Influx of Oxidants into Reduced Zones: Microbiological Controls Governing Metal Oxidation and Reduction

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Project Abstract:
The existing paradigm describes oxidation of reduced chemical species, such as Fe(II) and U(IV), following an influx of oxidants such as dissolved oxygen (DO) or nitrate. However, prior field results challenged current understanding of the oxidant's role controlling redox behavior of metals/radionuclides; low concentrations of an oxidant (DO) injected into a biostimulated reduced region of an alluvial aquifer stimulated a decrease in aqueous U concentrations *in situ*. Here we experimentally test the impact of a highly soluble oxidant, nitrate, on U redox state using organic-rich, naturally reduced-U bearing oxbow lake sediments (collected from Riverton, WY; SLAC SFA). Triplicate batch reactors of reduced sediments were amended with anoxic bicarbonate buffered medium with and without the addition of nitrate at varying concentrations (low nitrate <14 mg/L-N> high nitrate) following preincubation with added uranyl chloride (final concentration 5 mg/L). High nitrate amended batch reactors increased dissolved U(VI) consistent with oxidation of reduced species. However, low nitrate amendments resulted in a decrease of dissolved U(VI), consistent with reduction. No significant change in dissolved U(VI) was observed in controls amended with anoxic DI water. XANES analysis of collected sediments revealed an increase in sedimentary U(IV) (85% of U) in reactors amended with low nitrate relative to the control (40% U(IV) of sedimentary U). Thus indicating U(VI) reduction in response to low nitrate amendment. An increase in aqueous Fe(II) further supported the onset of reducing conditions. A decrease in sulfide was observed. PHREEQC modeling of geochemical data indicated Fe-sulfide precipitation, which would account for the observed decrease in aqueous sulfide. Reduction activity in low nitrate amended treatments occurred concurrent with an increase in dissolved organic carbon (DOC) and cell and virus abundance. Metagenome assembled genomes revealed the metabolic potential for both lithotrophic and organotrophic nitrate reduction as well as metal/radionuclide and sulfur cycling. Recovery of metagenome assembled virus genomes from microbial (>0.2μm) and virome (<0.2 μm and >0.05 μm) samples indicated a change in viral community in response to nitrate amendments. These results indicate the potential of microbially-mediated cell lysis and recycling of organic carbon. To verify that the observed geochemical processes were stimulated by microbial activity, batch reactors were amended with the antibiotic chloramphenicol and demonstrated suppression of both nitrate reduction and removal of aqueous U. Together these results demonstrate that in organic rich sediments a "tipping point" exists where an influx of an oxidant can lead to the increase in DOC supporting microbial activity and reducing conditions.