Transport and remobilisation of metals in the sediments of the contaminated Gromolo Torrent (Eastern Liguria, Italy)

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Introduction: The Gromolo Torrent is an Apennine watercourse located near the town of Sestri Levante (Eastern Liguria, Italy). Inside its basin, the abandoned Libiola Cu mine is located. This mining site was the most important sulphide (chalcopyrite + pyrite + sphalerite + pyrrhotite) deposit of the Ligurian ophiolites and was exploited until 1962. Intense Acid Mine Drainage (AMD) processes are active, leading to the generation of solutions characterised by low pH values and high amounts of dissolved SO_4^{2-}, Fe, and other chemical elements such as Cu, Zn, Pb, Al, Co, and Ni. An extensive precipitation of Fe and Cu-rich secondary minerals from AMD occurs, controlling the dispersion of elements of environmental concern outside the mine area. Moreover, AMD flows in the uncontaminated Gromolo Torrent in two points, causing the formation of amorphous Fe^{3+} oxy-hydroxides. These amorphous precipitates constitute a blanket which covers the torrent bed for several km. The aims of the work were: a) to characterise metal dispersion in the Gromolo Torrent bed and in the marine sediments of the "Baia delle Favole", where the torrent mouth is located; b) to evaluate the potential remobilisation of selected elements (Cd, Cr, Co, Cu, Mn, Ni, Pb, V, and Zn) from the amorphous precipitates using Bulk Leaching Tests (BLT); c) to assess the fraction of easily exchangeable metals using modified BCR Sequential Extraction (SE) on the amorphous precipitates and on marine sediments.

Methods: The precipitates of the Gromolo Torrent bed were sampled with a plastic syringe and stored in polypropylene bottles. Marine bottom sediments were sampled using a 5-L Van Veen grab. Two reference stations were also sampled, representative of the Gromolo Torrent sediments before the confluence AMD and marine sediments on the other side of the headland of Sestri Levante, respectively.
The mineralogical and chemical characterisation was performed by means of X-Ray Diffraction (XRD) and Inductively Coupled Plasma (ICP).
BLT were performed with deionised water to simulate the interaction with rain waters and with seawater to reproduce the interactions between the precipitates at the mouth of the torrent.
Modified BCR SE was performed following the method of [1]. The Certified Reference Material (CRM) BCR 701 was also tested, and the results obtained compared with those reported in [2], in order to test the accuracy of the measurements.

Results: The mineralogical and chemical results on the Gromolo Torrent showed the presence of an amorphous Fe-Al-Cu-rich phase, with cuprite (Cu_2O) present as accessory minerals. Rietveld refinement showed that, at the mouth of the torrent, these precipitates still constitute the major part of the sediments (≈56%). Marine sediments were constituted by the detrital minerals of the surrounding lithologies, such as quartz, plagioclase, chlorite, illite, and serpentine. No direct evidence of the presence of the amorphous precipitates was detected. However, in the sediments near the mouth of the Gromolo Torrent higher concentrations of Cu and Zn were observed.
BLT with deionised water showed a significant release of Pb, Fe, Al, Cu, and Zn. On the contrary, Cd, Co, Mn, Ni were more efficiently mobilised by seawater, with Cu and Zn showing still high concentrations in the leachates.
The results of BCR SE showed that in front of the mouth of the Gromolo Torrent, the adsorbed and Fe-oxy-hydroxides fraction were higher than in other samples, while Mn concentration, which was mainly contained in the adsorbed fraction, tended to rise moving along the coast.

Discussion: The amorphous precipitates control the dispersion of elements in the Gromolo Torrent, and are the cause for the high Cu and Zn concentrations in the marine sediments in front of the mouth of the torrent. The release of elements from the precipitates in seawaters is mainly controlled by exchange reaction with seawater cations and by the formation of soluble chlorocomplexes [3]. Also the currents play an important role, as their action tends to concentrate the materials transported from the torrent. Mn concentrations on the contrary seem to be controlled by sediments from another torrent of the area (the Entella Torrent).

References: [1] Rauret et al. (1999) *J. Environ. Monit.* **1**:57-61. [2] Pueyo et al. (2001) *J. Environ. Monit.* **3**:243-250. [3] Elbaz-Poulichet et al. (1987) *Mar. Chem.* **22**:125-136.