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Determination of Pre-Mining Geochemical Conditions and Paleoecology in the Animas River Watershed, Colorado

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ABSTRACT

Determination of the pre-mining geochemical baseline in bed sediments and the paleoecology in a watershed impacted by historical mining activity is of utmost importance in establishing watershed restoration goals. We have approached this problem in the Animas River watershed using geomorphologic mapping methods to identify old pre-mining sediments. A systematic evaluation of possible sites resulted in collection of a large number of samples of pre-mining sediments, overbank sediments, and fluvial tailings deposits from more than 50 sites throughout the watershed. Chemical analysis of individual stratigraphic layers has resulted in a chemical stratigraphy that can be tied to the historical record through geochronological and dendochronological studies at these sites.

Preliminary analysis of geochemical data from more than 500 samples from this study, when coupled with both the historical and geochronological record, clearly show that there has been a major impact by historical mining activities on the geochemical record preserved in these fluvial bed sediments. Historical mining activity has resulted in a substantial increase in metals in the very fine sand to clay sized component of the bed sediment of the upper Animas River, and Cement and Mineral Creeks. Enrichment factors for metals in modern bed sediments, relative to the pre-mining sediments, range from a factor of 2 to 6 for arsenic, 4 to more than 10 for cadmium, 2 to more than 10 for lead, 2 to 5 for silver, and 2 to more than 15 for zinc. However, the pre-mining bed sediment geochemical baseline is high relative to crustal abundance levels of many ore-related metals and the watershed would readily be identified as a highly mineralized area suitable for mineral exploration if it had not been disturbed by historical mining activity. We infer from these data that the water chemistry in the streams was less acidic prior to historical mining activity in the watershed.

Paleoentologic evidence does not indicate a healthy aquatic habitat in any of the stream reaches investigated above the confluence of the Animas River with Mineral Creek (fig. 1) prior to the impact of historical mining activity. The absence of paleoentologic remains is interpreted to reflect the poor preservation regime of the bed sediment materials sampled. The fluvial sediments sampled in this study represent higher energy environments than are conducive to the preservation of most aquatic organisms including fish remains. We interpret the sedimentological data to indicate that there has

been substantial loss of riparian habitat in the upper Animas River above Howardsville as a result of historical mining activity.

INTRODUCTION

Determination of the metal concentrations present in stream reaches in watersheds affected by historical, inactive mines is necessary to help define remediation and restoration goals facing federal land-management agencies (FLMA). We estimate that more than forty percent of the headwaters in watersheds in or west of the Rocky Mountains have been impacted by past mining activities (Church and others, 1998b). The determination of water quality, stream habitat, and aquatic community structure that existed prior to mining are needed to define pre-mining conditions and guide watershed restoration. There are no direct measures of water quality prior to historical mining activities; an alternative approach must be found to evaluate pre-mining water-quality conditions.

Historical mining activity has also profoundly changed the ground-water flow regime in most watersheds where mining has occurred. Waters flowing from adits represent the focusing of this modified ground-water flow regime. However, this increased artificial porosity within the ground-water system has resulted in an accelerated rate of oxidation of sulfide minerals in the near-surface environment, which increases the metal loads contributed by these anthropogenic features. Partitioning metal loads between the pre-mining component caused by chemical weathering processes, and that caused by the increased rate of oxidation as a result on the increased porosity caused by mining is not generally possible.

Determination of the pre-mining geochemical baseline in watersheds affected by historical mining activities is a difficult task if one is limited to the water-quality measurements that can be made today. Metals and acidity are released from the chemical weathering of mine waste dumps as well as from the hydrothermally altered rocks that occur within the watershed. One approach to determining what the pre-mining conditions were is to determine the anthropogenic contribution of metals from mine adits and waste dumps, and subtract these measured loads from the geochemical baseline measured today. This approach is a difficult one to apply in watersheds, and is limited by the completeness of data from anthropogenic point sources of metals, transport rates of metals from these point sources to streams, and pathways of metals from these point sources to the streams. This approach is also severely limited by the assumption that the ground-water baseflow has not been significantly changed by mining activity, an assumption we challenge.

An alternative approach to determining the pre-mining background conditions has been developed and tested in the Animas River watershed. The fluvial sedimentological record provides an indirect measure of pre-mining water quality through the analysis of the trace metal concentrations in the iron oxy/hydroxide and oxy/sulfate minerals that precipitated out of stream waters as colloidal fractions (Church and others, 1997). We have applied geomorphologic mapping methods to determine the relative ages of various river-terrace gravel deposits preserved within the stream reaches. These river-terrace deposits are generally erosional remnants of earlier fluvial gravel deposits, although a few overbank deposits representing high water flooding events and representative fluvial

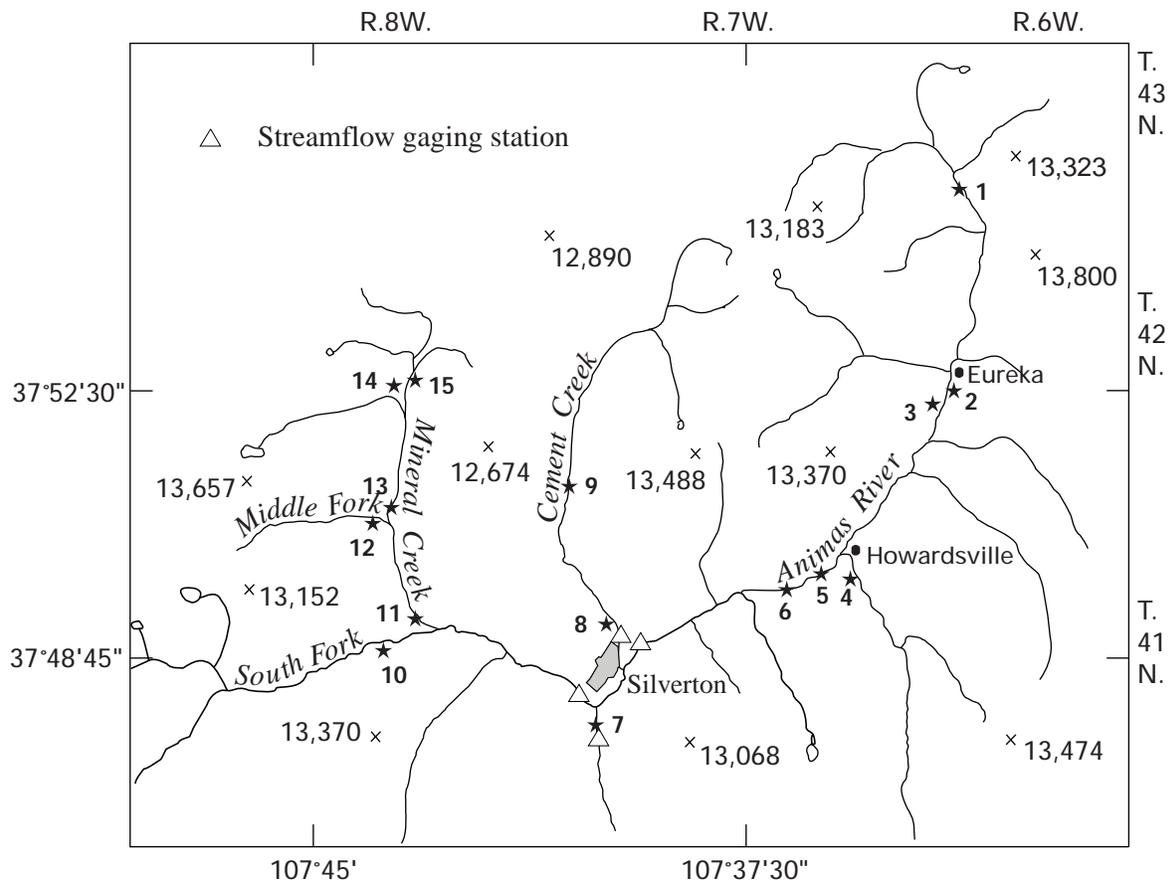
tailings deposits have also been sampled. We sampled fluvial gravels in terraces preserved above the maximum flood-stage level, as determined by overbank deposits left by the 1911 Gladstone flood, and determined trace metal concentrations in these bed sediments using the same sampling, processing, and analytical methods used to determine trace metal concentrations in the bed sediments today (Church and others, 1997). In some cases where the sedimentary samples represented sedimentary sites where the deposition rate was slow, we also initiated ^{210}Pb (lead), ^{14}C (carbon), and ^{137}Cs (cesium) geochronological studies to provide an absolute age of the deposits. Dendochronology has been used to determine minimum ages of the terraces. These pre-mining terrace sediment sites have proven to be relatively easy to identify in the watershed, although they are not readily available everywhere within the watershed. Preliminary results of our investigation of the trace metal concentrations in pre-mining fluvial sediments were initially reported in Church and others (1998a).

We also sampled and dated pre-mining sediments from a trench dug across a braided section of the upper Animas River between Eureka and Howardsville (site 3, fig. 1). Details of this investigation are reported in Vincent and others (1999). In this report, we will document the field methods and summarize the analytical results available from these samples.

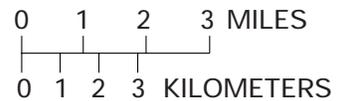
Paleontological analyses was conducted on a subset of these samples that represented low-energy sites of deposition. Analysis of the biotic material from the watershed habitats, as preserved in the fluvial sedimentological record, also can provide valuable information on both terrestrial and aquatic community structure. Analysis of trace element chemistry of the various organisms preserved in the various core materials could be used to provide another indirect measure of water chemistry. Results from these investigations provide permissive data if organisms are preserved, but not definitive data if the results are negative. Our studies to date do not provide any indication of a healthy aquatic community in the study area prior to mining.

Geology of the Study Area

The Animas River drainage basin (fig. 1) has its headwaters in the mountainous terrain above Silverton, Colo. and drains south into the San Juan River in northern New Mexico. Elevations range from more than 13,000 ft. (4,000 m) at the headwaters to less than 6,000 ft. (1,800 m) at the confluence with the San Juan River south of Aztec, New Mexico. The major population center in the basin is the city of Durango, Colo. The geology exposed at the surface and underlying the basin is varied. Precambrian rocks crop out in the eastern part of the drainage basin in the Animas Canyon area south of Silverton forming the high rugged mountainous area of the Animas Canyon. Paleozoic and Mesozoic sedimentary rocks crop out in the southern part of the drainage basin. The headwaters of the Animas River watershed are underlain by Tertiary igneous intrusive and volcanic rocks that formed as a result of a late Tertiary age episode of andesitic to dacitic volcanism followed by a later episode of ash-flows, lava flows and intrusions of dacitic to rhyolitic composition (Lipman and others, 1976). During this later episode of volcanism, the Silverton caldera formed. Pervasive and intense hydrothermal alteration and mineralization events postdate the formation of the Silverton caldera by several million years (Casadevall and Ohmoto, 1977). This area of the Animas River watershed



Base from U.S. Geological Survey
 Silverton, Colo. 1:100,000, 1982
 Altitudes shown in feet



★₅ Sample locality

Figure 1. Map of the upper Animas River watershed showing localities of samples taken to determine pre-mining background. The map area shows only the upper Animas River watershed which is the focal area of the current study. Additional samples are discussed in the text from localities as far downstream as Durango, about 75 river kilometers south of Silverton, Colo. on the Animas River. Bakers Bridge is located at the base of the Animas River Canyon section about 50 river kilometers south of Silverton, Colo.

above Silverton has been extensively fractured, hydrothermally altered, and mineralized by Miocene hydrothermal activity.

Placer gold was discovered in 1871 on Arrastra Creek above Silverton by soldiers exploring the Bakers Park area. Following the signing of a treaty with the Ute Indians in 1873, between 1,000 and 1,500 mining claims were staked in the Animas River watershed upstream from Silverton. Mining activity spread rapidly throughout the area. The chimney deposits associated with Red Mountain located in the headwaters of Mineral Creek were discovered in 1881. The railroad was brought up from Durango in 1882 providing cheap transportation for ore concentrates from the many mills in and above Silverton to the smelters in Durango (Sloan and Skowronski, 1975). Mining continued in the Animas River watershed at various levels of activity until 1991 when the Sunnyside Mine closed. The Sunnyside Gold Corp. initiated restoration activities throughout the watershed in 1994.

Geomorphology of Fluvial Deposits

Many of the sediment samples in this study come from fluvial deposits associated with stream terraces. An understanding of the geomorphic evolution of the stream valleys and these terraces is necessary to properly evaluate the meaning of the geochemical data. Surficial deposits of the Animas River watershed were mapped using color aerial photographs (Blair, 1998) resulting in a surficial geologic strip map of the major tributaries representing an area of about one kilometer in width and extending about 125 m above the active flood plain.

The upper Animas River and Mineral Creek follow the concentric fracture system created during the formation of the Silverton caldera (fig. 1). These fractures predisposed the volcanic rocks to accelerated weathering and erosion by allowing water seepage both from hydrothermal as well as meteoric sources. Today, surficial deposits in the stream valleys are dominantly glacial, fluvial, and colluvial. Although there have been multiple glacial episodes over the past 2 million years (Atwood and Mather, 1932; Gillam, 1998) only vestiges of the most recent glaciation (maximum extent about 18,000 years BP) are present today. For example, Mineral Creek and the upper Animas River have classic U-shaped valleys and both contain morainal deposits (Blair, 1998).

Fluvial deposits, representing both overbank deposits left by flood waters and erosional remnants, are found in stream terraces on the valley floors along with alluvial fan deposits, glacial deposits, colluvial deposits, and modern flood plain sediments. Stream terraces indicate that some change has taken place in the fluvial energy of the stream. Changes in energy are caused by changes in discharge, stream gradient, and sediment load. These changes can come about from long-term climatic change, short-term weather phenomena, temporary channel blockage, and human impact. All of the stream terraces in the Animas River watershed north of Durango, with one possible exception near Bakers Bridge, are post glacial. Terraces with elevations greater than 2 meters above the modern channel are probably the result of long-term climatic changes associated with neoglacial events, such as the "Little Ice Age" which spanned from about 1350 to 1750 AD. Terraces less than 2 meters above the modern stream channel are more likely associated with short-term weather phenomena, such as rare intense thunderstorms, or from human impact such as damming or altering discharge. This

interpretation has been confirmed by the detailed trenching study of the upper Animas River between Howardsville and Eureka where human activity has induced braided stream channel conditions causing aggradation. These studies have shown that old sediments, that is greater than 2,000 years BP by ^{14}C geochronological methods, are buried beneath the gravels that are present in the upper Animas River below Eureka (Vincent and others, 1999).

Field investigations indicate that fluvial gravel deposits preserved in terraces at greater than 2 meters above the active stream level are probably older than 1860. The fluvial sediments in these terraces were laid down prior to mining activity and reflect the pre-mining geochemical background for the representative drainage, assuming no post-depositional human impact has occurred. These older terraces are relatively rare in narrow canyons less than 100 m wide, such as between Howardsville and Silverton, and just north of Eureka (fig. 1). These narrow canyons act as high energy funnels during major storm events which flush out and redistribute previously deposited sediment. Where valleys widen to several 100 meters, older gravel terraces are usually preserved above the modern stream level; for example, at Bakers Park where the town of Silverton is located, along upper Mineral Creek (sites 13-15, fig. 1), and along selected reaches of the Animas Canyon between Silverton and Durango. Historical evidence of the age of these elevated remnant terrace deposits can also be deduced from a study of the overbank deposits resulting from the 1911 Gladstone storm. On October 5, 1911, the largest historic flood on record occurred in the upper Animas River watershed. This flood, called the Gladstone storm, reworked existing alluvial channel sediment and deposited overbank sediments on midstream bars and new flood plain deposits at elevations less than 2 meters above the active flood plain in several localities in the upper Animas River watershed (Pruess, 1996).

Human impact on the floodplain in the Animas River watershed has been significant, particularly in the modern active flood plains. It is estimated from the geomorphic mapping studies (Blair, 1998) that forty percent of the entire channel length within the Upper Animas watershed has been altered in some way (Blair, 1998). The flood plain between Howardsville and Eureka has been totally impacted directly or indirectly by human activity as shown by the dramatic change in channel morphology at the trench site (Vincent and others, 1999). A great deal of sediment movement has occurred here over the past 130 years to establish the now defunct town of Eureka (fig. 1), stabilization of the channel to maintain the old bridge crossing, road construction, gravel mining, and mineral processing. Another example of human impact on the active flood plain occurred when aggressive stoping beneath an alpine lake in 1978. This activity resulted in collapse of the mine roof and lake floor into the mine, draining the water from Lake Emma into the Sunnyside Mine. The associated flush of sediment-laden waters from the Gladstone portal down Cement Creek coated the entire active flood plain with muddy sediment.

METHODS

Field Sampling Methods

Using the geomorphological maps, we walked the segments of the river channels

where pre-mining sediments might be preserved in old terrace deposits. Terraces were sampled a number of sites in the watershed above the confluence of the Animas River with Mineral Creek. These localities are shown schematically on fig. 1. Terrace deposits were also sampled at several sites in the Animas Canyon between Silverton and Bakers Bridge about 25 km upstream from Durango Colo. These terrace deposits were sampled, whenever possible, beneath old large Engelmann Spruce which were cored if live or sampled where dead for dendochronological determination of the minimum age of the terrace deposits. These terrace deposits were generally composed of poorly sorted fluvial gravels containing lithic clasts ranging from 10 to 30 cm in diameter. These sections generally had no discernable stratigraphy, so the sections were sampled in lifts taken on 15 to 30 cm intervals throughout the exposed section. The gravels were sieved to pass a 2 mm stainless steel screen, and sent to the laboratory for further processing. In the laboratory the samples were dry-sieved to pass 100 mesh in the same manner as the stream sediments (Church and others, 1997). The sample material analyzed (that is, <150 micrometers) constitutes the very fine sand, silt, and clay sized fraction of the pre-mining fluvial sediments.

Below Bakers Bridge, the Animas River is a mature, meandering river with numerous oxbow lakes. We sampled the fluvial deposits in these oxbow lakes, one of which was active circa 1896 (see the historical photographs by Whitman Cross, in Atwood and Mather, 1932, plate 25; U.S. Geological Survey, 1898) just above the town of Durango in what was known at the turn of the century as the town of Animas City. Five-cm diameter cores of fluvial sediments up to depths of 3 meters were taken from these oxbow lakes and the core intervals divided along stratigraphic boundaries for sampling. Sandy layers were sieved as described above prior to chemical analysis. Stratigraphic intervals from this youngest meander contain deposits that have elevated concentrations of Ag, As, Cd, Cu, Pb, and Zn resulting from the transport and deposition of fluvial tailings in the Animas River whereas the stratigraphic intervals sampled in the older oxbow lakes at this site contain metal concentrations at or near crustal abundance levels.

Analytical Methods

Samples from the cores and lift sequences of the fluvial sediments were analyzed using two different analytical procedures: a mixed-acid total digestion, and a weak partial-dissolution extraction, both followed by ICP-AES (inductively-coupled plasma atomic emission spectroscopy) analysis.

The total digestion procedure utilizes a combination of HCl, HNO₃, HClO₄, and HF acids applied to 0.2g of sample (Briggs, 1996). The resulting solution is analyzed for 40 elements. This procedure is very effective in dissolving most minerals, including silicates, oxides and sulfides. Some refractory minerals such as zircon, chromite and tin oxides are only partially attacked. However, these minerals and the elements associated with them are not of concern to this study. To monitor the quality of the analyses, laboratory duplicates were analyzed to assess precision, and three standard reference materials (SRM's) were analyzed with each set of samples to assess accuracy. The reference materials were NIST-2704, NIST-2709 and NIST-2711, available from the National Institute of Standards and Technology (NIST, 1993a, 1993b, and 1993c).

Whereas the mixed-acid procedure releases all of the metals contained in a sample, the application of a partial-digestion technique releases metals bound within different mineral phases. These data can be quite informative in the study of metal enrichment in bed sediments due to the coating of grain surfaces by iron- and manganese-oxide minerals with metals released during weathering (Chao, 1984). We used a weak, warm-acid leach (50°C 2M HCl-1% H₂O₂) to dissolve hydrous amorphous iron- and manganese-oxide colloids or sediment-coatings which contain sorbed metals of interest (appendix II and III; Church and others, 1993). In this procedure, a 2-gram sample is leached with 15 mL of the solution for three hours, centrifuged and analyzed for 35 elements by ICP-AES. Replicates and the same reference materials were also analyzed with each sample set to access analytical quality and reproducibility.

Geochronology

Where the data on pre-mining sediment quality needed to construct a strategy for restoration is absent, other means of determining environmental changes may be obtained by examining the changes in fauna and flora coupled to chronological scales defined by the distribution of radioactive isotopes. This method of establishing chronologies is based on a known property of radioactive material, the half-life. A half-life of an isotope is the amount of time it takes for half a given number of parent atoms to decay to an isotope of another daughter element. The age of sediment containing a radioactive isotope with a known half-life is calculated by knowing the original concentration and measuring the percent of the remaining radioactive material. The requirements for a radioisotope to be a candidate for dating are that: (1) the chemistry of the parent isotope is known; (2) the half-life is known; (3) the initial amount of the isotope per unit substrate is known or can be accurately estimated; (4) once the isotope is encapsulated within the substrate, the only change in concentration is due to radioactive decay, that is the sample has remained a closed system; (5) the abundance of the daughter isotope must be relatively easy to measure if the technique is to be useful, and (6) the effective age range must be applicable to the time span required to solve the problem (about 8 half lives). In the Animas River watershed, there are four radioisotopes that satisfy these criteria and provide useful data: ⁷Be, ¹⁴C, ¹³⁷Cs, and ²¹⁰Pb.

Beryllium-7

⁷Be is formed in the atmosphere by the interaction of cosmic rays and nitrogen. This isotope has a short half-life of about 54 days. Since ⁷Be is a very reactive, it readily sorbs to soils and sediment upon being swept from the atmosphere by rainfall. The presence of ⁷Be in the sediment is a useful indication that the sediment was in contact with the atmosphere within a few months of the time of collection of the sample. Furthermore, if the ⁷Be activity is relatively uniform between different samples sites within the same watershed, the uniformity of the ⁷Be activity is very useful in establishing that the parent isotope activity of longer-lived isotopes are also in equilibrium with atmospheric processes producing the parent isotope, and that the assumptions necessary for ²¹⁰Pb dating are reasonable assumptions for the ²¹⁰Pb flux.

Lead-210

^{210}Pb , with a half-life of 22.8 years, is ideal for environmental studies. A member of the ^{238}U series, the disequilibrium between ^{210}Pb and ^{226}Ra is caused by the physiochemical activity of the intermediate gaseous progenitor, ^{222}Rn . This isotope, in turn, rapidly decays to form ^{210}Pb . The highly reactive lead is rapidly sorbed to or incorporated in the depositing sediment. This flux produces a concentration of unsupported or excess ^{210}Pb activity, which is the lead that has an activity higher than that of the ambient ^{210}Pb which is in equilibrium with ^{226}Ra . Ages of deposition of individual layers of sediment are calculated by determining the decrease in ^{210}Pb activity at consecutive intervals. If the initial concentration of ^{210}Pb is known, or can be estimated using ^7Be activity data, then the "age" of a horizon is calculated by the following:

$$T_{\text{age}} = \ln(A^{210}\text{Pb}_0 / A^{210}\text{Pb}_h) \times 1/\lambda \quad (1)$$

or substituting the constants,

$$T_{\text{age}} = \ln(A^{210}\text{Pb}_0 / A^{210}\text{Pb}_h) \times 1/0.03114; \quad (2)$$

where

$A^{210}\text{Pb}_0$ is the unsupported or "excess" ^{210}Pb activity in disintegrations per minute at time zero (the present),

$A^{210}\text{Pb}_h$ is the activity in disintegrations per minute at depth h, and

λ is the decay constant, or half-life of ^{210}Pb .

Carbon-14

^{14}C is also produced in the Earth's atmosphere by the interaction of cosmic-ray particles with nitrogen (N), oxygen (O), and carbon (C). Of these, nitrogen (N) is the most important in terms of the amount of ^{14}C produced. An additional source of ^{14}C was thermonuclear activity in the late 1950's and early 1960's. This additional contribution reached its peak between 1963 (northern hemisphere) and 1964 (southern hemisphere). From whatever source, the ^{14}C atoms produced are rapidly oxidized to CO_2 and are assimilated into the carbon cycle. ^{14}C has a half-life of 5,568 years producing an effective range of applicability of 100 to 70,000 years. The dates are reported as radiocarbon years before present, where present is, by international convention, 1950. The modern reference standard is 95 percent of the ^{14}C content of the National Bureau of Standards Oxalic Acid and calculated using the Libby ^{14}C half life (5,568 years). The bomb produce carbon is determined by comparing the 1950 carbon activity to the present carbon activity and is represented by the symbol δ . Prior to 1950 the atmospheric (^{14}C value was about -50 ‰, as a result of the thermonuclear activity the (^{14}C increased to 200 ‰ in 1964-1965. This value has been slowly decreasing as the "bomb" carbon is removed from the atmosphere. The "bomb" carbon signature provides a valuable reference marker against which other "dating" methods can be calibrated.

Cesium –137

^{137}Cs , with a half-life of 30.3 years, is a thermonuclear byproduct. Its presence is directly related to the atmospheric testing of nuclear devices during the latter half of the 1950's and early 1960's. Under ideal conditions, ^{137}Cs activity in the sediments deposited should mirror the ^{137}Cs production curve. With the exception of the Chernobyl failure, there has been no ^{137}Cs released to the atmosphere since the cessation of atmospheric nuclear testing. ^{137}Cs activity is now below the limit of detection in modern sediments. In the acidic bogs and wetlands sediments, ^{137}Cs has been demonstrated to be mobile and thus not a reliable isotope for "dating" purposes. However, since it is a group one element like sodium and potassium, it should behave conservatively in aqueous mediums.

All measurements of continuous variables are made with a degree of uncertainty (error). There are random errors, systematic errors, or observational errors, which all combine to introduce a degree of measurement uncertainty. Random errors arise from radioactive decay processes, or from the statistical uncertainty of measurements of parent and daughter isotope radioactivity. Systematic errors occur if there is a miscalibration of the instrumentation. Observational errors arise from unrecognized "contamination or disturbance" of the sample which violates the closed system behavior required for geochronological applications. In isotopic dating of sediment, it is assumed that the "law of superposition" is applicable. If sedimentary mixing, either natural or anthropogenic is unrecognized, the parent/daughter systematics have been destroyed and the results will be erroneous. In addition to the sources of error enumerated, there is a problem inherent in measurements of radioactivity. The ^{210}Pb procedure requires the precise measurement of the activity ^{210}Pb and its parent ^{226}Ra . Each of these measurements have an inherent degree of statistical uncertainty. As the differences in these two activities become small, it becomes impossible to differentiate between the two. For this reason, the lower limit of age measurements for the ^{210}Pb procedure is approximately 150 years. However, as most of the historical mining activity in the western U. S. has occurred following the Civil War, the ^{210}Pb geochronometer is ideally suited to study the environmental impacts caused by historical mining activity in fluvial systems.

As defined, the age of a layer of material is determined by the ratio of activity between T_0 and the activity at the horizon investigated. In determining the ages of a horizon, there are two levels of precision possible. The first is a crude estimated based solely on the determination of presence or absence of "excess" ^{210}Pb over the ambient parent ^{226}Ra . If "excess" ^{210}Pb activity exists, then the sediment is less than 150 years old. The second level of precision is necessary to provide the high degree of time resolution required in most environmental investigations. In these studies, the high age precision is determined by measuring the "excess" ^{210}Pb activity of sequential samples in homogenous sediment. In this procedure, each measurement validates the previous and succeeding one resulting in a smooth curve of decreasing "excess" ^{210}Pb activity with depth. As a result, the age measurements are internally consistent. This type of curve is the norm in lake environments where one can reasonably expect a uniform rate of sedimentation, but this behavior can not be expected in fluvial systems.

In fluvial sediments where sedimentary sequences are not deposited at a uniform rate, the use of radioisotopes to "date" stratigraphic horizons is more complex. In such situations, there are a number of parameters, which must be determined to refine a date

beyond the simple interpretation that the sample is less than 150 years old. These parameters are: (1) the flux of the parent and daughter isotopes to the system and (2) the adsorption coefficient of the isotopes in the sediment as they were deposited. A series of sites were sampled within the Animas River watershed to determine these parameters. To date, the top portions of eight cores have been examined to determine the flux of ^{210}Pb to the Animas River watershed and have yielded data consistent with the ^{210}Pb flux rate that has been determined in cores taken throughout the country. From our preliminary data, the incident ^{210}Pb flux is about 1.0 ± 0.3 dpm/cm²/year in the Animas River study area. The measurements needed to determine the adsorption factors for ^{210}Pb have not yet been completed.

Paleontologic Studies

Fine-grained sediments from cores taken along the Animas River watershed were examined for the remains of terrestrial and aquatic flora and fauna that might be preserved in the historical sedimentological record. Aquatic and terrestrial invertebrates, vertebrates, and plant megafossils would represent a qualitative proxy for the variety of habitats sampled along the Animas River, including active river and stream channels, abandoned oxbows, riparian habitats, and ponded systems such as beaver dammed ponds. Each of these habitats can be characterized by a distinct group of organisms, many of which have hard body parts, such as chitinized or sclerotized exoskeletons, cellulose or woody stems, or silicified or calcified skeletal components, that are preserved in the sediments. In some skeletal systems, particularly those with calcified body parts, trace elements are incorporated into the lattice structure and provide an additional quantitative proxy for water composition (De Deckker and Forester, 1988; Timmermans, 1993).

Samples examined for this study represent fine-grain sands, silts, and clays taken from cored localities. Lift samples and terrace gravels represent environments that are not conducive either to organism survival or to preservation of microscopic-sized remains, and so these lithologies were generally not examined. Samples from sites 2, 3, 7, 9, and 14 (fig. 1) were examined as were two sites in the Animas Canyon reach and many of the samples from the fluvial sediments in the oxbow lakes sampled near Durango. All samples were processed using methods that avoid agitation, chemicals, or high temperatures; in this manner, very delicate remains such as insect wings are recovered. Additionally, any analyses for trace elements, stable isotopes, or amino acids can be conducted on the organic remains without concern for thermal or chemical alteration of samples recovered. Samples were wet-weighed, placed in warm water with sodium bicarbonate and Calgon (sodium hexametaphosphate), and frozen. Subsequent thawing allows physical disaggregation of the clays. Sediment was washed through a 230 mesh-sieve (63 micrometers,) and all material larger than 150 micrometers was examined under a binocular microscope. Sample residues were examined and characterized for all organic remains of fauna and flora, preservation, and associated grain-size and lithology of the microscopic minerals and rock fragments.

RESULTS AND SUMMARY

Geomorphologic mapping of the fluvial deposits in the study area has identified

numerous sites where pre-mining bed sediments may be preserved. We have examined many of these sites and collected fluvial sediments from fifty-two sites plus the trench site (site 3, fig. 1). Fluvial materials from these sites represent pre-mining bed sediments, old historical bed sediments, overbank flood deposits, both pre-mining and historical, fluvial tailings deposits representing different milling processes, pre-mining riparian habitat, and historical and modern beaver ponds. More than 500 samples from these sites have been analyzed for their total metal concentrations. Preliminary analysis of the geochemical data, when coupled with both the historical and geochronological record, clearly show that there has been a major impact by historical mining activities on the geochemistry of the fluvial bed sediments. The impact of historical mining activity is clearly recorded in the sedimentological record as shown in the study of sediments from the trench section (Vincent and others, 1999). Historical mining activity has resulted in a substantial increase in metals in the very fine sand to clay sized component of the bed sediments of the upper Animas River, and Cement and Mineral Creeks. Enrichment factors for metals in modern bed sediments, relative to those sediments that are clearly pre-mining in age, range from a factor of 2 to 6 for arsenic, 4 to more than 10 for cadmium, 2 to more than 10 for lead, 2 to 5 for silver, and 2 to more than 15 for zinc.

Preliminary geochronological results from the silt layer exposed in the trench from the braided reach under a gravel bed in the upper Animas River between Howardsville and Eureka (site 3, fig 1) indicate that this layer was deposited just prior to the start up of mining. The data from samples from the top portion of the silt layer exhibit ^{210}Pb disequilibrium. This suggests that the top of the silt deposit is less than 100-to-150 years BP. Preliminary geochronological results from sediments from the oxbow lakes in the lower Animus River flood plain near Animas City indicate that these cores do show ^{210}Pb disequilibrium and one core, 98ABB270B, has been dated. The age profile from this core indicates episodic sedimentation. The top 8 cm of sediment in this core appears to have accumulated slowly over the past 40 years. The flat nature of the ^{210}Pb distribution between 8 and 20 cm is indicative of very rapid sedimentation. The ^{210}Pb and concurrent ^{137}Cs data suggest that this layer was deposited about 50 years ago. The bottom most stratigraphic interval from this core indicates another period of rapid sediment deposition and has a calculated ^{210}Pb age of about 70 years. The lack of equilibrium in these samples means that the core did not reach older sediment.

Nearly all of the samples examined for paleontologic evidence included some vegetative material, ranging from fine matted material characteristic of subaquatic plants from ponds, quiet streams, or overbank water accumulations, to concentrated fecal pellets laden with plant material, most probably representing sediments deposited in beaver ponds, to woody material characteristic of terrestrial upright plants growing in established riparian soils some distance from the main river channel. Cores that have been dated as pre-mining, especially those with significantly older sediments from the trench (site 3, fig. 1), show significant peatification of the woody plant remains, ranging from recognizable but altered stems to clumps of highly altered material. These intervals have been dated using ^{14}C methods. Most of the associated mineral grains consist of fine sand and silty material; occasional samples contain angular, fresh, uncoated sulfide mineral grains with essentially no fine-grained sediment or organic remains. This depositional environment clearly represents a rapid influx of mill tailings from an upstream source related to mining. In general, upstream samples from overbank habitats contain only

floral remains; aquatic invertebrates and vertebrates are conspicuous by their absence. These are interpreted to represent riparian habitat.

Crustaceans were recovered from two cores, from a modern beaver pond along an old channel of the Animas River near Needleton abandoned in 1927 (Osterwald, 1995) and from an old abandoned oxbow near Durango. The modern beaver pond, which is fed by groundwater, included a number of calcified valves of a freshwater crustacean, with the valves coated with iron oxides. The abandoned oxbow occurrence included a single daphniid ephippia (a chitinized egg case). The abundance and excellent state of preservation of ostracods from the beaver pond core indicate that neutral to alkaline pH waters without elevated trace element concentrations existed for a period of months. The daphniid occurrence in the oxbow sediments represents a nektonic or swimming crustacean with a short life cycle and is probably indicative of a flush of clean water probably from snowmelt; associated mineral grains with small amounts of vegetative debris further support a rapid influx of sediment from upstream sources.

Paleoentologic evidence does not indicate a healthy aquatic habitat in any of the stream reaches investigated above the confluence of the Animas River with Mineral Creek (fig. 1) prior to the impact of mining activity. The absence of paleoentologic remains is interpreted to reflect the poor preservation regime of the bed sediment materials sampled. The fluvial sediments sampled in this study were deposited in higher energy environments than are conducive to the preservation of most aquatic organisms including fish remains. In comparison with water quality observed today in the streams (Church and others, 1997), the bed sediment chemistry of the sediments today would suggest that pre-mining water was less acidic prior to mining and carried a smaller colloidal sediment load than is found in these stream reaches today.

Restoration goals and objectives for the upper Animas River watershed must take into account the evidence from the pre-mining fluvial record which indicates that metal loads and acidity in the water column were substantially lower than they are today. However, the profound changes in the ground-water flow system caused by mining activity and the substantial dispersed metal source in the fluvial sediments caused by the industry practice of discharging mill tailings into mountain streams throughout the west prior to 1935 are environmental impacts that may have prolonged influence on the overall restoration plan for the upper Animas River watershed. Additional studies that focus on the impact of removal of known point sources within the upper Animas River watershed are required before it is feasible to determine the extent to which watershed restoration can approach the original pre-mining bed sediment geochemical baseline.

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