



Effects of Mine Waste Dumps on the Exchange Processes of Potentially Toxic Elements at the Water/Sediment Interface in an Abandoned Sulfide Mine

Conference

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Background/Objectives

Caveira's mine, an abandoned sulfide Cu-Pb-Zn-Ag-Au mine, is situated in the southern part of the Iberian Pyrite Belt in Portugal. Historically exploited since the period of Roman Empire, the mine was ultimately abandoned in the late 1960s without any implementation of environmental remediation strategies. In February 2023, following a prolonged drought and subsequent rainfall, samples of sediment, water, and interstitial water were collected. This study specifically selected samples influenced by mine waste piles to investigate chemical exchanges at the sediment/water interface in a sulfide-rich environment. The objectives are to (i) compare the chemical composition of water and sediment, (ii) correlate potentially toxic elements (PTE) concentrations in sediments and water to elucidate the linear relationships among PTE, and (iii) identify the most effective approach for sediment reclamation.

Approach/Activities

Five sampling points impacted by mine waste piles were chosen for collecting stream sediments, water column, and interstitial waters. Physical-chemical parameters (pH, Eh) and PTE concentrations (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn, V) were analyzed in the sediments to assess labile fractions (exchangeable and soluble). The performed activities included *Aqua Regia* digestion to determine contamination levels, extraction of exchangeable forms using ammonium acetate at pH 4.5, and extraction of interstitial waters from sediments using *rhizon* samplers with a porosity of <0.45 µm. All three PTE fractions were analyzed using ICP-OES. In situ measurements of physical and chemical

parameters of the water column were conducted, followed by immediate filtration, acidification, refrigeration, and subsequent ICP-OES analysis. Descriptive statistics, Pearson correlations, and multivariate analysis were conducted using R language.

Results/Lessons Learned

Sediment pH levels ranged from 2.35 to 5.25, with redox potentials between 373 and 807 mV, indicating high toxicity levels, particularly for Pb (2232 to 18,135 mg/kg) and As (46.6 to 145.9 mg/kg). The exchangeable PTE analysis revealed high concentrations of Pb (434.8 to 38,467.3 mg/kg). Interstitial waters exhibited elevated Zn concentrations (11.4 to 157.9 mg/L), and water column pH varied from 1.42 to 4.53, with high concentrations of Zn (7.6 to 162 mg/L), Cu (10.1 to 35 mg/L), and As (<0.05 to 22.2 mg/L). Fe concentrations were exceptionally high across all samples (sediments: 2216.4 to 25,450.8 mg/kg; interstitial waters: 0.19 to 3173.5 mg/L; water column: 1.3 to 4533.43 mg/L). The As showed very low mobility, with exchangeable fractions below 1 mg/L. Strong Pearson correlations (≈ 1) between Fe, As, and Cu with pH levels suggest these elements form a cluster. In contrast, Zn and Fe displayed no correlation in either sediments or river water (≈ 0). Pb demonstrated weak correlations with the Fe-As-Cu cluster in water (≈ 0.5) but no correlation in sediments (≈ 0). This study suggests that sediment capping with a carbonate layer, such as marble or limestone powder, is the most effective method for increasing pH and minimizing toxic elements solubility, thus optimizing conditions for sediment reclamation.

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