

Simulation of pre-mining metal concentrations in mine-impacted catchments: Redwell Basin, Colorado, USA

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With the increased importance of water resources the remediation of impacts from historical mining becomes ever more important. Making decisions about remediation for a catchment must rely on the identification of the principal sources of metal loading in the catchment and the classification of the sources as natural or anthropogenic. Simulations can help to evaluate different options for removal of anthropogenic sources. Goals for remediation, however, must be based on understanding the pre-mining conditions in the catchment, so that remediation does not under or over correct the impacts of mining. A field experiment combining tracer injection and synoptic sampling in Redwell Basin, Colorado, provided a setting to demonstrate this approach, and to evaluate pre-mining concentrations through reactive solute-transport modeling. The spatially detailed stream and inflow samples were the basis for calibrating the OTEQ reactive solute-transport model. The model not only accounts for the mass-balance removal of mining inputs, but also the chemical reactions that result from the subsequent changes in pH and metal concentrations. The field setting indicated that only two inflows were affected by mining. One drains from a mine adit and the other drains from an unplugged artesian exploration well. Pre-mining conditions were estimated by removing the loads of the two mine-impacted inflows. The resulting simulation included all the non-mining inputs and eliminated the anthropogenic inputs. Downstream from the two mining inflows, the simulated pre-mining pH would have been 5.1, up from 3.8 observed in the sampling. Pre-mining Al, Cu, and Zn would have been 140, 28, and 1,300 µg/L, respectively, all substantially lower than post-mining concentrations of 1,100, 93, and 3,440 µg/L. Equilibrium calculations suggest amorphous Al(OH)₃ would be undersaturated, so that the streambed would not be coated with Al precipitate at the higher pH. But the pre-mining Cu and Zn concentrations would have exceeded USEPA aquatic life criteria. Thus, even the pre-mining natural acid-rock drainage would have limited the viability of the stream for aquatic life. This understanding provides a critical context for setting realistic remediation goals.

Using TEM and µ-XRF to characterize bacterially-mediated precipitation of dissolved Copper

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This study focuses on interactions of dissolved Cu with the Fe- and S-oxidizing Proteobacterium *Acidithiobacillus ferrooxidans*, a prokaryote found in acid rock drainage, and the abundant ferric minerals that form during *A. ferrooxidans* growth. We used Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray Spectroscopy (EDS) to image and characterize cells grown at pH 2.0 in medium with 0, 0.1, 1, and 10 mM Cu added. We also used micro-X-ray fluorescence microscopy (µ-XRF) to characterize the chemistry of single cells and surrounding precipitates.

We analyzed precipitates with no cells (abiotic), precipitates with live cells, and precipitates with dead cells. Abiotic precipitates were globular, 0.5 – 0.75 µm in size after 2 days, contained O, P, S, Fe, and trace Cu, and were noncrystalline. Live biotic precipitates were 0.5 µm after 2 days and 1.5 µm after 7 days, chemically similar to abiotic precipitates but lacked P, and were crystalline. These precipitates were jarosite based on X-ray diffraction. Dead biotic precipitates were 20 – 50 nm in size after 6 days, were chemically similar to abiotic precipitates, and did not diffract electrons.

Cells grown in all experiments exhibited granules, with an average P/O = 0.37 ± 0.08 (atomic %) based on EDS, indicative of polyphosphate granules. Copper (and Fe) was associated with these granules. Copper was also a component of the jarosite precipitates. Copper likely coprecipitated with jarosite since the pH was too low for adsorption.

Preliminary µ-XRF results showed higher Cu concentrations within a dead cell relative to extracellular precipitates, with the highest concentration in the polyphosphate granule. We expect further µ-XRF on live cells to reveal cytoplasm free of Cu, and polyphosphate granules with only trace Cu, if any. This work reveals that live and dead *A. ferrooxidans* cells, as well as ferric precipitates, can remove dissolved Cu from solution at low pH. Future work aims to determine how significant these potential sinks are in affecting metal mobility in natural environments.