

Spatiotemporal evolution of manganese speciation at biofilm-fluid interfaces

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The speciation of manganese (Mn) dictates its mobility and reactivity in saturated soils. For example, enzymatic Mn(II) oxidation, or biomineralization, facilitates precipitation of Mn(IV) oxide nanoparticles with a high sorption capacity and redox potential, while Mn(II) sorption and subsequent mineral surface-mediated oxidation can produce less reactive Mn(III)-rich particles. Batch experiments have demonstrated that the degree of solid-phase alteration from Mn(IV)-rich to Mn(III)-rich particles depends on fluid chemistry, in particular Mn(II) concentration. However, in complex porous environments, Mn(II) availability for Mn-oxidizing biofilms is dictated by flow heterogeneity and transport limitation, and thus Mn oxide composition at biofilm-fluid interfaces is not well understood. To this end, we performed flow-through microfluidic experiments with the Mn-oxidizing bacterium *Pseudomonas putida* GB-1 to promote Mn biomineralization in a model porous medium. At Beamlines 2-3 and 7-2 at the Stanford Synchrotron Radiation Lightsource, we combined optical microscopy and X-ray fluorescence spectro-microscopy to visualize Mn oxide precipitation and quantify Mn mass. We then used principal component analysis and linear combination fitting to identify Mn oxidation states and track their pore-scale spatiotemporal evolution. Preliminary data show that regions near the aqueous Mn(II) source contained about an order of magnitude more mass than regions near the reactor outlet. Additionally, these inlet regions contained a higher fraction of Mn(IV) (~42-54%) than outlet regions (~18-30%) at the final experimental time point. While the Mn(II) fraction increased towards the outlet, we observed similar Mn(III) fractions throughout the pore space. This suggests that enzymatic oxidation was most prevalent closest to the Mn(II) source, leading to an accumulation of Mn(IV) and likely drawing down the dissolved Mn concentration for downstream biofilms. In multiple inlet and outlet regions, Mn(II) and Mn(IV) appeared spatially segregated, which may indicate that local transport conditions determine the relative contribution of enzymatic oxidation and sorption to Mn accumulation within biofilms. Tracking pore-scale Mn speciation offers insights into mechanisms underlying microbe-mineral-fluid interactions and the associated effects on soil nutrient cycling and contaminant attenuation.