

EFFECT OF ACID MINE DRAINAGE ON A RIPARIAN AREA: ELEMENT CONCENTRATIONS IN SOILS AND PLANTS¹

by

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Abstract. The Stillwater River headwaters, located above Cooke City, Montana, have received acid mine drainage (AMD) from the McLaren gold mine since about 1935. To determine the cumulative effects of AMD on the riparian zone, we collected plant leaf material and soil from the upper 15 cm of the rooting zone of *Carex paysonis* plants along a gradient of decreasing river water pH. Sampling locations were above the source of AMD into the river, at the source of AMD, and below the source of AMD. Soil metal concentrations (Al, Cu, Fe, Mn, Pb, and Zn) were generally related to pH or percentage OM. Plant metal concentrations were poorly correlated with soil metal concentrations. Plant available metals may have been lower in highly organic soils near the AMD source due to the formation of stable complexes, or high concentrations of some metals may have resulted in toxicity and reduced plant uptake. Concentrations of Cu in plant leaves were higher than suggested maximums for plants and livestock forages at and below the source of AMD.

Additional Key Words: Payson sedge, Cu, metals

Introduction

One of the consequences of unregulated heavy-metal mining during the early and mid-1900s in mountainous areas of the Western United States has been the generation of acid mine drainage (AMD). In many cases, AMD has flowed unchecked into high-elevation stream systems for decades. The AMD is often characterized by low pH and high concentrations of heavy metals. The cumulative effects of AMD on streams are potentially numerous and are dependent

upon the environmental characteristics of the stream system and the type and amount of AMD. Aquatic organisms may be unable to survive for miles downstream of the AMD source. Also, the riparian zone adjacent to the stream may be negatively impacted through accumulation of heavy metals in the soils, uptake by vegetation, and bioaccumulation in food-chains.

The Cooke City Mining District, located above Cooke City, Montana, has been the site of mining activity and mineral exploration and, consequently, AMD since the 1880s. The Cooke City ore body is a highly mineralized hydrothermal pyritized-copper deposit that also contains gold and silver (Loverling 1929). Past mining consisted of both shallow open-pit and underground hard-rock operations with numerous small mines and exploration sites of varying age and extent throughout the area (Brown et al 1976). Two of the larger mines in the area, the McLaren and the Glengary, were actively mined from about 1935 until 1950 and 1967, respectively. Development of cyanide extraction technology for finely disseminated gold has resulted in renewed interest in the McLaren mine and adjacent areas. New plans are currently being developed by

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Noranda Exploration Inc., for mining this area, which has been designated the New World Project.

The New World Project is located at the headwaters of 3 major stream systems within the Greater Yellowstone Ecosystem. Miller Creek and Fisher Creek eventually flow into the Yellowstone River, and Daisy Creek is a tributary of the Stillwater River, which also flows into the Yellowstone River. Daisy Creek has been affected by AMD from the McLaren mine and Fisher Creek has been impacted by AMD from the Glengary mine for about 50 years. Information about the long-term effects of AMD on the riparian areas adjacent to these streams can provide baseline data for (1) establishing standards for new mining operations and (2) devising methodology for reclamation of degraded riparian areas. The purpose of this preliminary study was to investigate the effects of long-term AMD on riparian zone soils and vegetation of Daisy Creek.

Methods

This study examined the upper 2.5 km length of Daisy Creek, 1 of 3 tributaries that form the headwaters of the Stillwater River. Elevation over the study reach drops from 2,805 m at the stream's source (45°03' N, 109°49' N) to 2,609 m where it is joined by the other tributaries. Environmental characteristics of the area include 60-to 70-day growing seasons, low summer temperatures and relatively high solar radiation (Johnston et al 1975). Annual precipitation ranges between 110 and 150 cm and arrives primarily during the winter months (Johnston et al 1975). Riparian vegetation at the upper reach of the stream is characterized by wet meadow species, including elk slip marshmarigold (*Caltha leptosepala*), Holmes Rocky Mountain sedge (*Carex scopulorum*), water sedge (*Carex aquatilis*), Payson sedge (*Carex paysonis*), and several willow species. The lower reaches of the stream are more steeply downcut and riparian vegetation includes subalpine fir (*Abies lasiocarpa*), bluejoint reedgrass (*Calamagrostis canadensis*), Holmes Rocky Mountain sedge (*Carex scopulorum*), Payson sedge, and glaucous willow (*Salix glauca*).

AMD from the McLaren mine flows into Daisy Creek within 500 m of its source, a perennial spring. To determine the effects of AMD on the riparian zone, soil and vegetation samples were collected at the following locations: (1) above the source of AMD into Daisy Creek; (2) along the AMD tributary from the McLaren mine; (3) immediately below the source of

AMD into Daisy Creek; and (4) at 500 m intervals along the remaining 2 km of Daisy Creek. Since Payson sedge occurred along the entire reach, it was selected for analyses. At each of the 7 sample sites, plant leaf material and soil from the upper 15 cm of 4 individual Payson sedge plants were collected. All samples were collected within 1 m of the active stream channel.

Plant leaf tissue was washed with distilled water and dried prior to analysis. Leaf samples were analyzed for P, K, Mg, Ca, S, total N (TN), Al, Cu, Fe, Mn, Zn, and Pb. For all elements except TN, plant tissue samples were digested using a nitric perchloric acid digestion and analyzed by inductively coupled argon plasma spectrometry (ICAP). TN was analyzed using Kjeldahl digestion. Soil samples were analyzed for particle size distribution by the hydrometer method, organic matter (OM) (modified Walkely-Black), pH (saturated paste), cation exchange capacity (CEC) (1 N NH₄OAC at pH=7), P (Bray-1), S₀₋₅-S (0.1 M CaH₂PO₄), KCl extractable Al, and HCl extractable Cu, Fe, Mn, Pb, and Zn. Analyses were conducted by the Utah State University Soil, Plant and Water Analysis Laboratory and methods are outlined in Benton (1989) (plants) or Page et al (1982) (soils).

One-way ANOVA was used to determine differences in plant and soil variables among sites. Mean separations were computed using Fisher's Protected LSDs (Steele and Torrie 1980). Relationships among soil element concentrations, pH, OM, CEC, and soil texture were evaluated with Pearson's product-moment correlation coefficients for sites at or below the source of AMD (Sokal and Rohlf 1981). These coefficients measure the degree of association between any two variables, and test if it is greater than expected by chance alone.

Results and Discussion

Soil Physical and Chemical Properties

Upstream sampling locations were characterized by wet meadow vegetation and soils. These sites had generally higher percentages of silt or clay and OM than downstream sites (see Figure 1). Soil pH reflected the proximity of the AMD source into Daisy Creek (see Figure 1). The highest pH values were found at sites above the AMD source and furthest downstream of the source. The lowest soil pH was at the source of AMD into Daisy Creek. These values were similar to those for stream pH (Brown and Amacher 1990). As

expected for wet meadow soils, CEC was highly related to percentage OM ($R^2 = 0.93$; $p < 0.001$) with high OM soils having high CEC (see Figure 1). Soil concentrations of inorganic P are frequently pH dependent, and in this study inorganic P was negatively related to pH (see Table 1), indicating that soil inorganic P was highest at low pH values.

Soil concentrations of Al, Cu, Fe, and SO_4-S were highest along the AMD tributary or at the AMD source into Daisy Creek (see Figure 2). Although highly variable among samples, these elements tended to decrease with increasing distance downstream. Concentrations of Mn, Pb, and Zn were high above the source of AMD (see Figure 2) because that particular

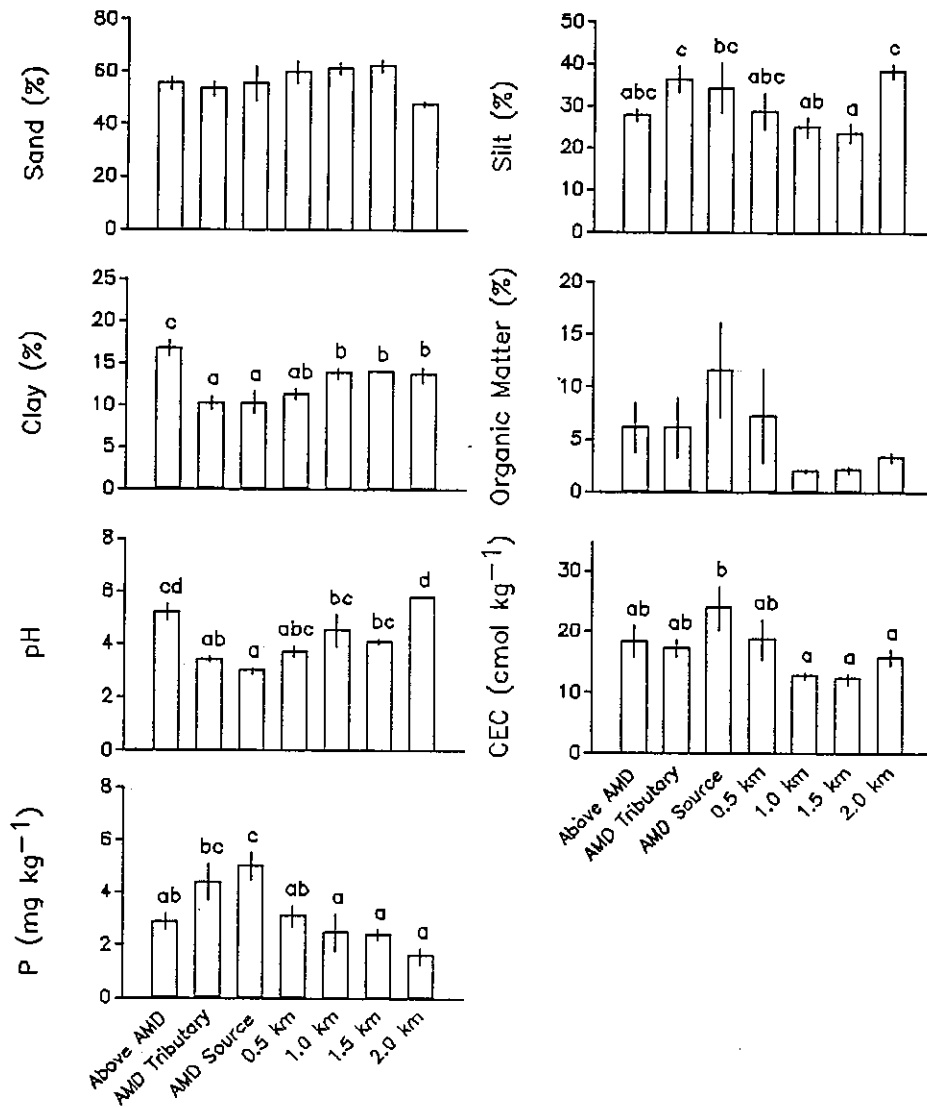


Figure 1. Selected physical and chemical properties of soils from the Daisy Creek riparian area above the AMD source, along the AMD tributary, at the AMD source and at 4 distances downstream of the source. Heights of histogram bars show means and error bars represent ± 1 SE; $n = 4$, except TN = 1. Unlike letters indicate significant differences among sites ($p < 0.05$) if shown.

Table 1. Product-moment correlation coefficients comparing soil elemental concentrations with pH, OM and CEC.

Element	pH	OM (%)	CEC (cmol kg ⁻¹)
Al (mg kg ⁻¹)	-0.69 ^{***}	0.53 ^{**}	0.45 [*]
Cu (mg kg ⁻¹)	-0.18	0.36	0.21
Fe (mg kg ⁻¹)	-0.52 [*]	0.72 ^{***}	0.76 ^{***}
Mn (mg kg ⁻¹)	0.20	0.01	-0.01
Pb (mg kg ⁻¹)	0.50 [*]	-0.17	-0.35
Zn (mg kg ⁻¹)	-0.20	0.45 [*]	0.29
SO ₄ -S (mg kg ⁻¹)	-0.49 [*]	0.33	0.22
P (%)	-0.76 ^{***}	0.47 [*]	0.54 ^{**}

* = $p < 0.05$; ** = $p < 0.01$; *** = $p < 0.001$.

area is part of a Mn deposit and has naturally high concentrations of these metals (Alan Kirk, Noranda Exploration Inc., personal communication). Concentrations of these metals did not differ among sites below the source of AMD.

Retention and movement of individual elements in soils depend on several factors, including soil pH, OM, and soil texture. In general, metal availability decreases with increases in pH, clay content, or OM. Soil pH has a major influence on solution concentrations of many metals and the solubility of metal compounds often increases with decreasing pH. With increasing pH, the number of sorption sites increases (Safaya et al 1987) and many metals are precipitated as insoluble compounds. Al has a very steep solubility curve and is largely unavailable above pH 5 (Donahue et al 1977). Concentrations of Al in the soil were highly negatively correlated with pH (see Table 1). The low concentrations of Al above the source of AMD and at the most distant site from the source may be attributable to high soil pH at these sites. Cu, Fe, Zn, and SO₄-S have less steep solubility curves than Al, but soil concentrations of these elements were also negatively correlated with pH (see Table 1).

Most metals can form stable complexes with OM. Concentrations of all of the metals, except Mn and Pb, were positively correlated with OM (see Table 1). The stability of these complexes varies among metals and may be greater for Cu and Pb (McBride 1981) than for Zn (Safaya et al 1987). The failure of Mn and Pb to follow the same patterns as observed for the other metals may be the result of several different factors. Low levels of Mn and Pb occurred in the AMD (Brown and Amacher 1990). Under natural conditions, Mn and Pb often form highly localized deposits and sample intensity may have been inadequate to explain either their distribution or chemistry. The low concentrations of Pb in high-OM soils ($R^2 = -0.17$) may have been due, in part, to the stability of the complexes that Pb forms with organic matter (McBride 1981). HCl may have been an inadequate extractant for these types of complexes. The redox status of the AMD and riparian soils (not measured specifically) will also influence the solubility of Mn. Metals can be adsorbed onto clay surfaces depending upon the exchangeable cation present on the clay surface and the metal species. The clay content at all study sites was low (see Figure 1). Consequently, metal concentrations were not positively correlated with clay content (data not presented). For this riparian system, pH and OM had

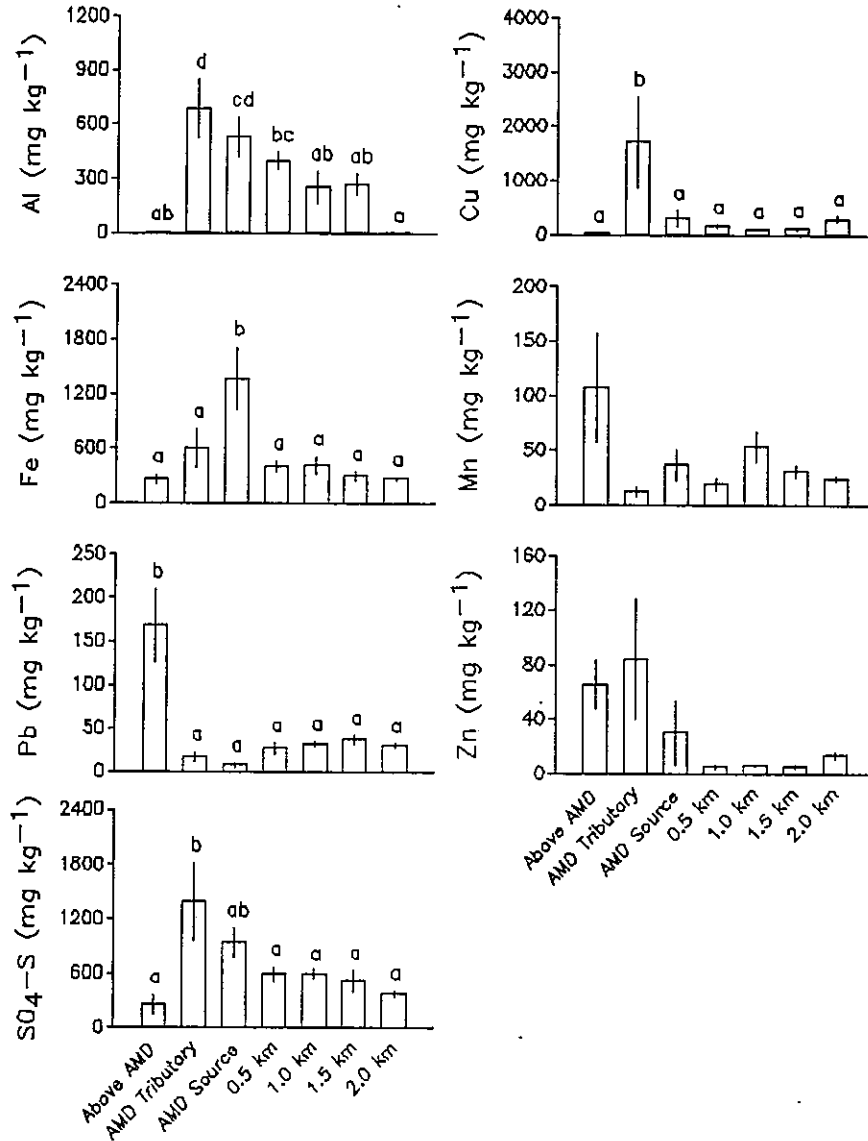


Figure 2. Metal and SO₄-S concentrations in soils of the Daisy Creek riparian area above the AMD source, along the AMD tributary, at the AMD source and at 4 distances downstream of the source. Heights of histogram bars show means and error bars represent ± 1 SE; n = 4, except TN = 1. Unlike letters indicate significant differences among sites if shown.

a greater effect on soil retention and plant availability of the metals than clay content.

Plant Elemental Concentrations

Concentrations of P, K, Mg, Ca, S, and TN in Payson sedge above the AMD source were generally similar to those at the site farthest from the AMD

source (see Figure 3). Percentages of P, K, and S were highest along the tributary into Daisy Creek, at the AMD source or immediately below the source of AMD (see Figure 3). P and S were positively correlated to soil concentrations of these metals and P, K, and S were negatively correlated with soil pH (see Table 2). Concentrations of Mg and TN varied little among sites (see Figure 3). Percentage Ca was lowest along the

Table 2. Product-moment correlation coefficients comparing plant elemental concentrations with soil concentrations of the same element, pH, OM and CEC.

Element	Soil Concentration (mg kg ⁻¹)	pH	OM (%)	CEC (cmol kg ⁻¹)
Al (mg kg ⁻¹)	-0.02	-0.12	-0.16	-0.22
Cu (mg kg ⁻¹)	-0.06	0.00	-0.05	-0.15
Fe (mg kg ⁻¹)	0.30	-0.53**	0.13	0.11
Mn (mg kg ⁻¹)	0.24	0.37	-0.32	-0.38
Pb (mg kg ⁻¹)	0.23	0.23	-0.24	-0.27
Zn (mg kg ⁻¹)	-0.10	0.49*	-0.39	-0.49*
S (%)	0.59*	-0.66***	0.00	0.05
P (%)	0.34	-0.53**	0.08	0.06
Ca (%)	-	0.82***	-0.32	-0.40
K (%)	-	-0.52*	0.00	0.04
Mg (%)	-	0.15	-0.33	-0.41

* = $p < 0.05$; ** = $p < 0.01$; *** = $p < 0.001$.

tributary into Daisy Creek or at the AMD source and increased with distance downstream from the source (see Figure 3). Levels of plant Ca were highly positively correlated with soil pH (see Table 2). The relationships of the different elements with soil pH were consistent with their solubility curves (Donahue et al 1977).

Concentrations of Al, Mn, and Pb in Payson sedge did not differ significantly among sites (see Figure 4). Plant concentrations of Mn and Pb tended to reflect soil concentrations and were positively related to pH, but negatively related to OM (see Table 2). Concentrations of Fe in Payson sedge were highest along the AMD tributary, at the source of AMD, or immediately below the source of AMD (see Figure 4). Plant Fe concentrations were positively related to soil concentrations, but negatively related to soil pH (see Table 2) reflecting the solubility curve for Fe (Donahue et al 1977).

Concentrations of plant Cu were significantly lower above the AMD source than at any of the other sites (see Figure 4). There were no differences in Cu concentrations in Payson sedge among sites at or below the AMD source. Plant concentrations of Cu were unrelated to soil characteristics (see Table 2), despite high soil concentrations of Cu at some of the sites and large differences in soil Cu among sites. Many plant species exclude Cu from shoot tissue (Marschner 1986) and concentrations in roots are often several times higher than in shoots (Neuman et al 1987). Uptake curves for Cu in aboveground plant tissue frequently plateau above a certain level of soil availability. Concentrations of Cu in Payson sedge at or below the AMD source may have reflected the upper limit for this species.

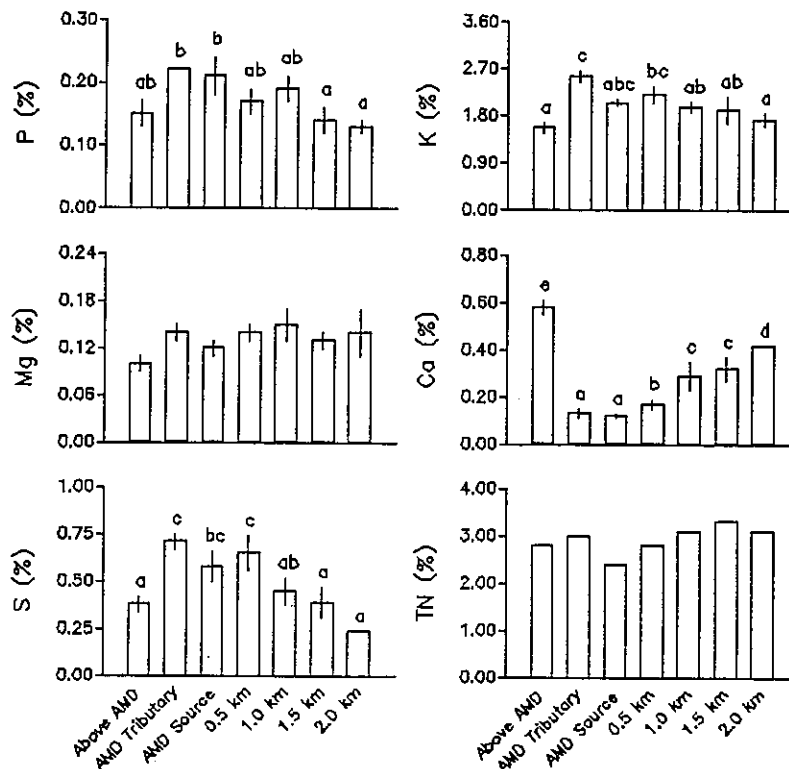


Figure 3. Foliar concentrations of selected elements in Payson sedge above the AMD source, along the AMD tributary, at the AMD source, and at 4 distances downstream of the source. Heights of histogram bars show means several times higher than in shoots and error bars represent ± 1 SE; $n = 4$. Unlike letters indicate significant differences among sites if shown.

Concentrations of Zn in Payson sedge were lowest above the AMD source, along the AMD tributary, or at the AMD source (see Figure 4). Plant Zn concentrations were positively correlated with pH, but negatively correlated with CEC (see Table 2). Plant Zn concentrations were lowest at sites with the highest soil Zn concentrations, indicating that other soil factors resulted in reduced plant uptake of Zn.

Conclusions

The Daisy Creek riparian area was affected by the AMD from the McLaren mine in several ways. The AMD lowered the pH of the riparian zone soils, which increased the solubility of many naturally occurring metal compounds and, consequently, increased the availability of these metals to plants and other living organisms. Also, the AMD contributed additional

metals to the system in solution, including Mn, Fe, Al, Zn, and especially Cu (Brown and Amacher 1990). Soil pH was lowest along the AMD tributary and at the source of the AMD into Daisy Creek. As pH increased with distance downstream of the AMD source, soil concentrations of most of the metals that occurred in the AMD decreased (Fe, Al, Zn, and Cu). High levels of OM in wet meadow soils at or near the AMD source were positively correlated with CEC and soil concentrations of those metals in the AMD. The ability of OM to form stable complexes with metals is a well-known phenomenon that has led to the use of wetlands for AMD treatment.

Metal concentrations in Payson sedge were often poorly correlated with soil metal concentrations. High metal concentrations coupled with low pH may have resulted in toxicity and reduced plant uptake. Also,

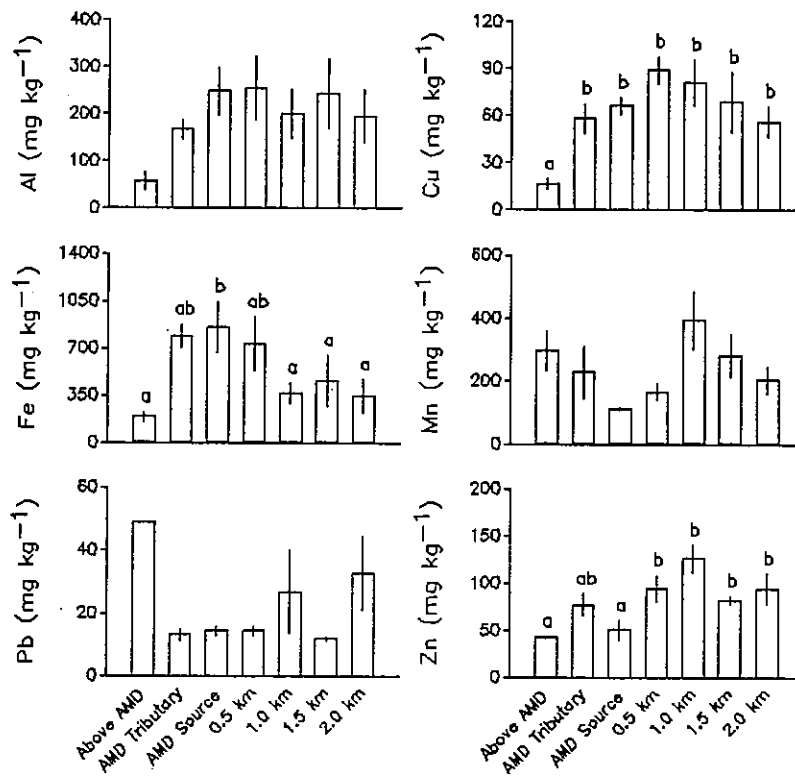


Figure 4. Foliar concentrations of metals in Payson sedge above the AMD source, along the AMD tributary, at the AMD source, and at 4 distances downstream of the source. Heights of histogram bars show means several times higher than in shoots and error bars represent ± 1 SE; $n = 4$. Unlike letters indicate significant differences among sites if shown.

plant availability of some metals may have been lower in highly organic soils near the AMD source due to the formation of stable complexes.

The riparian area is being negatively impacted by the AMD at distances greater than 2 km downstream. Leaf concentrations of Cu in Payson sedge exceeded suggested maximum concentrations for plants (Northeastern Coordinating Committee 1985) and livestock forages (National Research Council 1980) at all of the sample sites affected by the AMD. Payson sedge appears to exhibit relatively high-tolerance levels to AMD from the McLaren mine (Brown and Amacher 1990). Plant species more sensitive to the effects of the AMD may have already been excluded from the riparian area. Many animal species have low tolerance for Cu, and food-chain movement and bioaccumulation of metals within the area are of real concern.

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