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Geochemistry of Rio Guadiamar Sediments Following the April 1998 Spanish Aznalcollar Mine Tailings Dam Failure and Subsequent Clean-up

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The Aznalcóllar tailings dam at Boliden Apirsa's Aznalcóllar/Los Frailes Ag-Cu-Pb-Zn mine 45 km west of Seville, Spain, was breached on 25 April 1998, flooding approximately 4600 hectares of land along the Agrio and Guadiamar rivers, with an estimated 5.5 million m^3 of acidic water and 1.3 million m^3 of heavy metal-bearing tailings (Sassoon, 1998). Extensive clean-up work by Boliden Apirsa S.L., the Confederacion Hidrografica de Guadalquivir and the Consejería de Medio Ambiente was carried out immediately after the spill until January 1999, removing most of the deposited tailings and approximately 4.7 million m^3 of contaminated soils to the Aznalcóllar open pit. To evaluate the long-term fate of sediment-borne metal contaminants, an interdisciplinary geomorphological-geochemical research programme began in December 1998 (Macklin et al., 1999), to (1) monitor and model the recovery of the river, especially in terms of the geochemical and physical (erosion, sediment reworking, deposition) controls on the distribution of potentially hazardous elements between sediment and waters, and (2) provide data for establishing guidelines for the prevention and clean-up of tailings dam failures globally. This paper reports on the post-clean-up (post-January 1999) geochemistry of the Rio Guadiamar channel and floodplain sediments.

Detailed baseline geomorphological and geochemical surveys of the post-cleanup channel, floodplain and valley floor were carried out in January and May 1999 at six reaches representative of the types of river channel and floodplain environments in the Rio Guadiamar catchment affected by the spill. Sediment samples were taken from the channel bed and banks, the floodplain and higher river terraces. Several samples of deposited tailings and older, 'pre-spill' alluvium, were also taken at all of the reaches. The samples were digested in HF-$HClO_4$-HNO_3 and analysed by ICP-MS for Ag, As, Cd, Cu, Pb, Tl and Zn. Water-soluble metal was determined by shaking 1 g of sediment in 10 ml of de-ionised water (DIW) for one hour and analysing the filtered extract by ICP-AES. Total sulphur was analysed on a LECO C-S analyser. Sediment pH was measured in a 1:2.5 air-dried sediment: DIW slurry.

Total sediment-borne concentrations of metals are variable, exhibiting the following ranges (for 63 samples): Ag 0.2-7.4 mg/kg (average 2.3 mg/kg), As 30-1000 mg/kg (average 250 mg/kg), Cd 0.1-12mg/kg (average 3.8 mg/kg), Cu 45-730 mg/kg (average 260 mg/kg), Pb 71-2400 mg/kg (average 790 mg/kg), Tl 0.5-16 mg/kg (average 6.0 mg/kg) and Zn 190-3200 mg/kg (average 1100 mg/kg). There is a general downstream decline in average metal concentrations at the study reaches. Average elemental concentrations in the post-cleanup alluvial sediment are 7 to 11 times lower than those in the spilled tailings material, but typically exceed concentrations in older, pre-spill alluvium by 3 to 13 times. Total S contents range from 0.01-13.3% (average 4.90%).

Total element concentrations correlate well ($r = 0.62$-0.89) with total S contents, suggesting that the metals are largely bound to sulphide or sulphate minerals. This is confirmed by XRD and SEM analysis which shows the presence of sulphide minerals such as sphalerite and sulphate minerals including jarosite, although the relative proportion of these is not yet known. Total metal concentrations show extremely poor correlations with sediment pH. DIW-extractable metal concentrations show poor correlations ($r < 0.40$) with their respective total metal concentrations, suggesting that other factors influence the potential release of metals. Weak correlations of DIW-extractable Zn ($r = 0.50$) and Pb ($r = 0.60$) with total S, and of sediment pH with As ($r = 0.60$), Cu ($r = 0.62$) and Zn ($r = 0.64$) suggest that breakdown of sulphide or sulphate minerals, or interaction with acidic pH water, respectively, may result in the release of these metals.

The long-term behaviour and fate of these metals is key issue that faces environmental protection agencies responsible for the conservation and management of the Guadiamar catchment. Geochemical (chemical extraction) and mineralogical work is ongoing to develop predictive models of metal behaviour under varying conditions.

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