

## Chromium Diffusion and Reduction in Soil Aggregates

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**Introduction:** Predicting the transport and transformation of redox-sensitive metal contaminants in the subsurface environment remains challenging because of extreme differences in the permeabilities and diffusivities associated with macropores (fractures) and aggregates (sediment blocks). While the composition and activity of the microorganisms in such environments is constrained by transport limitations (oxygen, other terminal electron acceptors, carbon, and other nutrients), microbial communities can also exert dominant influences on transport and transformations of redox-sensitive elements including metal contaminants. A mechanistic understanding of interrelations between sediment physical structure, microbial populations, and transport-transformation of metal contaminants needs to be developed. This can not be obtained solely through studies of either model batch systems or of large columns since neither approach provides the necessary information on small-scale gradients in chemical and microbial composition. Thus, spatially-resolved studies integrating chemical transport and microbial dynamics within sediments are needed. Measurements of chromium diffusion and reduction in natural soil aggregates are being obtained to better understand its fate in contaminated field settings. Spatially-resolved microbiological characterization is also being done on the same systems.

**Methods and Materials:** Experiments were conducted on Altamont clay soil aggregates, saturated with a neutral salt solution containing either 0, 80, or 800 ppm organic carbon (OC), in order to stimulate growth of the indigenous microbial community to different levels. Following 14 days of incubation, the aggregates were placed in contact with a 1,000 ppm Cr(VI) solution for 3 days. This solution also contained 1,000 ppm bromide as a nonreactive tracer. One set of aggregates was then frozen, freeze-dried, epoxy-fixed, and sliced for micro-XANES mapping. Another set of aggregates was further incubated for 31 days, and then prepared in the same manner. The x-ray microprobe was used to map total Br and total Cr. The local Cr(VI) to total Cr ratio was determined from the relative intensity of the Cr pre-edge peak.

**Results and Conclusions:** X-ray microprobe and micro-XANES maps showed distinctly different patterns of total Cr, Cr(VI), and Cr(III) distributions within the soil aggregates, depending on the level of OC supplied in the initial wetting solution. In contrast, the Br- tracer exhibited similar diffuse distributions, independent of OC level. With higher OC, transport of Cr(VI) into aggregates and subsequent reduction to insoluble Cr(III) was higher, but restricted to shallower depths below aggregate surfaces. In the high OC aggregates, Cr(VI) typically diffused only about 10 to 15 mm before being reduced to Cr(III). The sharp termination of Cr diffusion fronts in high OC aggregates is indicative of rapidly increasing reduction rates with distance. These results, obtained on intact, natural aggregates, are similar to those from our previous work on homogeneous, synthetic soil aggregates. Separate experiments on Cr(VI) reduction by the soil microbial community, and by the OC amendment alone revealed much slower reduction rates. In these alkaline soils, the microbial role in Cr reduction appears to be dominated by dissimilatory Fe reduction, which in turn permits Cr(VI) reduction by Fe(II). In biologically active aggregates, gradients in redox conditions can be substantial over mm distances, such that redox reaction rates can be highly variable as well. In high OC soil profiles containing large aggregates, the combined effects of preferential flow and diffusion-limited Cr(VI) reduction can restrict the actual reactive soil volume to a small fraction of the bulk volume. Bulk chemical and microbiological characterization of such soils ignore important spatial relations needed to understand reactive transport.

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