# The geochemistry of pore waters in riverbed sediments in a mining-impacted landscape: sources of potentially toxic elements

M. Perotti[1]*, L. Ghezzi[1], C. Casiot[2], M. D'Orazio[1], R. Giannecchini[1], R. Petrini[1]

[1] *Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, 56126 Pisa, Italy*
[2] *HydroSciences UMR CNRS 5569 – IRD 050 – Université de Montpellier, CC0057, 163 rue Auguste Broussonet, 34090 Montpellier, France*

**Abstract** Pore-waters and sediment cores were collected from the bed of the Baccatoio Stream, receiving the outflows of acid mine drainages in Alta Versilia (Italy). The data indicate that sediments are composed by different layers for mineralogy and elemental distribution; it is observed that the uppermost level is characterized by iron oxyhydroxides that act as efficient scavengers for arsenic. Pore-waters invariably show higher concentration of potentially toxic elements with respect to the stream waters, in particular thallium. Observations indicate that this contaminated reservoir may be mobilized depending on the stream flow regime, yielding transient of contamination on the surface water.

**Key words** Alta Versilia minesites (Italy), streambed sediments, pore-water, potentially toxic elements, thallium

## Introduction

Hydrodynamic and biogeochemical processes govern the fate and transport of potentially toxic elements (PTE) in surface environments impacted by mining activity (Nordstrom 2011, Druschel et al. 2004). In particular, in these settings the water and solutes exchanges between stream water and pore water underlying the streambed and defining the hyporheic zone may modify the solute chemistry of both the near-stream groundwater and stream water (Bencala et al. 1993, Benner et al. 1995) including the fate and partitioning of PTE when contaminated sediments are buried in the streambed. These processes are mostly depending on the streambed structure and permeability that determine the mixing between the solutes that characterize the reducing and oxidized conditions that usually occur in the pore- and surface water, respectively. Such processes influence the sulfate reduction and sulfide stability and the reactivity of iron oxyhydroxides (HFO) particles, with implication on trace metal and metalloid sorption and release. In the present study, pore-waters were extracted from the riverbed sediments of the Baccatoio Stream, receiving acid drainages from abandoned minesites in the southern Apuan Alps. These drainages were characterized by a high sulfate (up to about 25 g/L) and iron (up to about 7 g/L) content, in addition to Al, Mn, Cu, Zn, As, Ni, Co, Se, Cd, Sb, Tl and Pb exceeding the limit of Italian Regulations for groundwater (Petrini et al. 2015). A sharp increase in pH follows the inflow of spring waters and tributaries along the Baccatoio stream course, allowing extensive precipitation of HFO. Suspended particles are carried downstream, then settle forming a bedload and bedded sediments in the Plain.

## Methods

Pore-waters were collected in two stations along the stream course by a passive method using a ceramic suction lysimeter at 15 cm depth in the riverbed. In one station waters were at both 15 and 40 cm and during low and high flow conditions. Waters were filtered in the field 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 determined immediately after sampling. Major anions and cations were determined by ion chromatography respectively on filtered and stabilized samples using ultrapure $HNO_3$. Trace elements, including PTE, were determined by ICP-MS using a Perkin-Elmer-NexION 300X. The certified reference standard IV-STOCK-1643 was used to evaluate analytical errors that were usually lower than 10% In one station were pore-water was collected riverbed sediments were also sampled to a depth of 40 cm using the piston coring technique. The sediment mineralogy was obtained by XRD using a Bruker D2 Phaser; the sediment chemistry was determined on the bulk by HHXRF using a NITON XL3t GOLDD+.

## Results

### Sediment core

The mineralogy of the sediment core is reported in tab. 1

***Table 1*** *Mineralogy of riverbed sediments at different depth.*

| Depth (cm) | Mineral phases |
|---|---|
| 0 – 7 | Qtz, Ill, Cal, Ab, Chl, Brt, Dol, Py |
| 7 – 16 | Qtz, Ill, Brt, Py |
| 16 – 18 | Ill, Qtz, Brt, Py |
| 18.5 – 21 | Qtz, Ill, Brt, Dol, Ab, Chl, Py |
| 21 – 38 | Qtz, Ill, Cal, Chl, Dol, Chl, Tur, (Brt) |

Ab, albite; Brt, barite; Cal, calcite; Chl, chlorite, Dol, dolomite; Ill, illite; Py, pyrite; Qtz, quartz; Tur, tourmaline

The chemiostratigraphy of sediments for Fe, As, Ba and S at depth of 17 cm (the depth of most pore-water extractions) is shown in fig. 1, and for Pb, Sb, Mn and K in fig. 2.

It is observed that As and Fe mostly concentrate in the uppermost sediment layer, suggesting precipitation or sedimentation of HFO particles and the scavenging of As from the aqueous phase by adsorption on HFO surface. Destabilization of HFO due to redox changes has hence the potential to release As to pore- and stream waters. Deeper in the core an increasing in S and Ba concentration and Pb, Sb and K can be noted; the latter observation indicate possible adsorption processes of trace metal on clay minerals. The bottom of the core (not shown) is characterized by the highest Ca concentration, likely due to the occurrence of stable carbonate mineral phases. Thallium was not detectable through HHXRF.

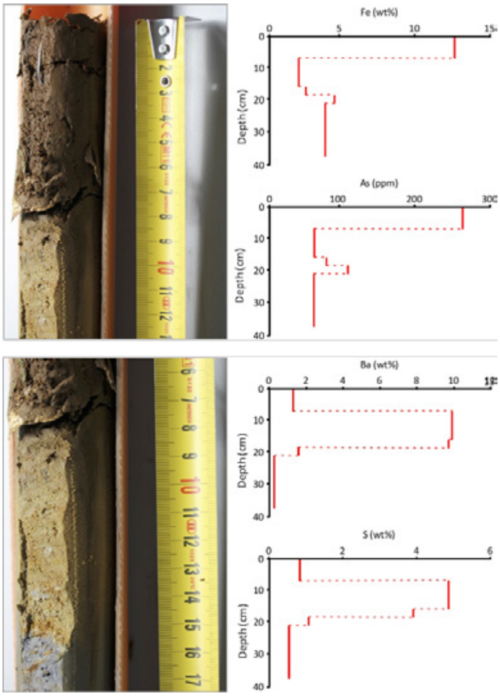

***Figure 1** Riverbed sediment chemiostratigraphy (for Fe, As, Ba and S to a depth of about 17 cm)*

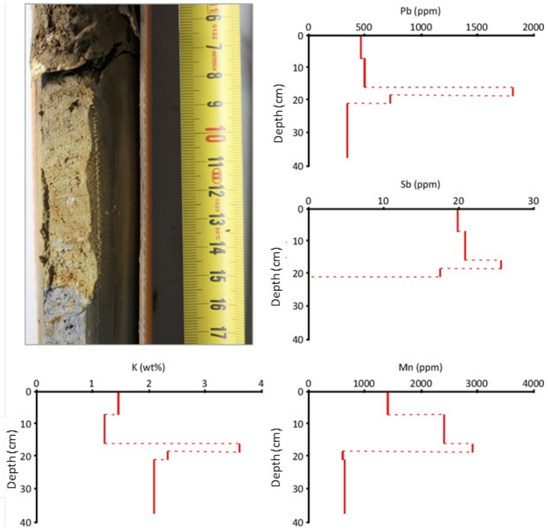

***Figure 2** Riverbed sediment chemiostratigraphy (for Pb, Sb, Mn, K to a depth of about 17 cm)*

Pore-waters

Pore-waters are characterized by circumneutral pH; Eh of 0.38 V, quite similar to the corresponding stream water, and DO of 3.7 mg/L during a low-flow regime, much lower compared with the oxidized stream water at the same station (9.4 mg/L). During high-flow DO increases approaching what measured in superficial water, suggesting that stream water moves through the riverbed sediment.

The trace element pattern in pore-waters and stream waters at the same sampling station during both low flow and high flow conditions is shown in fig. 3.

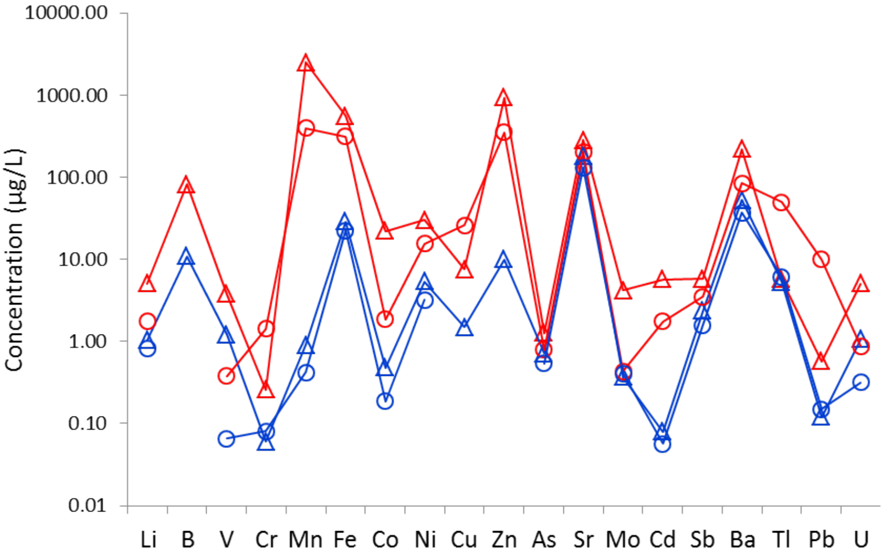

***Figure 3*** *Pore-water (in red) and stream water (in blue) trace element content. Open triangle: low flow conditions; open circle: high-flow conditions*

It is observed that pore-waters are characterized by a higher amount of PTE, in particular Mn, Fe, Zn, Pb and Tl. It can be also noted that the highest concentrations are observed during low-flow conditions, suggesting that pore-water contaminants are mobilized from the riverbed sediments during flooding events.

## Conclusions

Pore-waters and sediments were collected from streambed sediments of Baccatoio Stream, flowing through the Versilia Plain in Tuscany Region (Italy) and receiving highly polluted acid mine drainages from minesites in its upper course. The data indicate that some PTE concentrate in the pore-waters with respect to the flowing stream water, representing a possible source of contaminant release. Actually, the results indicate that changes in the stream hydrodynamic regime may mobilize pore-waters determining transients of high PTE concentration in the surface waters.

## References

Bencala KE, Duff JH, Harvey JW, Jackman AP, Triska FJ (1993) Modeling within the stream-catchment continuum. In: Jakeman AJ, Beck MB and McAleer MJ eds. Modeling change in environmental systems. Wiley

Benner SGE, Smart E.W, Moore JN (1995) Metal behavior during surface-groundwater interaction, Silver Bow Creek, Montana. Environ. Sci. Technol. 29:1789—1795

Nordstrom DK (2011) Hydrogeochemical processes governing the origin, transport and fate of major and trace elements from mine wastes and mineralized rock to surface waters. Applied Geochemistry 26:1777—1791. doi: 10.1016/j.apgeochem.2011.06.002

Druschel GK, Baker BJ, Gihring TM, Banfield JF (2004) Acid mine drainage biogeochemistry at Iron Mountain, California Geochem. Trans. 5:13—31

Petrini R, D'Orazio M, Giannecchini R, Bramanti E (2015) Thallium ecosystem diseases in dismissed mine sites as a threat for public health: the Valdicastello-Pietrasanta (Italy) case history. Congresso SIMP-SGI-SoGeI-AIV. Firenze, Italy. 2-4 Settembre 2015