PRELIMINARY RESULTS: RELEASE OF METALS FROM ACID-MINE DRAINAGE CONTAMINATED STREAMBED SEDIMENTS UNDER ANAEROBIC CONDITIONS [1]

Barbara A. Butler[2] and David J. Reisman

Abstract. Many miles of streams in the western U.S are contaminated with acid-mine drainage (AMD) from abandoned metal mines. Treatment of these streams may include removal of the existing sediments, with subsequent burial (e.g. in a repository). Burial of previously aerobic sediments may result in release of metals through multiple processes, including reductive-dissolution of metal oxyhydroxides, with concurrent release of previously sorbed metals. This paper discusses preliminary results from a laboratory study examining the release of Cd, Cu, Fe, Mn, and Zn from aerobic streambed sediments collected from an AMD-impacted stream (North Fork Clear Creek, CO). The pH, Eh, and metal release were monitored over twenty-eight days in an anaerobic chamber from sediment slurries prepared using filtered stream water. Additionally, the effect of sediment size was examined by using two size fractions: 2 mm to 63 μm and less than 63 μm. Dissolved Cd, Cu, Fe, and Mn were released and re-sequestered over time from both sediment size fractions. Dissolved Zn, however, demonstrated a continual decrease in concentration over time, relative to the concentration present in the stream water used to prepare the slurries. Releases of Cd, Cu, Fe, and Mn varied for each of the size fractions over time. In the case of Cd and Cu, no further release was observed in either size fraction after one week. Releases of Fe and Mn declined after the first week in the smaller size fraction and after the second week in the larger size fraction. Because of the presence of SO_4^{2-} in the stream water, it is hypothesized that the metals were re-sequestered as sulfide precipitates. Future studies will include replication, measurement of sulfur species, and the use of surface chemical techniques to examine the solids for the presence of metal oxides and sulfides.

Additional Key Words: Iron oxyhydroxides, manganese oxyhydroxides, and metal sulfides, AMD

Introduction

Thousands of miles of streams in the United States are contaminated by acid-mine drainage (AMD), resulting from predominantly coal mining in the eastern U.S. and from metal mining in the western U.S. Once AMD enters stream water having a neutral pH, a variety of chemical processes can occur, including neutralization of acidity and oxidation and subsequent precipitation of metal oxyhydroxides, such as aluminum oxyhydroxide (ALO), iron oxyhydroxide (HFO), and/or manganese oxyhydroxide (HMO) (Butler, 2005), known to strongly sorb metals (Jenne, 1968). The term sorption encompasses absorption, adsorption, and surface precipitation (Sposito, 1989). Another process that may occur is co-precipitation. This may entail: 1) adsorption of ions onto a freshly precipitated solid; 2) solid solution formation by incorporation of ions into a metal hydrous oxide lattice; 3) physical entrainment of ions in solution by the precipitate; or 4) any combination of these processes (Karthikeyan et al., 1997). The main distinction between co-precipitation and adsorption processes is that there is not a new three-dimensional solid formed via adsorption, simply an addition to the existing surface of a solid (McLean and Bledsoe, 1992). Metals associated with such solids can be transported downstream in the suspended sediment fraction and/or aggregate and settle to the streambed (Stumm, 1992; Schemel et al., 2000).

Remediation of these streams is desired to restore the aquatic ecosystem. Remedial efforts may include active and/or passive treatment of point-source inputs, non-point source inputs, and physical removal of tailings and contaminated streambed sediments. Disposal of these sediments may be into an existing tailing impoundment (EPA, 2001; 2004) or into a repository also containing tailings, waste rock, or other material removed during remediation (EPA, 2004; 2005a; 2005b). In some cases, these repositories are unlined (e.g. Bunker Hill Complex – EPA, 2005a), which may lead to release of metals to groundwater, if they are mobilized by anaerobic conditions and remain mobile.

When a metal oxyhydroxide is exposed to anaerobic conditions (as would be expected with burial), it is likely that metals will be released via reductive-dissolution. Changes in pH and Eh are also expected to release metals that are co-precipitated and/or sorbed to the oxyhydroxides. Dissolved metals released may be precipitated (i.e. re-sequestered) as insoluble metal sulfides, providing there is sufficient sulfate-reduction occurring. In the absence of SO_4^{2-} for reduction to

sulfide and subsequent precipitation, metals may continue to be mobile in the anaerobic environment.

The objective of this research was to assess the release and re-sequestration of metals from aerobic streambed sediments collected from an AMD-impacted stream (North Fork Clear Creek, CO) under anaerobic conditions over time. Metals were assessed in two different size fractions (63 μm ≤ x < 2 mm and x < 63 μm). Results are presented for Cd, Cu, Fe, Mn, and Zn.

Methods

Study Site

The North Fork of Clear Creek (NFCC) is Operable Unit #4 of the Clear Creek (CC) Superfund Site in the Rocky Mountains of Colorado, about 16 km (10 mi) west of Golden. Mining in the late 1800's for Au, Ag, Cu, Pb, and Zn in the Colorado Mineral Belt (CMB) has led to this region being impacted by AMD from multiple point and non-point sources (Cunningham et al., 1994; Wildeman et al., 1974). Figure 1 shows the study site with the locations of the primary sources of AMD input to NFCC: the National Tunnel Adit, Gregory Gulch, and Gregory Incline, each originating in the Black Hawk/Central City region of the CMB. When the AMD water mixes with upstream NFCC water, there is transformation from Fe^{2+} to Fe^{3+} iron, resulting in visible precipitation of ferric oxyhydroxides (variety of minerals collectively referred to as HFO) (Butler, 2005). These precipitates scavenge (co-precipitation and sorption) other metals present in the water column and are transported downstream and also aggregate and settle to the bed sediment. Additionally, during some parts of the year, manganese oxyhydroxide coatings (variety of minerals collectively referred to as HMO) are evident on rock surfaces (Butler, 2005).

Field Sample Collection

Aerobic sediments and associated pore water were collected in April 2007 from the top 5-cm of the streambed in 50 locations over a distance of 38-m (Fig. 1) using polypropylene scoops; material much larger than 2 mm was avoided. The sampling region provided sediment representative of what is typically found throughout the stream below the AMD inputs (personal observation). Sediment was composited into two new 1-gallon high-density polyethylene (HDPE) jars, previously rinsed with stream water.
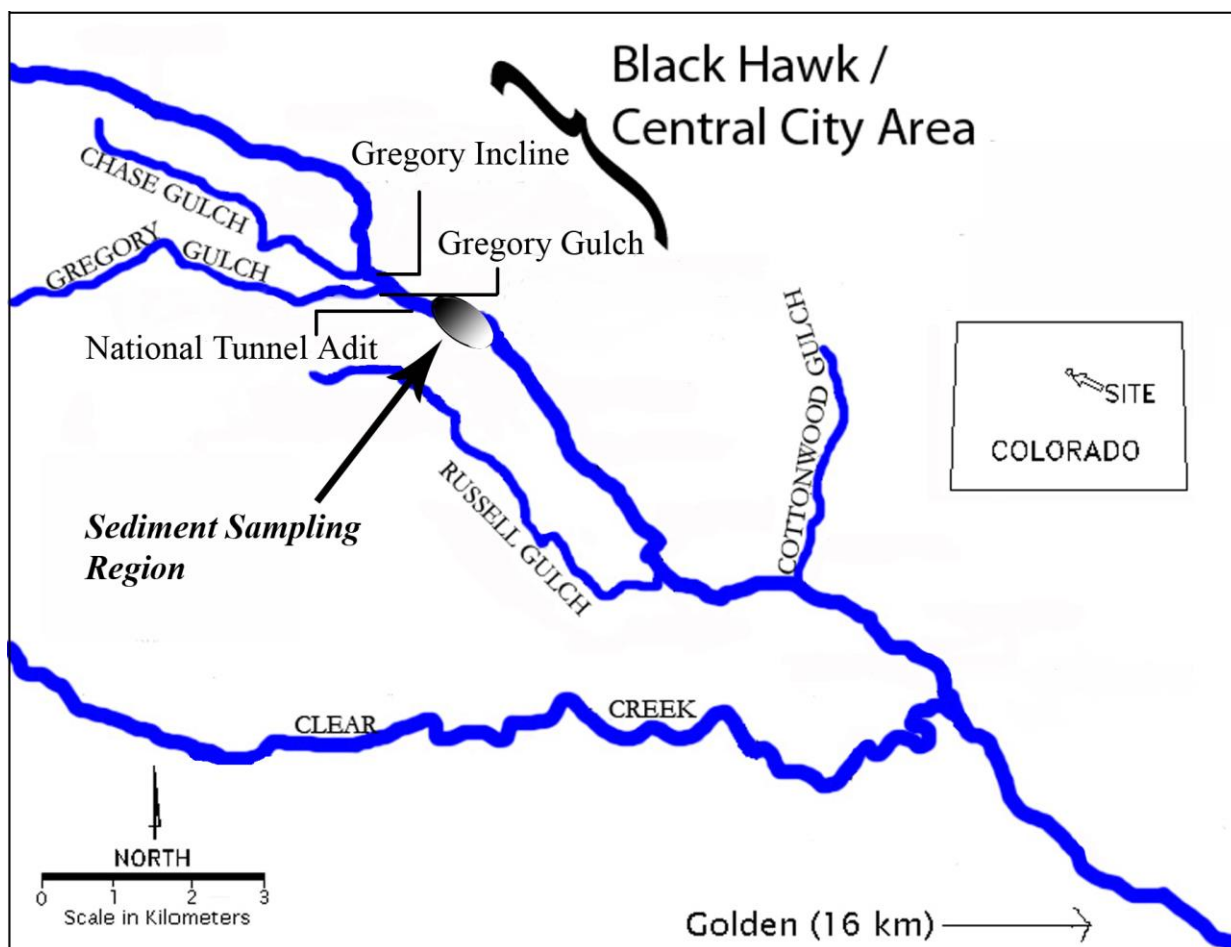
Figure 1. North Fork Clear Creek, CO watershed with sediment sampling location (adapted from Butler, 2005).

Water samples were collected in replicate from the central portion of the stream along the 38-meter reach in 1-L HDPE bottles. Collection included rinsing the bottles three times with stream water, placing them upside down under the water, inverting them, and then slowly bringing them upward through the water column to obtain a sample from the majority of the stream depth. Water samples were collected in replicate for DOC in a similar manner, but in brown borosilicate glass vials. The water was filtered through previously rinsed (250 ml DI) Target™ nylon 25 mm, 0.45 µm disposable filters and acidified to pH < 2 (1 ml acid per 1 L water) with H_2PO_4 (U.S. EPA, 2003). This process was repeated for a filter blank.

Aliquots from the bulk water samples were obtained for SO_4^{2-}, dissolved analytes (Cd, Ca, Cu, Fe, K, Mg, Mn, Na, and Zn), alkalinity, and pH. The pH field meter was inoperable; thus, pH was measured (within ≈ 2 hours of sample collection) at the Colorado School of Mines

(CSM) following a 3-point (4, 7, and 10) calibration and a check standard measurement of 7.03. Samples for dissolved analytes and SO_4^{2-} were filtered at 0.45 μm. The aliquots for metals were acidified in the field to pH < 2 with trace metal grade concentrated nitric acid (U.S. EPA, 1992). Additionally 2-gallons of stream water were collected for use in laboratory experiments.

All containers were sealed and shipped on ice to the laboratory, following EPA chain of custody procedures. Once received at the laboratory, samples were refrigerated at 4 ˚C until use.

Field Sample Processing

The bulk sediment/pore water slurry was homogenized in a 3-gallon tub by hand-mixing with a wooden spoon for 30-minutes; clumps observed were broken by hand while wearing nitrile gloves. Following homogenization, the bulk sample was wet-sieved (using stream water) into two size fractions: 1) 63 μm ≤ x < 2 mm and 2) x < 63 μm; material greater than 2 mm was discarded. The overlying water in the sediment slurries was allowed to settle and then was decanted. This process was repeated for the small size fraction over several days to minimize the amount of water remaining before commencing laboratory experiments; sediments were kept refrigerated between manipulations. A sub-sample of the homogenized sediment was sieved separately and the fractions dried at room temperature to determine the relative percentages of each size fraction in the bulk sediment, which were determined to be 83% and 17% for the 63 μm ≤ x < 2 mm and x < 63 μm fractions, respectively.

Laboratory Experiments

Bulk stream water was filtered through Gelman Sciences Type A/E glass fiber filters to remove particulates and purged for 1 hour with PurityPlus™ pre-purified N_2. Following purging, the water was placed into a Coy Laboratory Products (MI) anaerobic chamber and left to equilibrate with the atmosphere (7-10% H_2; 90-93% N_2, standard method for this chamber) for 24 hours.

Sieved sediment samples were homogenized for 10-30 minutes using a wooden spoon before removing aliquots for experiments. Wet sediment from each of the size fractions was added to one of two 4.2-L Scienceware® polypropylene tubs: 259 grams of the 63 μm ≤ x < 2 mm size fraction and 407 grams of the x < 63 μm size fraction (Mettler PC2200 balance). Triplicate sub-samples of wet sediment (3-10 mg each) from each size fraction were massed on an AND GR-202 Alpha-Liberty Company balance, dried at room temperature, and massed again for later

conversion of metal concentrations to a dry mass basis. The tubs were placed into the anaerobic chamber, two liters of anaerobic water were added to each, along with a stir bar, and then placed on stir plates. The sediment and water were homogenized and time zero (t_0) samples were obtained from each of the sediment slurries. Sampling included measuring of pH, Eh, and collection of dissolved water (filtered at 0.45 μm) for metal analyses via ICP-AES. Subsequent sampling was conducted at 1, 2, 5, 10 and 24 hours; then at 2, 3, 7, 9, 14, 21, and 28 days. Replicates were obtained at 5 hours and 7 days. Between sampling events, the slurries were covered loosely to allow atmospheric exchange with the chamber, while minimizing evaporative losses.

Dissolved Ca, Cd, Cu, Fe, K, Mg, Mn, Na, and Zn were measured on a Perkin-Elmer Optima 2100DV inductively coupled plasma atomic emission spectrometer (ICP-AES), dissolved SO_4^{2-} was measured on a Dionex ICS 2000 ion chromatograph (IC). Initial DOC was measured on a Phoenix 8000 UV-Persulfate TOC Analyzer and initial alkalinity was measured using the Hach® titration method. All analyses were conducted following internal EPA standard operating procedures. Containers were either new or rinsed with DI water, or were washed with Alkanox, followed by soaking for 24-hours in a 10% nitric acid solution, and triple rinsed with DI water.

Data Reduction and QA/QC

Before measuring pH, the meter was calibrated using a 3-point calibration (4, 7, and 10) and checked using a check standard from a different source. The pH check standard was within ± 0.05 units (stream samples and experimental samples) and measured pH in the replicate stream samples were below 10% relative percent deviation (RPD). Eh values were normalized to the standard hydrogen electrode (SHE) by adding the potential of the redox electrode (Mettler-Toledo Pt4805, potential of 210.5 mV obtained from the technical support center) to measured values. The SO_4^{2-} control check standard (CCS) was within 10% of the known value. ICP CCS samples were within ± 10% of their known values, blanks were less than 2 times the detection limit (DL), and all reported measurements were within the linear calibration range. DLs were 1.1, 1.3, 3.7, 4.6, 5.6, 18.0, 12.1, 166, and 52.7 μg/l for Cd, Cu, Fe, Mn, Zn, Ca, Mg, Na, and K, respectively and 0.02 mg/l for SO_4^{2-}. All analytes in replicate samples were within ± 20% RPD, with the exception of copper at 5 hr in the < 63-μm sample, which had an RPD of 22%. Errors associated with measurement of mass and volume were ± 1% for each.

Results and Discussion

Dissolved Cd, Cu, and Fe were below the detection limit (BDL) in the replicated stream water samples. The mean concentrations of Mn, Zn, and SO_4^{2-} were 0.49, 0.40, and 69 mg/l, respectively. The mean pH was 6.92, the mean DOC was 2 mg/l C, and alkalinity was 15.3 mg/l as $CaCO_3$. Water chemistry in NFCC varies depending on hydrologic season and the interested reader is referred to Butler et al. (2008) and Butler (2005). The dry mass / wet mass ratios for conversion of metal concentrations to a dry mass basis were 0.80 and 0.25 for the 63 μm ≤ x < 2 mm and x < 63 μm size fractions, respectively.

Dissolved Cd, Cu, Fe, Mn, and Zn (mg/kg dry mass) released from the sediments over time in the anaerobic chamber are shown in Fig. 2a-e. Metals from the larger sediment size fraction (63 μm ≤ x < 2 mm) are shown on each graph by the blue circles and those released from the smaller size fraction (x < 63 μm) by the red squares. Because the exposure water contained initial concentrations of Mn and Zn, these initial values were converted to dry mass sediment and are plotted as solid lines for each size fraction in Fig. 2e and f, respectively. Eh and pH over time are shown in Fig. 3.

Cd, Cu, Fe, and Mn were released from both size fractions of sediment, and with the exception of Fe, each was present in the first sample (t_0). Potential reasons for this immediate release to the water include: 1) displacement by ion-exchange; 2) physical perturbation of the sediments from mixing, perhaps releasing weakly bound metals; and/or 3) desorption of sorbed metals resulting from changes in Eh and pH. A trend of metal concentrations released from the smaller-sized sediment fraction being higher than that released from the larger-sized sediment fraction was observed at most times, with the exception of Cu at ≥ 5 hours and Mn at times ≥ 220 hours, which were measured in lower concentrations.

Unlike the other metals, the concentration of Zn present in the stream water used for experiments was greater than the concentration measured at any of the sampling times. The fact that the Zn concentrations are below the initial concentration over time in each of the size fractions indicates solely sequestration of the dissolved Zn, with no release of the metal from the solids greater than what was present in the water initially.
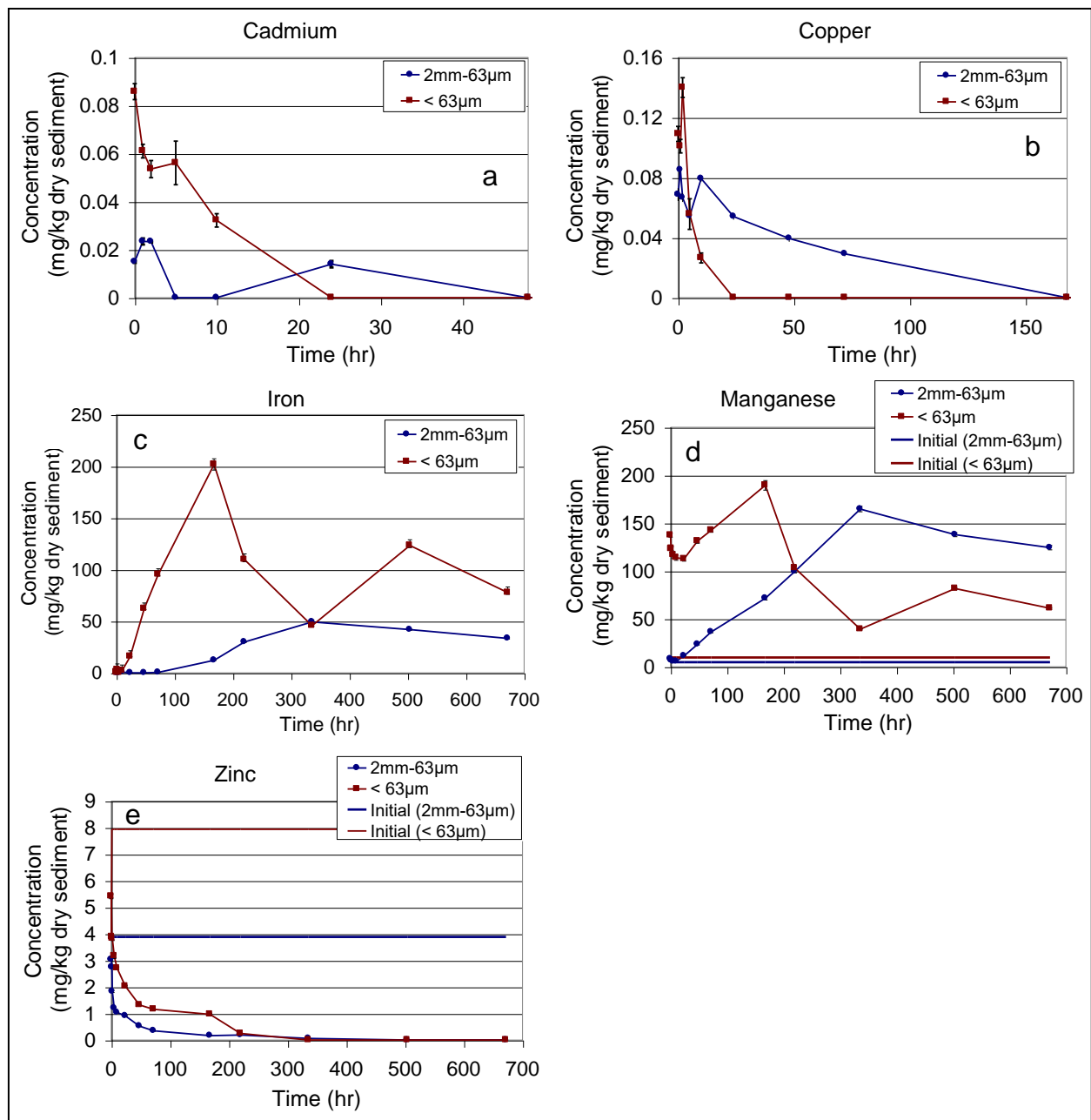
Figure 2. Dissolved metal concentration released from sediment (mg/kg dry mass) over time. Error bars (not all visible) represent instrument standard deviations (triplicate measurements) and analytical measurement error (propagated through all calculations); at times of 5-hr and 7-days, the error bars include these calculations for replicated samples.
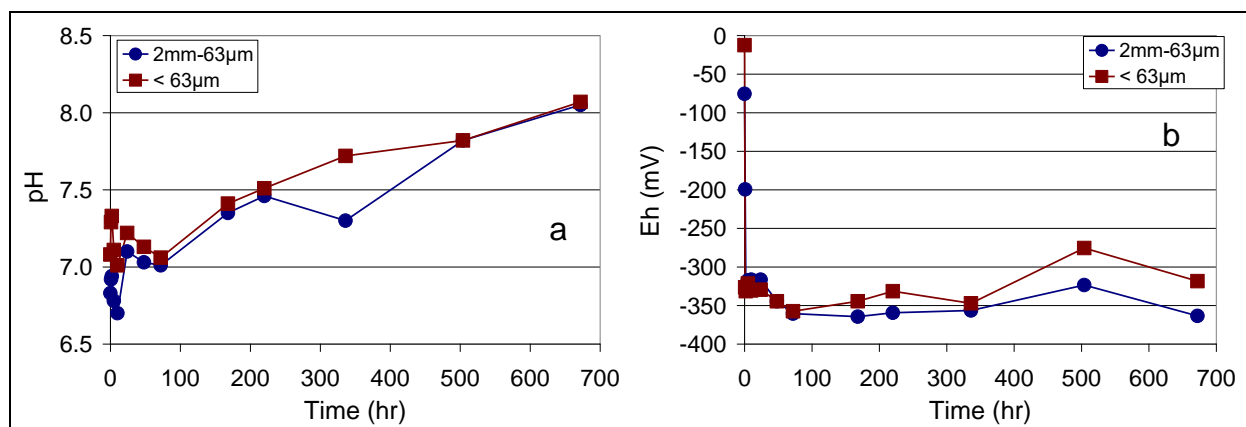
Figure 3. pH (a) and Eh (normalized to H_2) (b) over time.

Release of Fe was slow in both size fractions, beginning at ≈ 24 hours in the smaller size fraction and at ≈ 72 hours in the larger size fraction. A peak in concentration was observed at 1 week in the smaller size fraction and at 2 weeks in the larger fraction. The fact that no (or very little) release was observed in the early stages of the experiment indicates that Fe is more strongly associated with the sediments than were the other metals. This is most likely due to its being covalently bonded in amorphous and/or crystalline HFO minerals, requiring reductive-dissolution for release. HFO minerals that have previously been observed in suspended sediments in NFCC include ferrihydrite, goethite, and schwertmannite (Butler, 2005). Other studies in NFCC have indicated that the streambed sediments comprise similar minerals as the suspended sediments (Butler et al., manuscript in prep).

All metals released showed decreases over time, indicating that they were being re-sequestered. The mechanism for re-sequestration could be sorption onto solids, such as ALO, HFO, and/or HMO, and/or due to precipitation of the metals as metal sulfides. The sediments were not characterized for mineral composition, but ALO, HFO, and HMO are known to be present from previous studies at the Colorado School of Mines, Golden, CO (Butler and others, unpublished data).
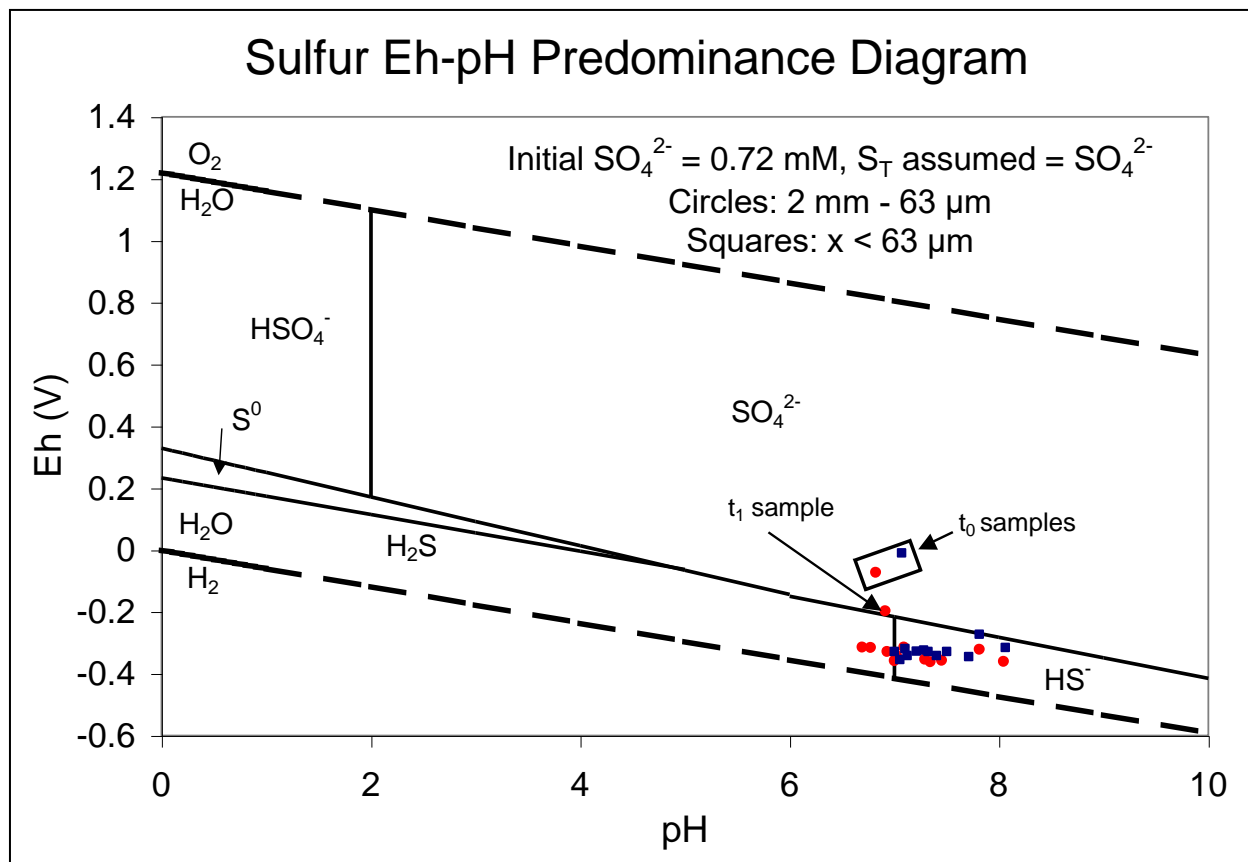
Figure 4. Sulfur Eh-pH predominance diagram with samples plotted in stability fields (using redox equilibrium equations and data from Pankow, 1997).

Figure 4 presents the sulfur Eh/pH diagram for the system, assuming total sulfur was equivalent to the measured sulfate in the added stream water (69 mg/l, 0.72 mM). The pH and SHE normalized Eh values are also plotted for each time sample. The t_0 samples from each size fraction and the 1-hour sample from the larger size fraction fall in the SO_4^{2-} field of the predominance diagram, suggesting that metal re-sequestration in the larger size fraction at 1 hour is not due to the formation of metal sulfide precipitates. All other data fall within the hydrogen sulfide/bi-sulfide (H_2S/HS^-) stability regions; thus, it is believed that the loss of dissolved metals over time is due to precipitation as metal sulfides, although some may be due to metal carbonate precipitation from the existing alkalinity.

Losses of Cd and Cu from the dissolved phase were much more rapid than with the other metals. Cd released in the beginning of the experiment was completely re-sequestered at times ≥ 48 hours in the 63 μm $\leq$ x < 2 mm sample and at times ≥ 24 hours in the x < 63 μm sample.

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The same was observed for re-sequestration of Cu in the smaller size fraction sample, but complete removal of the Cu from the dissolved phase took longer in the larger size fraction sample (BDL between 3 and 7 days).

In the smaller size fraction, there may be both reductive-dissolution and FeS formation occurring simultaneously over time, indicated by the observed increases and decreases in dissolved Fe concentrations after 2 weeks. Reductive-dissolution of crystalline goethite to form amorphous FeS requires a much higher concentration of sulfide (11.5 mM) than does amorphous HFO (2.14 µM) (Langmuir, 1997); thus, it appears that Fe released and re-sequestered from these sediments was derived from amorphous HFO.

The Mn released in both size fraction samples at t_0 was removed within 10 hours (larger size) and within 24 hours (smaller size). After these times, Mn was again released to the dissolved phase, with decreases in dissolved concentrations following at times of ≥ 1 week and ≥ 2 weeks for the x < 63 µm and 63 µm $\leq$ x < 2 mm samples, respectively. The re-release of dissolved Mn after 10 and 24 hours (larger and smaller size fractions, respectively) is likely due to reductive-dissolution of the HMO. There was also an increase in dissolved Mn in the 3-week sample and a decrease in the 4-week sample in the smaller size fraction, similar to that observed for Fe and corresponding to an increase (3 weeks) and decrease (4 weeks) in Eh. The 3- and 4-week samples from the smaller size fraction are represented by the two blue squares closest to the sulfate/bi-sulfide stability boundary (Fig. 4).

The sulfide solubility constants (K_{sp}) for Equation 1 are given in Table 1 for each metal examined (represented in Eq. 1 as Me).

$$MeS(s) + H_2O \leftrightarrow Me^{2+} + HS^- + OH^- \tag{1}$$

Table 1. Solubility constants for metal sulfides (Chang, 1991).

Metal Sulfide	K_{sp}
CdS	8×10^{-28}
CuS	6×10^{-37}
FeS	6×10^{-19}
MnS	3×10^{-14}
ZnS	3×10^{-23}

Based on solubility, the expected formation of metal sulfides over time would follow the series: CuS > CdS > ZnS > FeS > MnS. It appears that this trend may be true for metals released from the smaller size fraction (with Fe ≈ Mn), but not for the Cu and Cd in the larger size fraction. Based on the expected trends in metal sulfide precipitation and on the measured Eh and pH values (as seen in Fig. 4), it is very likely that the metals released from the sediments were rapidly precipitated as metal sulfides at times greater than 1 hour.

There are several potential reasons for the fact that dissolved Fe and Mn were still present in the sediment slurries after 4 weeks. It is possible that the other metals were being released as well, but at concentrations in equilibrium with the sulfide produced, which resulted in no measurable dissolved metals and no sulfide remaining for complexation with the Fe and/or Mn. It is also possible that the rates of reductive-dissolution of HFO and HMO could be faster than the rates of FeS and MnS formation. Another possibility is that the reduction of sulfate to sulfide in the system is kinetically constrained, resulting in insufficient sulfide available at these sampling times for metal sulfide formation. Assuming complete reduction of sulfate to sulfide (i.e. H_2S and/or HS^-) and precipitation of the maximum concentration of each metal released as metal sulfides, there would be 0.62 mM sulfide remaining in solution. Thus, it is not expected that the experimental system is sulfate-limited, although the final SO_4^{2-} concentration was not measured.

Table 2 presents the mean concentrations of each metal released, mean pH (calculated from the hydrogen ion concentrations and converted back to pH), and mean Eh over all time points. With the exception of Cu, the x < 63 µm sample has a greater mean concentration of dissolved metals released. This was expected due to the fact that smaller particles have a larger surface area and thus, sorb a higher concentration of metals available for latter release. Additionally, the solubility of any material is increased with decreasing particle size (Pankow, 1991). The statistical significance of the observed differences between each of the metals concentrations released in each of the size fractions could not be assessed due to the experiments not having been replicated. It appears that there is a difference between size fractions for Cu at each of the individual time points (see Fig. 2b), but the dissolved concentration in the larger size fraction sample becomes greater than that in the smaller size fraction after 5-hours. This results in the mean over all time points being very similar between the two size fractions.

Table 2. Mean concentrations of dissolved metals, Eh, and pH over all timed samples for each sediment size fraction (n = 13).

Parameter	Mean (mg/kg dry mass) over all timed samples	
	63 μm ≤ x < 2 mm	x < 63 μm
Cd	5.8×10^{-3}	2.2×10^{-2}
Cu	3.7×10^{-2}	3.3×10^{-2}
Fe	1.3×10^{1}	5.7×10^{1}
Mn	5.4×10^{1}	1.1×10^{2}
Zn	1.1×10^{0}	2.2×10^{0}
pH[†]	7.04	7.27
Eh	-310	-306

The increases in pH over time in both size fractions are likely due to the combined processes of hydroxide release during metal sulfide formation (see Equation 1), and uptake of protons in the reductive-dissolution of HFO (Equation 2) (and similarly for HMO) and in the reduction of SO_4^{2-} to bisulfide (Equation 3) (Langmuir, 1997). The slightly higher pH observed in the smaller size fraction sample could be due to these processes occurring more rapidly than in the larger size fraction.

$$2Fe(OH)_3 + 3HS^- + 3H^+ \leftrightarrow 2FeS + S^0 + 6H_2O \tag{2}$$

$$SO_4^{2-} + 9H^+ + 8e^- \leftrightarrow HS^- + 4H_2O \tag{3}$$
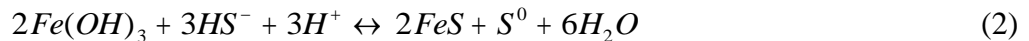
Metals released from sediments buried in waste piles could be expected to enter groundwater. The graphs in Fig. 5 show the concentrations of metals released in the experiments with the primary maximum contaminant level (MCL) for Cd (40 CFR 141.62) and the secondary MCLs for Cu, Fe, Mn, and Zn (40 CFR 143.3) (Electronic Code of Federal Regulations www.ecfr.gpoaccess.gov). The graphs show that only Fe and Mn exceed the MCLs and that these are exceeded even after 4 weeks.
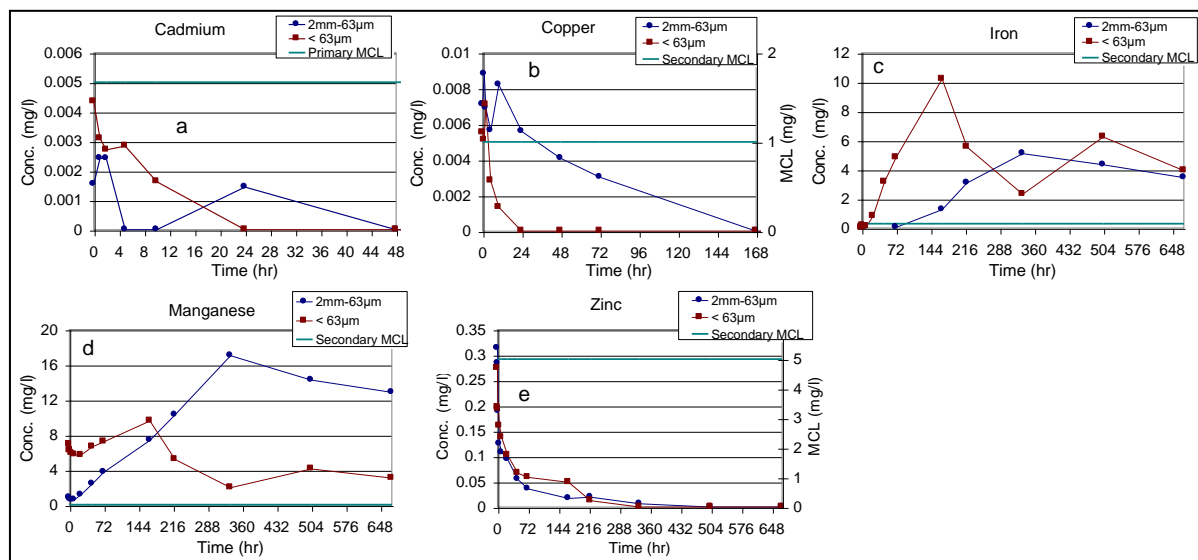
Figure 5. Dissolved metal concentrations over time with primary and secondary MCL values for comparison. Solid solution ratios: 103 g/L for the 63 μm ≤ x < 2 mm sample and 51 g/l for the x < 63 μm sample.

Conclusions

This study has shown that metals associated with aerobic sediments are released into the dissolved phase when held under anaerobic conditions. It is hypothesized that this is because of weak chemical and/or physical association with the sediments being altered, but the exact mechanism is not known. In the presence of sulfide from SO_4^{2-} reduction, these dissolved metals are rapidly precipitated (re-sequestered) as metal sulfides, which are stable to further dissolution in an anaerobic environment. If pH and Eh were to change, however, the sulfide precipitates could be re-dissolved and allow the metals to be mobile (e.g. increase in pH with Eh similar, or increase in Eh with pH similar, refer to Fig. 4). Higher concentrations of metals are released from smaller sized sediment particles as compared to larger size particles on an equal mass basis.

Releases of iron and manganese do not follow the same trends as Cd, Cu, and Zn. This is most likely because Fe and Mn are associated with the mineral composition of the sediment and not just associated by sorption or ionic exchange processes. Iron and Mn remain in the dissolved phase (presumably in their reduced forms at the measured Eh values) at much higher concentrations and for a much longer time than do the other metals (greater than 4 weeks in this study). This may allow them to reach groundwater at concentrations exceeding the current

drinking water standards, if the repository is not lined and/or capable of capturing leached metals prior to their reaching the water table. All pH and Eh data obtained after one hour plotted on the sulfide stability diagram in either the hydrogen sulfide or bisulfide stability fields. Thus, it is expected that dissolved iron and manganese remaining in the samples after 4 weeks is due to kinetic limitations and not to thermodynamic processes, especially since complete conversion of sulfate present would yield 0.72 mM sulfide, which is more than sufficient to precipitate with all dissolved metals measured.

Future studies will include replication of experiments, a longer experimental time frame (to assess complete loss of Fe and Mn from the dissolved phase), measurement of sulfide species over time (dissolved sulfate/sulfide and acid-volatile sulfide), measurement of DOC released from the sediments, spectroscopic assessment of solids for oxides and sulfides, and particle size distribution.

Acknowledgements

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