In Situ Observation of Mn Reduction in Soil by Plant Roots: Initial Results

C. Guest,[1] I. A. Thompson,[1] D.G. Schulze,[1] D, M. Huber,[1] S. Sutton,[2] M. Newville[2]

[1] *Purdue University, West Lafayette, IN, U.S.A.*

[2] *The University of Chicago, Chicago, IL, U.S.A.*

Introduction

Synchrotron x-ray microbeams allow spatially resolved analysis of complex systems, such as moist soil adjacent to live plant roots. Data collection is easy, but interpretation can be difficult because soils contain different minerals, water, air, organic matter, and micro- and macro-organisms, and the element of interest may occur in any or all of these "phases." We are interested in the speciation of Mn in the vicinity of live plant roots with the goal of understanding the role of Mn redox chemistry in some plant fungal diseases. Plants take up soluble Mn^{2+}, but oxidized Mn^{3+} and Mn^{4+} are very insoluble. Near plant roots, the Mn oxidation state should be influenced by root exudates that can be reductants themselves or a food source for Mn-oxidizing or Mn-reducing microbes. Mn in some soil minerals is not part of this microbially mediated redox process.

Reduction of Mn oxides by exudates from plant roots, particularly sunflower, has been demonstrated using a highly simplified Mn-impregnated filter paper technique.[1] Our objective was to determine whether microXANES could detect Mn reduction in the immediate vicinity of live plant roots growing in moist soil.

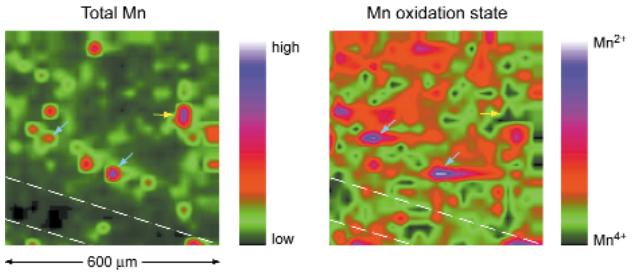

FIG. 1. Maps of total Mn distributions and Mn oxidation state in the vicinity of a live lateral root of sunflower (outlined by the dotted white lines) growing in soil that had been sieved to remove particles >50 mm in diameter. Note that areas high in Mn can contain either Mn4+ (yellow arrow) or Mn2+ (blue arrows).

Material and Methods

We filled sample cells[2] with the <50 µm fraction of an Elston soil and planted them with sunflower seeds. Maps of total Mn and Mn oxidation state in the vicinity of selected roots were prepared using microXANES.[3] We also isolated the 150-250 µm sand fraction, impregnated the grains in epoxy resin, and prepared a 30 µm thin section on a quartz glass slide. Minerals were identified by optical microscopy, and major element composition was obtained by electron probe microanalysis at Purdue. Trace element composition was obtained by XRF at beamline X26A at the NSLS. XANES spectra and oxidation state maps were obtained using the x-ray microprobe at GSECARS station 13-ID-C.

Results

In the mapping experiment, the path of the root was evident from the total Mn map (Fig. 1). There was no clear evidence for a gradient in Mn oxidation state from the root to the bulk soil, but there are spots of high Mn, some mainly Mn^{4+}, others mainly Mn^{2+}. The accumulation of Mn^{2+} by microbial processes is unlikely, and the most plausible explanation is that these apparent accumulations of Mn^{2+} are due to Mn in grains of primary minerals.

MicroXANES spectra were acquired for the soil immediately adjacent to a root and 2 mm away from the root (Fig. 2). These spectra, taken away from Mn hot spots, show higher Mn^{2+} content near the root. Even though no obvious redox gradient was evident from the maps, this limited microXANES data set is consistent with the notion of Mn reduction by exudates from plant roots.

Most of the individual minerals in the sand have Mn K XANES spectra (examples in Fig. 2 bottom)[4] that are quite different from the bulk soil spectra (Fig. 2, top).

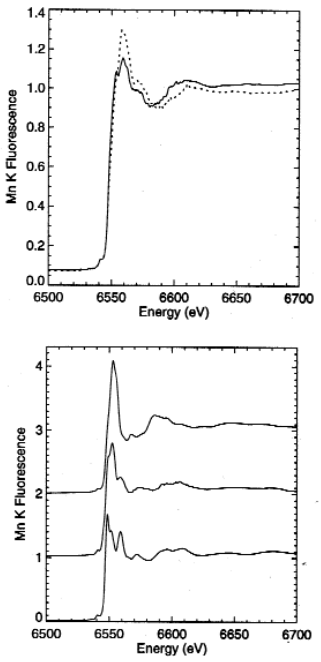

FIG. 2. Top: Mn K XANES spectra for soil immediately adjacent to the root (solid line) and 2 mm away from the root (dashed line) showing greater reduction near the root. Bottom: Mn K XANES spectra for 3 minerals in the soil thin section, garnet, mica, and pyroxene (upper to lower).

Conclusions

Manganese XANES spectroscopy is potentially valuable for studying redox reactions on a micrometer scale in soils. Our initial results support the notion of Mn reduction by root exudates in that Mn was more reduced in soil immediately adjacent to the root than farther away. Identifying the redox effects of roots in natural soils is difficult because of the presence of Mn-rich detrital grains. We conclude that the observed redox difference is not due to the influence of detrital grains based on comparisons with single-crystal spectra from a thin section of this soil. Additional work is needed to confirm this interpretation.

Acknowledgments

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