

## **Fine Scale Biogeochemical Processes in Hyporheic Zone Sediments**

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A series of experiments and model simulations were performed to derive kinetic models and parameters for describing the biogeochemical transformations of organic carbon, nitrate, and contaminant (Cr) in Columbia River hyporheic zone sediments. Denitrification of nitrate to nitrite and gaseous  $N_2O$  and  $N_2$ ; direct nitrate reduction to ammonium (DNRA); nitrification from ammonium to nitrate; and anaerobic ammonium oxidation (Anammox) were all observed in the hyporheic zone sediments. The relative importance of these multiple processes to nitrate transformation was influenced by contact water chemical composition, fluid residence time, and ion exchange reactions. Dissolved and sediment-associated organic carbon (OC) chemical properties including speciation, nominal oxidation state, and double bond counts changed significantly during nitrate transformation in response to the changes in contact water chemical composition. A reaction network has been established based on these findings to describe nitrate- and, more generally, N-transformation in the sediments. These results, combined with functional gene, enzymes measurements, and microbial community analysis, will be used to evaluate enzyme-based biogeochemical models to describe the evolution of microbial community functions and biogeochemical process kinetics.

Experiments and modeling simulations were also performed using the Cr redox reaction as a probe to investigate the redox properties of the hyporheic zone sediments. Kinetic studies indicated that Cr(VI) can be reduced to poorly soluble Cr(III) with a reduction rate that correlated with the sediment Fe(II) concentration. The reduced Cr was stable in presence of  $O_2$  and Mn oxides under circumneutral pH conditions. Microbial reduction of the sediments promoted by native OC can further enhance the redox capacity and the rate of Cr reduction. A reaction network linking Cr(VI) reduction with Fe(II) oxidation, the production of biogenic Fe(II) coupled with OC oxidation, and abiotic oxidation of Fe(II) by river water oxygen was developed and applied to simulate coupled biotic and abiotic reactions in the hyporheic zone under dynamic hydrological conditions. The results provide important insights to the functioning of the hyporheic zone as a redox barrier for Cr sequestration. The reaction network and associated kinetic parameters for N, Fe, and Cr redox transformations coupled with OC speciation forms the basis for an integrated multi-component, biogeochemical kinetic model applicable to the Columbia River hyporheic zone and up-scaled domains of the Hanford Reach.