acid Mine Drainage Impacted Watershed

Sabre M. Duren[1], Diane M. McKnight[1]

[1]Institute of Arctic and Alpine Research, University of Colorado at Boulder, Campus Box 450, Boulder, Colorado 80309–0450 USA

Abstract A diel study was performed on October 14, 2011 in a wetland spanning about 20 acres located in Summit County, Colorado. The purpose was to quantify the concentrations and reaction rates of DOC, H_2O_2, Fe^{2+}/Fe^{3+}, and other metals based on photochemistry. The results of the experiment confirmed photochemistry is a major control on iron redox chemistry. The diel fluctuation of dissolved ferrous iron was associated with nearly identical trends in 23 different metal concentrations (Al, Cd, Ni, Mn, Pb, Zn, Dy, Er, Eu, Gd, Ge, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, U, Y, Yb).

Keywords photochemistry, hydrology, acid mine drainage, dissolved organic matter, rare earth metals

Extended Abstract

Throughout the state of Colorado, over 1,900 km of surface waters are affected by acid mine drainage (AMD; IMCC 1992). AMD is caused by the weathering of pyrite through a series of biogeochemical processes, which can also occur through natural weathering processes. AMD-degraded surface waters and streambeds cause deleterious effects to stream ecosystems, in many cases greatly reducing periphyton, benthic invertebrate, and fish populations for many kilometers. It is important to have an understanding of the role of the wetlands controlling the cycling of metals because of the potential major influence on the chemistry of receiving waters.

To date, few studies have focused on iron photochemistry in acid mine drainage impacted wetlands, although several studies have addressed iron photochemistry in acid mine drainage streams and lakes (McKnight *et al.* 1988; McKnight and Bencala 1988; Hrncir and McKnight 1998; McKnight and Duren 2004; Gammons *et al.* 2005; Parker *et al.* 2008; Nimick *et al.* 2011). Wetlands are "hot spots" for dissolved organic matter (DOM) photochemistry because the shallow waters are influenced by high light intensity and high DOM concentrations in slow moving waters with residence time for reactions to take place. DOM is key in understanding dominant diel processes on hydrogen peroxide, iron speciation, trace metals, and rare earth metals. The oxidation of Fe^{2+} and cycling of iron has been correlated to the cycling of DOM (Voelker and Sulzberger 1996; Hrncir and McKnight 1998). H_2O_2 can be produced through photolysis of DOM in the presence of ultraviolet light and O_2 (Voelker and Sulzberger 1996). The rates of superoxide radical (O_2^-), and H_2O_2 formation are functions of DOM concentration and reactivity and ultraviolet light intensity (Craig *et al.* 2009). While Fe^{2+} is produced by photoreduction, it is also consumed in the photo-Fenton reaction: $H_2O_2 + 2Fe^{2+} \rightarrow 2\,Fe^{3+} + OH^{\cdot} + OH^-$ (Voelker and Sulzberger 1996). If wetlands control the cycling of DOM and metals, photochemistry may have a major influence on the chemistry of receiving waters.

A diel study was performed on October, 2011 in a wetland system located downstream of Pennsylvania Mine in Summit County, Colorado to quantify the concentrations and reaction rates of DOC, H_2O_2, Fe^{2+}/Fe^{3+}, and other metals of interest. Ten hourly samples were collected during daylight hours and 5 samples were collected after dark. The pH throughout the experiment ranged from 3.41 – 3.97. The results confirmed that photochemistry is a major control on the oxidation and reduction of iron in AMD-impacted wetlands. At midday the H_2O_2 concentrations reached a maximum and then decreased in the afternoon (Fig. 1). The dissolved ferrous iron concentrations were a mirror image of the H_2O_2 concentrations due to consumption in the photo-Fenton reaction (Fig. 2). The corresponding ferrihydrite ($FeOH_3$) concentrations are a major variable for trace metal transport. The diel fluctuations of dissolved iron concentrations driven by changing light intensity were associated with nearly identical trends in the concentrations of 23 different metals, all of which increased as ferrous iron decreased (Fig. 3 shows an example; all 23 metals show a very similar trend). In addition to metals commonly found in AMD streams (Al, Cd, Ni, Mn, Pb, and Zn), these metals included a number of rare earth

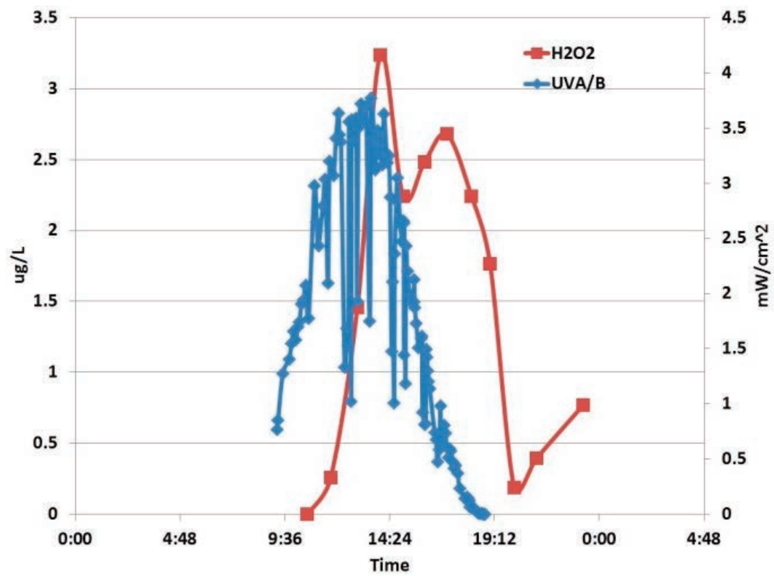

Fig. 1 *DOC photolysis produces hydrogen peroxide.*

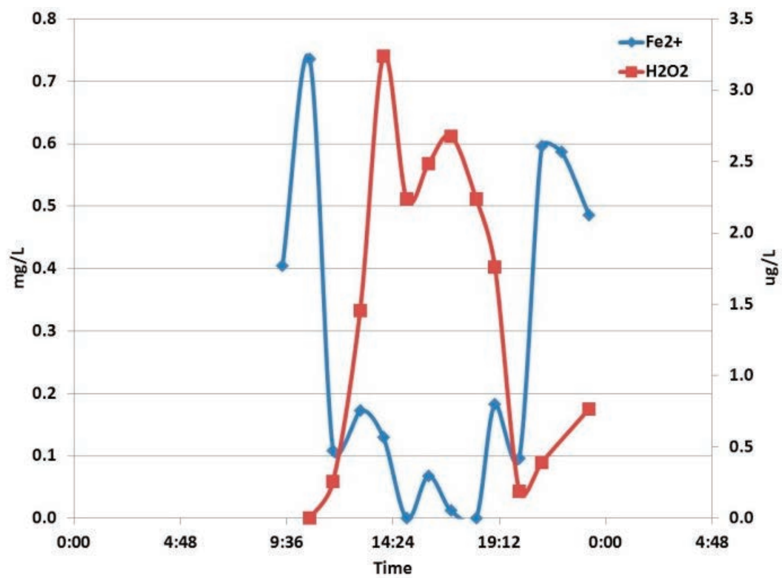

Fig. 2 *Ferrous iron is consumed in the photo-Fenton reaction.*

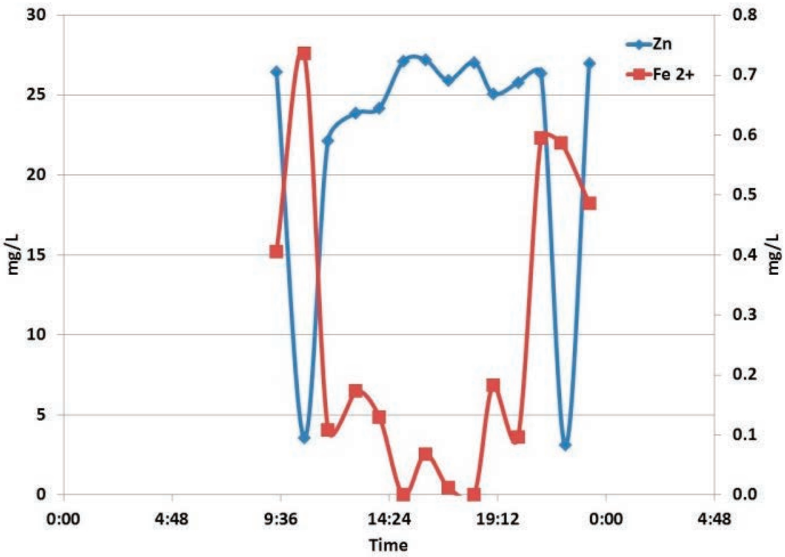

Fig. 3 Representative diel metal trends: ferrous iron and zinc.

metals (Dy, Er, Eu, Gd, Ge, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, U, Y, and Yb) some of which occurred in concentrations exceeding 200 µg/L. The data collected during the experiment confirmed the role of photochemistry in controlling the oxidation and reduction of iron, and the effect iron speciation has on other metal concentrations in a wetland.

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