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Two-year monitoring of water hydrochemistry in a Pb-Zn Mississippi Valley-Type mine (MVT) in the Southeastern Alps (Raibl, Friuli Venezia Giulia)

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The recent and past mining activities are among the main anthropic sources of dispersion of potentially toxic trace elements (PTEs) in the environment. In this study, a two-year monitoring of different water bodies in a decommissioned mining site located in the Southeastern Alps (Friuli Venezia Giulia, Raibl mine) was performed. Results have allowed to provide a characterisation of the hydrogeochemistry, the chemical signatures and the temporal-spatial variations of PTEs in a carbonate-hosted Pb-Zn Mississippi Valley-Type (MVT) mine, where no acid mine drainages (AMD) occur. Besides mineralogy and pH-Eh conditions, strong rainfalls and high-flow events are the main factors affecting the temporal variability of dissolved PTEs, promoting their dissolution and dispersion. Anomalous concentrations of trace metals (Zn, Pb, Tl) were found in near neutral pH-buffered groundwaters entrapped in tailings impoundments, whereas concentrations of metalloids (As, Sb and Ge) were more abundant in low-flow water drainage from mine adits. High concentrations of Tl were found in the saturated area of the tailings impoundments, related to relatively lower pH and sulfate ions contents, thus suggesting Tl-bearing pyrite/marcasite oxidation. At the same time, low concentrations of dissolved Ge and Cd in groundwaters entrapped in tailings are possibly associated to sphalerite-depleted post-flotation tailings. Based on chemical data, modeling and literature, attenuation processes of dissolved PTEs (mainly Pb) are mainly attributed to sorption onto Fe-oxy-hydroxides, which is pH-dependent, and precipitation of mineral phases (e.g., dissolved Zn to hydrozincite: $Zn_5(CO_3)_2(OH)_6$). The Tl/Zn and Tl/Pb ratios show that enrichments occur without notable attenuation inside the tailings impoundments, possibly indicating that Tl attenuation needs higher pH to effectively promote adsorption onto Fe-oxy-hydroxides [Coup and Swedlund, 2015], as, conversely, occurs in the Rio del Lago stream waters.

References

Coup K.M. and Swedlund P.J., (2015). *Demystifying the interfacial aquatic geochemistry of thallium(I): New and old data reveal just a regular cation*. *Chemical Geology*, 398, 97-103.