Smith, K.S., Walton-Day, Katherine, and Ranville, J.F., 2000, Evaluating the effects of fluvial tailings deposits on water quality in the Upper Arkansas River Basin, Colorado: Observational scale considerations, in Proceedings of the Fifth International Conference on Acid Rock Drainage (ICARD 2000), Denver, Colorado, May 21-24, 2000, Volume II: Littleton, Colorado, Society for Mining, Metallurgy, and Exploration, Inc., p. 1415-1424.

Evaluating the Effects of Fluvial Tailings Deposits on Water Quality in the Upper Arkansas River Basin, Colorado: Observational Scale Considerations

Kathleen S. Smith[1], Katherine Walton-Day[2], and James F. Ranville[3]

ABSTRACT

Four different scales of observation were used to evaluate the potential effects of a fluvial tailings deposit on water quality along the flood plain of the upper Arkansas River south of Leadville, Colorado. First, we collected surficial material and subjected it to batch water-leaching tests. Second, we excavated and leached an intact eight-inch-diameter core. Third, we examined the water quality of the shallow ground water beneath the fluvial tailings deposit; and fourth, we monitored water quality along a 5-km reach of the adjacent Arkansas River. Leaching of surficial samples indicates that there is a reservoir of readily water-soluble material yielding elevated metal concentrations and high acidity. However, there are minimal measurable water-quality effects of the fluvial tailings deposit on the adjacent reach of the Arkansas River.

INTRODUCTION

The upper Arkansas River, Colorado, has been the focus of a great deal of research on water-quality related impacts on the environment from past and current mining practices. Although treatment plants designed to remove metals have improved conditions for brown trout (the dominant species) in the upper Arkansas River, episodic events and nonpoint sources of pollution are still of concern (Colorado Division of Wildlife, 1998). The flood plain of the upper Arkansas River south of Leadville, Colorado, contains numerous deposits of tailings that have been transported downstream from historical mining operations in the Leadville area (URS Operating Services, 1997). These deposits are a possible source of acid and metal contamination to surface and ground water. The subject study site is located at one of these fluvial tailings deposits, approximately 13 km south of Leadville (fig. 1). The size of the site is about 0.1 km^2, and it is relatively flat and virtually devoid of living vegetation.

The fluvial tailings deposits are generally overbank and pointbar deposits containing fine-grained mixtures of tailings and other sediment. Cored material from the deposits is usually extremely heterogeneous. At our study site, the top of the fluvial tailings deposit commonly consists of a fine-grained pyrite-rich layer, the middle portion of the deposit is clay-rich with sand and silt lenses, and the bottom contains an organic-rich layer underlain by a sand and gravel shallow aquifer. The dominant minerals are quartz, feldspar, and mica.

We used four different approaches and observational scales to study and evaluate the effects of fluvial tailings on water quality at the study site. First, we collected surface and near-surface material from the fluvial tailings deposit and subjected it to batch water-leaching tests. Second, we excavated an intact eight-inch-diameter core from the deposit and determined its leaching behavior under unsaturated conditions. Third, we installed shallow ground-water wells at the site and collected ground-water-quality samples. Finally, we collected water-quality samples along a 5-km reach of the adjacent Arkansas River. These four approaches represent different scales of observation of the potential effects of the fluvial tailings on water quality. In this paper, we compare results and interpretations among these different scales of observation.

1 U.S. Geological Survey, M.S. 973, Denver Federal Center, Denver, CO 80225-0046 ksmith@usgs.gov
2 U.S. Geological Survey, M.S. 415, Denver Federal Center, Denver, CO 80225-0046 kwaltond@usgs.gov
3 Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401 jranvill@mines.edu

Use of brand names is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

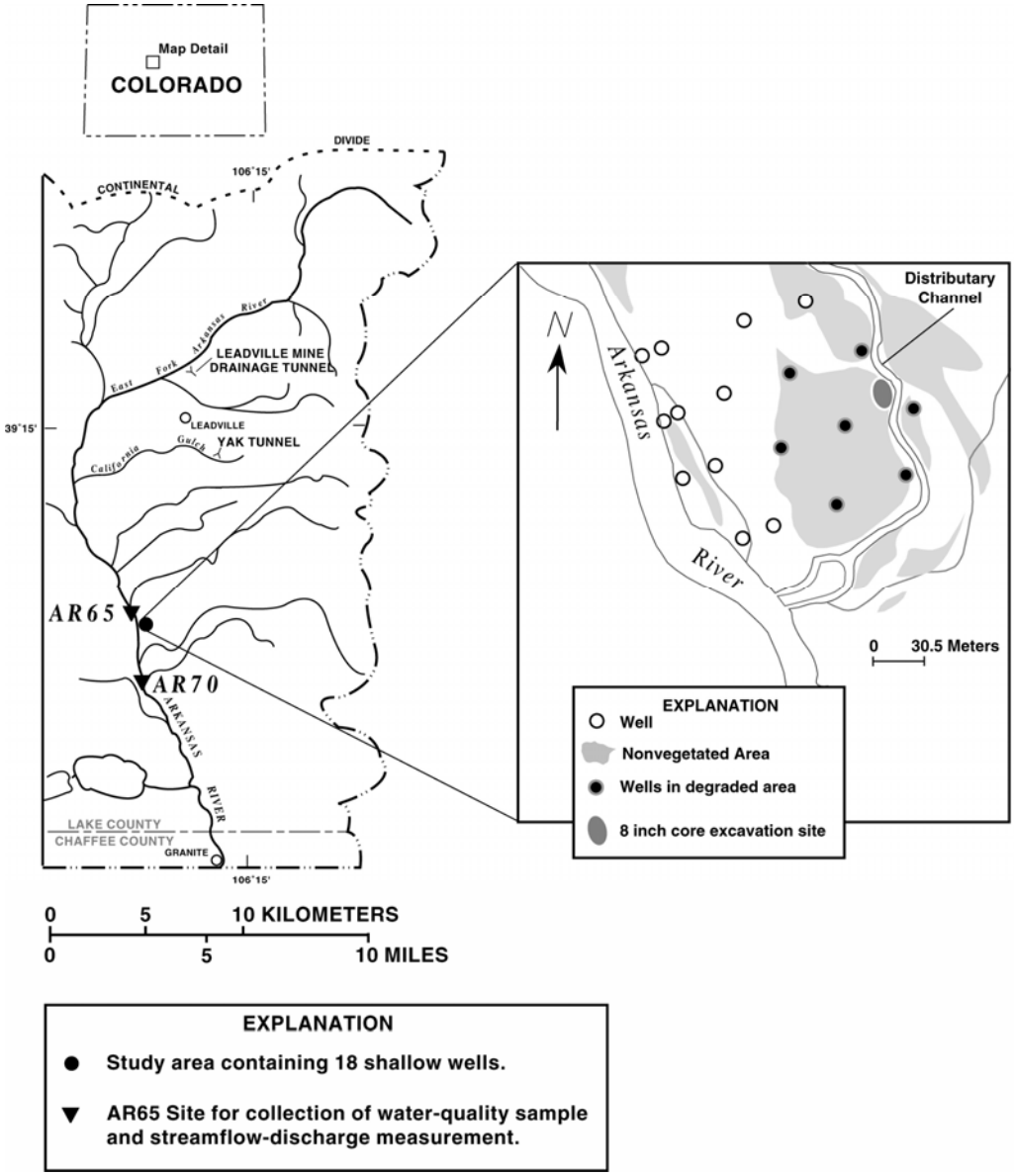

Figure 1 Map of the field site showing the study area where shallow ground water wells were installed and surficial materials collected. Also shown are the excavation site of the eight-inch-diameter core, and the upstream and downstream sampling sites along the Arkansas River, Colorado.

Related work at this study site is reported by Walton-Day et al. (1996; in press), Jerz (1998), and Smith et al. (1998b, 1999a, 1999b).

METHODS

Collection and Leaching of Surficial Fluvial Tailings-Deposit Material

We used a one-inch stainless steel soil core barrel with plastic liners to collect five cores at the site. After air drying the cores, we separated the cored material into visually distinct stratigraphic segments on the basis of color and textural differences. Leaching data for the surficial segments are given in this paper (surficial segments ranged from 5 to 15 cm in length). Batch water leaches of core segments were performed by combining 2 g of sample with 40 g of deionized water and shaking the mixture for 3 hours. After shaking, pH measurements were made and the leachate suspension was filtered through a 0.45-µm filter. Filtered leachates were acidified with nitric acid and analyzed by inductively coupled argon plasma - mass spectroscopy (ICP-MS). A more detailed description of the collection and leaching methods is contained in Smith et al. (1998b).

Collection and Leaching of an Intact Eight-Inch-Diameter Core

An eight-inch-diameter core was excavated intact from the bank of a distributary channel that cuts through the fluvial tailings deposit (fig. 1). A clear polymethylmethacrylate tube was placed on top of the bank. The fluvial tailings around the tube were slowly excavated and the tube pushed down to encase the remaining material. The process was repeated until the shallow aquifer material was reached (approximately 60 cm of overlying material). The bottom of the tube was fitted with a polyvinylchloride (PVC) cap and the joint sealed with silicone cement. The cap contained sampling ports designed to separately sample water draining along the interface between the cored material and the inner edge of the tube and water draining through the center part of the core (center port). Deionized water was applied to the top of the core at a rate of 2 mL/min using a peristaltic pump. The deionized water was allowed to drain by gravity through the core. Effluent was collected from the center port at the bottom of the core at various times. Forty sequential effluent samples were collected under unsaturated conditions over a 23-day period. Specific conductance and pH measurements were made on the effluents, and a portion of the unfiltered effluents was acidified with nitric acid and analyzed by ICP-MS. A more detailed description of the core leaching method is in Smith et al. (1999a).

Installation and Sampling of Shallow Ground-Water Wells

Eighteen shallow ground-water wells, ranging in depth from 0.5 to 2 meters, were installed in a grid throughout the study area (see fig. 1). The 3.8-cm-diameter wells were designed to contain a screened interval within the zone of water-table fluctuation. The annulus of each well was filled with sand to a depth approximately 15 cm above the screened interval. The annular fill of each well was completed with a bentonite seal topped by concrete containing a 7.5-cm-diameter PVC collar. The wells were developed by repeated surging and pumping until the well water was visibly clear. Prior to water-quality sampling, the wells were pumped until at least three well volumes of water had been pumped and pH and specific conductance remained steady. Values of pH and specific conductance were determined using a Hydrolab multiparameter sampling probe installed in a flow-through cell downstream from the peristaltic pump. Unfiltered samples were collected and acidified with concentrated nitric acid to pH less than 2.0 and analyzed by inductively coupled argon plasma - atomic emission spectroscopy (ICP-AES). All equipment that contacted sample water was pre-cleaned using the procedure described by Horowitz et al. (1994). Detailed methods are given in Walton-Day et al. (in press).

River Sampling

Water samples were collected and streamflow discharge measurements were made at two sites along the upper Arkansas River that were upstream and downstream from the study site. Sampling at each site was conducted from a bridge so that a composite water-quality sample could be obtained across the entire stream width and depth using the equal-width increment sampling technique (Shelton, 1994). Standard USGS techniques were used to collect water-quality samples and to conduct streamflow-discharge measurements (Rantz et al., 1982a, 1982b; Shelton, 1994). Field parameters, such as pH and specific conductance, were measured using a Hydrolab multiparameter-sampling probe. Unfiltered samples were acidified with concentrated nitric acid to pH less than 2.0 and analyzed by ICP-AES. All equipment that contacted sample water was cleaned using the procedure described by Horowitz et al. (1994). Instantaneous mass loads were computed for several elements and compared along the river reach. An instantaneous load for a particular element is the product of concentration and streamflow discharge and is expressed in units of mass per unit of time. Detailed methods are given in Walton-Day et al. (in press).

WATER-QUALITY RESULTS AT DIFFERENT OBSERVATIONAL SCALES

Average values for water-quality constituents and properties are presented in table 1 for the different scales of observation. Results for unfiltered samples are reported for eight-inch-core effluent, shallow ground water, and river water. Unfiltered samples represent the total amount of metal present in a given medium. More detailed results can be found in Smith et al. (1998b, 1999a) and Walton-Day et al. (in press). A brief discussion of the interpretation for each observational scale follows.

Table 1 Average values and ranges of various constituents and properties in 20:1 water leachates of surficial material, eight-inch-core effluent, shallow ground water for 7 wells in the most degraded area, shallow ground water for all 18 wells, and adjacent river water [pH values are median values; n, number of measurements; ND, not determined; µS/cm, microSiemens per centimeter; µg/L, micrograms per liter; mg/L, milligrams per liter; eight-inch-core effluent, shallow ground water, and river water are for unfiltered samples]

Constituents and properties	Surficial leachate (20:1 water:solid)	Core effluent	Ground water (7 wells)	Ground water (18 wells)	River water
pH					
n	5	40	34	85	58
range	2.1 - 2.9	2.8 - 3.5	2.3 - 6.1	2.3 - 8.1	7.2 - 8.2
median value	2.3	2.9	3.3	6.0	7.8
Specific conductance (µS/cm)					
n	ND	40	34	85	57
range	ND	1,560 - 3,480	210 - 2,760	90 - 2,760	79 - 230
average value	ND	2,530	850	500	150
Cadmium (µg/L)					
n	5	40	39	97	4
range	22 - 280	250 - 4,000	< 5 - 410	< 5 - 410	< 5 - 6
average value	95	1,520	55*	32*	< 5
Copper (µg/L)					
n	5	40	39	97	60
range	120 - 1,400	240 - 1,860	< 50 - 1,150	< 50 - 1,150	< 50
average value	570	940	120#	65#	< 50
Iron (mg/L)					
n	5	40	39	97	60
range	3.6 - 490	0.89 - 35	0.050 - 112	< 0.02 - 110	0.27 - 4.0
average value	180	16	24	10+	1.0
Lead (µg/L)					
n	5	40	39	97	38
range	140 - 3,500	40 - 96	< 5 - 2,100	< 5 - 2,100	6.0 - 120
average value	1,660	68	170*	74*	25
Manganese (mg/L)					
n	5	40	39	97	60
range	0.23 - 4.1	0.23 - 8.7	0.011 - 7.0	< 0.005 - 12	0.076 - 0.97
average value	1.2	2.3	1.6	1.6*	0.27
Zinc (mg/L)					
n	5	40	39	97	60
range	2.1 - 34	6.2 - 170	0.016 - 29	0.016 - 29	0.085 - 0.99
average value	11	62	4.8	3.4	0.31

* Detection limit = 5 µg/L; substituted 2.5 µg/L for all samples < 5 µg/L.
\+ Detection limit = 0.020 mg/L; substituted 0.010 mg/L for all samples < 0.020 mg/L.
\# Detection limit = 50 µg/L; substituted 25 µg/L for all samples < 50 µg/L.

Leachates of Surficial Fluvial Tailings-Deposit Material

Leaching of the surficial fluvial tailings-deposit material produced elevated metal concentrations and a median pH value of 2.3 (table 1). These results indicate that waters draining from the fluvial tailings deposit might degrade the quality of receiving waters. Degradation would likely be from surface runoff and subsurface flow following snowmelt and periodic rainfall.

Effluents from Eight-Inch-Cored Fluvial Tailings-Deposit Material Under Unsaturated Conditions

Effluents obtained by leaching an eight-inch-diameter core with deionized water contained elevated metal concentrations and pH values ranging from 2.8 to 3.5 (fig. 2). Results presented in table 1 represent average metal concentrations of 40 samples collected under unsaturated leaching conditions of the eight-inch core over a period of approximately 23 days. Most metals exhibit a large spike in concentration early in the leaching process followed by a gradual decrease in concentration (fig. 2). The elevated metal concentrations and acidity released from the eight-inch core indicate that uncontaminated shallow ground water should be degraded by infiltration of water through the tailings. Average iron and lead concentrations are higher in the most degraded shallow ground-water wells than in the eight-inch-core effluent (table 1). Metal concentrations in these effluents are not directly comparable with the metal concentrations in surficial leachates (above) because of uncertainties in the solid-to-solution ratio for the eight-inch-core effluents. The computed solid-to-solution ratio for the eight-inch-core experiment was approximately 1:3; however it is likely that not all parts of the core were fully contacted by the water due to preferential flow. Also, the material in the lower portions of the core is compositionally different from the surficial material that was subjected to the batch leaching experiments. Detailed results can be found in Smith et al. (1999a).

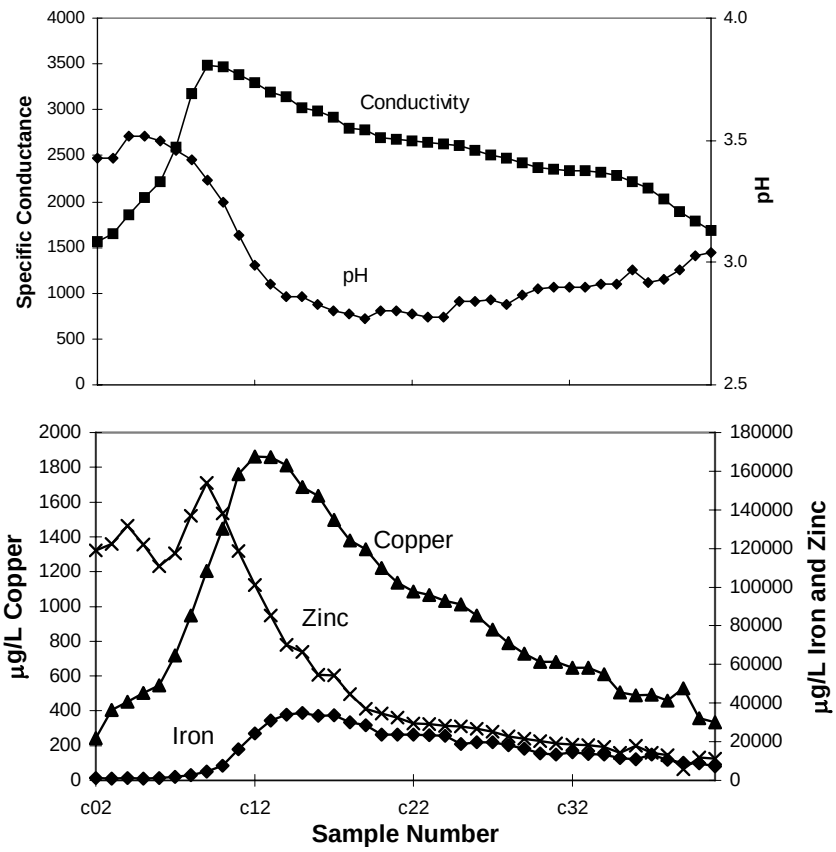

Figure 2 Composition of effluents obtained by leaching an eight-inch-diameter core of fluvial tailings with deionized water under unsaturated conditions for 23 days

Shallow Ground Water

The quality of shallow ground water beneath the fluvial tailings deposit is clearly degraded by the overlying tailings, as exhibited by depressed pH values (pH less than 3.0 in as many as four wells; fig. 3) and elevated specific conductance and unfiltered metal concentrations in some wells. Shallow ground-water quality shows some seasonal variability that affects the number of wells exhibiting degradation of water quality. Degradation of most water-quality constituents and properties is geographically restricted to wells located directly beneath tailings deposits (seven wells); table 1 presents results for these seven wells and for all 18 wells. Zinc contamination is most pervasive and is present in almost all wells. At this scale of observation, degraded water quality is demonstrated in the shallow ground water, but no conclusions can be drawn about the adjacent river water. Detailed results are given in Walton-Day et al. (in press).

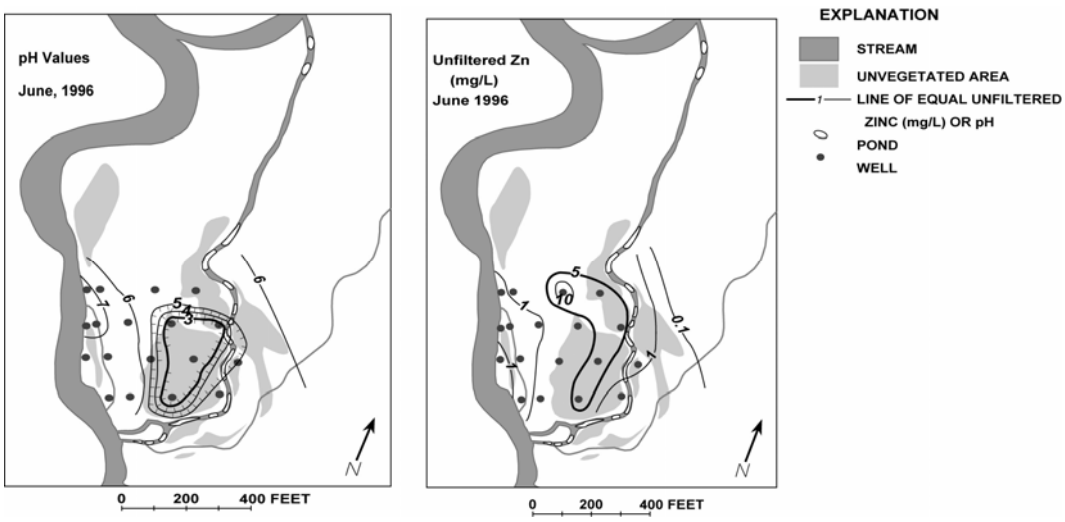

Figure 3 Shallow ground water pH and unfiltered zinc concentrations beneath the fluvial tailings deposit

River Water

Instantaneous loads for unfiltered metals increase between the upstream and downstream sampling sites for iron, lead, and zinc on two out of 18 sampling dates and for manganese on one date. For all other sampling dates there is either no statistical difference or a decrease in instantaneous unfiltered metal loads between the upstream and downstream sampling sites. Figure 4 shows instantaneous loads for unfiltered zinc concentrations to illustrate this point. In addition, pH values are circumneutral, indicating minimal to no effect from the low-pH waters. This result indicates that there is minimal evidence that the fluvial tailings deposits are degrading water quality along this river reach. It is likely that some metals from the study site reach the Arkansas River during certain times of the year, but metal inputs from the study site appear to be mostly undetectable when conventional mass-loading techniques are used. The variability in these mass-loading techniques can be as high as 20 percent. Therefore, load changes of less than 20 percent probably will not be detected. It is important to note that this data set does not include any stormwater sampling, so we are not able to evaluate degradation of water quality during storm events. May and June data represent snowmelt conditions. At this scale of observation, there is only a minimal effect on water quality from the fluvial tailings deposit. Detailed results are given in Walton-Day et al. (in press).

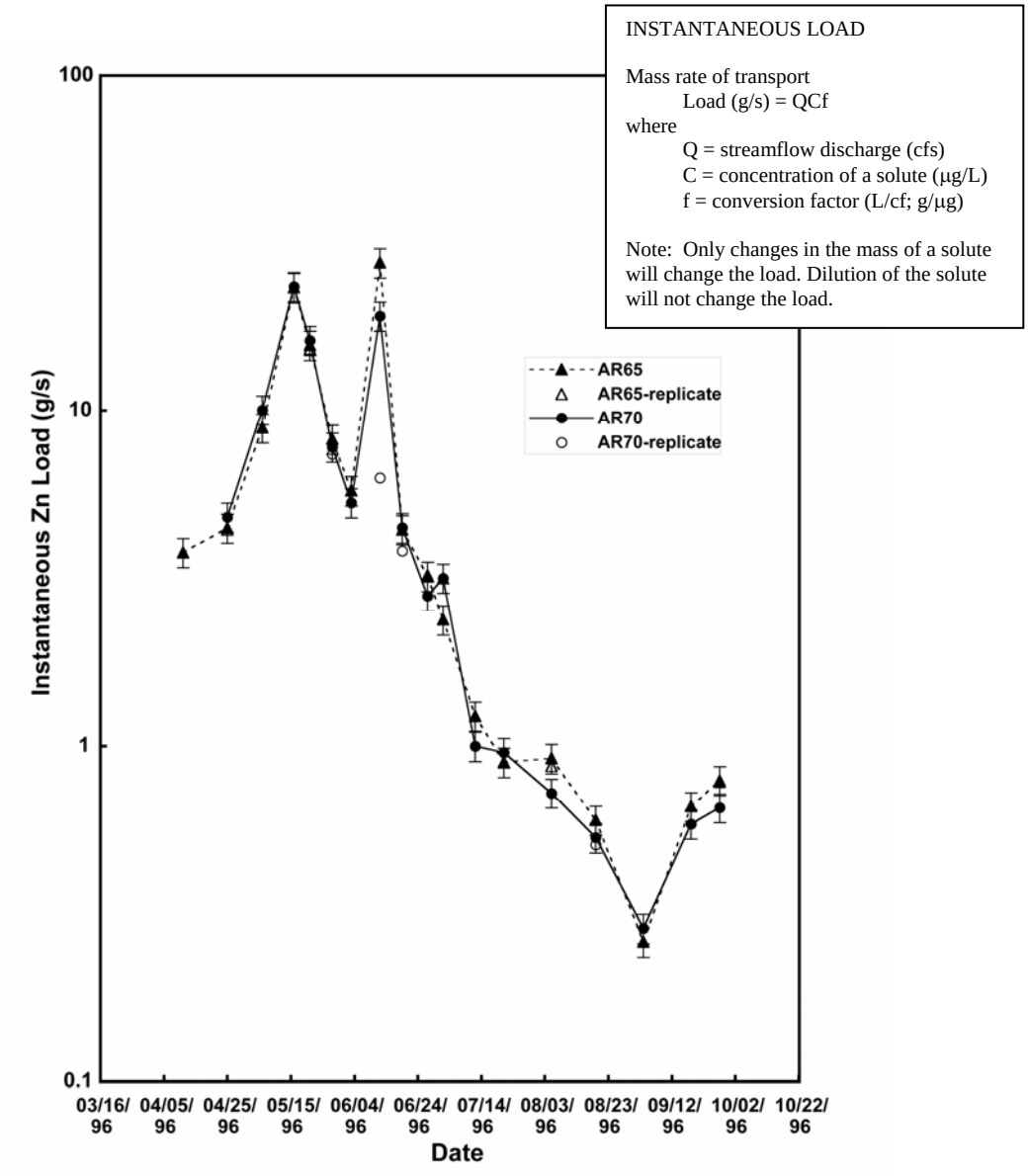

Figure 4 Instantaneous loads for unfiltered zinc concentration upstream (AR65) and downstream (AR70) from the study site for several dates

REMEDIATION IMPLICATIONS AT DIFFERENT OBSERVATIONAL SCALES

High concentrations of soluble metals at tailings-deposit surfaces have been explained by precipitation of hydrated metal sulfates resulting from soil moisture that is drawn to the surface and evaporated during warm, dry periods (Nimick and Moore, 1991; Bayless and Olyphant, 1993). We collected hydrated metal sulfate salts from the surface of the fluvial tailings deposit at the study site and dissolved them in deionized water (1:20 ratio). Iron concentrations were in the 1,000's mg/L, zinc in the 10's mg/L, manganese, copper, and lead in the 1,000's μg/L, and cadmium in the 100's μg/L. Dissolution of these salts probably is the source of most of the dissolved metals and acidity in leachates of tailings material from our study site. These salts may degrade water quality during storm events. Water-quality data from shallow ground-water wells indicate localized areas of elevated metal concentrations and acidity, but there is only a minimal effect on the quality

of the adjacent river water. It is likely that hydro-geochemical processes in the sediment column attenuate metals as they migrate through the fluvial tailings deposit. Some possible attenuation processes include dilution, precipitation of saturated mineral phases, sorption onto hydrated metal-oxide minerals (Walton-Day et al., 1996; Smith et al., 1998a) or organic material, and precipitation of sulfide phases in the organic-rich layer. Figure 5 shows the mean concentrations of selected metals for our four observational scales.

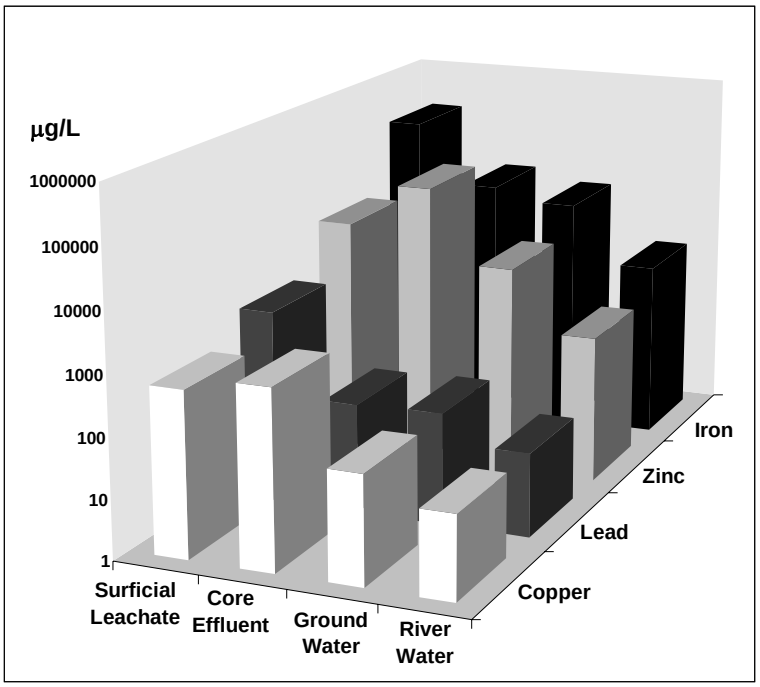

Figure 5 Three-dimensional bar graph showing mean concentration of copper, lead, zinc, and iron for four observational scales. Note general decrease as the scale changes from surficial material to river water.

When studies such as ours are done, the observational scale affects the results and interpretation at scientific, remediation strategy, and regulatory levels. The integration of the four scales of observation indicates that natural attenuation processes, including dilution, may decrease concentrations of some metals as the scale of observation goes from surficial samples to river-water samples. However, looking at any of these observational scales individually would not reveal any attenuation processes.

Remediation decisions depend on observational scale and on the remediation objectives. For example, if remediation objectives and the accompanying sampling plan only encompass water quality in the Arkansas River, our results indicate that the effects of the fluvial tailings are minimal, and no remediation may be necessary. However, if remediation objectives include the riparian ecosystem, it is clear that remediation is necessary to improve sediment and vegetation quality.

Since we did not evaluate storm events in our study, we do not know their short-term effects on water quality. Storm events have been shown to cause sudden influxes of metals into receiving streams in some mined areas (e.g., Nimick and Moore, 1991; Bayless and Olyphant, 1993; Ortiz et al., 1995; Wirt et al., this volume). In order to fully evaluate potential effects of the fluvial tailings on water quality, it would be necessary to develop a monitoring strategy that can evaluate the influence of storm events on water quality.

Our study illustrates that it is important to consider observational scale and remediation objectives when evaluating the effect of fluvial tailings on an ecosystem. Natural attenuation processes, including dilution, may play a role in metal transport from one observational scale to another. Collection of surficial samples likely represents a worst-case scenario since efflorescent salts tend to accumulate at the surface of the tailings deposit. With an awareness of the importance of observational scale, it may be possible to employ remediation actions that make use of the potential benefits of natural attenuation processes.

ACKNOWLEDGMENTS

We would like to acknowledge the landowner who has graciously allowed us to work on his property. Analytical chemistry was performed in the U.S. Geological Survey Mineral Resources Program Analytical Laboratories in Denver, Colorado, and at the Colorado School of Mines in Golden, Colorado. We acknowledge M. Adams, L. Gerner, P. Lamothe, A. Meier, and F. Rossi for their analytical assistance; J. Evans, P. Hageman, E. Sampson, M. Singleton, and C. Walker for their field assistance; J. Jerz and D. Macalady for their help with laboratory experiments; and J. Evans for his graphical assistance. S. Church, R. Leinz, R. Runkel, S. Wilson, D. Nimick, and D. Williams provided helpful reviews of this manuscript. This work was funded through the U.S. Geological Survey Toxic Substances Hydrology Program and the U.S. Environmental Protection Agency Rocky Mountain Headwaters Mining Waste Initiative.

REFERENCES CITED

Bayless, E.R., and G.A. Olyphant. 1993. Acid-generating salts and their relationship to the chemistry of groundwater and storm runoff at an abandoned mine site in southwestern Indiana, U.S.A. *Journal of Contaminant Hydrology* 12:313-328.

Colorado Division of Wildlife. 1998. *Fisheries inventories, Upper Arkansas River Basin*. Arkansas and Rio Grande River Basins Aquatic Biology Group, Colorado Department of Natural Resources, Division of Wildlife, 138 p.

Horowitz, A.J., C.R. Demas, K.K. Fitzgerald, T.L. Miller, and D.A. Rickert. 1994. *U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water*. U.S. Geological Survey Open-File Report 94-539.

Jerz, J.K. 1998. Mechanisms of acid and metal release from a fluvial tailings deposit. Golden: Colorado School of Mines, M.S. thesis.

Nimick, D.A., and J.N. Moore. 1991. Prediction of water-soluble metal concentrations in fluvially deposited tailings sediments, Upper Clark Fork Valley, Montana, U.S.A. *Applied Geochemistry* 6:635-646.

Ortiz, R.F., P.B. von Guerard, and Katherine Walton-Day. 1995. Effect of a localized rainstorm on the water quality of the Alamosa River upstream from Terrace Reservoir, south-central Colorado, August 9-10, 1993. In *Proceedings-Summitville Forum `95*, eds. H.H. Posey, J.A. Pendleton, and D. Van Zyl, 178-182. Colorado Geological Survey, Special Publication 38.

Rantz, S.E., and others. 1982a. *Measurement and computation of streamflow--v. 1, Measurement of stage and discharge*. U.S. Geological Survey Water-Supply Paper 2175, 1-284.

Rantz, S.E., and others. 1982b. *Measurement and computation of streamflow--v. 2, Computation of discharge*. U.S. Geological Survey Water-Supply Paper 2175, 285-631.

Shelton, L.R. 1994. *Field guide for collecting and processing stream-water samples for the National Water Quality-Assessment Program*. U.S. Geological Survey Open-File Report 94-455.

Smith, K.S., J.F. Ranville, G.S. Plumlee, and D.L. Macalady. 1998a. Predictive double-layer modeling of metal sorption in mine-drainage systems. In *Adsorption of metals by geomedia*, ed. E.A. Jenne, 521-547. San Diego: Academic Press.

Smith, K.S., S.J. Sutley, P.H. Briggs, A.L. Meier, Katherine Walton-Day, J.F. Ranville, and J.K. Jerz. 1998b. Trends in water-leachable lead from a fluvial tailings deposit along the upper Arkansas River, Colorado. In *Proceedings of the Fifth International Conference on Tailings and Mine Waste '98, Fort Collins, Colorado, January 26-29, 1998*, 763-768. Rotterdam: A.A. Balkema.

Smith, K.S., J.F. Ranville, P.J. Lamothe, A.L. Meier, and Katherine Walton-Day. 1999a. Metal leaching through a fluvial tailings deposit along the upper Arkansas River, Colorado. In *Proceedings of the Sixth International Conference on Tailings and Mine Waste '99, Fort Collins, Colorado, January 24-27, 1999*, 627-632. Rotterdam: A.A. Balkema.

Smith, K.S., Katherine Walton-Day, and J.F. Ranville. 1999b. Considerations of observational scale when evaluating the effect of, and remediation strategies for, a fluvial tailings deposit in the Upper Arkansas River Basin, Colorado. In *U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999--Volume 1 of 3--Contamination from Hardrock Mining*, eds. D.W. Morganwalp and H.T. Buxton, 131-138. U.S. Geological Survey Water-Resources Investigations Report 99-4018A.

URS Operating Services. 1997. *Sampling activities report, upper Arkansas River Fluvial Tailings, Leadville, Colorado*. URS Operating Services.

Walton-Day, Katherine, J.K. Jerz, J.F. Ranville, J.B. Evans, and K.S. Smith. 1996. Effects of fluvial tailings deposits on the quality of surface and ground water at a site in the upper Arkansas River basin, Colorado. In *Abstracts with Programs, Geological Society of America Annual Meeting, Denver, Colorado, October 28-31, 1996*, A-466.

Walton-Day, Katherine, F.J. Rossi, L.J. Gerner, J.B. Evans, T.J. Yager, J.F. Ranville, and K.S. Smith. In press. *Effects of fluvial tailings deposits on surface- and ground-water quality and implications for remediation--upper Arkansas River, Colorado, 1992-1996.* U.S. Geological Survey Water-Resources Investigations Report 99-4273.

Wirt, Laurie, K.J. Leib, and M.A. Mast. Chemical-constituent loads during thunderstorm runoff in a high-altitude alpine stream affected by acid drainage. This volume.