Thallium and other potentially toxic elements in surface waters contaminated by acid mine drainages in southern Apuan Alps (Tuscany)

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Abstract Geochemical surveys were carried out over three years in the mining area of Alta Versilia. The physico-chemical parameters and the concentrations of potentially toxic elements (PTE) were determined both in mine drainages and in waters of the Baccatoio Stream receiving AMD.
AMD have an average pH of 2.2 and contain high concentrations of Al, Fe, Mn, Cu, Zn, As, Ni, Co, Se, Cd, Sb, Pb and Tl. The discharge of AMD into the stream results in a severe contamination. Downstream of the mines, the pH increases and most PTE are readily scavenged from the stream waters by precipitation and adsorption. On the contrary, Tl behaves almost conservatively, undergoing only dilution.

Key words Alta Versilia mine sites (Italy), mine drainage, potentially toxic elements, thallium

Introduction

Weathering of iron sulfide minerals is the primary source of the generation of acid mine drainages (AMD), which represent a major environmental problem in areas with many active and abandoned mine sites world-wide (Chen et al. 2007; Moore and Luoma 1990; Nordstrom et al. 2015). The southern sector of the Apuan Alps (northern Tuscany, Italy) is characterized by the occurrence of sulfide-bearing mineral deposits worked up to the beginning of 1990's, and whose Tl-rich nature was recognized in the last years. Recent geological studies show Tl concentration levels up to 600 μg/g in the pyrite ores (D'Orazio et al. 2017). The mine sites of Pollone and Mt. Arsiccio are located in the catchment area of the Baccatoio Stream (27.6 km^2). Mine drainages directly discharge into the stream, that crosses the Valdicastello Carducci village and reaches the coastline flowing through a densely populated area. Despite the stream water has been used by local population to irrigate gardens and vegetable gardens, a detailed geochemical characterization of both AMD and their impact on the surface water quality has never been so far reported for this area.

In the present work the physico-chemical properties and major and trace element content were determined on acid mine drainages and superficial waters in the Baccatoio Stream catchment, with special reference to Tl.

Methods

Acid mine drainages, ground- and surface-waters were collected during repeated surveys from 2013 to 2016. Waters were filtered at the sampling stations using 0.45 μm nylon filters, and stored into pre-cleaned high-density polyethylene bottles. Temperature, pH, redox potential (Eh), dissolved oxygen (DO), electrical conductivity (EC) and HCO_3^- were deter

mined in the field. Major anions and cations were determined by IC (Thermo-Dionex ICS-900) respectively on filtered and on filtered and acidified (using ultrapure HNO_3) sample aliquots. Trace element analysis were performed on filtered and acidified samples by ICP-MS (PerkinElmer-NexION 300X) using ^{103}Rh, ^{187}Re and ^{209}Bi as internal standards. The certified reference solution IV-STOCK-1643 was used to evaluate analytical errors that were usually lower than 10%.

Results

In AMD the pH, EC and DO range between 1.3 to 2.9; 1 mS/cm to 30 mS/cm and between 1.2 mg/L to 8.7 mg/L, respectively. The observed variability reflects the relative contribution of sulfide oxidation and rainwater inputs in determining the dynamics of the processes inside the tunnels, and highlight the dependence on seasonality. AMD are also characterized by high concentration of potentially toxic elements, as graphically shown in Figure 1, exceeding the Italian Regulation guidelines for groundwaters for Al, Fe, Mn, Cu, Zn, As, Ni, Co, Se, Cd, Sb, Tl and Pb.

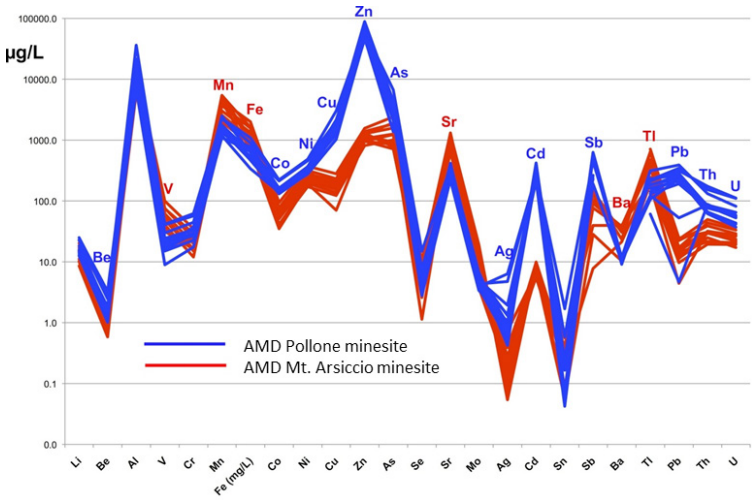

Figure 1 *Plots showing the elemental patterns (including PTE) in acid mine drainages from Pollone and Mt.Arsiccio mine sites. Note the high Tl concentration, in particular at the Mt. Arsiccio mining area*

The Baccatoio Stream waters are characterized by a pH ranging from 2.4 in its upper course to 8.3 downstream and towards the coastline. The progressive increase of pH along the watercourse reflects freshwater inputs and the evolution towards equilibrium conditions with atmospheric CO_2 under calcite saturation. The pH increase causes a rapid drop of EC from 3600 µS/cm to about 320 µS/cm, and contributes to the scavenging of most contaminants by precipitation and adsorption processes mostly on iron oxyhydroxides (HFO) (Edraki et al. 2005; Nordstrom 2011) that characterize the riverbed sediments. This is shown in Figure 2, where the Fe and As contents in the different stations along the stream course are reported.

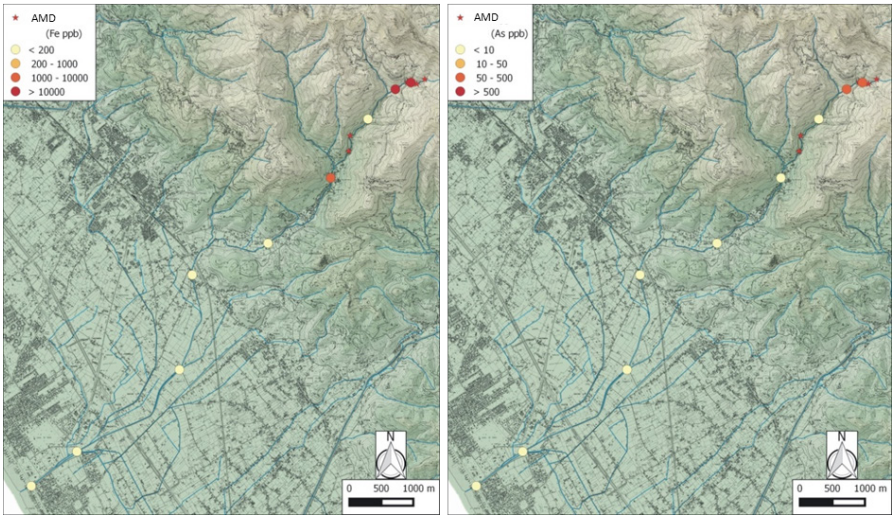

Figure 2 *Fe and As distribution in different stations along the Baccatoio Stream, as an example of decreasing PTE concentration along the flowpath due to HFO precipitation. AMD are also superimposed (stars)*

It is worth to note that Tl remains invariably above the threshold of 2 µg/L, except at the mouth of the stream due to dilution effects by seawater intrusion (Figure 3). This suggests that the decrease of Tl concentration mostly results from dilution, and that sorption is not a significant process for immobilization of this element, at least in these environmental conditions. These observations support the high mobility for Tl through the aqueous system and its low affinity for the precipitates (Xiao et al. 2012), representing an environmental and human health hazard.

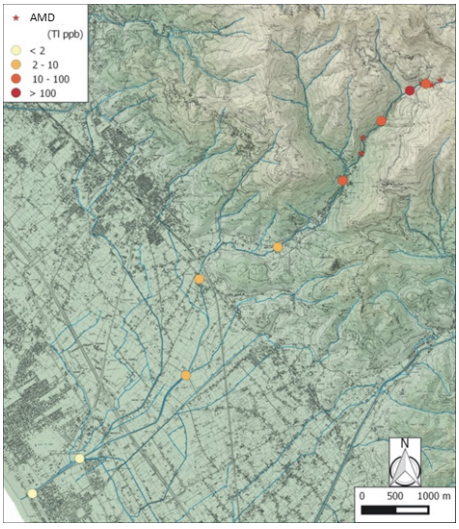

Figure 3 *Tl distribution in different stations along the Baccatoio Stream, showing concentration exceeding the 2 µg/L threshold along most of the watercourse. AMD are also superimposed (stars)*

Conclusions

High concentrations of PTE characterize the AMD from mine sites in the Baccatoio Stream catchment, in Alta Versilia (Tuscany, Italy), reflecting the large abundance of sulfides, in particular pyrite, in the ore bodies they drain. Drainages are characterized by high Tl content, in particular the M. Arsiccio mine drainages, due to the Tl-rich nature of the pyrite ores occurring in this mine. AMDs impact the Baccatoio Stream water quality; however, most of the pollutants decrease in concentrations along the Baccatoio flowpath towards the coastline due to dilution and HFO precipitation. Thallium migrates almost conservatively along the Baccatoio Stream maintaining concentrations above 2 μg/L. The use of the Baccatoio Stream as irrigation source may cause a Tl-contamination in agricultural soils, creating the conditions for environmental and human health hazards.

Acknowledgements

The authors thank the Regione Toscana for financial support.

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