

Incongruent weathering of Cd and Zn from mine tailings

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ABSTRACT

Weathering of discharged mine tailings contaminates streams, rivers and floodplains with toxic metals on a vast scale. The magnitude of the problem depends on input tailings mineralogy, storage and dispersal, and climatic conditions. To better understand the mechanisms of long-term tailings weathering, a leaching column study was established, incorporating tailings and soil from Potosí, Bolivia, with the aim of modelling a 25 year field period. The Zn/Cd molar ratio of the tailings leachate water, initially 738 for the unaltered tailings, is highly variable over 15 model years of leaching, particularly in the mixed tailings-soil columns. Columns with soil have ratios as high as 2563, while pure tailings columns reach ratios of <376. We employ complementary techniques, involving atomistic computational modelling, leachate analysis and mineralogical characterization, to elucidate the mechanisms governing these incongruent Cd and Zn weathering dynamics.

Introduction

MINE tailings are a significant source of potentially toxic metallic elements to fluvial environments when discharged directly to rivers either intentionally or accidentally during tailings dam spills (Hudson-Edwards *et al.*, 2001, 2003). These tailings add to the sediment load of river systems, where they are deposited in channels and floodplains. Once deposited, they undergo accelerated chemical weathering, releasing metallic elements such as Cd and Zn to waters, sediments and organisms. To fully understand the short- to long-term fate of Cd and Zn in fluvial systems, quantitative data on weathering leachate compositions and Cd and Zn speciation in the tailings and their secondary weathering products are required.

Potosí, Bolivia, was the world's richest city for almost two centuries since its foundation in 1546, with a population equal to London and larger than that of Paris or Rome (Pretes, 2002). The silver mines of the adjacent Cerro Rico were remarkably rich, with initial grades near 19% Ag (Waltham,

2005). Currently there are many small-scale mining cooperatives at Potosí, and Zn is the principal metal extracted. The ore is crushed in small-scale mills and the tailings are frequently discharged directly into nearby rivers and streams or are stored in impoundments behind often unstable dams. Dam breaks, for example at Porco in 1996 where 235,000 m³ of tailings were released into the Pilcomayo River, have severe environmental consequences (Hudson-Edwards *et al.*, 2001; Miller *et al.*, 2004). Metals from such tailings-dam spills and from direct discharge have contaminated Pilcomayo floodplain sediments with Cd and Zn for at least 200 km downstream of the mines (Hudson-Edwards *et al.*, 2001). The aim of the current study is to better understand the mechanisms of Cd and Zn release during long-term mine tailings weathering and floodplain storage through leaching-column studies on tailings and soil from Potosí, Bolivia.

Methods

Leaching experiments were conducted using four opaque HDPE columns (5.5 cm diameter × 55 cm

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high). Two columns contained 850 g of tailings only, a third column 500 g of floodplain soil from the Río Pilcomayo mixed thoroughly with 100 g of tailings, and the fourth, a mixture of soil and tailings as in column 3, but with a 50 g surface layer of pure tailings to simulate a tailings dam spill. To reproduce wet season conditions, 200 ml of 6 μM CaSO_4 , adjusted where necessary to pH 5–6 with H_2SO_4 to mimic the composition of continental-type Bolivian rainwater, was added to the columns weekly for three weeks. The columns were then allowed to dry for three weeks to simulate dry-season conditions. Each 6-week cycle represents a modelled field year of weathering. All solutions added to the columns were prepared with high-purity water (18 M Ω Milli-Q; Millipore). Leachate volume, pH and conductivity were measured bi-weekly during the model ‘wet’ seasons, and the leachate waters subsequently filtered to 0.2 μm . Ten and 30 mL sub-samples were then collected for anion and cation analysis, respectively. The cations were stabilized by the addition of 100 μl of 50% v/v HNO_3 and stored in acid-washed bottles until analysis. Anions (Cl^- , SO_4^{2-}) were analysed by ion chromatography (Dionex ICS-2500), Cd by ICP-MS (Varian 810) and Zn by ICP-AES (Varian VISTA PRO). Data quality was monitored by measuring element concentrations in laboratory blanks and in certified reference materials (ION-96.3 and TMDA-64 from the National Water Research Institute, Environment Canada), and by analyzing duplicates of 50% of the leachate samples.

Results and discussion

Fifteen model years of column leaching have been completed. For each model year, masses of Cd and Zn in the leachates show an inverted V-shape, with particularly large metal masses released in the first two model years (e.g. 3.8 mg Cd, 1140 mg Zn in model year one), a sharp decline in model year 3, a slight rise in model year 4, rises in model years 9 to 12, and declines again thereafter (Fig. 1). Within each model year, masses of Cd and Zn in the leachates rise above the previous year’s final masses after the first rainwater addition, rise sharply after the second addition, then decline after the third addition (Fig. 1). We interpret the first rise as a ‘wash out’ due to the dissolution of soluble Cd and Zn salts that formed (possibly by evaporation) and the flushing out of metal-rich pore waters, which accumulated during the model dry seasons (cf. Drever, 1997). This phenomenon has been observed previously for major ion concentrations in the Río Pilcomayo (Smolders *et al.*, 2004), and emphasizes the importance of a full seasonal water sampling regime to capture the complete temporal variability in water chemistry. We attribute the second rise in leachate Cd and Zn masses to the dissolution of Cd- and Zn-bearing tailings minerals by the model rainwater. The decline in metal concentrations after the third rainfall event is interpreted as due to the formation of secondary minerals within the columns, or a decline in mineral dissolution rates.

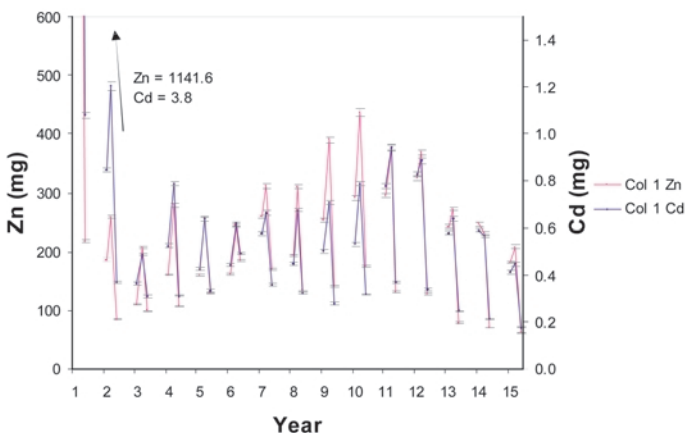


FIG. 1. Masses of Cd and Zn in leachate waters from the tailings-only filled Column 1. Data points for leachate resulting from the three irrigation events per simulated year are joined. Each data point is a mass summation of two individual collections. The first irrigation produced no leachate, so model year one is represented by two data points only. Columns 2 to 4 show similar trends. Error bars represent the median of coefficients of variation of duplicate analyses taken over the 15 model years.

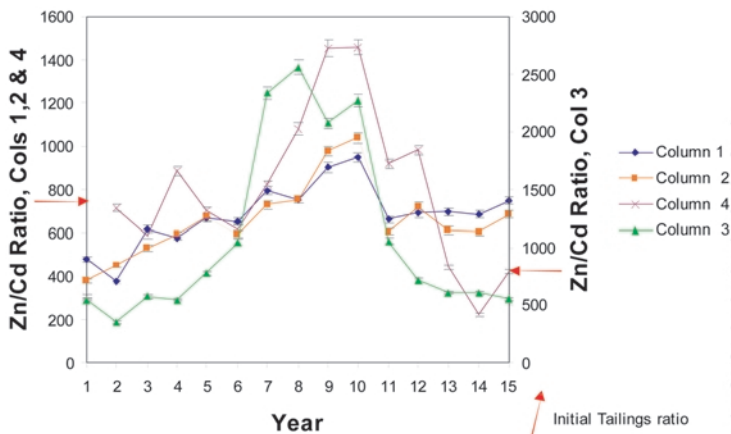


FIG. 2. Zn/Cd molar ratio in column leachate waters. Each data point is a mass summation of 6 individual measurements. Error bars represent the median of coefficients of variation of duplicate analyses taken over the 15 model years.

The Zn/Cd molar ratio for the unaltered tailing is 738 (Kossoff, unpublished data), while that for leachates from all columns over model years 1 to 15 are illustrated in Fig. 2. In the early model years, the leachate Zn/Cd ratios in all columns are below that of the unaltered tailings, suggesting either preferential weathering of a Cd-rich phase, or retention of Zn in secondary phases in the columns, or both. By model year 8, the Zn/Cd leachate ratio in column 3 is 2563, and the ratios peak to 950 (year 10), 1038 (year 10) and 1457 (year 8) in columns 1, 2 and 4, respectively. If the release of Cd and Zn from tailings weathering were congruent, this ratio should be observed consistently in the leachate throughout the time series, assuming no differential re-sorption of Cd or Zn. The increases in the ratios with each successive wetting cycle suggest the loss of highly soluble Cd-rich phases, weathering of a different Cd-poor, Zn-rich phase, or retention of Cd by the column solids, or all three. After model year 10, the Zn/Cd molar ratios decline in all leachates.

The dissimilar behaviour of Cd and Zn in our columns contrasts with that shown for mine tailings weathering in other studies, for example that by Acero *et al.* (2007), who observed similar temporal trends in pore water concentration for both Cd and Zn in unsaturated mine tailing columns. We are currently investigating the Potosí tailings further using mineral characterization and atomistic computational modelling techniques to provide explanations for the

incongruent and dissimilar Cd and Zn weathering patterns presented here.

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