Mn Speciation in Poplar Roots

S. J. Naftel,[1] R. R. Martin,[1] F. Courchesne,[2] S. M. Macfie,[3] V. Séguin[2]
[1]Department of Chemistry, University of Western Ontario (UWO), London, Ontario, Canada
[2]Départment de Géographie, Université de Montréal, Montréal, Québec, Canada
[3]Department of Plant Sciences, UWO, London, Ontario, Canada

Introduction

The transport of metals **C** both micronutrients and toxins **C** from soils into plants is vital for life on earth, yet the processes involved are poorly understood. This poor understanding stems in part from the low concentrations of metals and the small scale over which the transport occurs.

X-ray fluorescence (XRF) and x-ray absorption near-edge structure (XANES) using a mirofocussed x-ray beam provide a powerful means of examining both the distribution (XRF) and chemical state (XANES) of metals in the rhizosphere (soil immediately around the root) and within plants.

In this preliminary study, we used μ-XRF and μ-XANES to examine the distribution and chemical state of Mn in the roots of a poplar tree.

Methods and Materials

Poplar root samples with soil clinging to them were supplied by F. Courchesne. The samples were dehydrated in a graded acetone series, then infiltrated with Spur=s resin. The roots were then hand sectioned to approximately 20- to 50-μm thickness by using a razor blade. The sections were mounted on a silicon wafer with carbon tape for analysis.

The XRF maps and XANES spectra were taken on beamline 20-ID-B (Pacific Northwest Consortium Collaborative Access Team [PNC-CAT]) at the APS. The beamline is equipped with a channel-cut Si(111) monochromator. A pair of Kirkpatrick-Baez mirrors were used to focus the incident beam down to 5×5 μm. The sample was held at 45° to the incident beam, and the emitted Mn Kα fluorescence was monitored with a 13-element detector placed at 90° to the incident beam. The map was created with the photon energy set at 10 keV.

Results and Discussion

The Mn distribution map of one of the roots is shown in Fig. 1. The image size is 450×450 μm with a pixel size of 5×5 μm. The highest Mn concentrations (green/yellow) are found in a ring around the root. Some internal root structures corresponding to lower Mn concentrations (blue) can be seen. At this time, it is not clear where the root/soil interface is located, and the origin of the internal structures (anatomical or artifacts of preparation) is not understood.

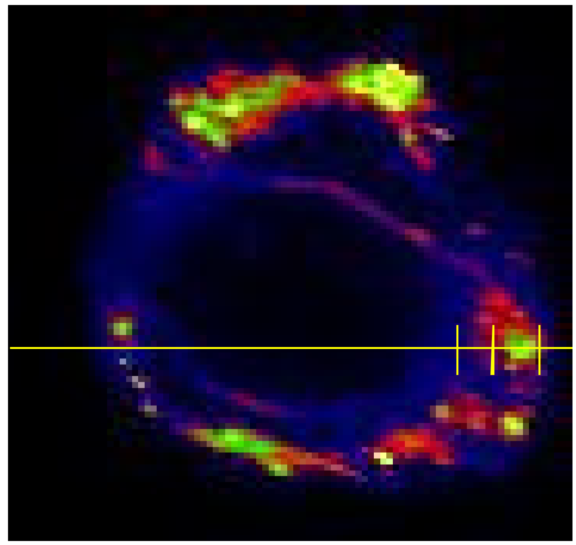

FIG. 1. Mn fluorescence intensity map. For details see text.

However, it is clear that Mn is not uniformly distributed around and within the root.

Mn XANES spectra were taken at 10-μm intervals along the horizontal line in Fig. 1. These spectra are numbered from 1 to 11 starting from the right of Fig. 1 and can be grouped (indicated by the vertical lines on Fig. 1) into three similar regions. We believe these regions represent the soil, rhizosphere, and root (from right to left). The XANES spectra for each region are shown in Figs. 2-4. The spectra shown have not been calibrated or normalized; they are single spectra with the background removed.

The spectra from the outer edge of the image are shown in Fig. 2. They are likely from a combination of Mn oxides.

The next region covers the highest concentration of Mn in the map (Fig. 3). Here the spectra change from a mixed oxide spectrum (5 and 6) to a distinct spectrum (8) that is representative of all the spectra from within the root (see Fig. 4).

The Mn spectra from within the root are all the same (Fig. 4) and probably indicate an organic Mn compound such as Mn oxalate. The position of the edge relative to Mn metal (not shown) indicates that the Mn is in the $2+$ oxidation state.

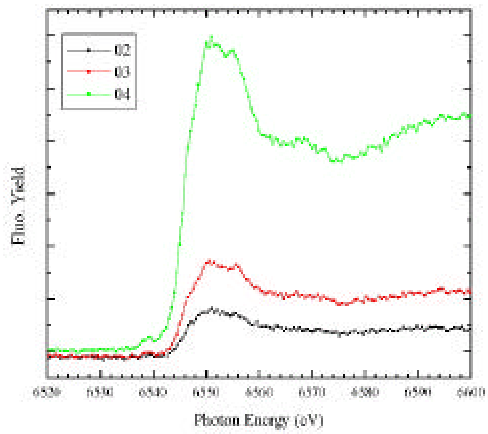

FIG. 2. Mn XANES from the soil region.

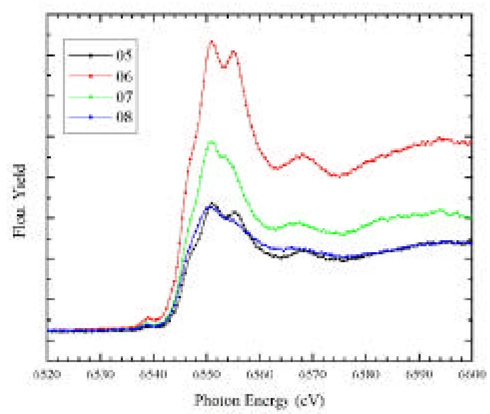

FIG. 3. Mn XANES from the rhizosphere region.

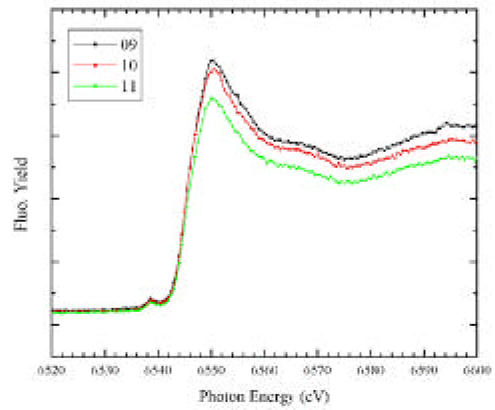

FIG. 4. Mn XANES from within the root.

Discussion

This study examined a poplar root and associated rhizosphere with μ-XRF and μ-XANES. The speciation of Mn was found to change from Mn oxides in the soil to an organic Mn compound within the root as the rhizosphere was traversed. The change was rapid, occurring over a space of 20 μm. More work is underway to determine the exact Mn species present both inside and outside the root and to reliably match the elemental distributions with anatomical structures.

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