USE OF STABLE ISOTOPES TO EXAMINE METAL ATTENUATION AND RELEASE PROCESSES IN A FLUVIAL TAILINGS DEPOSIT [1,2]

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Abstract. The upper Arkansas River south of Leadville, Colorado, contains deposits of fluvial tailings from historical metal-mining operations. These sulfide-bearing deposits are possible non-point sources of acid and metal contamination to surface- and ground-water systems. We conducted a pilot study to evaluate the use of stable-metal isotopes to help ascertain metal retention and release mechanisms that influence metal transport from the deposits to shallow ground water. To accomplish this, we excavated an intact core from a small fluvial tailings deposit and performed laboratory column experiments to examine the amount of metals leaching through the core under different geochemical conditions. Deionized water was continuously applied to the top of the core, and effluent was collected from the bottom of the core for a period of about 2 months. The core was sequentially leached under unsaturated, partially saturated, and fully saturated conditions to simulate changing water-table levels within the deposit. Reducing conditions developed upon partial and complete saturation of the core. During all leaching phases, core effluents were acidic (pH 2.8-3.5) and contained elevated metal concentrations. During a portion of the unsaturated leaching phase, stable-metal isotope spikes (^{111}Cd, ^{65}Cu, ^{54}Fe, ^{207}Pb, and ^{68}Zn) were applied to the top of the core along with conservative tracers. None of the isotope spikes exhibited breakthrough with simultaneously added conservative tracers during the unsaturated leaching phase. However, some of the isotope spikes did break through when reducing conditions developed (during partial- and complete-saturation conditions). By comparing the behavior of metal-isotope spikes with total-metal concentrations in the effluent from the core, we were able to gain insights into geochemical conditions that might promote release of particular metals from the fluvial tailings deposits to the shallow ground-water system at our field site. Hence, use of stable-metal isotopes facilitated the determination of

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different metal-attenuation processes, metal-release processes, and metal sources in the fluvial tailings deposit in response to changing geochemical conditions.

Additional Key Words: cadmium, copper, iron, lead, zinc, prediction, geochemical, leaching, column experiments

Introduction

Tailings from historical mining operations near the Leadville, Colorado, area have been washed downstream and deposited along portions of the upper reaches of the Arkansas River over the past 100+ years (URS Operating Services, 1997, 1998). These tailings are mine wastes of processed gold, silver, lead, and zinc ores from the Leadville Mining District. The resulting fluvial tailings deposits are possible sources of acid and metal contamination to surface and ground water.

The upper Arkansas River has been the focus of a great deal of research on water-quality related impacts on the environment from past mining practices. Although water treatment facilities designed to remove metals have improved water-quality conditions for brown trout (the dominant species) in the upper Arkansas River, episodic metal releases and non-point sources of metals are still of concern (Colorado Division of Wildlife, 1998; Davies et al., 2000).

Our study site is located at one of these fluvial tailings deposits, approximately 13 km south of Leadville, Colorado. The site is about 0.1 km^2 in size, is relatively flat, and was virtually devoid of living vegetation (Fig. 1). The site is typical of numerous deposits along the upper Arkansas River, and was selected because of ease of access and because its lack of vegetation suggested potential impact of the deposit on adjacent ground and surface water. Our subsequent findings show that the local ground water beneath the fluvial tailings deposit exhibits lower pH and elevated metal concentrations (Walton-Day et al., 2000; Smith et al., 2000).

The fluvial tailings deposits along the upper Arkansas River are generally overbank and pointbar deposits containing fine-grained mixtures of tailings and other sediment. Material from the deposits is compositionally 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.

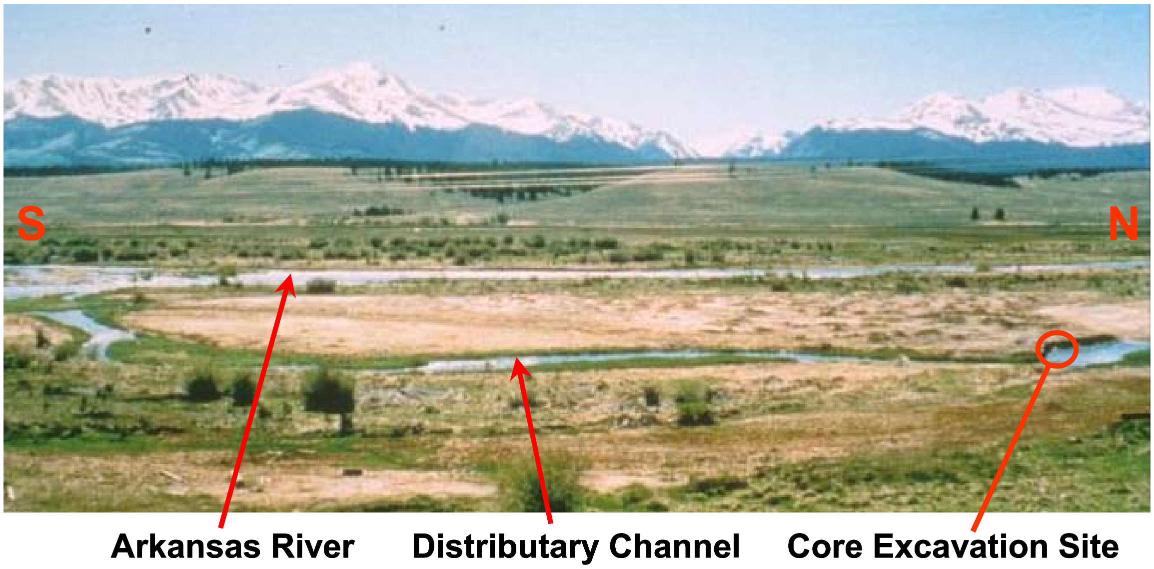

Figure 1. Photo of the study site showing the fluvial tailings deposit along the upper Arkansas River south of Leadville, Colorado.

The objective of our study was to evaluate the use of stable-metal isotopes to examine processes that control metal transport from the deposit to the underlying ground water. We excavated an intact 20-centimeter-diameter (60 cm in length) core of the deposit from the bank of a distributary channel that cuts through the deposit (Fig. 2). We sequentially leached the core in the laboratory under unsaturated, partially saturated, and fully saturated conditions for a period of about two months, and collected the effluent at various times. This procedure was intended to simulate the impact of water infiltration through the deposit (seasonally) and into the shallow ground-water system. We employed stable-metal isotope spikes to identify processes within the core that control metal retention and release in response to changing geochemical conditions. Related work at this study site is reported by Walton-Day et al. (1996, 2000), Jerz (1998), and Smith et al. (1998b, 1999a, 1999b, 2000).

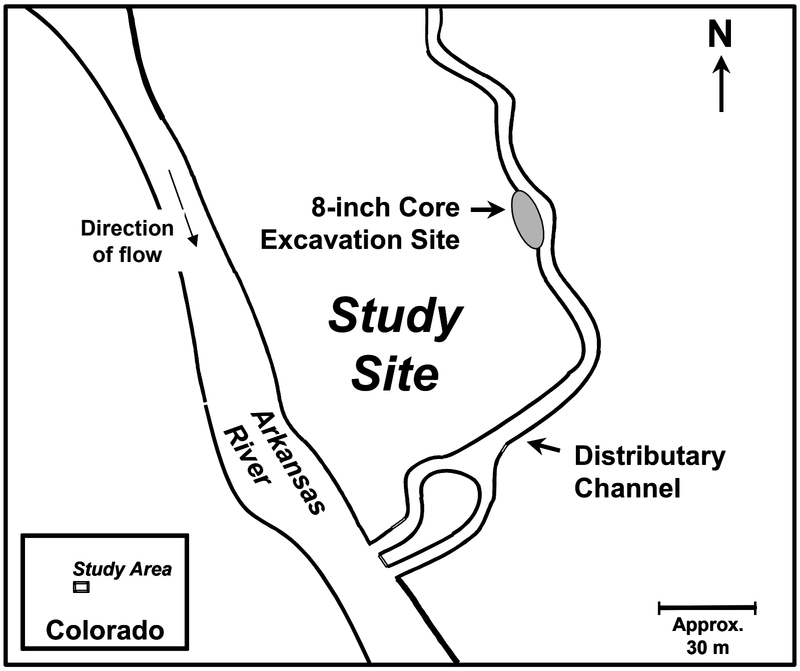

Figure 2. Map of the study site showing the excavation site of the 20-centimeter-diameter core along a distributary channel of the upper Arkansas River, Colorado.

Methods

Core Collection and Design

A 20-centimeter-diameter 60-centimeter-length core was excavated intact from the bank of a distributary channel that cuts through the fluvial tailings deposit (Figs. 1, 2, and 3). 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 sand and gravel aquifer 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 (side-wall flow, edge port), and water draining through the center part of the core, making full contact with the core material (center port). A perforated acrylic plate separates the cored material from the cap, and polypropylene cloth on top of the plate prevents fine material from passing from the cored material into the cap. The cap was filled with clean quartz sand to eliminate any void space.

Core Leaching Procedure

Three saturation conditions were used for the core leaching experiments, beginning with unsaturated, followed by partially saturated (lower half of the core flooded), and ending with fully saturated (entire core flooded). Effluent was collected in containers from both the center and edge ports at the bottom of the core (only data for the center port are reported in this paper). Effluent was collected at varying times, and sample volume, pH, and specific conductance were measured. Each effluent analysis represents a composite value over the time period between collection times. A total of 87 sequential effluent samples were collected over the 57-day period of the leaching experiment. Results presented in this paper are for unfiltered samples. Filtered samples (0.45 μm) were also collected, but little difference was noted between filtered and unfiltered results.

In the unsaturated flow core-leaching phase, deionized water was continuously dripped on the top of the core at a rate of 2 mL/min using a peristaltic pump (Fig. 4). The deionized water was allowed to freely drain by gravity through the core, which resulted in the unsaturated flow

Figure 3. Excavation of an intact 20-centimeter diameter 60-centimeter length core from a fluvial tailings deposit along the upper Arkansas River, Colorado.

conditions of the core.

A mixed isotope spike solution was introduced during the unsaturated flow phase (at about 265 hours). The spike solution consisted of ^{111}Cd, ^{65}Cu, ^{54}Fe, ^{207}Pb, and ^{68}Zn, with Na and ClO_4 added as conservative tracers. The mixed isotope solution was continuously dripped on the top of the core from 265 hours until 373 hours into the experiment. At 373 hours, deionized water was again continuously dripped on the top of the core. After 490 hours into the experiment, the drip rate was changed from 2 mL/min to 1 mL/min to determine if flow rate was an important factor.

At 565 hours, partial saturation conditions were introduced by allowing water in the core to back up from the bottom to flood up to about 15 cm from the top of the core (the water level was just below the pyritic zone of the fluvial tailings). Partial saturation was accomplished by raising the height of the outlet tube at the bottom of the core (with a continual deionized water drip rate of 1 mL/min on the top of the core). This partially saturated condition is intended to simulate rising of the underlying shallow ground water table into the fluvial tailings deposit. At about 912 hours, a ^{207}Pb isotope solution was introduced, which consisted of a ^{207}Pb spike with Li added as a conservative tracer. The ^{207}Pb isotope solution was continuously dripped on the top of the core

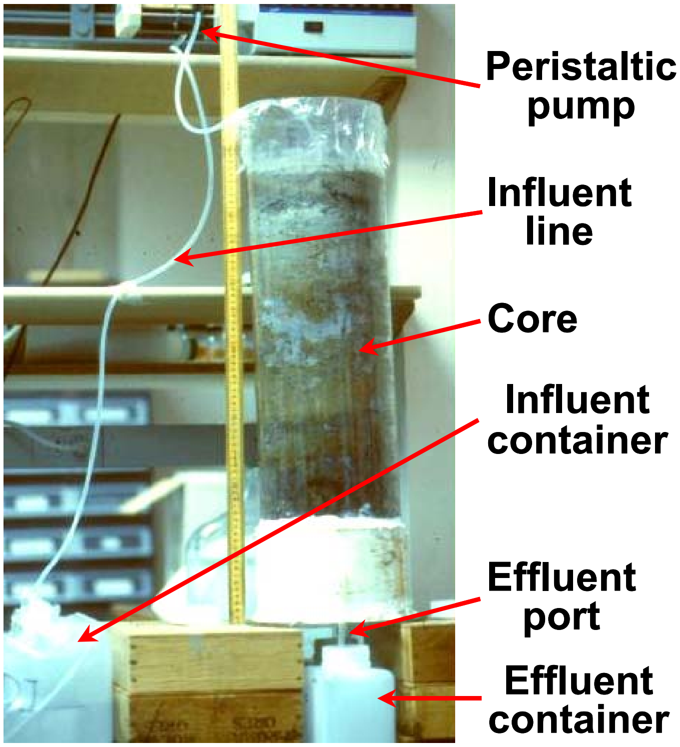

Figure 4. Setup for the core leaching experiments.

from 912 hours until 1,016 hours into the experiment. At 1,016 hours, a conservative tracer consisting of Na and ClO_4 was introduced and continuously dripped into the partially saturated core at a flow rate of 1 mL/min.

Complete saturation of the core was initiated at 1,152 hours into the experiment. At that time, the conservative tracer drip was changed to one containing Li, Na, and ClO_4. The complete saturation phase was maintained for about 9 days with continual dripping at a rate of 1 mL/min. At 1,271 hours, the tracer drip was replaced with a deionized water drip. The core was drained at 1,369 hours into the experiment.

During the partial and complete saturation phases, determination of ferrous iron, sulfate, and dissolved oxygen in the effluent was performed in addition to pH and specific conductance measurements. Ferrous iron and sulfate were determined using Hach® kits, and dissolved oxygen and sulfide were determined using CHEMetrics® kits. Acidified (nitric acid) subsamples of unfiltered effluent were analyzed for metals by inductively coupled plasma-mass spectrometry (ICP-MS; Lamothe et al., 2002). Analytical replicates were run on about 10 % of the samples.

Preparation and Determination of Stable Metal Isotope Spikes

Stable metal isotopes were purchased from the Oak Ridge National Laboratory, with ^{111}Cd, ^{65}Cu, ^{54}Fe, and ^{68}Zn in the oxide form, and ^{207}Pb in the carbonate form. The natural abundance of ^{111}Cd, ^{65}Cu, ^{54}Fe, ^{207}Pb, and ^{68}Zn is 12.8%, 30.8%, 5.8%, 22.1%, and 18.8%, respectively. The use of an enriched stable-isotope spike significantly shifts the isotope ratio away from the natural abundance, thus allowing the isotope spike to be discriminated in the core effluent. Isotope concentrations in the effluent were determined by ICP-MS. To discern different behavior of each isotope spike in the system, the isotope spike value was ratioed to another isotope (not used in the spike) of the same metal. This value was then ratioed to the natural abundance. If the isotope spike is enriched in the effluent, then the ratio of isotopic ratios is > 1. Hence, a ratio equal to 1 means that the introduced metal spikes are retained in the core, and a ratio greater than 1 means that the introduced metal spikes are released from the core. The added stable metal isotope spikes do not greatly perturb the metal balance within the core, but their concentrations are adequate to be individually detected by ICP-MS. The pH of the stable metal isotope spike solutions was within a pH unit of the effluent pH values.

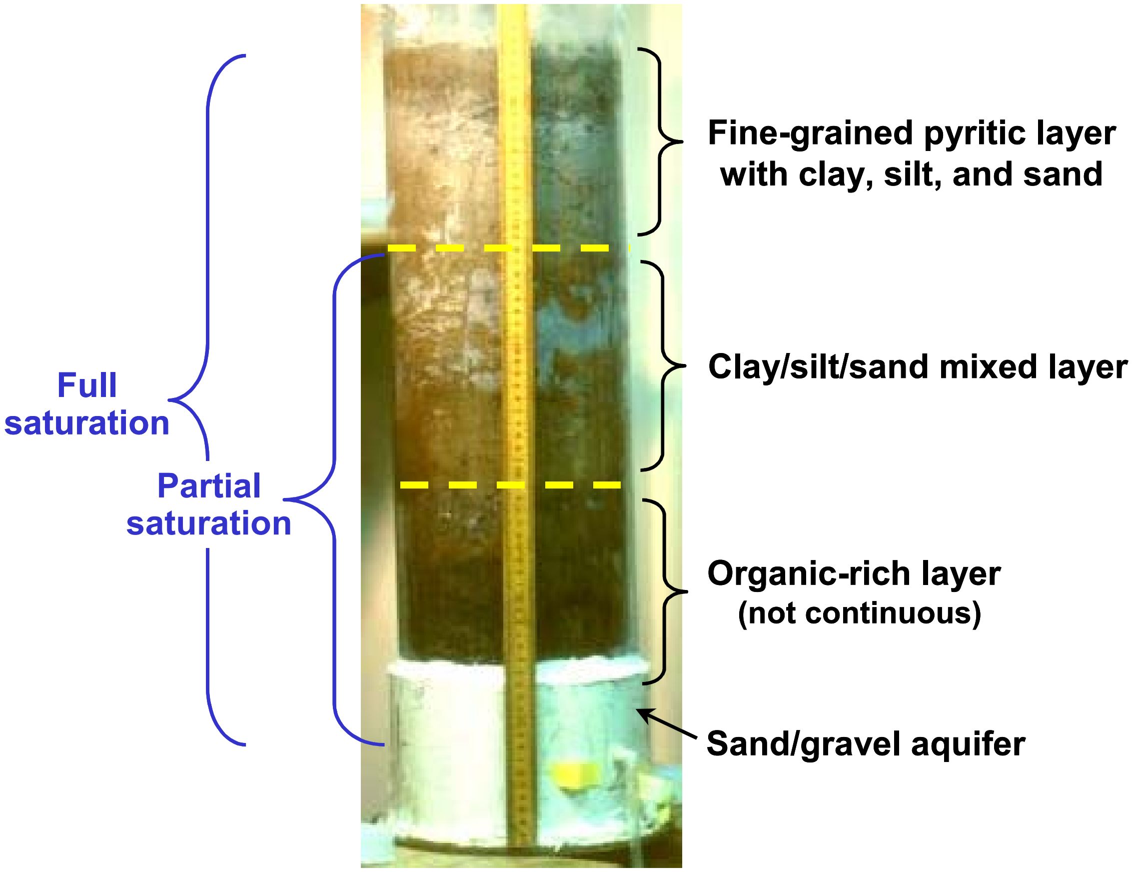

Figure 5. Graphic illustrating the spatial complexity of the intact 20-centimeter diameter 60-centimeter length core excavated from a fluvial tailings deposit along the upper Arkansas River, Colorado.

Results and Discussion

As described in the methods section, our core was collected intact. Consequently, the spatial heterogeneity of the fluvial tailings system was preserved in the core. Figure 5 shows the spatial variation of materials within the core. The top portion of the core 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 sand and gravel aquifer material. Composition of this core was determined by visual inspection. Adjacent cores of the fluvial tailings deposit were collected and mineralogically and chemically characterized (Smith et al., 1998b, 1999a). The dominant minerals are quartz, feldspar, and mica.

Our approach of collecting an intact core is intended to better simulate onsite field conditions. More traditional approaches, such as grab sampling, sampling of surficial material, batch or column studies with mixed materials from the site, or humidity cells, do not address the potential complexity of geochemical processes likely to take place in the field. For example, at our field site 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 (Smith et al., 1998a; Smith, 1999; Smith and Huyck, 1999) or organic material, and precipitation of sulfide phases in the organic-rich layer. Another advantage of using an intact core is the ability to simulate conditions of changing ground water levels. The partially and fully saturated conditions in our core leaching experiment are intended to simulate seasonal rising of the underlying shallow ground water table into the fluvial tailings deposit.

Effluents obtained from the core leaching experiment contained elevated metal concentrations, and had high specific conductance and low pH values (ranging from 2.8 to 3.5) (Fig. 6). This indicates that there is a reservoir of readily leachable material in the core, and that the sources of metals and acidity are from within the core itself. The results in Figure 6 also demonstrate that the deposit material can continue to generate acidity over long periods of time. After 900 hours of leaching, the pH levels off to about 3.3, and the conductivity reaches a near-constant value of about 700 μS/cm. This low pH and high conductivity, present even after over 100 liters of water (approximately 17 pore volumes) had been passed through the core, illustrate the long-term release of soluble constituents from the core, and likely from the fluvial tailings deposit. Given an average annual precipitation at the site of about 40 cm/year, this represents the amount of precipitation over a period of 7-8 years. Based on the mass of core material, the volume of water introduced over the course of the experiment, and 30 % porosity, the computed solid-to-solution ratio for the overall core leaching experiment is approximately 1:3. However, it is likely that not all parts of the core were fully contacted by the water due to preferential flow.

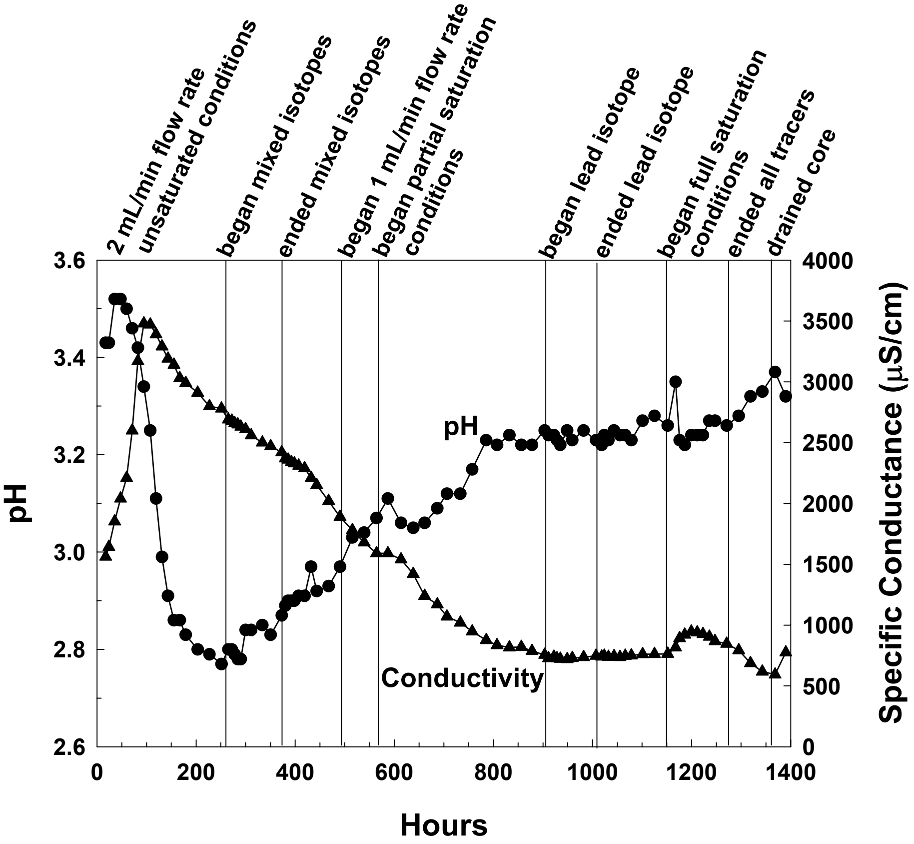

Figure 6. Specific conductance and pH of core effluents over the course of the leaching experiment.

Most metals exhibited a large spike in concentration early in the leaching process followed by a gradual decrease in concentration (Fig. 7 and Fig. 8). High concentrations of soluble metals from tailings deposits have been explained by precipitation of hydrated metal-sulfate salts 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 our study site and dissolved them in deionized water (1:20 ratio). Iron concentrations were in the 1,000s mg/L, Zn in the 10s mg/L, Mn, Cu, and Pb in the 1,000s μg/L, and Cd in the 100s μg/L. Similar salts were present in the top portion of our core, and these salts were visibly depleted over the course of the leaching experiment. Hence, dissolution of salts is the likely source of most of the metals and acidity in the core effluents, which is consistent with the observed rapid release of metals.

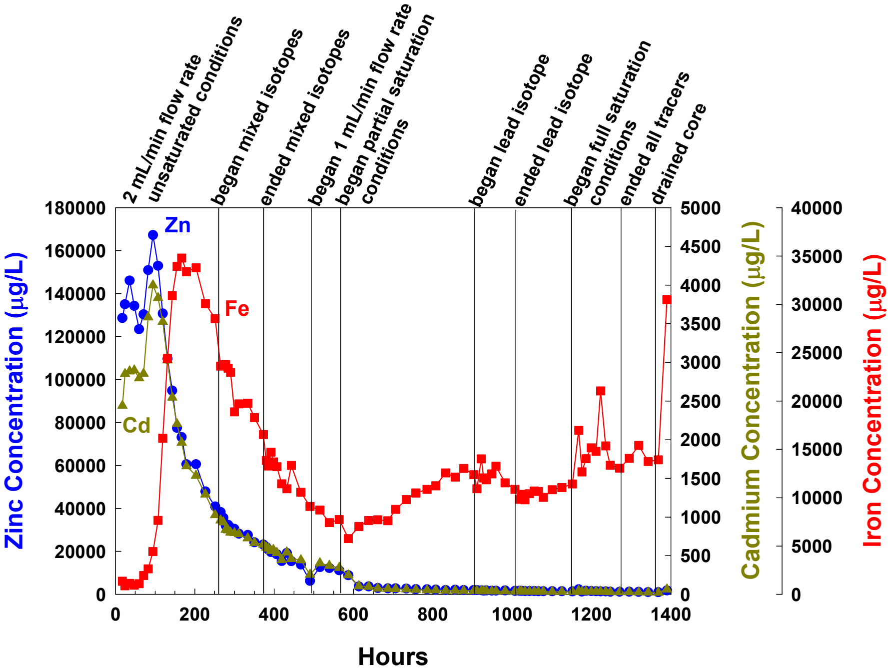

Figure 7. Total iron, zinc, and cadmium concentrations in core effluents over the course of the leaching experiment.

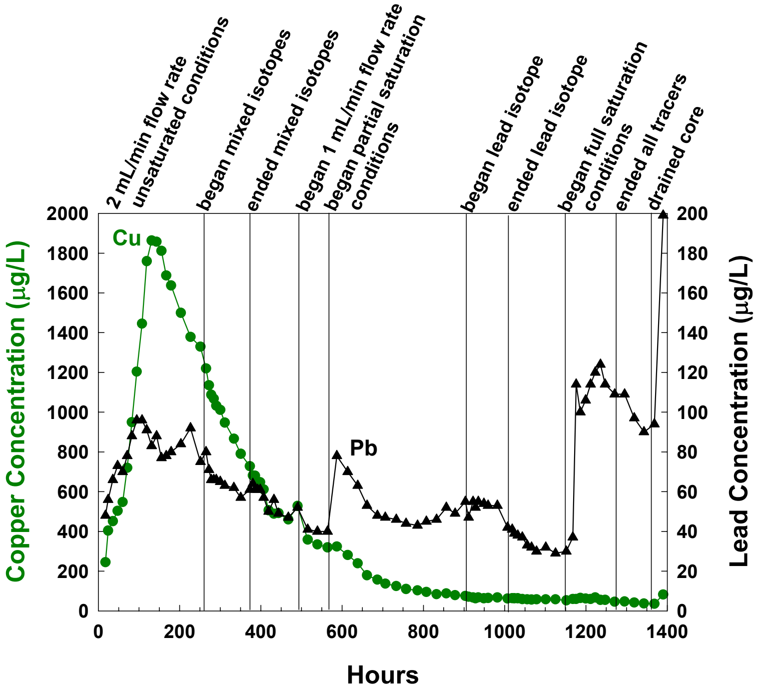

Figure 8. Total copper and lead concentrations in core effluents over the course of the leaching experiment.

Total Fe concentration gradually increases upon partial and complete saturation of the core (Fig. 7). This increase corresponds to the detection and subsequent increase in ferrous iron concentrations in the effluent, and indicates that reductive dissolution of iron oxides is taking place within the core. The behavior of total Pb (Fig. 8) is different from the other metals in that there is a less obvious peak in concentration and a very broad tail. There are also spikes in the total Pb concentration upon partial and complete saturation of the core (Fig. 8).

Figure 9 shows the tracer concentrations in the core over the course of the leaching experiment, and Figure 10 shows the isotope ratios for the stable metal isotope spikes added to the core. The tracers, including ClO_4, Na, and Li, all exhibited breakthrough shortly after they were introduced into the core (Fig. 9). In contrast, none of the stable metal isotope spikes exhibited breakthrough during the unsaturated phase of the leaching experiment (Fig. 10). This indicates that the spiked metals were being retained in the core. Iron exhibits some erratic behavior, which is difficult to interpret. When partial saturation conditions are introduced (along with subsequent anoxic conditions and reductive dissolution of iron phases), Cd and Zn isotope ratios indicate that the spikes are partially released from the core. This partial release of the spiked Cd and Zn is likely a result of the reductive dissolution of iron phases with which the metals were associated. In contrast, Cu and Pb spikes do not show any release from the core. Copper and Pb are more strongly sorbed by hydrous iron oxides than are Cd and Zn (Smith, 1999), which might explain the preferential release of spiked Cd and Zn from the core. Alternate explanations might include 1) Cu and Pb release followed by precipitation inside the core (perhaps as sulfide minerals or anglesite ($PbSO_4$)), or 2) Cu and Pb release followed by resorption onto another phase (perhaps in the organic-rich layer near the bottom of the core (see Fig. 5)).

Another interesting contrast is the difference in metal behavior when total metal concentrations are compared with isotope ratios. In the case of Cd and Zn, total concentrations in the core effluent (Fig. 7) show little variation when anoxic conditions develop (during the partial and full saturation phases of the experiment). Conversely, isotope ratios for Cd and Zn (Fig. 10) indicate increased concentrations of metal isotope spikes in the effluent (i.e., release of spiked Cd and Zn from the core). In the case of Pb, total concentrations in the core effluent (Fig. 8) are variable, and total concentration increases both when partial saturation and full saturation conditions are initiated. Conversely, the Pb isotope ratio (Fig. 10) remains constant at 1.0. In the

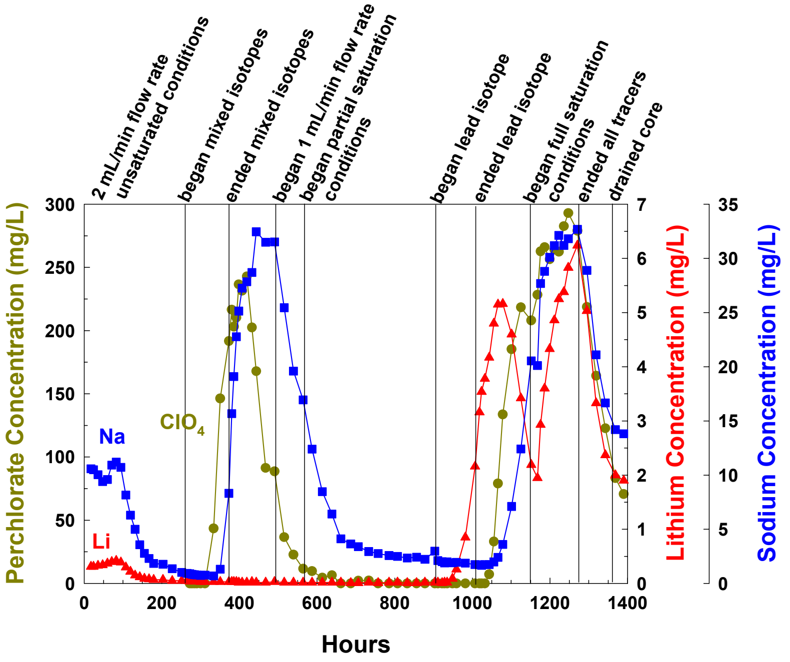

Figure 9. Total lithium, sodium, and perchlorate conservative tracer concentrations over the course of the leaching experiment.

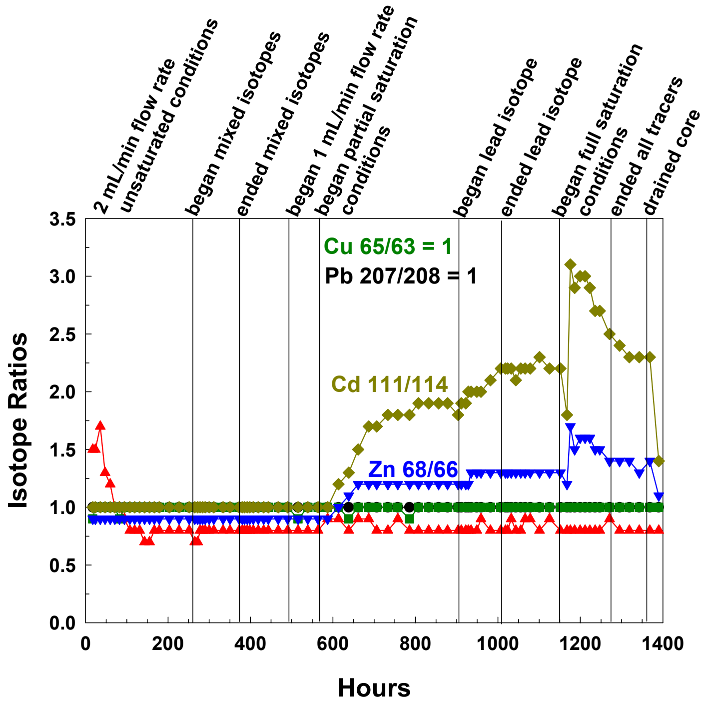

Figure 10. Isotope ratios for stable metal isotope spikes added to the core during the leaching experiment.

case of Cu, both total concentration in the core effluent (Fig. 8) and the Cu isotope ratio (Fig. 10) show little variation during the partial and full saturation phases of the experiment.

These contrasts between the behavior of total metal concentrations and isotope ratios in the core effluents highlight the utility of stable metal isotopes to distinguish between different metal release and retention processes. The behavior of Cd and Zn indicates that they become mobile under anoxic conditions. Hence, during seasonal fluctuations of the shallow water table beneath the fluvial tailings deposit, Cd and Zn would be expected to be more mobile when the water table is high. The behavior of Pb indicates that there is likely a combination of sorption and solubility mechanisms that control Pb retention and release in the core. The reasoning behind dual mechanisms for Pb is that the increases in total Pb concentration in the effluent do not correspond with fluctuations in the Pb isotope ratios. Therefore, the source of total Pb in the effluents originates from something present in the core, rather than from the introduced Pb isotope spike. Anglesite was determined to be present in the fluvial tailings deposit material (Smith et al., 1998b); hence, there may be a dynamic steady state involving anglesite solubility in the core. The behavior of Cu indicates that Cu is strongly retained under both oxic and anoxic conditions and therefore would not be expected to be very mobile in the fluvial tailings deposit system.

Summary

We conducted a pilot study to evaluate the use of stable-metal isotopes to help ascertain metal retention and release mechanisms that influence metal transport from a fluvial tailings deposit to the underlying ground water. To accomplish this, we excavated an intact core from a small fluvial tailings deposit and performed laboratory column experiments to examine the amount of metals leaching through the core under different geochemical conditions.

We found that the advantages of collecting an intact core include (1) preservation of the spatial heterogeneity of the fluvial tailings system, and (2) the ability to simulate changing hydro-geochemical conditions found in the field. More traditional approaches, such as grab sampling, sampling of surficial material, batch or column studies with mixed materials from the site, or humidity cells, cannot address the potential complexity of geochemical processes likely to take place in the field.

The intact core was transported to the laboratory and sequentially leached under unsaturated, partially saturated, and fully saturated conditions for a period of about two months. The core effluent was collected at various times. The different saturation conditions were intended to simulate seasonal changes, including water infiltration through the deposit and into the shallow ground-water system, and rising water-table levels into the deposit. The different saturation conditions also were able to simulate changing geochemical conditions (e.g., oxic/anoxic or pH fluctuations) likely to take place under field conditions. During all leaching phases, core effluents were acidic (pH 2.8-3.5) and contained elevated metal concentrations, and reducing conditions developed upon partial and complete saturation of the core.

We evaluated the use of stable-metal isotope spikes to help identify processes within the core that control metal retention and release in response to changing geochemical conditions. By comparing the behavior of metal-isotope spikes with total-metal concentrations in the effluent from the core, we were able to gain insights into geochemical conditions that might promote release of particular metals from the fluvial tailings deposits to the shallow ground-water system at our field site. For example, Cd and Zn appear to be mobilized under anoxic conditions whereas Cu does not appear to be mobile under either oxic or anoxic conditions.

The combination of use of intact material from the field site and use of stable metal isotopes in this study facilitated determination of different metal-attenuation processes, metal-release processes, and metal sources in the fluvial tailings deposit in response to changing geochemical conditions. Consequently, the use of stable-metal isotopes seems to be promising for revealing important processes that influence metal transport in natural systems.

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