

***In Situ* Reduction of Cr(VI) in Contaminated Soils through Organic Carbon Amendment**

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Introduction

Chromium is used in a wide variety of processes and products and has become a common metal contaminant in soils [1]. In soils and sediments, Cr occurs primarily in two oxidation states having very different behavior [2]. Cr(VI), as CrO_4^{2-} and HCrO_4^- , is generally more soluble and more mobile. Hexavalent Cr is also more toxic, especially through inhalation, when it can be carcinogenic. In the reduced, trivalent state, Cr is generally much less soluble, less mobile, and less hazardous. In soils that have been contaminated with Cr(VI), overall rates of reduction to Cr(III) forms are of great interest because of the vastly differing toxicities associated with these two oxidation states.

One approach to remediating Cr(VI)-contaminated soils involves accelerating *in situ* reduction to Cr(III) through organic carbon (OC) infusion. The effectiveness of OC amendments in reducing Cr(VI) will generally depend on the concentration of the metal contaminant, the reactivity and bioavailability of OC, and microbial activity. Net Cr(VI) reduction in soils occurs through a complex network of synergistic and competing processes. These include direct enzymatic reduction by microorganisms, reduction by various forms of OC, reduction by ferrous iron and sulfide (for which sustained availability requires microbial mediation), and catalytic influences of mineral surfaces.

Despite the fact that some Cr-contaminated soils and groundwater do contain very high levels of Cr(VI), exceeding 1000 ppm [1], very few laboratory studies have been conducted at concentrations relevant to remediating such conditions where microbially dependent pathways can be impaired.

A common limitation of *in situ* remediation is the fact that delivery of reagents is typically ineffective. Infiltrating water, contaminants, and injected reducing agents all tend to distribute, initially primarily through interconnected higher-permeability pathways and secondarily through lower-permeability domains that can make up most of the subsurface volume. Transport in these latter domains (soil aggregates and sediment blocks) can be diffusion-dominated and slow. Thus, in order to understand the dynamics of contamination and *in situ* remediation processes, it is essential to include transport influences. One approach to including these effects

involves conducting experiments in soil columns where transport can become diffusion-dominated.

In this study, competing effects of the initial level of Cr(VI) contamination and the amount of OC added were tested in small soil columns. Our primary goals are to determine (a) the overall effect of OC availability on Cr reduction in soils, (b) the collective importance of microbially dependent Cr(VI) reduction pathways vs. abiotic pathways in highly contaminated oxidizing soils, and (c) whether spatial heterogeneity of Cr develops during OC-stimulated Cr reduction.

Methods and Materials

Small soil columns were used to represent transects into subsurface domains where transport is diffusion-limited [3]. One end of each column represents the exterior of an aggregate, through which components (water, O_2 , CO_2 , Cr(VI), OC) are exchanged between the soil and its environment. Columns were packed with soil from the C horizon of Altamont clay (Alameda County, CA). The native Cr concentration of this soil is 60 ppm, with more than 95% as Cr(III). Soils were infiltrated with solutions containing 1,000 or 10,000 ppm Cr(VI) added as K_2CrO_4 . Five days later, the hydrostatic columns were ponded with solutions containing OC as either tryptic soy broth or sodium lactate. Solutions with 0 (deionized water control), 800, or 4000 ppm of organic carbon were ponded on each column. Tryptic soy broth was used as a carbon source, representing decomposing plant tissue. Lactate was used in several columns since it is an easily metabolized carbon source, with related compounds now being tested for use in *in situ* bioremediation [4]. Redox potential profiles were periodically measured through a series of Pt electrodes embedded along columns. Measurements of pH were also obtained at the exterior surface of each column.

Profiles of Cr concentrations and oxidation states in soil columns were obtained at various times after exposure to Cr(VI) solutions by using micro x-ray absorption near-edge structure (micro-XANES) spectroscopy. Micro-XANES measurements were obtained at the GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS) beamline 13-ID-C and at beamline X26A of the National Synchrotron Light Source. Large beam sizes of about 300 μm were used in all measurements in order to average over a large population

of mineral grains and pores. The broad beam size also helped minimize x-ray beam-induced Cr(VI) reduction, which was a problem encountered when obtaining micro-XANES data at the brighter GSECARS beamline. Soil columns were scanned with the monochromatic beam set at the pre-edge peak energy and at energies in a range of 150 to 205 eV above the pre-edge absorption energy.

In order to determine the extent to which microorganisms contributed to Cr(VI) reduction in these soils, a separate set of sterile columns was tested under conditions that covered the range of Cr(VI) and OC additions used in the main experiment. The extent of Cr(VI) reduction in the sterile columns (day 84) was determined by micro-XANES analyses.

Results

Total chromium concentration profiles were relatively uniform within individual columns. Reduction of Cr(VI) occurred more rapidly with higher OC for both levels of initial Cr(VI), although the more highly contaminated soils [10,000 ppm initial Cr(VI)] generally required longer times to achieve low Cr(VI)/ΣCr ratios.

Comparisons between the various sterile soils showed greater Cr(VI) reduction in response to OC addition. Nonsterile soils exposed to 1000 ppm Cr(VI) had about 3 to 4 times greater reduction than their sterile counterparts, indicating that microbially dependent pathways were dominant (Fig. 1). In the systems exposed to 10,000 ppm of Cr(VI), without additional OC, relative differences between sterile and nonsterile soils were not significant, indicating negligible microbial influences at these extremely high Cr concentrations. However, nonsterile 10,000-ppm initial Cr(VI) systems did exhibit significantly enhanced reduction upon the addition of OC.

Discussion

The relatively uniform distribution of Cr(VI) at any given time within individual systems indicated reduction rates that were spatially fairly uniform. The reaction-limited condition observed in these columns is in strong contrast to the diffusion-limited cases examined in our previous experiments [3]. Chromate reduction in soils is accelerated by organic carbon through abiotic and microbially dependent processes. Both natural native humic substances and added OC support abiotic Cr(VI) reduction, which occurs even at initial Cr(VI) concentrations as high as 10,000 ppm. Under the slightly alkaline-oxidizing conditions of these experiments, the efficiency of microbially dependent pathways dominated abiotic reduction in all of the 1000-ppm initial Cr(VI) systems and in the OC-amended 10,000-ppm initial Cr(VI) system. These results demonstrate the importance of stimulating microbially dependent reduction pathways

with OC in order to remediate extremely Cr(VI)-contaminated soils. Future studies need to address reoxidation of Cr(III) and practical strategies for inhibiting reoxidation.

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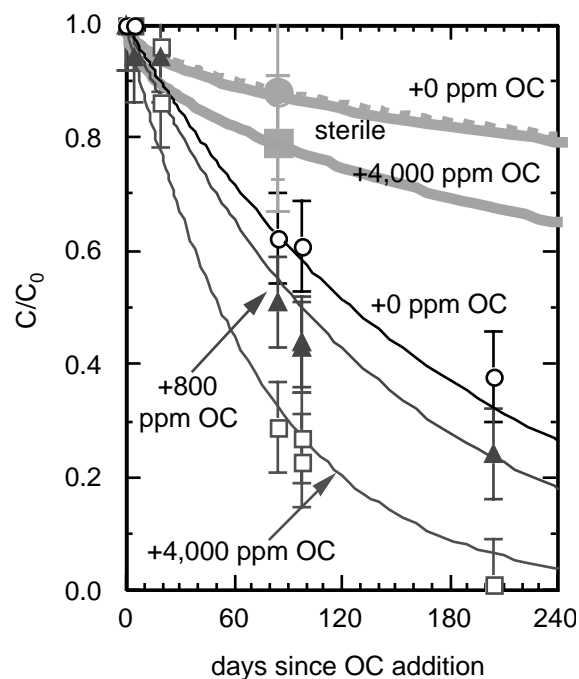


FIG. 1. Cr(VI) reduction trends in soils exposed to 1,000 ppm of Cr(VI) solutions, then treated with varying amounts of organic carbon.

References

- [1] C. D. Palmer and P. R. Wittbrodt, Environ. Health Perspectives **92**, 25-40 (1991).
- [2] D. Rai, L. E. Eary, and J. M. Zachara, Sci. Total Environ. **86**, 15-23 (1989).
- [3] T. K. Tokunaga, J. Wan, M. K. Firestone, T. C. Hazen, E. Schwartz, S. R. Sutton, and M. Newville,

Environ. Sci. Technol. **35**, 3169-3174 (2001).

- [4] P. J. Evans and S. S. Koenigsberg, "Bioremediation of inorganic compounds," edited by A. Leeson, B. M. Peyton, J. L. Means, and V. S. Magar, in Proc. of 6th Int. in situ and on-site Bioremediation Symp. **6**(8), 209-215 (Battelle Press, Columbus, OH, 2001).