THE BIOGEOCHEMISTRY OF WETLAND ECOSYSTEMS AND TREE RINGS IN THE SAN LUIS VALLEY, COLORADO—THE EFFECT OF NATURAL AND HUMAN-INDUCED METAL-RICH, ACID DRAINAGE

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INTRODUCTION

The Summitville Mine, located near the old mining town of Summitville in Rio Grande County, Colorado, operated between July 1986 and December 1992 as a large-tonnage open-pit heap-leach gold mine. During its 6 years of existence the trace metal levels in drainage water from the mine site were elevated over historical (pre-1986) levels (Moran and Wentz, 1974) due to input from three sources—heap leach water, seeps that occur throughout the mine workings, and an increase in the metal load of water coming from the old Reynolds Adit. Mine-drainage waters flow into Wightman Fork, a small tributary of the Alamosa River, which in turn flows east into the San Luis Valley. The increase in the trace metal burden of the Alamosa River watershed is of concern to farmers, land owners, and Federal and State wildlife agencies.

The information presented here is largely abstracted from reports previously published (Balistrieri and others, 1995; Gough and others, 1995).

PURPOSE AND OBJECTIVES

This study seeks to chart potential spatial and temporal trace metal trends in drainage water chemistry through the analysis of metal levels in individual tree rings from narrow-leaf cottonwood *(Populus angustifolia* James) and, to a lesser extent, quaking aspen *(Populus tremuloides* Michx.). As stated below, the use of tree ring chemistry in the characterization of contaminated sites is a viable technique and its use in this regional study has promise.

Also, this study assesses the impact of acid drainage on selected wetlands in the San Luis Valley. We compared the biogeochemistry of wetlands that receive surface water from the Alamosa River with wetlands that receive surface water from sources that carry little or no drainage from mineralized areas (e.g., Rio Grande River). We collected and analyzed water and stream-bed sediment from the Wightman Fork and Alamosa River to identify elements that are indicative of drainage from mineralized areas (i.e., indicator or tracer elements) and to assess the extent of their transport throughout the Alamosa River system. We also collected and analyzed water, sediment, and rooted aquatic vegetation from wetlands that receive surface water from several sources— Alamosa River, La Jara Creek, and Rio Grande River—particularly those located in the Alamosa National Wildlife Refuge.

The wetlands are seasonal hosts to migratory birds such as the endangered whooping crane, and the U.S. Fish and Wildlife Service is concerned about the possible impact of metal- enriched drainage on the stability, productivity, and quality of these wetland ecosystems.

METHODS

The field studies were conducted between June 24–29, 1993. Details of field and laboratory methods are published (Balistrieri and others, 1995; and Gough and others, 1995) and are only summarized here.

Tree-ring samples

Samples of aspen were collected from riparian, mixed coniferous forest communities along the Wightman Fork and the Alamosa River from just above the confluence to just below (Sites B, C, and D, fig. 1). Samples of narrowleaf cottonwood were collected from the same communities along the Alamosa River at Sites E, F, G, H, I, J, and K. These sites were spaced about 5 kilometers apart from just below the confluence of the Alamosa River with the Wightman Fork to a point down river about 50 kilometers (fig. 1). Aspen was collected at Sites B-D because Site E was the elevational upper-most extent of cottonwood. The last four sites (H, I, J, and K) were located within the San Luis Valley.

Samples consisted of cores of xylem material collected at 1.5 m above the ground. At each site cores were extracted from each of two adjacent mature trees. From one of the two trees a second core was extracted immediately parallel to the first one as a within-tree replicate sample.

River samples

Stream-bed sediment and water were collected from the Wightman Fork and 10 locations along the Alamosa

River; the same localities as were sampled for tree-ring cores (fig. 1).

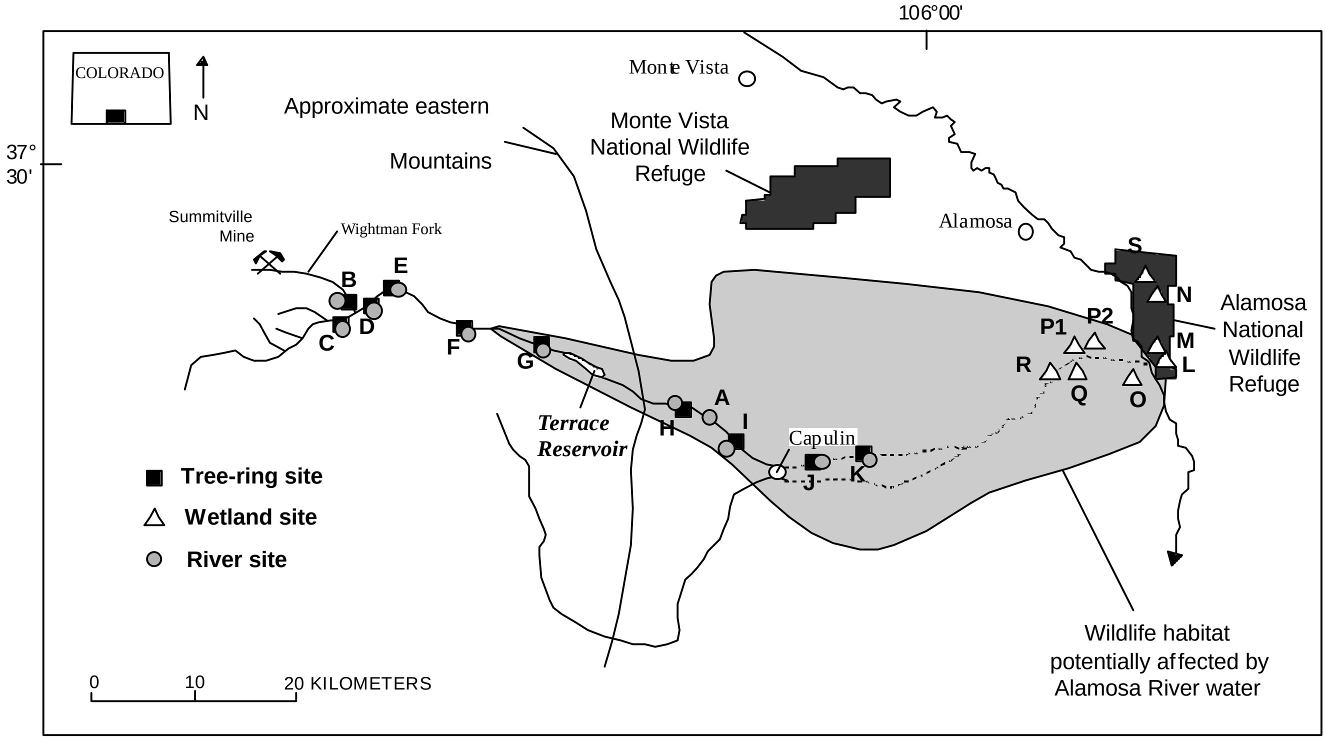

Figure 1. Map showing sampling sites for tree-rings, sediments, and water (Wightman Fork and upper Alamosa River), and wetland water, sediment, and aquatic plants (lower Alamosa River and Alamosa National Wildlife Refuge). The dashed lines indicate that down stream of Capulin the Alamosa River and La Jara Creek are channelized and the subsurface hydrology of these streams is poorly understood.

Wetland samples

Sediment, water, and wetland plants were collected from nine areas within wetlands just west of (Sites O, P1, P2, Q, and R) or within (Sites L, M, N, and S) the Alamosa National Wildlife Refuge (fig. 1). The character of the wetlands was variable and included permanent (M and S) and small evaporative ponds (P2), wetlands along sloughs (L), oxbows (O), ditches (P1), or canals (N and R), and flooded fields (Q). The wetlands received surface water from different sources. The wetlands within the Refuge appeared to be topographically isolated from receiving surface water from the Alamosa River or La Jara Creek and, most likely, received surface water from the Rio Grande River. The wetlands west of the Refuge appeared to receive surface water from the Alamosa River or a combination of Alamosa River and La Jara Creek waters.

DISCUSSION

Dendrochemical Trends

We discuss results from the analysis of tree-rings from four separate years and from six of the 10 sites. These rings represent periods before modern mining began at Summitville (1970 and 1980), the year mining was initiated (1986), and the period during active mining (1990).

The translocation of elements between rings is a concern in the interpretation of dendrochemical trends. The small number of analyses per core in this study precludes definitive interpretation of element movement among rings; however, elements such as Br, Cl, Mg, Na, and P are mobile within some trees to some extent (Yanosky and others, 1995).

Cottonwood

Lead

Except for cottonwood rings collected at Site K (the site furthest from the mine) the uptake of Pb does not show either temporal or spatial trends (fig. 2). An order of magnitude increase is present at Site K over a 30-year period. Several explanations are possible: either the amount of available Pb increased over time or the absolute amount of Pb did not change and the bioavailability of what was present did change. Baes and Ragsdale (1981) found that Pb was laterally mobile in selected southeastern hardwood tree species, i.e., Pb concentrations were greater in older than younger rings. The radial Pb concentration pattern that we observe (fig. 2) did not follow this pattern; however, our data covered only 30-40 years. The increase in Pb from older to younger rings remains unexplained.

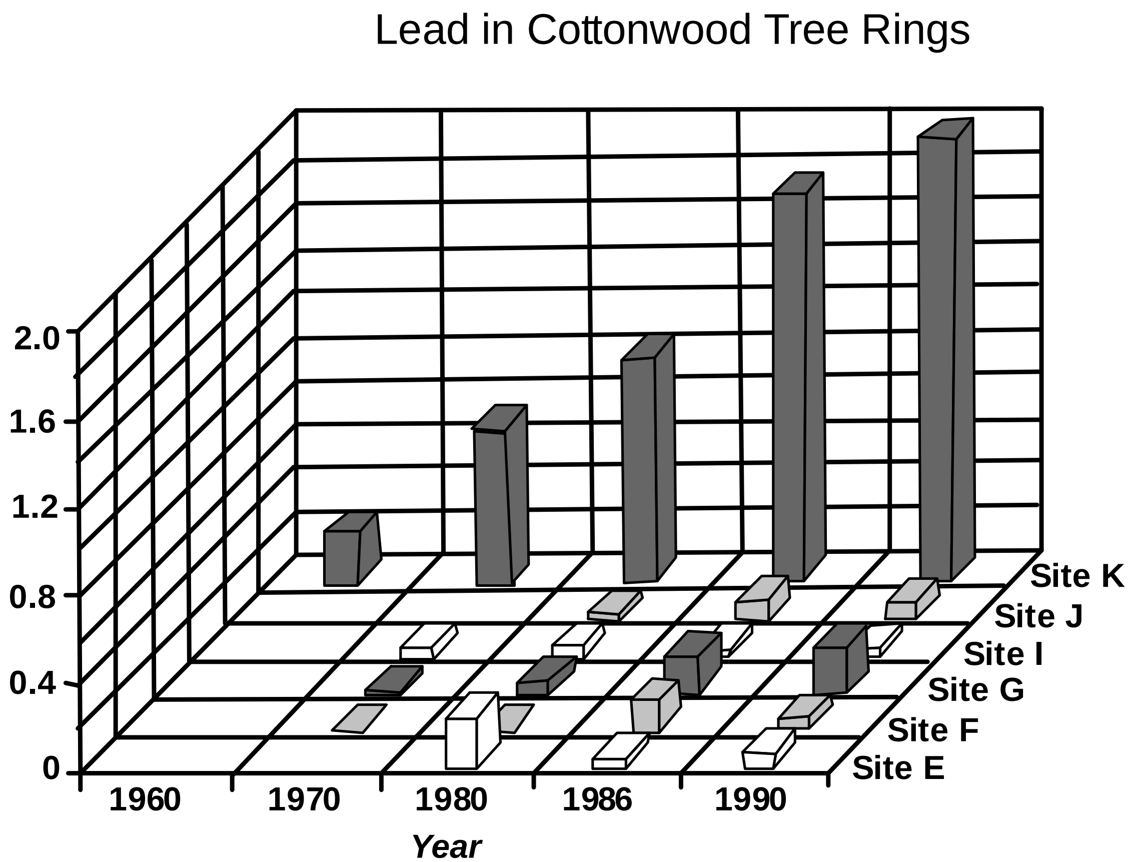

Figure 2. Lead in cottonwood tree rings (Gough and others, 1995; see Fig. 1 for position of study sites).

Copper and Zinc

Copper and Zn are two of the major metals associated with area mineralization and are of great concern because of their toxicity to aquatic biota. High concentrations were found in the associated stream sediment and water samples (Balistrieri and others, 1995). Patterns in tree rings show that (a) they are most abundant in older tissue, (b) there are no obvious down-gradient trends, (c) there is a very high correlation between Cu and Zn in both their temporal and down gradient patterns, particularly within rings from the upper sites (E, F, and G). High concentrations of Cu in ground water are toxic to tree roots and uptake inhibition is a consideration.

Phosphorus

Both temporal and down-gradient trends are noted; P is translocated to younger tissue; P concentrations increase at Sites I, J, and K (valley floor) and may be due to agricultural input or increases in its bioavailability.

Bromide and Sodium

In this river basin environment, Br and Na are highly mobile. In addition, both elements appear to be laterally mobile within the trees (i.e., there is possibly some movement from younger to older rings). This mobility complicates down-gradient interpretations. The increased uptake of Br and Na at Site K is possibly due to oxic, saline soil conditions.

Aspen

The aspen and cottonwood data are not directly comparable because they are different species, may represent different ecological physiologies, and can occupy entirely different habitats. The aspen collected were from riparian communities, however, and occupied the same basic ecological niche as cottonwood. We note only general trends and do not compare absolute element concentrations.

Copper and Zinc

Cu and Zn are elements of environmental concern; there is no obvious impact from Wightman Fork because values above the confluence with the Alamosa River and in Wightman Fork were about the same; higher concentrations occur in older tissue.

Bromide

Both temporal and down-gradient trends are possible; impact from mine drainage may be observed; highly mobile element is associated with mineralization.

Barium

Both temporal and down-gradient trends are possible; impact from mine drainage may be observed.

River Samples

Water

Water in the Wightman Fork (Site B) was characterized by low pH values and elevated concentrations of dissolved major (Na, Ca, Mg, Cl, and sulfate) and minor (Al, B, Co, Cu, Fe, Mn, Ni, Sr, and Zn) ions relative to water in the Alamosa River above the confluence with the Wightman Fork (Site C). The Wightman Fork had a distinct influence on the composition of Alamosa River water downstream of the confluence. Values of pH were lower and dissolved concentrations of major (Na, Ca, Cl, and sulfate) and minor (Al, Cu, Fe, Mn, Sr, and Zn) ions were elevated in the Alamosa River just below (Site D) as compared to above (Site C) the confluence. Elevated dissolved concentrations of major (Na, Ca, Cl, and sulfate) and certain minor (Cu, Mn, Sr, and Zn) ions persisted far downstream (at least 49 km) in Alamosa River water. Dilution plays the major role in attenuating dissolved concentrations of ions downstream from the confluence; however, dissolved Cu concentrations far downstream also appear to be affected by a removal process such as sorption (Balistrieri and others, 1995). The dissolved chemical characteristics of the Wightman Fork and Alamosa River are variable with time and highly dependent on pH (Ward and Walton-Day, 1995; Walton-Day and others, 1995). Hence, our sampling during June 1993 only provides a single, instantaneous picture of the dissolved chemical characteristics of these rivers.

Sediment

The composition of stream-bed sediments from the Wightman Fork and Alamosa River is summarized in Balistrieri and others, 1995. The data indicate that sediments in the Wightman Fork (Site B) have higher concentrations of Fe, S, As, Cr, Cu, Hg, Pb, and Zn relative to sediments in the Alamosa River above the confluence with the Wightman Fork (Site C). Of these elements, Cu and As show the greatest enrichment (13.5 to 14.2 x). Sediments in the Alamosa River downstream of the confluence with the Wightman Fork tend to have higher concentrations of As, Co, Cr, Cu, Ni, and Zn relative to sediments above the confluence (Site C). Higher concentrations of Co, Ni, and Zn in Alamosa River sediments tend to occur much farther downstream (>18–29 km from the confluence) than the other elements.

The composition of water and sediments in the Wightman Fork most likely reflects drainage from the Summitville Mine; however, enrichments of elements in the Alamosa River downstream of the confluence with the Wightman Fork also include elements supplied by other streams and from diffuse runoff. Based on the compositional data of Wightman Fork and Alamosa River, the following elements appear to be indicative of drainage from mineralized areas in this watershed: Al, As, B, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, S, Sr, Zn. Some of the minor elements (e.g., As, Co, Cr, Cu, Ni, and Zn) are enriched far downstream of the confluence with the Wightman Fork. This latter group of elements is used as potential tracers or indicator elements for assessing the impact of drainage from mineralized areas on wetlands in the San Luis Valley.

Wetland Samples

Water

The composition of surface water in selected wetlands in the San Luis Valley is summarized in Balistrieri and others, 1995. In June 1993, the wetlands were alkaline (pH > 7), had variable dissolved major ion (e.g., Na, K, Ca, Mg, Cl, and sulfate) concentrations, and low concentrations of many minor ions (e.g., Co, Cu, Ni, and Zn). Variations in the major ion chemistry of the water and our observations of salt crusts in the vicinity of many wetlands suggest that evaporation was occurring and causing the concentration and precipitation of certain dissolved elements. The low concentrations of the minor cations are consistent with their ability to sorb onto particles or precipitate at higher pH values (Stumm and Morgan, 1981). In contrast, the mobility of anions, like As, is usually greater at the higher pH values observed in the wetlands due to lower sorption of anions at high pH (Pierce and Moore, 1982). Dissolved concentrations of As tended to be higher in wetlands within the Refuge as compared to wetlands outside of the Refuge. This observation may, in part, reflect different source waters as well as the effects of evaporative concentration.

Differences in the ratio of two conservative elements, Na and Cl, between the wetlands and Alamosa River water below Terrace Reservoir provide support for different source waters. The ratio in Alamosa River water (Na/Cl = 100±4) is less than half of the ratio in wetland waters within the Alamosa National Wildlife Refuge (Na/Cl = 229±19). The ratio for wetlands west of the Refuge ranges from 114 to 189 and suggests input from the Alamosa River.

Sediment

The composition of wetland sediments is summarized in Balistrieri and others, 1995. Concentrations of the indicator elements of mineral/mine influence (i.e., As, Co, Cr, Cu, Ni, and Zn) for selected wetland sediments that receive water from different sources were examined. Results indicate that sediments in wetlands that receive some Alamosa River water clearly have higher concentrations of Cu, Ni, and Zn than wetlands receiving surface water from other sources. In addition, the metal contents of sediments in wetlands receiving Alamosa River water do not significantly change with depth. If wetlands receiving Alamosa River water received additional metals from drainage derived from open-pit mining activities at Summitville, then the down core composition of wetland sediments should change significantly provided that the collected sediment represents a time frame that brackets the beginning of open-pit mining activities at Summitville Mine (i.e., before and after 1984–1986) (Pendleton and others, 1995).

Two wetland cores (Site O core 1 and Site M core 2) were age dated using ^{210}Pb techniques. Mass accumulation rates were determined from ^{210}Pb activity and water content as a function of depth using a one-dimensional, two-layer, steady-state sedimentation model in which mixing occurs only in the surface mixed layer (Robbins and Edgington, 1975; Carpenter and others, 1982). The model assumptions are that (1) the sedimentation rate is constant; (2) there is no post-depositional mobility of ^{210}Pb; (3) the flux of unsupported ^{210}Pb to the interface is constant; and (4) the deepest sample represents the amount of supported ^{210}Pb in this area and is constant throughout the core. The porosities of the two cores were calculated from water content data and by assuming that the density of the dried sediment was 2.5 g cm^{-3}. The supported ^{210}Pb in the sediments was estimated to be 0.8 dpm g^{-1}. Accumulation rates were calculated as 0.74 g cm^{-2} y^{-1} at Site M (core 2) and 0.70 g cm^{-2} y^{-1} at Site O (core 1). Sedimentation rates in cm y^{-1} do not include natural compaction and, hence, decrease with depth. The sedimentation rates are between 0.33 and 0.52 (average = 0.38) cm yr^{-1} for Site M (core 2) and 0.33 and 0.43 (average = 0.35) cm yr^{-1} for Site O (core 1).

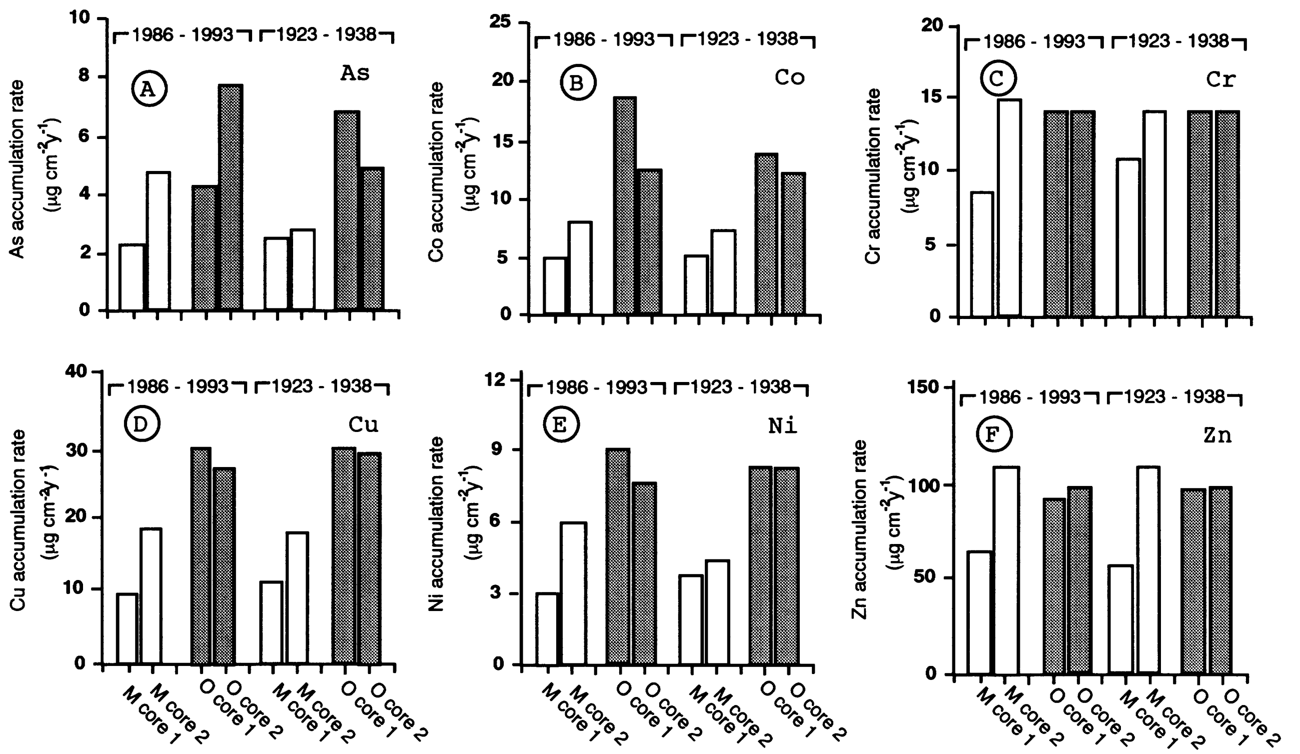

Figure 3. Examples of accumulation rates for indicator elements at two wetland sites for two rime periods: pre (1923-1938) and post open-pit mining at Summitville Mine (Balistrieri and others, 1995). Site O receives Alamosa River water whereas site M receives surface water from other sources.

Accumulation rates of the indicator elements were calculated by multiplying the metal content at a given depth by the mass accumulation rates for two time periods at Sites M and O (fig. 3). These time periods represent pre- and post-open pit mining activities at Summitville Mine. Only Site O receives surface water from the Alamosa River. We conclude (1) variations in the metal content of the two cores collected at a given site result in a range of element accumulation rates for that site; (2) the site that receives Alamosa River water (Site O) tends to have higher accumulation rates of As, Co, Cu, Ni, and, possibly, Zn; and (3) there is little difference between accumulation rates at the site receiving Alamosa River water (Site O) for pre- and post-open pit mining activities because there are no significant changes in metal contents down core.

Increases in certain indicator elements (i.e., Co, Cr, Cu, and Ni) in the wetlands receiving Alamosa River water compared to those that receive surface water from other sources may be related to the accumulation of Fe in the wetlands. Iron oxyhydroxides have a strong affinity for many elements and, thus, can sequester trace elements in the sediments. Higher Fe contents and accumulation rates are observed for wetlands receiving Alamosa River water. There are good correlations between the concentrations of Fe and certain indicator elements in almost all wetland sediments.

Aquatic Plants

The same species of aquatic plant (*Persicaria amphibia* and *Potamogeton natans)* was not present in all of the wetlands; however, each species came from wetlands that received water from different sources.

Rooted aquatic macrophytes can assimilate dissolved metals from the water through their leaves, but most uptake is thought to occur through their roots. Therefore, their chemical composition often reflects the geochemistry of the sediments in the wetlands (Pip and Stepaniuk, 1992; Flessa, 1994).

The concentrations of the indicator elements on a dry weight basis in the aquatic wetland plants are compared for wetlands receiving surface water from different sources. Both *P. amphibia* and *P. natans* growing in wetlands receiving Alamosa River water tend to have higher concentrations of Co and Cu. Zinc also appears to be enriched in *P. amphibia* in wetlands receiving Alamosa River water. These observations are consistent with the enrichment of these elements, particularly Cu and Zn, in the sediments of wetlands receiving Alamosa River water. In contrast, aquatic plant concentrations of As tend to be higher in wetlands receiving water from other sources. Dissolved concentrations of As also tended to be higher in these wetlands.

SUMMARY

The element concentration levels in tree rings (dendrochemistry) of cottonwood and aspen, stream sediment, and surface water were examined at 10 sites along the Wightman Fork and Alamosa River in southern Colorado. Tree-ring chemistry is used to chart potential spatial (down gradient) and temporal (over about 30 years) trace metal trends in drainage waters. Preliminary results for Ba, Br, Cd, Cu, Na, P, Pb, and Zn are presented. Spatial and temporal trends are noted; however, cause and effect relations are hard to establish with these data. Results for Cu and Zn do not show a clear association with mine drainage; trends for P are complicated by valley soil conditions and agricultural practices. The analytical method proved especially suited to this type of study.

Concentrations of As, Co, Cr, Cu, Ni, and Zn in surface water were used as possible tracers of acidic, metal-enriched drainage from mineralized areas in the Alamosa River watershed. These elements appeared to be transported throughout the Alamosa River system downstream of its confluence with the Wightman Fork.

The composition of surface water in selected wetlands in the San Luis Valley appeared to be affected by evaporation during June 1993. These waters tended to be alkaline and have low dissolved concentrations of all of the indicator elements, except As.

The chemical composition of sediments in wetlands receiving surface water from the Alamosa River or Alamosa River and La Jara Creek tended to be enriched in Fe, Cu, Ni, and Zn relative to sediments of wetlands receiving surface water from other sources. A comparison of metal accumulation rates in two wetlands receiving water from different sources indicates that the wetland receiving surface water from the Alamosa River has higher accumulation rates of Fe, As, Co, Cu, and Ni. The higher concentrations and accumulation rates of certain indicator elements in wetlands receiving some surface water from the Alamosa River appear to be related to the content and accumulation of Fe. However, there are no major differences in the accumulation rates or down core concentrations of indicator elements during the past 70 to 100 years in wetlands receiving Alamosa River water. The effects of recent mining activities (e.g., open-pit mining at Summitville) on wetland sediment geochemistry is not readily apparent.

Aquatic wetland plants (i.e., *P. amphibia* and *P. natans*) tend to have higher concentrations of certain indicator elements (i.e., Co, Cu, and Zn) in wetlands receiving Alamosa River water. These enrichments reflect similar trends observed in the sediments of these wetlands. Finally, a direct link between specific mining activities at the Summitville Mine and the geochemistry of the studied wetlands was not found. However, the studied wetlands west of the Alamosa National Wildlife Refuge that receive Alamosa River water tended to have higher concentrations of indicator elements, except As, in their sediment and aquatic plants relative to the studied wetlands within the Refuge that receive surface water from other sources. In addition, Cu appears to be the best overall indicator element for wetlands that receive water from the Alamosa River.

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