

## Natural attenuation of contaminants in mine drainage at abandoned mines

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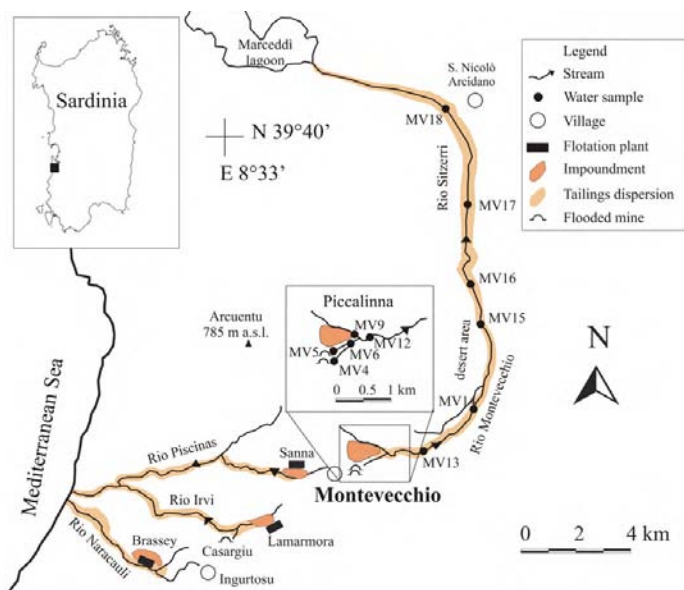
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**Abstract** Since 1996, hydrogeochemical surveys have been carried out in the Montevecchio Pb-Zn mining district (Sardinia, Italy) to investigate variations in the aqueous occurrence of contaminants. Overall results showed decreasing concentrations of Zn, Cd, and Pb in 2009 as compared with values recorded in 1996. The lowest dissolved concentrations of sulphate and metals were observed in correspondence of less acidic conditions. Despite the ongoing natural attenuation, very high concentrations of toxic metals continue to be observed after 15 years since the mine flooding. Treatment of mine drainages before their discharge into the local streams is recommended to reduce the dispersion of contaminants.

**Key Words** mine closure, rebound, hydrogeochemistry, heavy metals, Sardinia

### Introduction and study area

This paper is aimed to investigate variations occurring in the chemical composition of mine drainages since the mine closure. The study area is located in the Arburese mining district (SW Sardinia, Italy). The Pb-Zn vein ores are mainly comprised of quartz, galena, and sphalerite, with local occurrences of siderite, ankerite and calcite. Pyrite, marcasite, and other sulphide minerals are associated with the ore. These ores, hosted in silicate-dominant rocks, were exploited intensively from 1850 to 1990. Underground workings extended in a system of overlapping galleries for a depth of 600 m below ground level. Peaks in Pb-Zn production were reached in the middle-1900. The decline of mining industry, due to the fall in base-metal value and increasing labour costs, led to the closure of Pb-Zn mines over the 1970–1990 period. Figure 1 shows the location of mines, flotation plants and tailings in the Arburese mining district. Different sources of surface water contamination occur in this area. After the dewatering plants were stopped and underground workings became flooded, mine drainages were observed since 1996. These contaminated waters have been discharged directly into the local streams. Other sources of contaminants comprise flotation tailings and waste rock dumps (Fig. 1).



*Figure 1* Map showing the Montevecchio mining district and location of water samples.

### Temporal variation of mine drainages

In 1973, under active mining and dewatering conditions, the water pumped out of Montevecchio showed near neutral pH (6.2), 2000 mg/L SO<sub>4</sub>, 290 mg/L Zn, 1 mg/L Cd and 1.2 mg/L Pb (Biddau 1978). Mine drainages at the first outflow showed acid pH and dissolved concentrations of SO<sub>4</sub>, Zn, Cd and Pb much higher than those observed under dewatering conditions.

At Montevecchio, the MV4 and MV5 adits (Fig. 1) collect drainages of underground workings. Flow rate at MV4 is ≤2 L/s, and varies at MV5 (1–10 L/s) due to inputs from surface drains. Figure 2 shows pH and SO<sub>4</sub> variations in the MV4 and MV5 waters, and the local monthly precipitation in 1996–2009. The acidity produced by the oxidation of sulphide minerals (especially pyrite) has been preserved at MV4 (pH = 3.9±0.3) due to the paucity of carbonate minerals in this system. The pH at MV5 varied from 3.4 to 7.4; the lowest values were observed when sampling was carried out after long droughts.

Figure 3 shows the variation of metals in the MV4 and MV5 adit waters during the monitoring period. Dissolved Zn and Cd in the MV4 drainage are higher than those observed in MV5. In both mine drainages concentrations of metals increase when pH is more acidic. Such increase is particularly marked for Pb, which is consistent with the higher mobility of Pb under acidic conditions. Overall results of the hydrogeochemical surveys show a significant decrease (≥50%) in SO<sub>4</sub>, Zn and Cd concentrations in the MV4 drainage sampled in 2009, as compared with values recorded in 1996. Dissolved Pb concentrations show a larger variability depending on pH.

### Impact of mine drainages on surface waters

Mine drainages from Montevecchio are directly discharged into the Rio Montevecchio-Rio Sitzerri stream (Rio Montevecchio and Rio Sitzerri refer to the upper and lower course, respectively, see Fig. 1), which flows into the Marceddi lagoon. This stream also receives seeps from the Piccalinna tailings (0.1 to 0.3 L/s), and further downstream, inputs from uncontaminated tributaries, whose flow rates largely depend on rainfall. Figure 4 shows pH values and metal contents in waters sampled along the Rio Montevecchio-Rio Sitzerri stream. Sampling was carried out in September 2004 and September 2008, following long droughts. It should be noted that the drainages from mine adits are the main water suppliers to the Rio Montevecchio during the dry season.

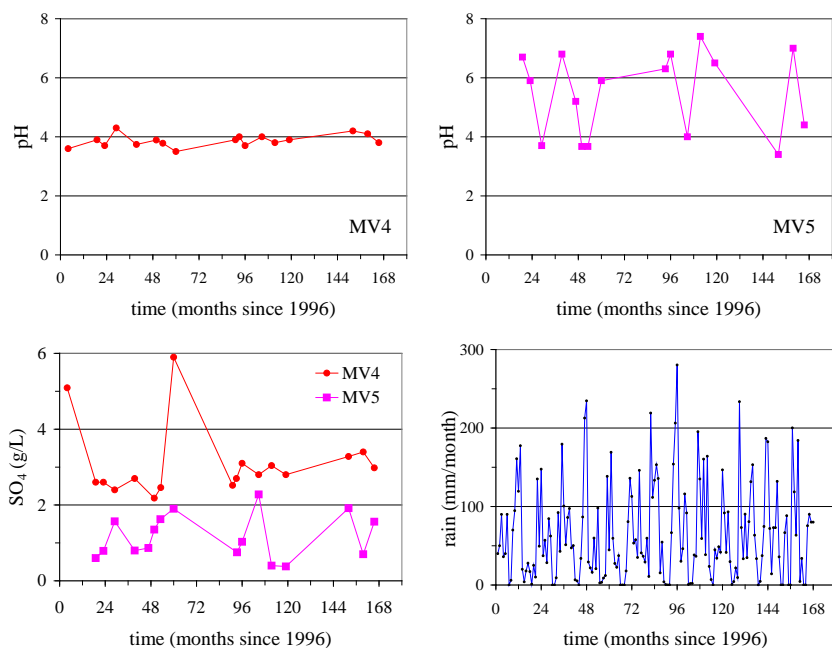
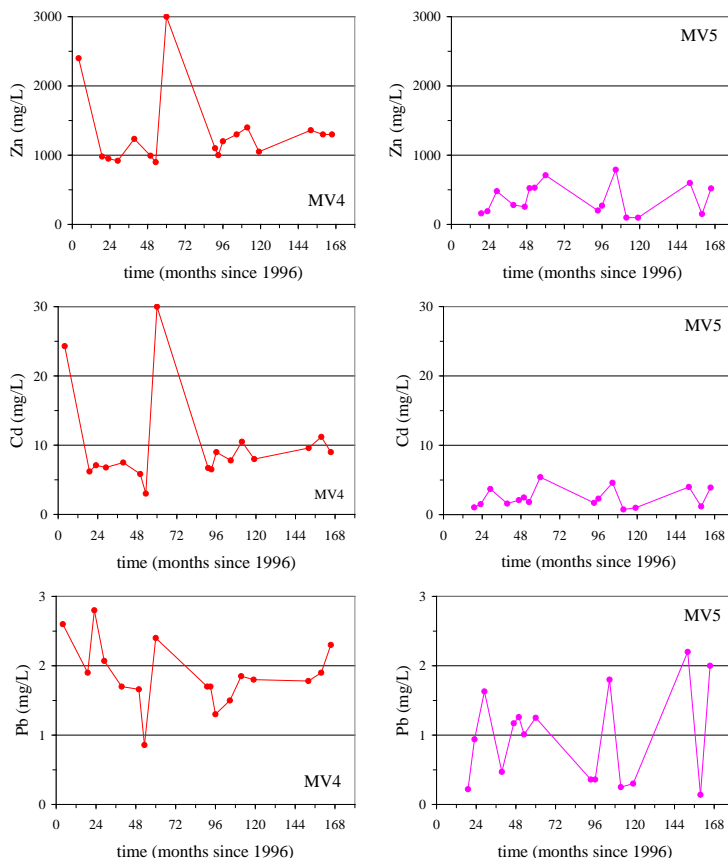


Figure 2 Temporal (1996–2009) variation of pH and sulphate in the MV4 and MV5 adit waters and monthly precipitation in the Montevecchio area



*Figure 3* Temporal variation of sulphate, zinc, cadmium and lead in the MV4 and MV5 adit waters at Montevecchio (sample locations are shown in Figure 1)

Iron precipitation occurs in a relatively short (< 3 km) distance from the source (Fig. 4b). The acidity (pH 3.3) produced by Fe precipitation allows Pb to remain in solution, mainly as  $Pb^{2+}$  (38%) and  $PbSO_4^0$  (56%) aqueous species. Concentrations of Pb in the stream decrease significantly only further 7 km downstream when the pH rises to 6.2 and dissolved Fe is very low (<0.1 mg/L).

In contrast, Zn, Cd and Mn persist in the stream at high concentrations even under near neutral (6.2) pH condition. Under this condition, the stream water shows low alkalinity ( $HCO_3^- = 12$  mg/L), and thus the water is strongly undersaturated with respect to carbonate minerals. Speciation of Zn, Cd and Mn is dominated by divalent cations and uncharged aqueous sulphate-complexes. The observed behaviour of Cd and Zn is consistent with their mobility being higher than Pb under near neutral conditions. When occurring as divalent cations, Pb is completely adsorbed at pH 6 while Cd and Zn are poorly adsorbed (e.g. Stumm and Morgan 1996). The behaviour of Mn is consistent with its higher mobility with respect to Fe: for the precipitation of Mn-oxide phases is required a redox potential much higher than that required for Fe precipitation (Stumm and Morgan 1996). Then, the Mn precipitation as carbonate minerals observed in mining environments (Kruse and Younger 2009) is hampered in the Montevecchio area by the low availability of alkalinity. Concentrations of Zn, Cd and Mn only drop when an uncontaminated tributary flows into the Rio Sitzerri (Fig. 4c, e, f).

Despite the attenuation in dissolved contaminants, the estimated amount of dissolved metals discharged daily into the Marceddi Lagoon is significant, especially when the flow of streams rises dramatically soon after storm events.

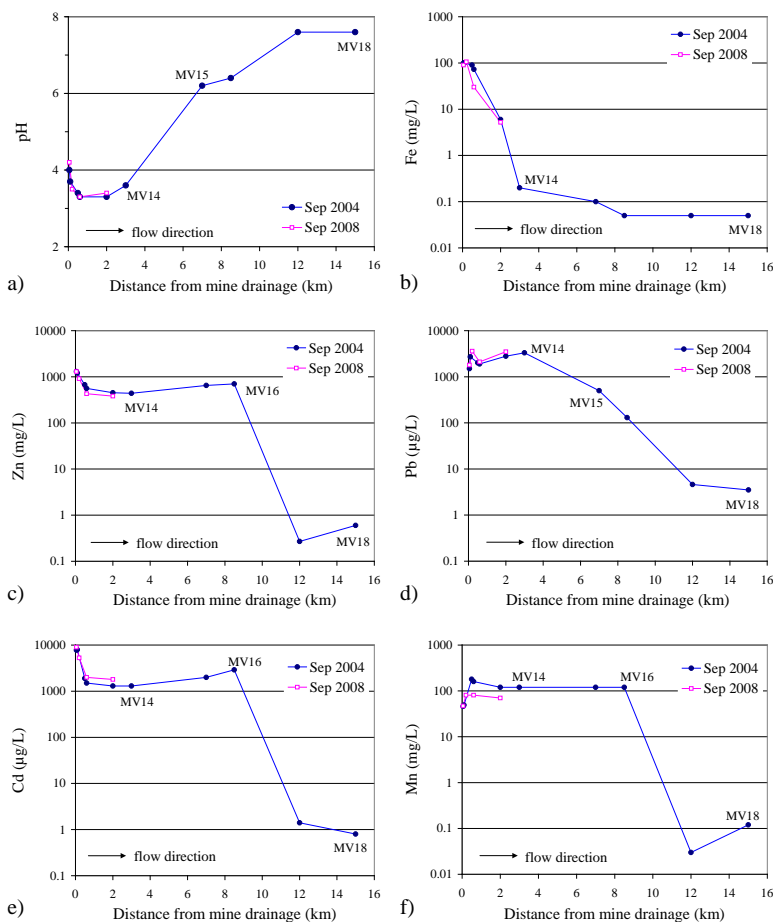


Figure 4 Variations of pH and dissolved metals in waters sampled along the Rio Montevecchio – Rio Sitzerri (sample locations are shown in Figure 1)

**Conclusions**

A very high contamination level still persists in the Montevecchio mine drainages after 15 years of flushing. These contaminated mine drainages flow directly into the Rio Montevecchio – Rio Sitzerri stream. Attenuation in the dissolved load of contaminants occurs by precipitation of solid phases and by dilution via uncontaminated tributaries. Concentrations of Zn, Cd and Pb in the stream water increase under high runoff conditions, due to the weathering of the exposed mining-related residues. Under such conditions, the dispersion of contaminants is favoured by transport via adsorption processes onto very fine particles (<0.4 µm) and/or associated to colloids.

**Acknowledgements**

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