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Trends in water-leachable lead from a fluvial tailings deposit along the upper Arkansas River, Colorado

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ABSTRACT: Fluvial deposits of mine tailings occur along the upper Arkansas River south of Leadville, Colorado. We examined material collected from a small fluvial tailings deposit (approximately 0.1 km²) located about 13 km downstream of Leadville. The deposit is predominantly barren of living vegetation. We collected continuous cores of one-inch diameter that ranged from 10 to 58 cm deep. We separated the cored material into visually distinct sections based on color and textural differences, and determined bulk chemical composition, mineralogy, and water-leachable chemical constituents for the distinct sections. There is a large reservoir of water-leachable lead in the fluvial tailings deposit. Comparison of bulk lead and water-leachable lead concentrations reveals that bulk lead concentrations are not a good indicator of water-leachable lead concentrations.

1 INTRODUCTION

The floodplain of the upper Arkansas River, south of Leadville, Colorado, contains several deposits of fluvial tailings. These deposits are a possible nonpoint source of acid and metal contamination to surface and ground water. Studies at other fluvial tailings sites document that stormwater runoff from tailings can be a source of acidity and metals to surface water (Nimick & Moore 1991). In our study we examine the water-leachable chemistry, bulk chemistry, and mineralogy of selected sediment cores collected from a fluvial tailings deposit along the upper Arkansas River. We discuss our results for lead in this paper.

2 STUDY SITE DESCRIPTION

The study site is in the upper Arkansas River basin approximately 13 km south of Leadville, Colorado (Figure 1). The size of the site is about 0.1 km². There is a distributary channel that flows through the study site and the tailings mainly are deposited between the Arkansas River channel and the distributary channel. The tailings deposits generally are fine-grained overbank deposits containing mixtures of tailings and other sediment. The tailings are composed of mine waste washed downstream from the Leadville Mining District, which contains gold, silver, lead, and zinc ores mined over the last 100+ years. The study site is predominantly barren of living vegetation, but there are vestiges of dead willows. Recently the land use in the area has been for cattle grazing.

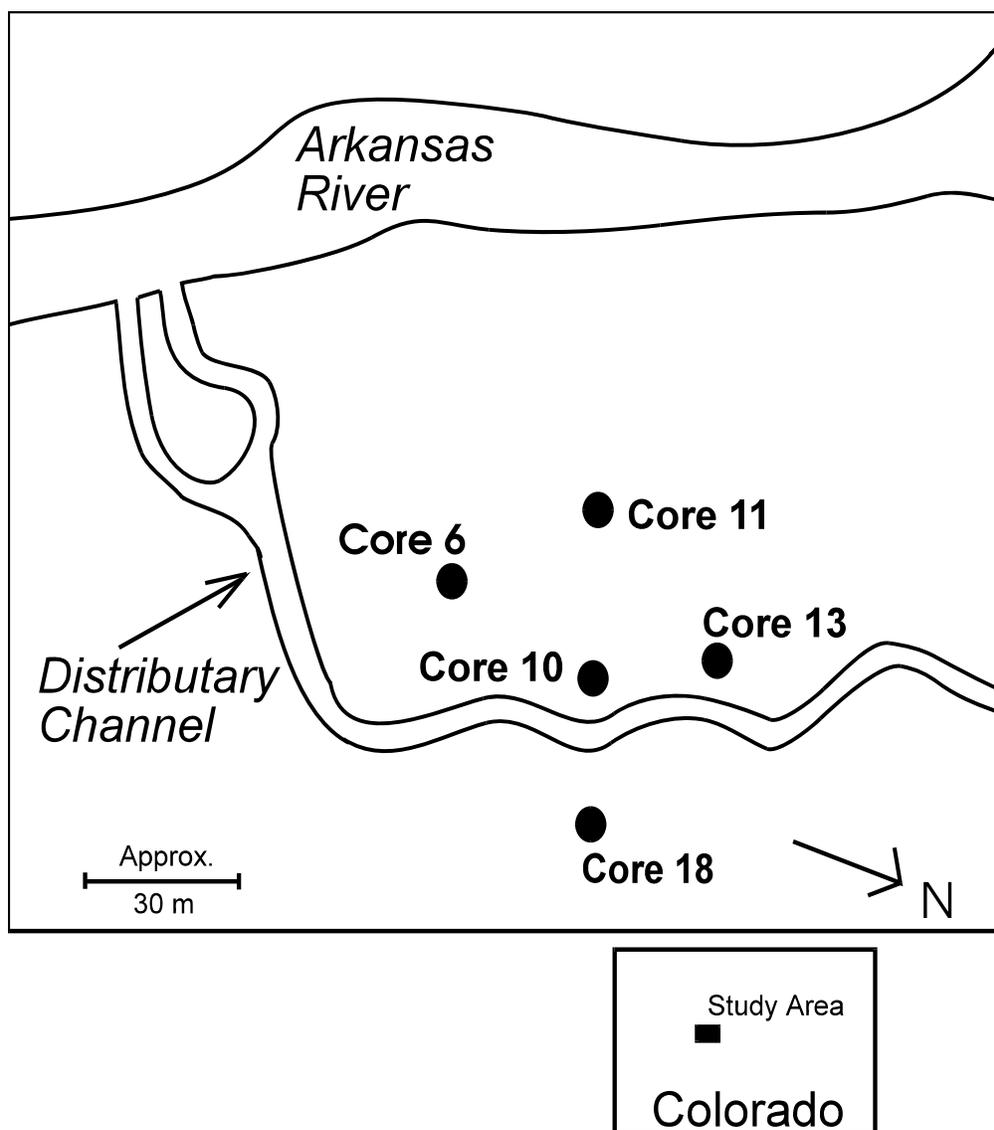


Figure 1. Schematic of the study area showing location of sediment cores.

3 METHODS

We used a one-inch stainless steel soil corer with plastic liners to collect 20 continuous cores ranging from 10 to 58 cm deep. Data from five selected cores are presented in this paper (see Figure 1 for location of cores). Upon air drying, we separated the cored material into visually distinct segments based on color and textural differences, and determined water-leachable constituents, bulk chemical composition, and mineralogical composition of the segments as a function of depth.

Water extracts of core segments were made by combining 2 g of sample with 40 g of deionized water. The mixtures were shaken for 3 hours and filtered through a 0.45 μm filter. Extracts were acidified with nitric acid and analyzed by inductively coupled argon plasma - mass spectroscopy (ICP-MS). ICP-MS can directly determine as many as 70 elements in a sample with detection limits in the sub-part-per-billion range and a linear range of nine orders of magnitude or more without the need for dilution. Calibration for this elemental coverage is accomplished by using a standard containing known concentrations of some of the elements across the elemental mass range to construct a response curve for the instrument. By using the

response curve derived, the degree of ionization, and the natural isotopic abundance, quantitative estimates of concentration for all elements can be made in samples without the need for a calibration standard for every element. The main limitations of the technique come from drift due to clogging of sampling orifices, changes in ion transfer efficiencies due to sample matrix effects, plasma conditions, nebulizer, or electronics, and isobaric interference from polyatomic or doubly charged ions. Internal standards are used to correct for drift; interference is minimized by selection of the isotope used for determination or by mathematical correction.

Semi-quantitative mineralogy was determined for pyrite and jarosite in selected cores using x-ray diffraction (Klug & Alexander 1974). Percentages of pyrite and jarosite were determined using pyrite from the core samples and jarosite from the Skouriotissa Mine, Cyprus, as calibration standards for semi-quantitative mineral determinations. Relative standard deviation is $\pm 20\%$ of the reported value. Values should not be used as absolute numbers but rather as relative concentrations from one sample to another. Qualitative mineralogy was determined for other constituents by x-ray diffraction.

Bulk chemistry was determined for core segments using inductively coupled argon plasma - atomic emission spectroscopy (ICP-AES). Samples were completely digested using a mixture of HCl, HNO₃, HClO₄, and HF acids for this analysis (Briggs 1996).

4 RESULTS AND DISCUSSION

4.1 *Deposit mineralogy*

Based on visual inspection, cored material from the fluvial tailings deposit is very heterogeneous. However, some generalizations can be made. Generally the top of the deposit 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 is organic-rich underlain by a sand and gravel shallow aquifer. The dominant minerals are quartz, feldspar, and mica.

Figure 2 illustrates semiquantitative pyrite and jarosite content in selected cores as a function of depth. The pyrite and jarosite content of the cores is extremely variable. Pyrite content in the cores ranges from less than detection (detection limit is about 2%) to nearly 80%, and jarosite content ranges from less than detection to 23%. Jarosite is predominantly in the hydronium form. Although jarosite is a possible weathering product of pyrite, there is no consistent relationship between pyrite and jarosite content in the cores.

4.2 *Deposit chemistry*

Figure 3 shows water-leachable lead concentrations and bulk lead concentrations as a function of depth in the cores. Both water-leachable and bulk lead concentrations generally are greater near the top of the cores. High concentrations of soluble metals at a tailings-deposit surface have been explained by precipitation of hydrated metal sulfates resulting from soil moisture that is drawn to the surface and evaporated during warm weather (Nimick & Moore 1991). It is clear that there is a large reservoir of water-soluble lead at or near the surface of this tailings deposit. There is little evidence of downward lead migration in cores 6 and 11. However, cores 10, 13, and 18 show elevated water-leachable lead concentrations below the surface layer. This may be indicative of lead migration in these cores or evidence of evaporation at greater depth due to coarser grain sizes in these cores.

The range in lead concentrations is highly variable (see axis scales in Figure 3). Figure 4 illustrates that there is no consistent relationship between bulk lead concentration and water-leachable lead concentration. For example, the top portion of core 6 contains 30,000 ppm bulk lead of which 980 $\mu\text{g/L}$ (≈ 0.98 ppm or about 0.003% of the bulk content) are water soluble. For comparison, the middle portion of core 18 contains 4,200 ppm bulk lead of which 5,500 $\mu\text{g/L}$ (≈ 5.5 ppm or about 0.1% of the bulk lead content) are water soluble. It appears that the bulk lead content is not a good predictor of water-leachable lead concentrations in this system.

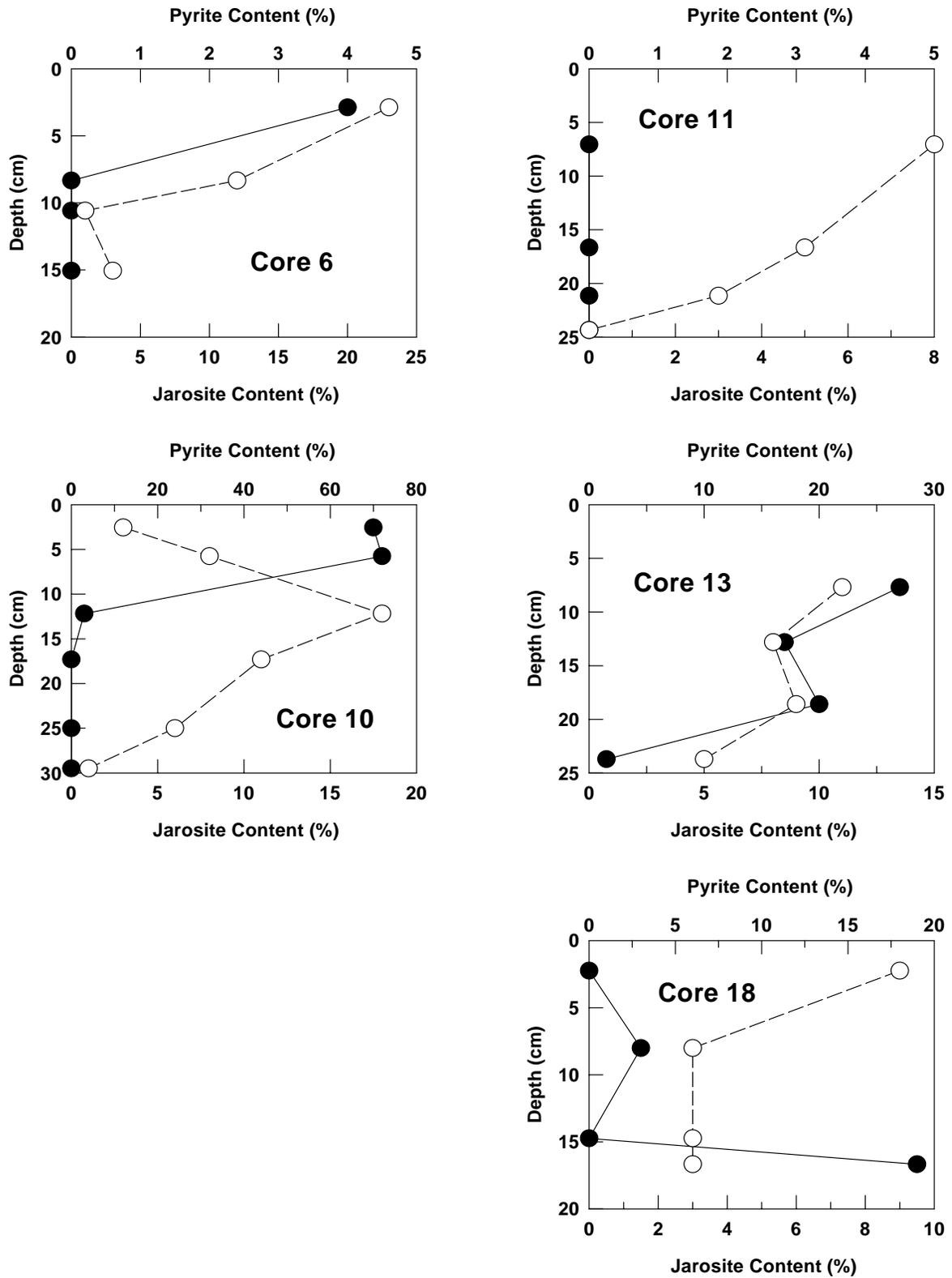


Figure 2. Depth profiles of semiquantitative pyrite (filled circles) and jarosite (open circles) content in selected cores collected from a fluvial tailings deposit along the upper Arkansas River, Colorado.

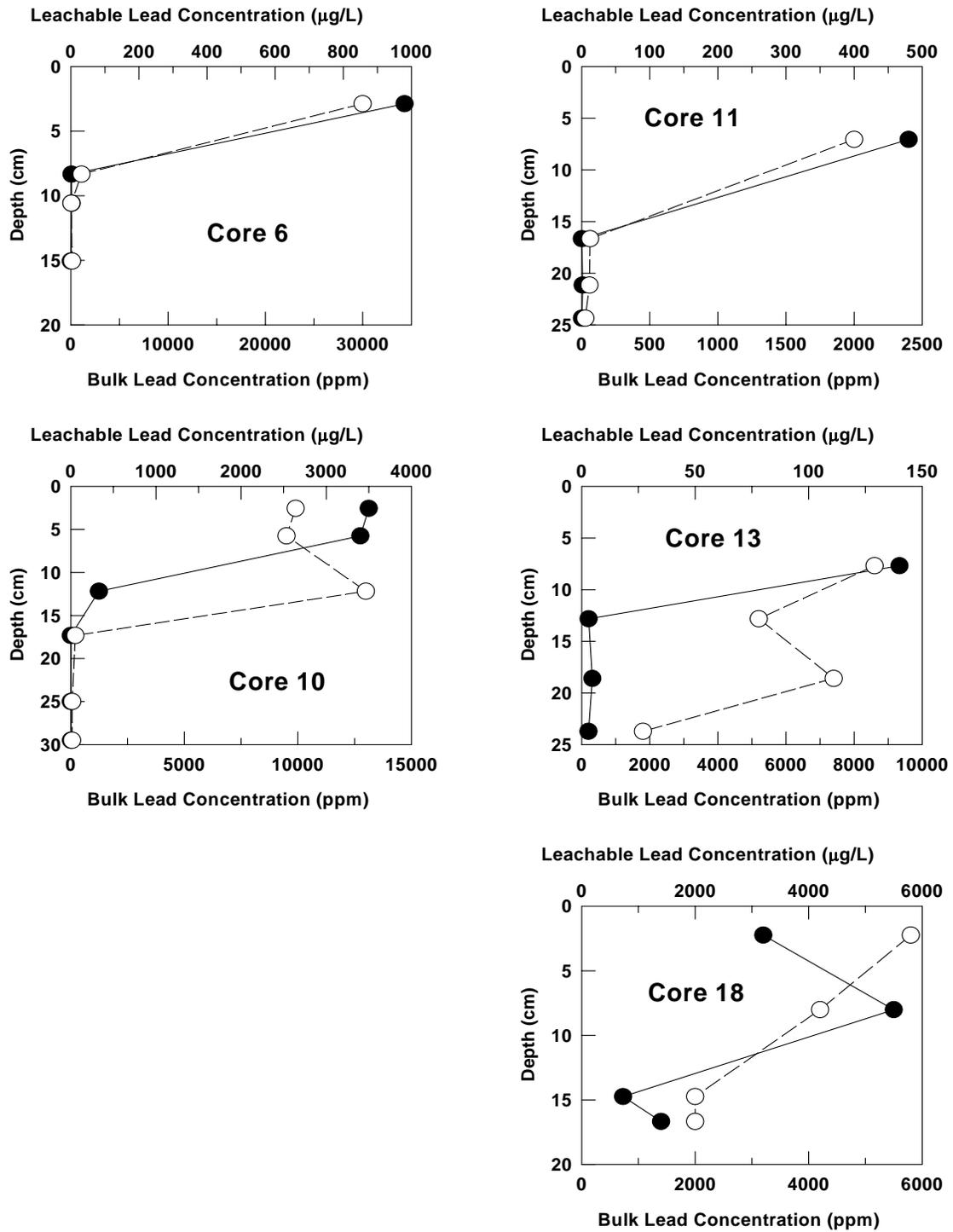


Figure 3. Depth profiles of water-extractable lead (filled circles) and bulk lead (open circles) concentrations in selected cores collected from a fluvial tailings deposit along the upper Arkansas River, Colorado.

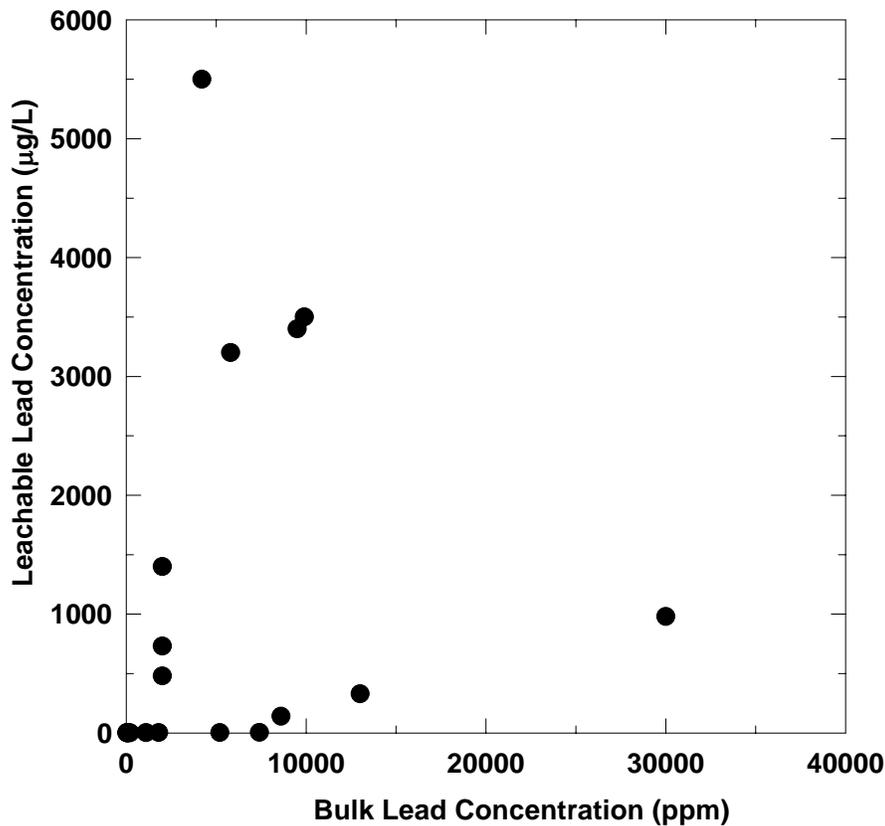


Figure 4. Bulk lead concentrations versus water-leachable lead concentrations for samples collected from a fluvial tailings deposit along the upper Arkansas River, Colorado.

However, bulk lead concentrations are much greater than water-leachable lead concentrations, so only a small fraction of the bulk lead content is water soluble.

Vertical profiles of water-leachable lead do not necessarily follow those for bulk lead. Bulk lead and water-leachable lead follow the same trend in cores 6 and 11, but the trends are very different in cores 10, 13, and 18 (see Figure 3). Therefore, bulk lead vertical profiles are not a good predictor of trends in water-leachable lead concentrations in this system.

5 SUMMARY AND CONCLUSIONS

Bulk lead and water-leachable lead concentrations were compared in cores collected from a fluvial tailings deposit. The following points summarize our findings.

1. There is a large reservoir of surface or near-surface water-soluble lead in the fluvial tailings deposit.
2. Bulk lead concentrations cannot be used to predict water-leachable lead concentrations.
3. Vertical trends in water-leachable lead concentrations cannot be reliably predicted from trends in bulk lead concentrations.

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REFERENCES

- Briggs, P.H. 1996. Forty elements by inductively coupled plasma-atomic emission spectrometry. In B.F. Arbogast (ed.), *Analytical methods manual for the Mineral Resource Surveys Program, U.S. Geological Survey: 77-94*. U.S. Geological Survey Open-File Report 96-525.
- Klug, H.P. & L.E. Alexander 1974. *X-ray diffraction procedures for polycrystalline and amorphous materials, 2nd edition*. New York: John Wiley and Sons.
- Nimick, D.A. & 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.