# Geochemical and microbiological response to oxidant introduction into reduced Hanford 300 Area sediments

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Pliocene-age Ringold Formation sediment from below the subsurface redox transition zone (RTZ) at the Hanford 300 Area site was employed in a study of the geochemical response to introduction of oxygen or nitrate in the presence or absence of microbial activity. The fine-grained reduced sediments contained large quantities of reduced Fe in the form of Fe(II)-bearing phyllosilicates, together with smaller quantities of siderite and pyrite. The purpose of the experiments was to assess the potential for native microbial communities to oxidize sediment-associated reduced Fe/S phases in response to oxidant influx, and thereby influence redox balance within the RTZ. A suite of reactors was constructed with dried reduced subsurface material and artificial Hanford groundwater. The reactors were amended with either 10 mM nitrate, an oxic headspace, or no added oxidant. They were inoculated with sediment containing native microbial communities from the either within or below the RTZ. A parallel set of uninoculated sterile controls were also constructed. During a 910-day incubation, a loss of ca. 50% of 0.5 M HCl-extractable Fe(II) (5-10 mmol Fe(II)/L), and detectable generation of sulfate (ca. 0.2 mM, equivalent to 10% of the reduced inorganic sulfur pool) was observed in sterile aerobic reactors. All of the inoculated and the sterile reactors amended with nitrate showed no Fe(II) loss or sulfate generation suspensions despite (1) the recent recovery of chemolithotrophic Fe(II)-oxidizing bacteria from Hanford/Ringold formation sediments, and (2) the detection of genes for $CO_2$ fixation (Rubisco) in sediments within the RTZ. In contrast, significant nitrate (and, putatively, oxygen) consumption occurred via heterotrophic metabolism took place in the inoculated reactors. In addition, detectable accumulation of Fe(II) and complete consumption of sulfate took place in inoculated oxidant-free reactors. The organic carbon (OC) content of the sediments employed in this study as well as measured OC concentrations within and below the RTZ was sufficient to account for the observed heterotrophic metabolism. Diffusion-reaction simulations of oxygen and nitrate consumption coupled to solid-phase OC oxidation indicate that heterotrophic consumption of oxidants could play a key role in maintaining the redox boundary at its current position. These findings are consistent with a variety of prior observations that Ringold Formation sediments contain active heterotrophic microbial communities, and reveal that such communities are poised to respond to oxidant influx and thereby act as barrier to vertical U, nitrate, and other redox-sensitive contaminant migration over millennial time scales.