

Diffusion-limited biotransformation of metal contaminants in soils/sediments: chromium

T. Tokunaga[♦], J. Wan[♦], D. Joyner[♦], T. Hazen[♦], M. Firestone[•], E. Schwartz[•], S. Sutton[■], and M. Newville[■]

[♦]*Lawrence Berkeley National Laboratory, Berkeley, CA 94720 USA*

[•]*University of California, Berkeley, CA 94720 USA*

[■]*University of Chicago, Chicago, IL 60637 USA*

Introduction

Understanding transport and reactions of metal contaminants such as chromium in soils is complicated by potentially ambiguous speciation obtained from indirect, chemical-extraction-based analyses and by small-scale variations in physical, chemical, and microbiological characteristics. The fate of elements with highly redox sensitive solubilities can be especially complex because of possible unwanted changes in redox potentials during chemical extraction and strong redox potential gradients that can develop over short (less than mm scale) distances in environmental systems. In soil and groundwater systems, Cr exists in the III and VI oxidation states, with the majority of the former being stable solids or strongly adsorbed species, and the majority of the latter being more soluble and mobile [1]. Transport and reactions of chromium in soils are critical concerns in many metal contaminated environments because of the carcinogenic effects of Cr(VI). Thus, transport and reduction rates of Cr(VI) in soils need to be measured in order to understand and possibly remediate Cr contamination. Both Cr transport and reduction rates ultimately reflect interdependent influences of physical (transport), geochemical, and microbial processes.

The process tested in this study is the response of soil aggregates (cohesive structural units comprised of many primary mineral particles) to a Cr(VI) contamination event. In cohesive soils, aggregate sizes can exceed 100 μm and contain a wide range of microenvironments. In structured soils, it is commonly hypothesized that contaminants rapidly move through a small subset of hydraulically active macropores and slowly diffuse into the adjacent soil matrix. Under such a scenario, the surficial region of soil aggregates may sustain oxidizing conditions favoring stability of Cr(VI), while interiors of aggregates are more reducing, hence permit conversion to Cr(III). It is expected that the level of microbial activity within aggregates is critical in controlling the extent of Cr(VI) reduction, primarily through control of intra-aggregate redox potentials. The availability of potential reductants [Fe(II), Mn(II), S(-II), and organic carbon] depends strongly on microbial activity. The interdependent influences that sediment structure and microbial communities have on transport and reduction of chromate are being investigated in various microcosm and batch systems of clay (Altamont, CA) and fine sand (Savannah River, SC) sediments.

X-ray absorption spectroscopy is an essential component in this work because it permits direct speciation on essentially undisturbed environmental samples [2]. In particular, the technique of micro-XANES (x-ray absorption near edge structure) spectroscopy was used because of primary interest

in oxidation state determination and the need for spatially resolved measurements [3, 4].

Methods and Materials

Synthetic soil aggregate microcosms were prepared with either Altamont clay or Savannah River fine sand. These microcosms were typically 30 mm in length, 10 mm in width, and about 5 mm in thickness. The long (30 mm) dimension represented a transect into a soil aggregate, with an aerobic boundary at one end and a potentially anaerobic core region on the opposite end. Microcosms included arrays of Pt electrodes (2 to 5 mm spacing) to measure redox potential profiles over the full course of the experiment. A Kapton window covered one side of each microcosm to permit x-ray profiling. Additional microcosms were constructed in modified 5 cc syringes to facilitate later extrusion and sectioning of sediments. The soils were saturated with either a neutral salt (KCl, CaSO₄), 80 ppm organic carbon (OC), or 800 ppm OC solution. Tryptic soy broth was used as the OC source. These soils had about 1% native OC, and the OC-amended soils permitted more rapid microbial growth, hence more reducing conditions. Sterilized (gamma irradiation) control soil microcosms were also saturated with the same three wetting solutions. Following 14 days of incubation, the exterior boundary of each microcosm was exposed to up to 5200 ppm Cr(VI) solution for three days, simulating an episodic contamination event. Micro-XANES (GSECARS, 13-ID-C) profiles of total Cr, Cr(VI), and Cr(III) were measured within the aggregates at various stages following Cr exposure. For this purpose, the monochromator was cycled through -10, 0, and +40 eV relative to the Cr(VI) pre-edge peak energy (5993 eV). Although a much finer spatial resolution (1 μm) is possible on this beamline, a defocused x-ray beam of $\approx 100 \mu\text{m}$ was used for this study. The larger spot size was selected (i) in order to volume average over a sufficient number of soil particles and pores, (ii) because of the moderately large CrO₄²⁻ diffusivity in these sediments, and (iii) to minimize x-ray-induced Cr(VI) reduction. This latter artifact was kept to less than 5% based upon separate time-dependent tests. Microcosms were sectioned at various times (3, 13, and 30 days) after exposure to Cr(VI) for characterization of microbial population profiles within aggregates [intergenic transcribed spacer (ITS), denaturant gradient gel electrophoresis (DGGE), and direct counting] and for other chemical analyses.

Results

Redox potential profiles typically stabilized within 10 to 14 days relative to initial wetting. Spatially resolved redox measurements in the sediment microcosms showed expected lower potentials in systems with higher OC addition and more oxidizing conditions within 2 to 4 mm of aggregate surfaces. Upon addition of CrO_4^{2-} , local increases in redox potentials were measured within several mm of the exposure boundary.

Spatially resolved micro-XANES spectroscopy typically showed short Cr penetration distances in the Altamont clay, with abrupt rather than diffuse termination. Micro-XANES analysis provided direct evidence of nearly complete Cr(VI) reduction to less toxic Cr(III) forms. The extent of Cr transport into sediment blocks was far less than expected by diffusion without reduction, inversely related to OC amendment and proportional to the boundary Cr(VI) concentration. In the case of the Savannah River fine sand, greater Cr penetration depths were measured, indicative of slower Cr(VI) reduction kinetics. Retardation of the CrO_4^{2-} diffusion front by adsorption onto minerals was negligible in the case of the Altamont clay because of lack of protonated surfaces under the alkaline pH (8.5). In the case of the Savannah River sand, low surface area and low Fe content minimized influences of CrO_4^{2-} adsorption.

The microbial communities and populations in sediment microcosms were characterized with DNA fingerprints, direct counting and enrichment culturing. ITS analyses of the Altamont soil microcosm incubated with 80 ppm added OC followed by contamination with 260 ppm Cr(VI) showed that the microbial community composition in the exposure region (only the outermost 2 mm of the microcosm) is different from those in sediments taken from greater depth. Several populations appear only in soil that was exposed to Cr suggesting they are chromium resistant and that they may play an active role in Cr reduction. These results were confirmed with DGGE, where again, certain bands appeared only in fingerprints taken from soil communities that were exposed to Cr(VI). Direct counting of microbial populations in the sediment microcosms showed higher population densities in the outer layers for the sample exposed to 260 ppm Cr. More growth occurred in the surface layer sediment due to the availability of oxygen. Similar patterns (i.e., unique populations developing in the Cr-contaminated zone) were observed in the other microcosms.

In related batch studies, several microbial cultures have been enriched from the sediments used in the microcosms on 800 ppm OC in the presence of 100 ppm Cr(VI). These cultures will be further characterized by sequencing their 16S ribosomal genes. Analyses of batch and microcosm samples are ongoing.

Discussion

These results show how a metal contaminant, Cr(VI), becomes very locally reduced within soil aggregates, depending on redox conditions established by microorganisms. Microbial respiration combined with low O_2 diffusivities in nearly water-saturated soils results in low redox potentials in interior regions of aggregates. Generation of reducing microsites within aggregates is also limited by available organic carbon. In systems with high microbial activity, reducing conditions can easily develop at the mm scale. The implications of anaerobic microsites in soils have been well known for many years in the context of denitrification [5], and the general process has relevance to the fate of other redox-sensitive elements, including chlorinated organic and trace-element contaminants [6, 7]. In general, the spatial resolution needed for understanding such systems is determined by characteristic transport distances, and these distances in turn are determined by characteristic reaction times. The need for measurements and models with at least mm scale spatial resolution was demonstrated for highly nonequilibrium reactive transport of Cr within soil aggregates. In such systems, coarser scale volume-averaged chemical speciation will not permit mechanistic characterization of reactive transport.

Acknowledgments

We thank Keith Olson, Andrew Mei, and H. Scott Mountford of LBNL, and GSECARS staff for assistance. Funding for this study was provided through the U. S. Department of Energy, NABIR and Basic Energy Sciences, Geosciences Research Programs. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38.

References

- [1] D. Rai, E. Eary, and J.M. Zachara, *Sci. Total Environ.* **86**, 15–23 (1989).
- [2] G.E. Brown, Jr. and G.A. Parks, *Rev. Geophys.* **27**, 519–533 (1989).
- [3] D.G. Schulze and P.M. Bertsch, *Adv. Agron.* **55**, 1–66 (1995).
- [4] S.R. Sutton and M.L. Rivers, *CMS Workshop Lectures*, Synchrotron X-ray Methods in Clay Science, **9**, 146–163 (1999).
- [5] K.A. Smith, *Soil Sci.* **123**, 284–291 (1977).
- [6] M.V. Enzien, F. Picardal, T.C. Hazen, R.G. Arnold, and C.B. Fliermans, *Appl. Environ. Microbiology* **60**, 2200–2204 (1994).
- [7] T.K. Tokunaga, S.R. Sutton, and S. Bajt, *Soil Sci.* **158**, 421–434 (1994).