

# Diffusion-Limited Reduction of Chromium in Soil Aggregates

T. K. Tokunaga,<sup>1</sup> J. Wan,<sup>1</sup> T. C. Hazen,<sup>1</sup> K. R. Olson,<sup>1</sup> E. Schwartz,<sup>2</sup> M. K. Firestone,<sup>2</sup>  
S. R. Sutton,<sup>3</sup> M. Newville,<sup>3</sup> A. Lanzirotti<sup>3</sup>

<sup>1</sup> Lawrence Berkeley National Laboratory, Berkeley, CA, U.S.A.

<sup>2</sup> University of California, Berkeley, CA, U.S.A.

<sup>3</sup> The University of Chicago, Chicago, IL, U.S.A.

## Introduction

The fate of metal contaminants in soils and sediments is controlled by interdependent influences of transport and biogeochemical reactions. Laboratory studies of biogeochemical processes that determine the fate of contaminants are commonly conducted in well-mixed suspensions and solution cultures. Limitations in applying results of laboratory studies to field environments often relate to the fact that the subsurface contains a broad spectrum of microenvironments, while individual laboratory batch studies apply to specific microenvironments. The gap between understanding of well-mixed batch systems and observations on very complex natural subsurface systems provides incentive to examine biogeochemical dynamics in systems of intermediate complexity, which include the critical characteristics and coupling of relevant microenvironments. Since individual soil aggregates (cohesive units comprised of individual mineral particles) can contain wide variations in chemical and microbiological composition, studies of intra-aggregate biogeochemical transformations provide opportunities to identify how microenvironments are coupled. Steep gradients in oxygen concentrations and redox potentials in soil aggregates that exhibit anaerobic interiors indicate that transformations experienced by redox-sensitive metal contaminants can occur within short distances. The studies presented here are aimed at understanding the interactions of aggregate microenvironments and microbial communities that control the fate of Cr(VI) contamination.

Chromium is used in a variety of industrial processes, and its hexavalent species have become a serious problem as a soil contaminant at hundreds of hazardous waste sites because it is a respiratory carcinogen and acutely toxic in high doses. In uncontaminated soils, Cr is found as Cr(III) because of the high pe range associated with Cr(VI)-Cr(III) transformations, and high proportions of Cr(VI) are largely restricted to contaminated sites. Cr(III) occurs in soil primarily as stable solids and strongly adsorbed species, while most Cr(VI) species are soluble and mobile. Recent comparisons of abiotic versus enzymatic Cr(VI) reduction kinetics indicate that aqueous Fe(II) is expected to be dominant in neutral to alkaline anaerobic soils.<sup>1</sup> Active microbial communities nevertheless exert dominant influences since they mediate the depletion of oxygen and the availability of reactive reductants [Fe(II) and S(-II)]. Soil microbial communities are also influenced by exposure to high concentrations of Cr(VI), with responses including death, resistance development, and enzymatic reduction. Thus, interactions between soil microbial communities and invading Cr(VI) solutions are complex but central to the fate of the contaminant.

## Methods and Materials

Experiments were conducted on small soil columns designed to represent transects into synthetic aggregates,<sup>2</sup> and on actual soil

aggregates. In the column studies, experiments on Cr diffusion and reduction were conducted in 30-mm-long soil columns. Prior to introducing Cr(VI), the columns were saturated with solutions containing from 0 to 800 ppm organic carbon (as tryptic soy broth) and incubated for 14 days. The carbon amendments were added to stimulate microbial respiration and develop more reducing conditions. The Cr(VI) solutions were then introduced to one end of each column (representing the exterior surface of an aggregate) and allowed to diffuse inwards. Redox potential profiles were measured with Pt electrodes. The GeoSoilEnviroCARS beamline 13-ID-C was used to obtain micro x-ray absorption near-edge structure (micro-XANES) spectroscopy profiles of Cr(VI) and Cr(III) distributions.

The second stage of experiments was designed to test for Cr redox zonation during contamination of natural, intact soil aggregates. The same solutions used in the previous experiments were used to wet these soil aggregates. Following 17 days of incubation, these aggregates were immersed in individual containers of Cr(VI) solutions (1000 ppm initial Cr) for 3 days, representing an episodic contamination event. After removal from Cr(VI) solution, aggregates were freeze-dried, fixed with a low-viscosity resin, and cut to obtain 5-mm-thick slab cross sections. One surface of each slab was polished for synchrotron x-ray microprobe mapping of Cr distributions. An additional set of aggregates was prepared in the same manner, without freezing and fixing with resin for micro-XANES determination of the percentage of Cr(VI). Portions of these aggregates were cored to obtain depth-profile analyses of microbial communities [phospholipid fatty acid (PLFA) analyses, enzymes, and the density and activity of total microorganisms] and for additional Cr XANES analyses.

## Results and Discussion

Under more reducing conditions (redox potentials < -100 mV), Cr(VI) diffusion and Cr(III) precipitation were limited to distances of a few mm in the synthetic soil aggregates, with abruptly terminated transport fronts. Thus, sharp boundaries between contaminated and uncontaminated regions can develop. Bacterial communities were characterized using DNA fingerprints. Principal component analysis of terminal restriction fragment length polymorphism patterns distinguished the region exposed to Cr(VI) from unexposed regions. Ribosomal intergenic spacer analysis of extracted bacterial DNA also showed that unique intergenic sequences were present in the soil sample exposed to Cr(VI). Control tests on Cr(VI) in sterile soils with carbon added showed negligible Cr reduction rates. With higher microbial activity, anoxic conditions are established at shallower depths. Such conditions facilitate Cr(VI) reduction within short distances below oxic surfaces, thereby sustaining large Cr(VI) concentration gradients at the surface, and larger diffusive influxes. The sharply terminated

Cr contaminant fronts indicate that Cr(VI) reduction rates increase rapidly with depth into the aggregates. Aqueous Fe(II) is likely to be the primary reductant,<sup>1</sup> but its concentration profiles were not obtained.

X-ray microprobe maps of Cr distributions in resin-fixed natural aggregates were obtained at beamline X26A of the National Synchrotron Light Source. Measured Cr distributions in natural aggregates are very similar to those obtained in the model synthetic aggregates. Aggregates with higher available organic carbon took up higher amounts of Cr(VI) and reductively precipitated Cr(III) within shorter distances. Micro-XANES analyses showed that transported Cr was largely reduced to Cr(III), with only 23, 11, and 4% remaining as Cr(VI) in the +0, +80, and +800 ppm organic carbon systems, respectively. Total microbial biomass (as measured by PLFA and by direct fluorochrome staining) was not significantly affected by exposure to Cr or by differing concentrations of organic carbon. The proportion of the total microorganisms that was active, however, was higher in aggregates that received the highest concentrations of organic carbon. This suggests that the spatial distribution of microbial activity in the aggregates is related to the creation of redox gradients and to Cr(VI) reduction. This was further supported by the measurement of dehydrogenase activity within the aggregates. The average dehydrogenase activity was highest in the outermost (0-20 mm) regions of aggregates presaturated with 800 ppm organic carbon (dehydrogenase concentrations of 686  $\mu\text{g/g}$  soil after 7 days incubation). In contrast, deeper parts of these same aggregates (the 20-60 mm depths) had average dehydrogenase concentrations that were no higher than 17% that of outer regions.

These results show the importance of intra-aggregate spatial relations for redox-sensitive contaminants as well as for the microbial communities responsible for redox gradients and reductants. By extension, similar stratification of redox potentials, metal contaminants, and microbial communities might occur within larger sediment blocks deeper in the subsurface. In soils and sediments comprised of aggregates or blocks that support internal redox gradients, bulk characterization of chemical and microbiological conditions does not allow mechanistic understanding of biogeochemical processes controlling the fate and transport of contaminants.

## Acknowledgments

We thank Andrew Mei, and Tracy Letain of LBNL, and GSECARS staff for assistance. Funding for this study was provided through the Basic Energy Sciences, Geosciences Research Program, and the Natural and Accelerated Bioremediation Research Program of the U. S. Department of Energy (DOE). Use of the Advanced Photon Source was supported by the U.S. DOE, Office of Science, Basic Energy Sciences, under Contract No. W-31-109-Eng-38. Research was carried out (in part) at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U. S. DOE, Division of Materials Sciences and Division of Chemical Sciences.

## References

- <sup>1</sup> S. Fendorf, B.W. Wielinga, and C. M. Hansel, *Int. Geol. Rev.*, **42**, 691-701 (2000).
- <sup>2</sup> T.K. Tokunaga, J. Wan, M.K. Firestone, T.C. Hazen, E. Schwartz, S.R. Sutton, and M. Newville, manuscript submitted.