Transport and Fate of Zinc in the Abandoned Mine District of Ingurtosu, Italy: A Mass- and Isotopic-Balance Approach

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The Rio Naracauli (RN) in SW Sardinia, Italy, drains a group of abandoned mines that produced primarily Zn and Pb until 1968, has near-neutral pH and Zn concentrations >10s of mg/L. In the upper reaches of RN, seasonal biomineralization of hydrozincite $\{Zn_5(CO_3)_2(OH)_6\}$ occurs. The hydrozincite forms on exopolysaccharide surfaces of a cyanobacterium [1], and selectively incorporates the heavier isotopes of Zn with a fractionation, Δ, of +0.35 ‰ [2]. In 2011, a tracer-injection experiment was conducted in the RN to quantify the sources and sinks of dissolved Zn and other metals. In the upper 600 m of the stream, where the hydrozincite forms, dissolved Zn concentrations decreased from 64 to 3.8 mg/L due to the biomineralization, and δ^{66}Zn of the dissolved Zn decreased from -0.04 to -0.24 ‰ relative to the JMC-3-0749-Lyon standard, as the heavier isotope went into the hydrozincite. From 200-600 meters along the RN, mass-balance calculations from the tracer experiment suggest that as much as 2.5 kg of hydrozincite forms annually in each meter of the stream.

Combining the mass- and isotope-balance calculations shows that the field data do not follow a Rayliegh distillation model. This result was expected because of the addition of isotopically heavier Zn in upwelling groundwater near 200m downstream from the origin of RN. If the Rayleigh calculation is reset to account for this added Zn, the distillation model fits the data more closely. The resetting is necessary because of both the different concentration and isotopic composition of the incoming groundwater. Thus, the model helps explain the loss of Zn due to hydrozincite biomineralization, as well as the gain of Zn from upwelling groundwater in the RN.

[1] Podda, Zuddas, Minacci, Pepi, Baldi (2000), *Appl. Env. Microbiol.* **66**, 5092-5098. [2] Wanty, Podda, De Giudici, Cidu, Lattanzi (2013), *Chem. Geol.* **337**-338, 1-10.