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Quantifying biomineralization of zinc in the Rio Naracauli (Sardinia, Italy), using a tracer injection and synoptic sampling

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ABSTRACT

Streams draining mined areas throughout the world commonly have high concentrations of Zn. Because Zn is not easily removed from stream water and because it can be toxic to aquatic organisms, its presence is a persistent problem. The discovery of biomineralization of Zn-bearing solids in the mine drainage of Rio Naracauli, in Sardinia, Italy, provides insights into strategies for removing Zn and improving water quality in streams affected by mine drainage. Until now, the transport and attenuation of Zn has not been quantified in this stream setting. A continuous tracer injection experiment was conducted to quantify the biomineralization process and to identify the loading of constituents that causes a change from precipitation of hydrozincite [$Zn_5(CO_3)_2(OH)_6$] in the upstream reach to precipitation of a Zn-silicate phase downstream. Based on the mass-load calculations derived from the tracer experiment, about 1.2 kg/day of Zn is sequestered in hydrozincite. This biomineralization represents nearly 90% removal of Zn. Other elements such as Pb and Cd also are sequestered, either in the hydrozincite, or in a separate phase that forms simultaneously. In the lower 600 m of the stream, where the Zn-silicate forms, as much as 0.7 kg/day Zn are sequestered in this solid, but additions of Zn to the stream from groundwater discharge lead to an overall increase in load in that portion of the Rio Naracauli.

1. Introduction

Zinc, derived from weathering of mine wastes and surrounding naturally altered rocks, is one of the most difficult metals to remediate from contaminated stream water because of its mobility under most chemical conditions. Although Zn is an essential element for life, in sufficiently high concentrations it is toxic to aquatic organisms (Schmidt et al., 2011). The Rio Naracauli (Fig. 1), which drains the Ingurtosu mine in the Arburese mining district in southwest Sardinia, has been studied because of the precipitation of unusual Zn minerals, including hydrozincite [$Zn_5(CO_3)_2(OH)_6$] and an amorphous Zn-rich phase (Medas et al., 2012a, 2012b; Medas et al., 2014a; Podda et al., 2014, and references therein). These are biologically mediated precipitation reactions (Podda et al., 2000; De Giudici et al., 2009; Medas et al., 2012a) and an understanding of how these Zn minerals form might provide insights into remediation of other streams affected by high Zn concentrations (Medas et al., 2014b). These reactions were studied in the Rio Naracauli by using a mass-loading approach (Kimball et al., 1994; Kimball et al., 2002) to quantify surface water and groundwater inputs to the stream, instream chemical processes, and to characterize the overall hydrologic conditions of the stream. In the mass-loading experiment, a conservative salt tracer is injected in the stream until a steady-state concentration is reached at each point along the entire reach of stream to be studied. By examining decreases in tracer concentration as a function of downstream distance, locations where water is added to the stream can be identified and the additions quantified. This hydrologic characterization allows for calculation of chemical mass balances so that the extent of the Zn precipitation process can be quantified with the stream as a laboratory.

1.1. Previous studies

Studies of heavy metal contamination from the Ingurtosu mine began in the 1990s by Luca Fanfani and his group at the University of Cagliari, and soon led to the discovery of precipitation of Zn-rich phases in the Rio Naracauli (Zuddas et al., 1998; Podda et al., 2000). The phenomenon occurs in two distinct sections of the stream, and yields two distinct Zn-bearing solids, one of which was recognized by X-ray diffraction as hydrozincite [$Zn_5(CO_3)_2(OH)_6$], whereas the other, informally described as "fango bianco" (= white mud), is actually a mixture of detrital quartz and an amorphous, Zn-rich phase, having a local atomic structure similar to hemimorphite ($Zn_4Si_2O_7(OH)_2H_2O$; Medas et al., 2014a; Podda et al., 2014); this phase will be referred to here as "Zn-silicate." Recent studies of Zn-isotope fractionation suggest that both precipitation processes are biologically mediated and likely depend on

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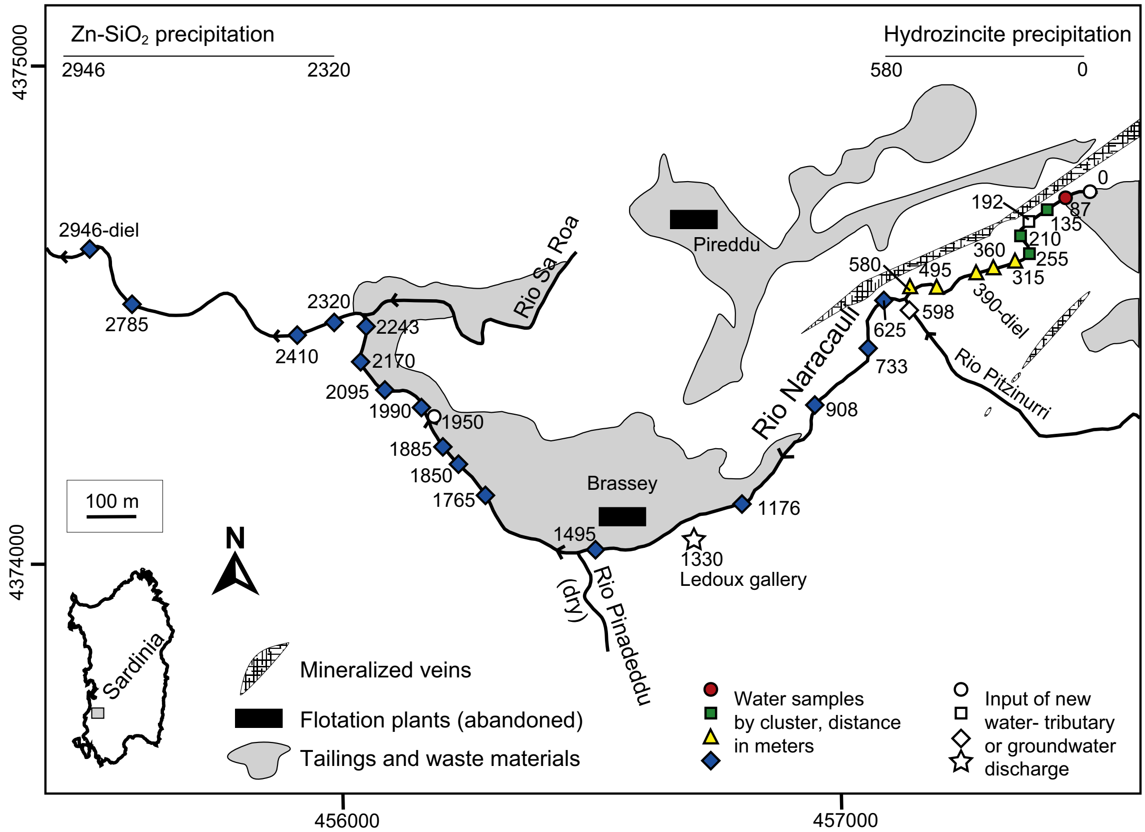

Fig. 1. Location map of the Ingurtosu study area. The town of Montevecchio lies approximately 6 km NE of the eastern side of this map, along the strike of the veins shown in the figure. X and Y coordinates in UTM Zone 32S. Symbols correspond to the cluster analysis results (circles for group 1, squares for group 2, triangles for group 3, diamonds for group 4, star for group 5). Inflows are shown as open symbols, stream samples are solid. Numbers next to each symbol correspond to distance downstream from the origin spring. At the top of the figure the approximate zones of precipitation of hydrozincite and Zn-silicate are shown.

establishment of microenvironments, with pH and carbonate concentrations much greater than the bulk solution, near bacterial surfaces (Wanty et al., 2013a, 2013b). In both cases, the formation of the Zn minerals is linked to specific microbiological assemblages (Podda et al., 2000, 2014). To our knowledge, this biomineralization of Zn is unusual and is documented only in the Rio Naracauli, although biomineralization involving other metals in mine drainage has been reported elsewhere (cf. Adlassnig et al., 2013). A detailed investigation of the causes leading to this phenomenon may open the way to novel approaches to remediation. Although concentrations of many elements were determined from repeated stream sampling from the late 1990s to present, the objectives of the study described here will focus on quantifying mass transport and precipitation derived from a tracer-dilution experiment conducted in June, 2011. From these results, we examine mass transport of Zn, SiO_2, and other selected elements that help establish the hydrologic and biogeochemical context for the reactions. Selected data appear in Table 1, and the full data set from detailed sampling in 2011 is included in the online supplemental data.

In previous papers (Podda et al., 2000; Medas et al., 2012a; Podda et al., 2014) we pointed out that cyanobacterial communities evolve along the Naracauli stream. In fact, according to our 20 years of data collection in Rio Naracauli, *Scytonema* sp. dominates in the upstream hydrozincite precipitation area, while *Leptolyngbya frigida* dominates in the downstream Zn-silicate precipitation area. These communities produce riverbed biofilms that have different basic physicochemical properties. *Scytonema* sp. has a hydrophilic surface, whereas *Leptolyngbya fr.* has a hydrophobic surface (Podda et al., 2014). On the surfaces of these biofilms, the two Zn minerals nucleate and grow according to substantially similar mechanisms that can be referred to as controlled biomineralization processes (De Giudici et al., 2009; Medas et al., 2012b; Wanty et al., 2013a; Podda et al., 2014). Podda et al. (2000) classified the strain responsible for hydrozincite precipitation as metallophile. Similarly, Sprocati et al. (2006) classified the Zn-silicate forming strain as metallophile (attribution of the strain to *Leptolyngbya frigida* is recent, Podda et al., 2014).

1.2. Field area

The Rio Naracauli originates from the Ingurtosu mine in southwest Sardinia. The mines, which have been inactive since 1968, produced mainly Pb and Zn from a laterally extensive vein system that extends for nearly 8 km from Ingurtosu to Montevecchio (Medas et al., 2012b and references therein). The headwaters of the Rio Naracauli are at an elevation of about 552 m asl, and within 8 km the Rio Naracauli empties into the Mediterranean Sea (Fig. 1). The tracer was injected at an elevation of just over 200 m, which at the time of our work was the highest elevation of perennial flow. The area experiences a Mediterranean climate, with an average annual temperature of about 17 °C, and approximately a half meter of precipitation that occurs mainly from September to April (Weatherbase, 2013). The 2011 samples were collected under near base-flow conditions in June. Further details of the study area are described in Medas et al. (2012a).

1.3. Mass-loading approach

Mass-loading studies have been used to quantify metal loads from abandoned and inactive mines and to support science-based decisions about remediation of streams and catchments. The approach is based on continuous injection of a tracer and synoptic-sampling methods that were developed in a series of studies in St. Kevin Gulch, Colorado, USA, for determining mass-loading in mine-drainage streams (Broshears et al., 1993; Kimball et al., 1994). The approach has since