

Quantifying biogeochemical controls on metal behaviour within Acid Rock Drainage environments: amorphous Mn oxyhydroxide biomineral formation and associated metal sequestration.

Elizabeth A. Haack* and Lesley A. Warren
School of Geography and Geology, McMaster University, Hamilton, Ontario, Canada L8S 4K1
(*primary contact) haackea@mcmaster.ca

Abstract

Identifying the processes controlling reactive metal transport is a necessary prerequisite to the design of effective, mitigative, strategies for contaminated aqueous environments, such as acid rock drainage (ARD). Our research employs a combined field and laboratory approach to: 1) examine the biogeochemical processes that influence metal speciation; and to 2) characterize solid phases that control reactive metal transport in ARD environments. Results indicate that biofilms associated with shallow acid-impacted tailings streams accumulate metals (Mn, Ni, Co and Cr) on a seasonal basis, and that on a diel basis, biological cycling of amorphous Mn oxyhydroxides impacts trace metal retention within the biofilm matrix (Haack and Warren, 2003).

Metal Retention within ARD-stream associated biofilms

The tailings site is located at the Falconbridge Strathcona Nickel Mine (Onaping, Ontario). Several shallow (<5 cm) seepage streams flow over the tailings and ultimately discharge into a tailings pond. On a seasonal basis (June-September 2001 and June-August 2002), microbial mats of up to 1-3 mm in thickness covered extensive portions of the streambeds. Geochemical conditions of the acid-impacted shallow streams varied on both spatial and temporal (seasonally, diurnal) scales (e.g. pH 2.8-3.6 and temperature variation by up to 20°C over 24 hours). Dissolved (0.2 µm filtered) metal loads in the streams were high; typically in the mM (Fe) and µM range (Mn, Ni, Co and Cr). Reflecting the overlying water column metal loads, mean seasonal total metal concentrations in the biofilms decreased in the order: Fe (4.9 mmol/g) >> Ni (13.5 µmol/g) > Mn (1.9 µmol/g) > Cr (0.5 µmol/g) ≈ Co (0.4 µmol/g). However, while Fe concentrations remained relatively invariant, total Mn, Co, Ni and Cr concentrations increased significantly and linearly over the sampling season. For all metals analyzed, total concentrations in the biofilm were not correlated to their respective overlying water concentrations or to overlying water column pH. These results indicate that biofilms act as long-term sinks for metals and that metal retention within the biofilm is not controlled by bulk water column geochemistry.

Biological Cycling of Amorphous Mn Oxyhydroxides

Analysis of biofilm solid phases by sequential extraction indicated that as much as 75% of metals retained within the biofilm materials were associated with the amorphous oxyhydroxide fraction. Mn concentrations in the amorphous oxyhydroxide fraction, $[Mn]_{\text{Amorphous}}$, showed a cyclical pattern on a diel basis; Mn concentrations reached minimum values during photosynthetically active hours (Figure 1). Dissolution and precipitation of Mn oxyhydroxides is known to occur at oxic/anoxic interfaces (e.g. Van Cappellan et al., 1998), and reflect the redox control on Mn cycling. *In-situ* analysis of geochemical conditions within the biofilms using microelectrodes (DO and pH) indicated that a highly dynamic microenvironment was created within the biofilms with diel cycle as a result of photosynthesis and respiration. Diel shifts in oxygen production and consumption rates caused shifts in the oxygenated region of the biofilm (Figure 1), and resulted in vertical migration of the oxic/anoxic boundary by as much as 1 mm over a 24 hour period. The magnitude of the loss of $[Mn]_{\text{Amorphous}}$ was correlated ($p < 0.05$) to shifts in the relative depth of the oxic/anoxic boundary. Fluctuations in $[Mn]_{\text{Amorphous}}$ are proposed to be the result of: 1) a microbially catalyzed process of Mn oxidation and formation of Mn oxyhydroxides during non-photosynthetically active hours; and 2) dissolution processes during photosynthetically active, daylight hours.

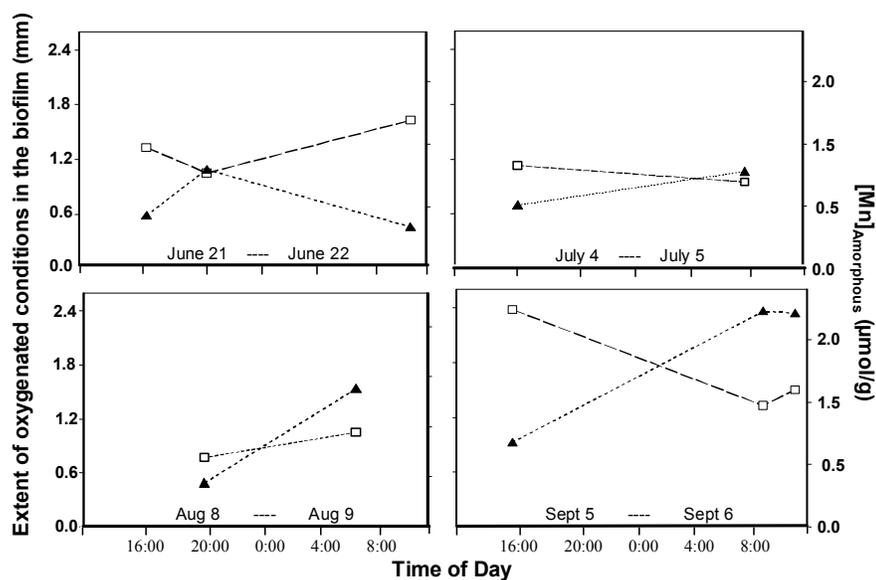


Figure 1: Amorphous Manganese oxyhydroxide concentration (solid triangles) and depth of oxygenated conditions in the biofilm (open squares) at all sampling times (Summer 2001). As oxygenated conditions extend deeper into the biofilm structure during photosynthetically active hours, amorphous Mn oxyhydroxide concentrations, $[Mn]_{Amorphous}$, decrease.

Trace Metal Dynamics

Ni, Co and Cr concentrations in the amorphous oxyhydroxides fraction were strongly and positively correlated to $[Mn]_{Amorphous}$. However, while Cr concentrations in the amorphous oxyhydroxide fraction showed diel fluctuation (constant Cr:Mn ratio), Ni and Co concentrations did not vary on a diel cycle resulting in enriched Ni:Mn and Co:Mn ratios during photosynthetically active daylight hours. These results suggest that Cr mobility, like Mn mobility is controlled by redox processes, while Ni and Co mobilities are likely controlled by sorption/precipitation processes. Currently, we are examining the reactive amorphous Mn oxyhydroxide phase on a fine scale (high resolution-TEM and associated EDX) and the oxidation state and local chemical environments of Mn and associated trace elements (XAFS). Results from these techniques will provide key insights into understanding the transport of contaminants as well as the biogeochemical processes controlling the redox cycling of Mn in this acid-impacted system.

Haack, E.A.; and Warren, L.A. Biofilms as geochemical solids: the role of microbial geochemistry in controlling trace metal dynamics in ARD seepage streams. **2003**, In review.

Van Capellen, P.; Viollier, E.; Roychoudhury, A.; Clark, L.; Ingall, E.; Lowe, K.; DiChristina, T. *Environ. Sci. Tech.* **1998**, *32*, 2931.