Impact of biogeochemical barriers on the fate of zinc (Zn) in the metal-polluted Iglesiente and Arburese mine districts (SW-Sardinia, Italy)

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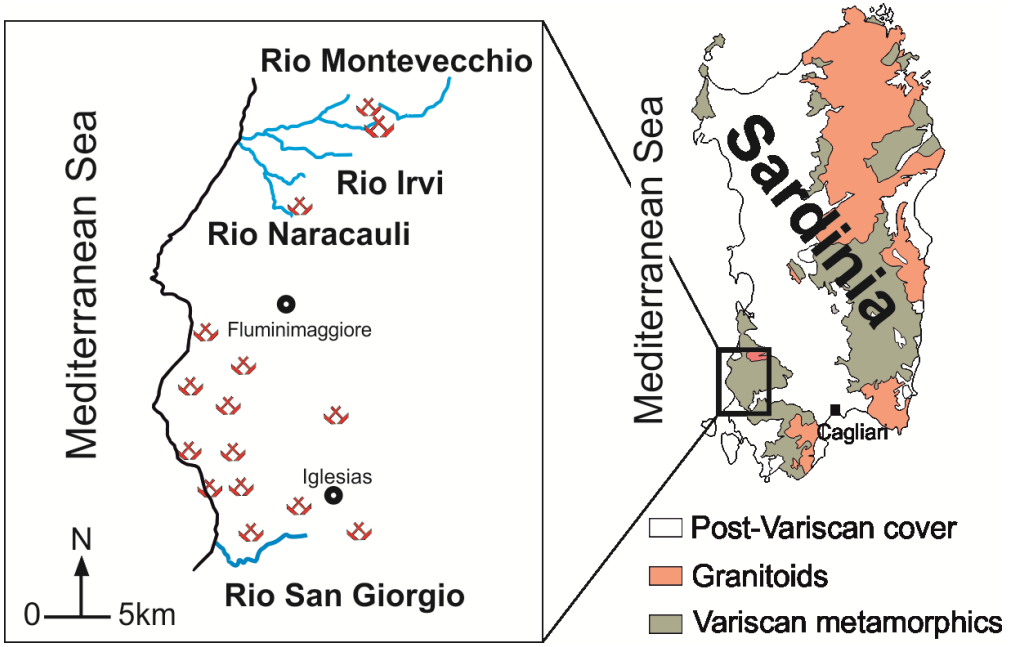
➢ Centuries of mining activity for the extraction of Zn and Pb from both sulphide and non-sulphide (calamine ores) mineralizations, left an heritage of deep landscape modification and serious heavy metal pollution in the Iglesiente and Arburese mine districts (SW Sardinia, Italy).



The "Fanghi Rossi" tailings dump, near Iglesias town (https://www.photosodini.com/fotografie-di-marco-sodini/book/galleria-immagini-sardegna/)

➢ Four streams flowing in the Iglesiente and Arburese mine districts (Rio Irvi, Rio Montevecchio, Rio Naracauli and Rio San Giorgio) have been studied, combining investigation techniques from the catchment scale (tracer-injection technique) to the microscale (scanning electron microscopy (SEM)), in order to understand the processes involved in the fate of contaminants.

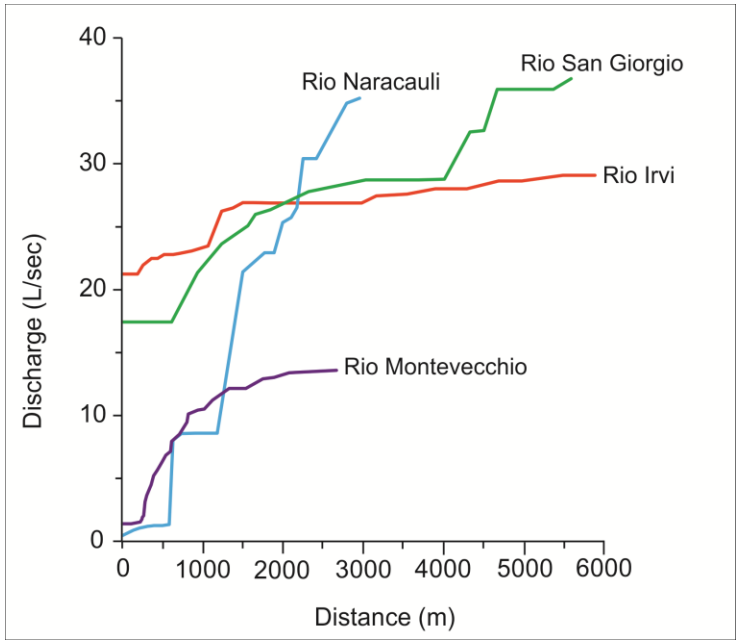
The outflow from Casargiu adit whose water flows into the Rio Irvi.

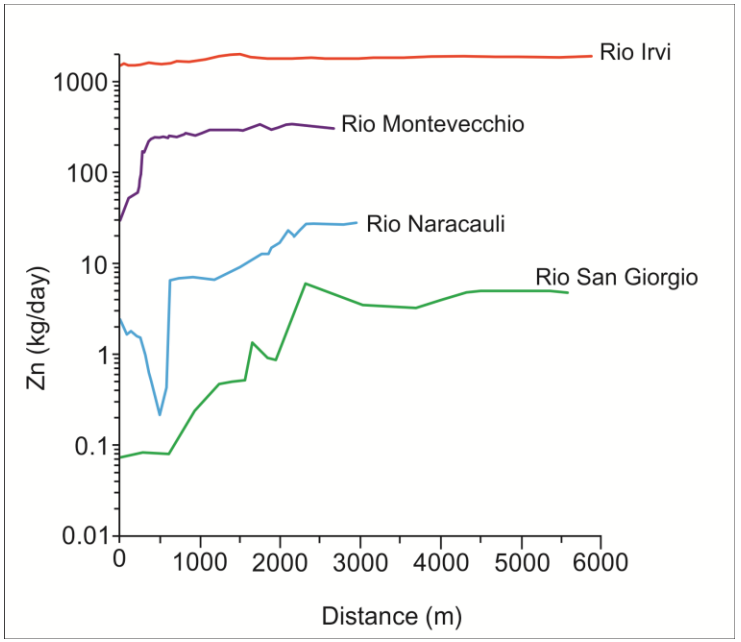
Investigation at catchment scale : hydrologic-tracer tecnique
(determination of metal loads, especially Zn load)

The tracers tecnique have been developed to identify and quantify the effect of mine drainage at catchment scale (Buxton et al., 1997).

It this study, the tracer-injection tecnique was combined with detailed sinoptic sampling to calculate the river discarge and the contaminant loads.

The streams have similar discharge but



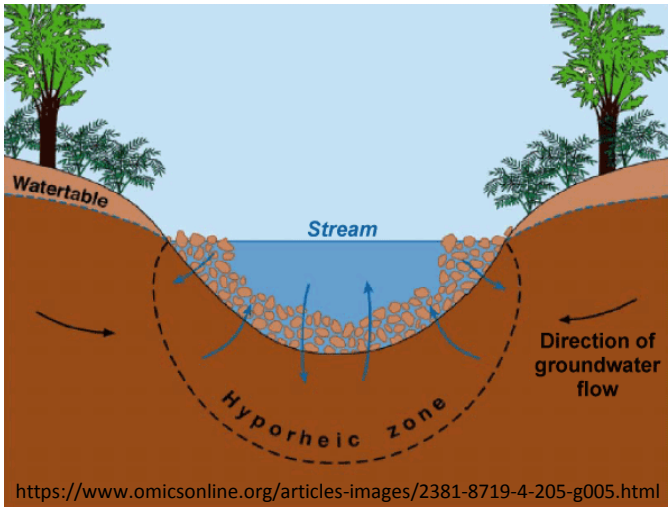


different Zn load, up to three order of magnitude, from 6 kg/day (Rio San Giorgio) to about 2000 kg/day (Rio Irvi).

Investigation at microscopic scale : SEM analysis

- The hyporheic zone is the ecotone where geosphere, biosphere and water meet, and the biogeochemical reactions take place (Byrne et al., 2014).

- Stream sediments (core samples) and plants (*Phragmites australis* and *Juncus acutus*) were collected from the riverbed of the studied streams to perform SEM analysis.



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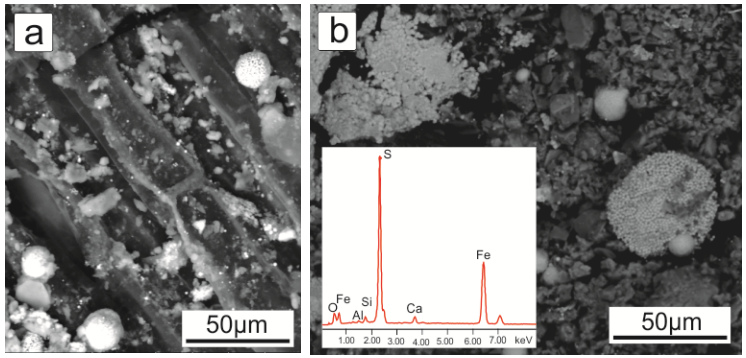
In the Rio San Giorgio sedimentation prevails. The sediments can attain more than three meters of thickness and are covered by dense vegetation. These conditions allow the onset and the development of processes, like the precipitation of authigenic secondary minerals under reducing conditions, limiting the metal mobility.

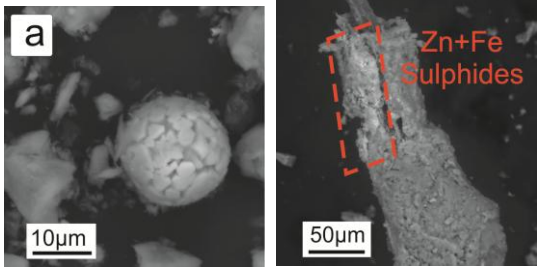


Pyrite framboids on roots of Phragmites australis (a) and sediments (b) collected in Rio San Giorgio riverbed.

Investigation at microscopic scale : SEM analysis

Rio Naracauli has sedimentation-dominated regime.

In the hyporheic zone, plants and microorganisms favour the precipitation of secondary minerals.

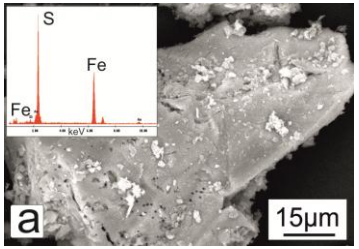


Framboidal iron sulphide (a) and metal sulphide plaques on roots (b) in core samples collected in Rio Naracauli.

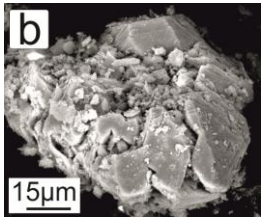
Moreover, the precipitation of Zn-rich phases can form encrustation on the riverbed: the white mud (an amorphous Zn-silicate) and the hydrozincite, biologically mediated, respectively, by *Leptolyngbia frigida and Scytonema* sp. .

Hydrozincite precipitation

Rio Montevecchio streambed presents thin sediments coverage or pebbles and reddish mud. In the core samples, primary minerals subjected to alteration are present



Altered pyrite (a) and galena (b) in core samples collected in Rio Montevecchio.



It is worth to mention that the precipitation of Fe oxy/hydroxides can influence the contaminants load.

In the Rio Irvi, erosional processes prevail and the riverbed is mainly rocky.
The precipitation of "*green rust*" (biologically mediated) and iron oxy/hidroxides influence the metal load.

Green rust and Fe oxy/hydroxides precipitation in the Ri o Irvi.

Biogeochemical barriers and resilience processes

In the studied streams several processes affect the metal loads. Natural attenuation of metals occurs through:

- the precipitation of Fe oxy/hydroxides and "green rust" which can incorporate or adsorb metals on surface
- precipitation of authigenic metal sulphides under reducing conditions mediated by microbial actions
- metal intake in roots and stems of plants (*Phragmites australis* and *Juncus acutus*) and metal immobilization in the rizosphere
- bioprecipitation of Zn-rich phases (hydrozincite and white mud)

Among them, the processes occurring at the hyporheic zone (i.e., bioprecipitation of metals sulphides and metal intake by plants) that lead significant abatement of metals load, constitute biogeochemical barriers that response to perturbations caused by mine activity, and therefore, can be considered part of the resilience of the system itself.

A thorough understanding of how different environmental compartments interact and the ecosystem responds to contamination can help to plan effective remediation actions.