SEASONAL CHANGES IN THE CHARACTERISTICS OF SUSPENDED SEDIMENT METAL TRANSPORT IN A MINING-IMPACTED STREAM[1]

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Abstract. An important source of metals to aquatic ecosystems is acidic, metal-rich effluents from active or abandoned mining sites. Natural processes and remedial activities both lead to the neutralization of acidity, which results in the removal of dissolved metals from the water column. This process produces sediment deposits and suspended particles having high metal concentrations. The amount and characteristics of metal-contaminated sediments and stream water, collected from a high-gradient stream reach (North Fork, Clear Creek) located in the Front Range of Colorado, were studied. Deposited sediments and suspended particulate material are dominated by very fine-grained (colloids and fine silts) iron oxyhydroxide precipitates that contain high levels of copper and zinc. Sediments of this type are susceptible to *in-situ* formation, re-dissolution, and aggregation/disaggregation processes. These fine-grained sediments are suspected to be the key to metal transport, fate, and toxicity in this system. We examined seasonal variations in the following: 1) water column dissolved and suspended metal concentrations, 2) relative size distributions of suspended and bed sediments, and 3) acid-soluble metal content in coatings from streambed rocks. Metals were found to be temporarily stored in loose flocculated sediments, which accumulated in periods of low flow. Significant metal transport occurred as these sediments were re-suspended during high-flow hydrologic events, including spring snowmelt and a localized summer rainstorm.

Additional Key Words: Acid mine drainage, AMD, colloids, iron oxyhydroxide.

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Introduction

Acid-mine drainage (AMD) is an important source of metal contamination in regions of current or past mining of sulfide ores. AMD impacted streams pose toxicity risks to a variety of aquatic and sediment-dwelling organisms. In the Blackhawk-Central City area of the Colorado Mineral Belt, gold, silver, copper, lead, and zinc were extensively mined in the late 1800's (Wildeman et al., 1974; Cunningham et al., 1994; U.S. EPA, 1999). Effects from these past mining activities are still seen today in the Clear Creek Watershed (Ficklin and Smith, 1994; Morris et al., 1999). For example, the North Fork of Clear Creek (NFCC), a major tributary of Clear Creek, does not support fish in locations below AMD inputs (U.S. EPA and CDPHE, 1997).

AMD enters NFCC, near the towns of Blackhawk and Central City, and results in high concentrations of heavy metals, including iron, zinc, copper, and manganese in the water and the associated sediments. Once the metal-laden water mixes with the upstream NFCC water, there is a transformation from ferrous to ferric iron. This results in the visible precipitation of colloidal ferric oxyhydroxides. These colloids can scavenge other metals present in the water column, and can either be transported downstream or aggregate and then settle to the bed sediment (Stumm, 1992; Schemel et al., 2000).

Sediments accumulated on the streambed can be resuspended and transported. Deposition and scouring of metal-laden bottom sediments is mostly controlled by flow conditions in the stream. NFCC is an example of a high-gradient mountain stream, where flows are quite variable over the year and depend on seasonal (snow-melt, fall/winter low-flow) and short-term (localized rain storms) weather conditions. In addition, drought during 2002 resulted in the lowest recorded flows for Clear Creek and likely affected metal transport.

Both the dissolved phase and suspended sediments were analyzed for a variety of metals (iron, copper, manganese, and zinc data are presented) over May-October, 2002. Water column samples were collected from both NFCC and the main-stem of Clear Creek (CC), Colorado. Bed sediment samples were collected from NFCC. The suspended and bed sediments were examined for relative particle-size distributions. Coatings on rocks, which were dissolved with acid, were examined for relative metal concentrations, based on estimated surface area. The results of the chemical analyses were used to determine the relative importance of suspended versus dissolved transport of metals over the study period.

Methods

Field Sampling

Samples were collected biweekly at two locations on the main-stem of Clear Creek (Kermit's SG, and Golden) and at the staff gage on NFCC (NFSG) (see Figure 1). The Colorado Department of Public Health and Environment (CDPHE) and the Colorado School of Mines (CSM) conducted a spatial study on May 21, 2002 at numerous sites in NFCC and CC, which are indicated in Figure 1. This paper presents the results from eleven sampling events from May 21 to October 1, 2002 in NFCC. Full results from the May 21, 2002 spatial sampling are available from CDPHE.

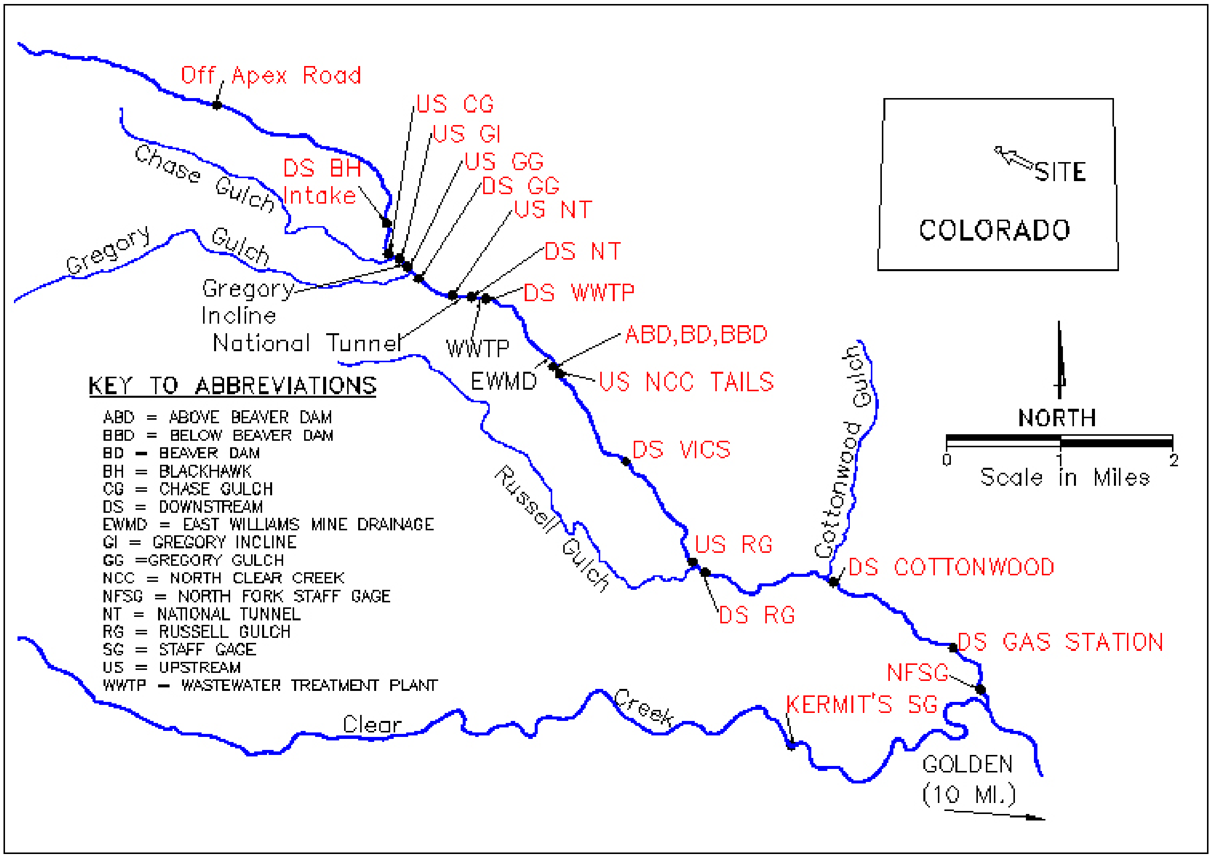

Figure 1. NFCC Study Area (adapted, with permission, from an electronic version of the Clear Creek Watershed Topography map provided by Rocky Mountain Consultants, Longmont, CO).

All water samples were grab samples collected in high-density polyethylene (HDPE) bottles. Bottles were rinsed three times with the stream water before sample collection. The bottles were placed below the surface water and then filled by moving the bottle through the water column. It was assumed that the water was well mixed due to the turbulent nature of the stream and thus, samples were not depth integrated. Water was filtered in the field using 25 mm filter holders (Gelman) with disposable 0.45-micron (Supor-450) filters. Filtered and raw water samples were acidified with metal-free hydrochloric acid to a $pH < 2$. Unfiltered samples were also collected for total organic carbon, alkalinity, and particle-size analysis (organic carbon and alkalinity results are not presented).

Bed sediments were collected at the NFSG, DS Gas Station, and BD sites on May 21, 2002. Based on visual observations, samples of varied sediment types were collected in order to assess the range of sediment types present in the stream. Loose sediments were collected using plastic beakers. The sediments were transferred to polyethylene bags with overlying stream water. Cobbles and rocks of approximately 5-25 cm diameter were collected twice at NFSG (10 on May 21, 2002 and 8 on August 20, 2002) and at two sites below the beaver dam (BBD) (6 rocks for each) in August.

NFSG flow data was obtained from the U.S. Geological Survey (USGS) Lakewood, Colorado office.

Analytical

Temperature and pH were measured in the field; all other analyses were performed in the laboratory. Samples were analyzed for total and dissolved metals on a Perkin-Elmer Optima-3000 ICP-AES using EPA Method 200.7.

Particle number and size distribution measurements were performed on unfiltered water samples using a Nicomp-780 Single Particle Optical Sizer (SPOS). SPOS uses a combination of light obscuration and scattering to determine the size distribution of a sample over the range of 0.4-250 micron. The upper limit of particles per ml for injection into the Nicomp-780 SPOS is $\sim 10^4$ particles/ml. Thus, samples were diluted in deionized water before analyses and the results were adjusted with the dilution factor to determine particles per ml in each original sample.

Bed sediments were wet sieved into > 2 mm, 2 mm to 63 μm, and < 63 μm fractions. The fraction > 2 mm was discarded and the two remaining fractions were dried. The 2 mm to 63 μm fraction was air-dried and the < 63 µm fraction was oven-dried at 50 ˚C. The dry mass in each size fraction was determined.

Sediment coatings on the rocks were removed by soaking the rocks in 0.5 M HCl for 3-10 days with occasional agitation. Loose, flocculated material was rubbed off the rocks (by hand, using nitrile gloves) before the rocks were submersed in the acid solution. The acidic solution was filtered and diluted before analysis for metals by ICP-AES. The dimensions of the rocks were determined and an approximate geometric surface area was computed and used to normalize the metals data.

Results and Discussion

Flow in NFCC was very low in 2002, with a range from 0.4 to 25 cfs (Figure 2).

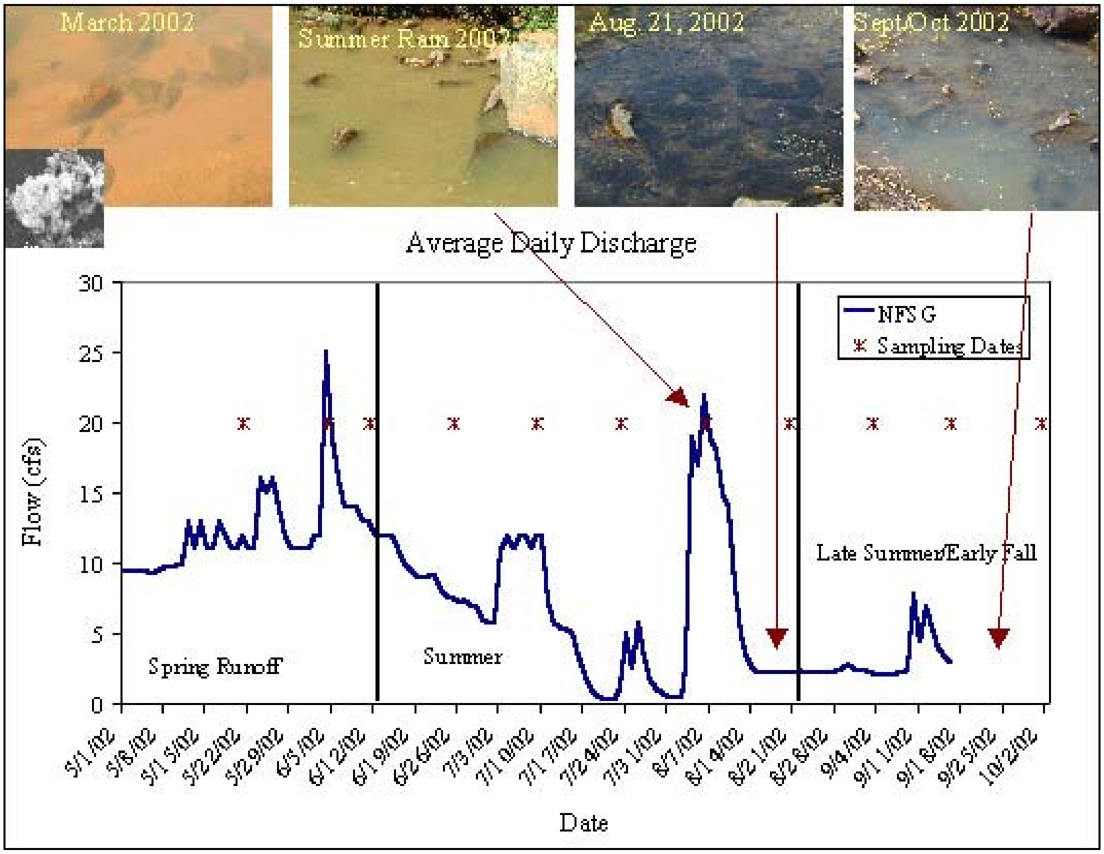

Figure 2. Flow, sampling dates, and photos showing sediment changes and transport during varied hydrologic events.

Flow dynamics in the creek were seen to control particulate-metal transport, as illustrated by the photographs in Figure 2. During the winter and early spring, very fine iron oxyhydroxides had accumulated and appeared to dominate the bed sediments (left-most photograph in Figure 2). These iron oxyhydroxides typically form initially as submicron colloids, as shown in the SEM photomicrograph (Figure 2 insert). These colloids aggregate and form a loose floc that deposits in the stream. As the flow increased during spring runoff, these iron oxyhydroxides were re-suspended and carried downstream. As the summer progressed, and flow decreased, iron oxyhydroxides re-accumulated on the creek bed. A summer rain event on August 5th increased the flow dramatically over a short period. This increased flow resuspended and transported the iron oxyhydroxides downstream (2nd photograph in Figure 2). Once these particles were scoured away by the increased flow, a black coating, suspected to be manganese oxide, was seen on the rocks (3rd photograph in Figure 2). Over several weeks of low flow, iron oxyhydroxides once again began to accumulate on the creek bed. In addition, increased turbidity in the stream was observed.

The particle-size distribution of the suspended sediments (0.4 to 250 µm) was determined using SPOS. The resultant data were simplified by summing the number of particles in each of three size ranges (< 1, 1-10, > 10 µm). The results for each of the sampling dates are presented in Figure 3.

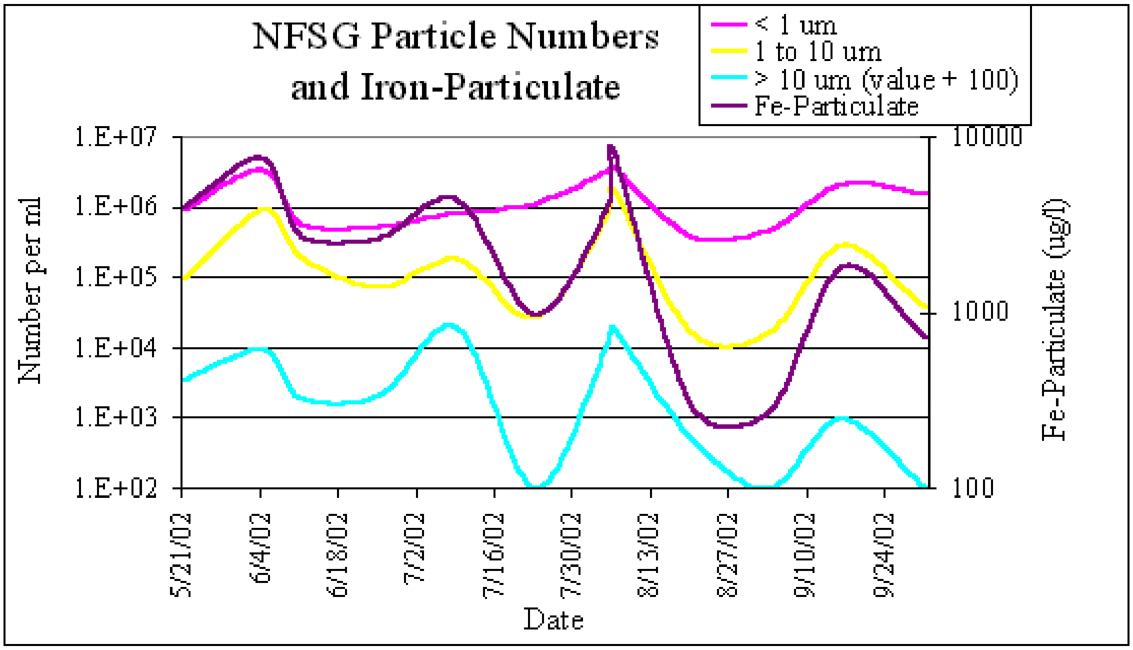

Figure 3. Concentration of suspended particles and iron-particulate.

These results show that the majority of suspended sediment particles are colloidal (less than 1 micron in diameter). The number of particles greater than 10 micron is very small (for ease of comparison to other data presented in Figure 3, 100 particles per ml was added to the particle numbers in this size fraction). Iron particulate in Figure 3 was computed as the difference between iron concentration in the raw (total) and filtered (dissolved) samples. Particle numbers in all size classes are correlated to particulate iron concentrations for all dates. This result is consistent with the fact that iron oxyhydroxide precipitates dominate the suspended sediments.

Particle number-based size distributions can be mathematically converted to volume-based size distributions assuming spherical particles. Particle-volume size distributions are directly related, assuming a relatively uniform density, to the size distribution of particle mass, and is used as a surrogate for mass-based size distributions.

As shown in Figure 4, during low flow conditions (e.g. July 23rd and October 1st), particles in the < 1 um fraction significantly contribute to volume % (~ mass %). This is consistent, especially for the latter date, with our observation of a greenish-white turbidity in the stream (see Sept/Oct photo in Figure 2).

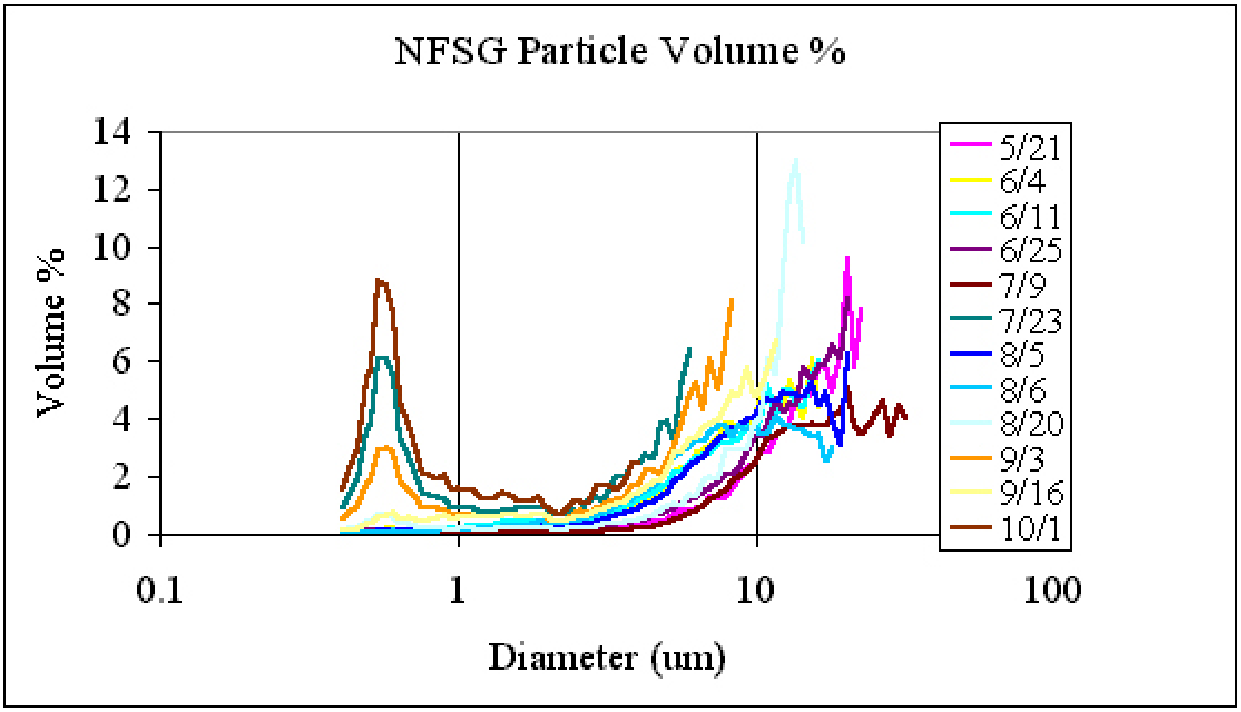

Figure 4. Volume-based size distribution over study period.

Filtration of samples left a reddish-orange colored material on the filter. This observation and the ICP-AES results for iron indicate the suspended sediments are primarily iron oxyhydroxides. The color in the water column may be a result of wavelength-dependent scattering by submicron colloids. The absence of larger particles is due to the low flow being unable to suspend these larger sediments. Thus, colloidal transport of metals may be important during low flows in NFCC. Larger particles (> 5 micron) are dominant at higher flows, during both spring runoff and the rainstorm event. During higher flows, the suspended sediments represent particles that are scoured from the streambed and re-suspended in the water column.

Results from ICP-AES analyses of four metals in the water column are shown in Figure 5.

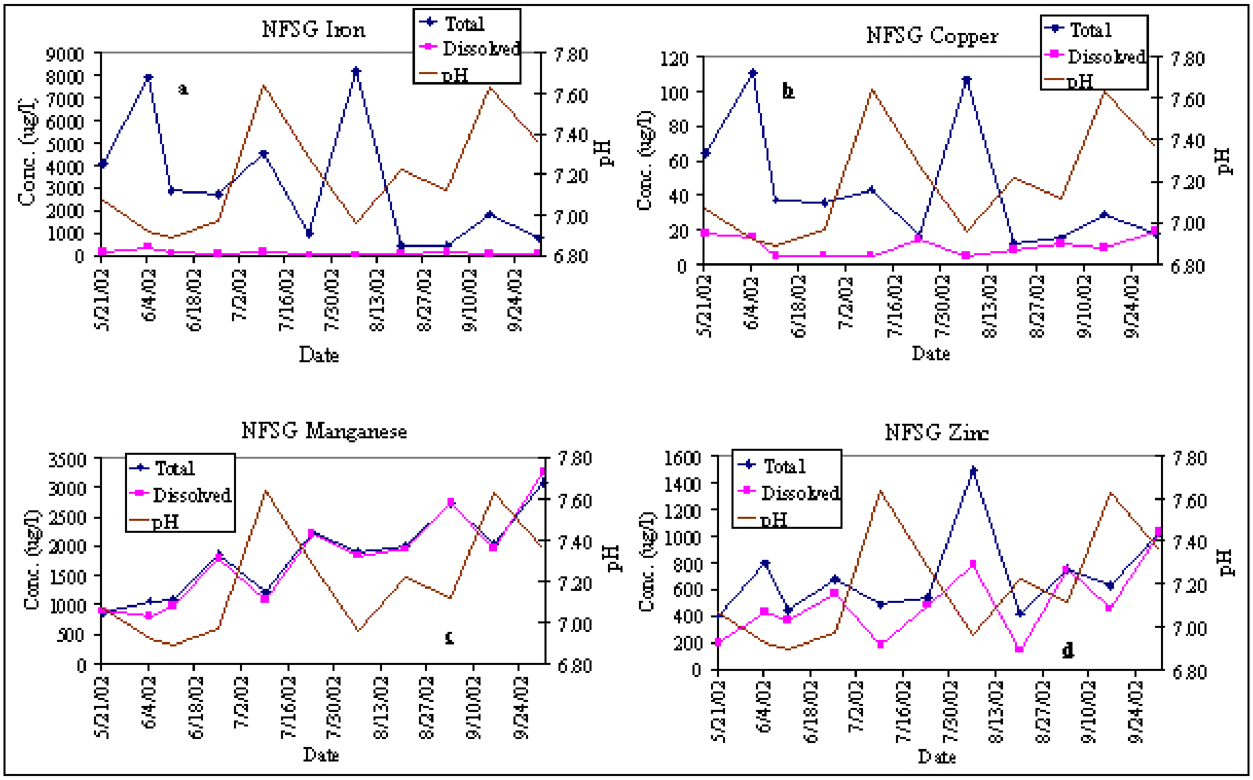

Figure 5. pH, total and dissolved iron (a), copper (b), manganese (c), and zinc (d) over time.

Although pH remains relatively constant over the study period (6.9 to 7.6, shown in Figure 5), it was observed that for the spring and summer rain events (June 4th and August 5th), the pH was lower. This has been seen in other AMD impacted stream systems (Ortiz et al., 1995; Rupert, 2001) and is likely due to flushing of more AMD into the creek during higher flow events. Figure 5a shows that iron is present only in the particulate phase at NFSG during the study period. Elevated levels of particulate iron coincide with the high flows that occur during spring runoff and the summer rainstorm.

Copper is predominantly in the particulate phase (66-96%) during higher flows and in the dissolved phase (0-26% particulate) during lower flows (Figure 5b). For most of the sampling dates, copper transport by suspended sediments was dominant.

Manganese (Figure 5c) is present only in the dissolved phase during all dates, with the exception of a spring rain event (June 4th), where 25% of the total manganese was in the particulate phase. Manganese concentrations are also seen to increase over the course of the year and dissolved phase transport is always dominant.

Zinc in the particulate phase varies widely (0- 66%) and does not appear to have a clear temporal trend (Figure 5d). These results suggest that both dissolved and particulate zinc transport is important in NFCC.

Bed Sediment

Sediment collected on May 21, 2002 from three different sites in NFCC varied greatly in size (Table 1) and sediment material.

Table 1. Bed sediment size distribution.

Sampling Site	Size Fraction	
	2 mm to 63 µm	< 63 µm
DS Gas Station (a)	98%	2%
DS Gas Station (b)	29%	71%
DS Gas Station (c)	82%	18%
Beaver Dam (BD)	4%	96%
NFSG	89%	11%

Three areas within a 15-foot reach of the creek were sampled at the 'downstream Gas Station' site. The sediment in this area was very diverse, including coarse sand, organic-rich sediments mixed with iron oxyhydroxides, and fine sand (Table 1 'DS Gas Station' a, b, and c, respectively). Very fine iron oxyhydroxide floc dominates the sediments in the beaver dam. NFSG sediments were a mix of iron oxyhydroxides and coarse sand. Acid digestion and metals analysis of these sediments is not complete.

Rock Coatings

The surface area of the rocks was estimated from measurements of the major faces performed after removal of coatings. Based on this computation, an estimate of metal concentrations on a surface area basis was made (Table 2). The 0.5 M HCl easily removed the coatings present on the NFSG and BBD rocks collected in May. The black coating on the NFSG rocks collected in August was removed more slowly (about 10 days of submersion in the acid with occasional agitation), and included a black/brown colored 0.5 M HCl-insoluble fraction. This material was dissolved in concentrated HCl. From Table 2, it is seen that the dominant component of the coatings for all May samples is iron, which is consistent with the observed reddish color of the coatings.

Table 2. Major components of rock coatings.

Analyte	Site Name and Concentration (mg/cm^2 rock surface)				
	BBD-01	BBD-02	NFSG May 2002	NFSG August 2002	
Soluble in:	0.5 M HCl	0.5 M HCl	0.5 M HCl	0.5 M HCl	Conc. HCl
Iron	1114	819	551	309	324
Calcium	438	469	274	145	143
Aluminum	168	142	238	169	151
Manganese	90	47	91	259	360
Phosphorus	97	149	71	24	27
Zinc	76	38	56	96	106
Lead	36	7	1	1.2	1.6
Copper	30	10	12	6	6

A comparison of the manganese and iron concentrations in the August versus May rock coatings shows that manganese was higher in August and iron was lower. This is consistent with the observation of the observed black coating (expected to have been manganese oxides) and the lack of an orange coating (see Figure 2). In addition, it was found that the insoluble fraction of the rock coating in August was predominantly manganese (~100 mg/cm^2 rock surface more Mn was present in the concentrated HCl versus the 0.5 M HCl) with an iron component. These results indicate that the amount and composition of the rock coatings is not consistent throughout the study period, and may indicate a seasonal trend.

Conclusions

Iron is present in the NFCC system nearly entirely in the particulate phase and iron oxyhydroxides are observed to dominate the suspended sediments present in NFCC. *In-situ* precipitation of iron oxyhydroxides appears to occur during low flows and is especially prevalent in locations close to AMD inputs. Copper is also seen to be present to a significant extent in the suspended sediments. In contrast, Mn is essentially only present as a dissolved phase. Zinc is present in both the dissolved and particulate phases with no clear trend. These results are consistent with the known behavior of metals in AMD. Copper is known to be more readily adsorbed than Zn. Mn is often problematic, as it has been shown to be difficult to remove from AMD.

During high-flow the suspended sediments are likely principally derived from the flocculated bed sediments. The amount of suspended sediments may represent an equilibrium between re-suspension and flocculation/settling, which is controlled by the hydrologic conditions. Elevated concentrations of metals associated with suspended sediments are transported during high flows, especially during rain events. Colloids dominate the suspended sediment during lower flow; these may be formed by precipitation in the water column. Colloids have been seen to be present during low flow conditions at various areas in the creek. These colloids are likely what is contributing to the increased mass % of suspended sediment in the < 1 um fraction during low-flow sampling dates.

There are a wide variety of bed-sediment types throughout the creek, as well as at a given site, using the 'DS Gas Station' site as an example. Bed-sediment composition and particle-size distribution changes during the year. As seen with the NFSG site, larger particles dominated in May, but over the sampling period, accumulation and loss of more fine-grained material (iron oxyhydroxides) was observed. Very fine iron oxyhydroxides dominate the May beaver dam sample and have been seen to dominate throughout the sampling period.

Fe, Ca, Al, and Mn (in decreasing order) comprise the majority of elements present in coatings on rocks at NFSG in May 2002. Mn, Fe, Al, Ca, and Zn (in decreasing order) comprise the majority of elements present in the black coatings (considering both the 0.5M HCl soluble and insoluble fractions) on rocks at NFSG in August 2002. Loosely associated rock coatings are likely to change over time in the creek due to scouring at higher flows and deposition at lower flows. It is currently uncertain as to the formation and fate of the harder, black (manganese-dominated) coatings on the rocks. The observed differences in both the rock coatings and the bed sediments may affect metal attenuation in NFCC.

Future studies will include further examination of particle formation, the relationship of particle formation to water column metal concentrations, particle transport, and the effect of the Waste-Water Treatment Plant (WWTP) on particulates and metal concentrations. Additionally, the relationship between suspended sediment and coatings (loose and armor) on rocks will be examined.

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