

# N and C *K*-edge XANES Spectroscopy of Rhizosphere and Non-Rhizosphere Soils

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## Introduction

The rhizosphere (or root-sphere) is loosely defined as the volume of soil that is affected directly by the presence of plant roots. In this region, plant root exudates, dead tissue and enhanced microbial activity combine to create an environment that differs greatly from that of bulk soil [1]. The rhizosphere is also the main point of entry for, and transformation of, organic carbonaceous

and nitrogenous materials in the terrestrial ecosystem. However, the rhizosphere presents formidable challenges to the analyst, and as such, whole-soil advanced analytical techniques such as XANES offer great potential to investigations of this complex environmental system.

## Science

### Objectives

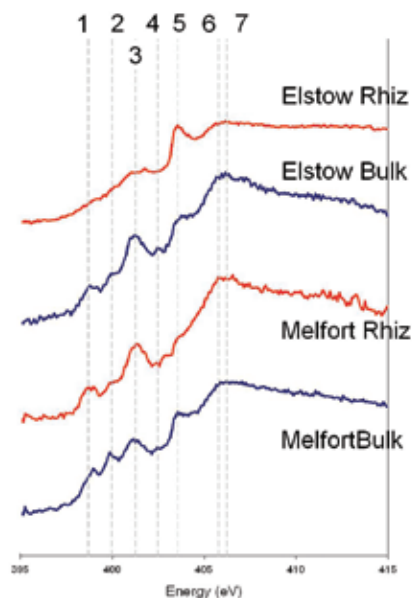
This study was undertaken to gain a stronger fundamental understanding of the molecular organic chemistry in the rhizosphere. Our goal was to employ techniques that are amenable to whole soil analysis with little pre-treatment. In this study, we used synchrotron-based N and C *K*-edge XANES to explore differences between *Pisum sativa* L. rhizosphere and bulk soils.

### Materials & Methods

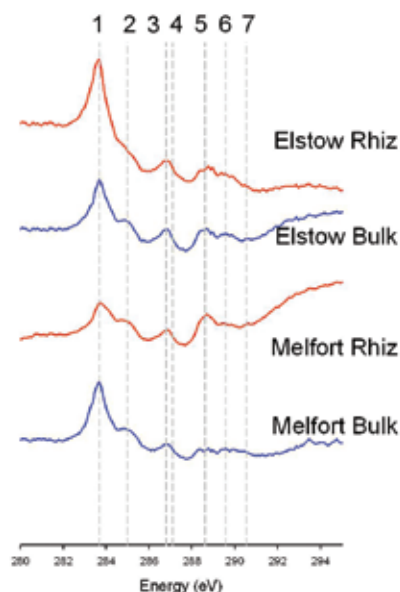
A growth chamber study was conducted using two agricultural soils from Saskatchewan. Pea (*Pisum sativum* L.) was planted in replicate pots containing either a Dark Brown Chernozem (Elstow; silty clay loam) or Black Chernozem (Melfort; heavy clay). The plants were grown for 28 days, at which time the bulk and rhizosphere soils were sampled.

For XANES analysis, soils were dried, ball-milled and pressed onto scraped indium metal, and affixed to a steel sample disc using conductive carbon tape. Nitrogen and carbon *K*-edge XANES spectra were recorded on the 11ID-1 spherical grating monochromator (SGM) beamline. Fluorescence and total electron yield spectra were collected at 250 mA and a beam intensity of 2.9 GeV. Incident flux was provided by in-line Au mesh for the N *K*-edge analysis, and by a freshly sputtered Au surface for C *K*-edge analysis.

Spectra were averaged, background corrected and normalized using AXIS 2000 and WinXAS.



**Figure 1:** N *K*-edge XANES fluorescence yield spectra and major transitions for rhizosphere and bulk soils from the Elstow and Melfort sites. Numbered resonance assignments are (1) pyridinic, (2) nitrile and pyrazole, (3) amide, (4) pyrrole, (5) nitroaromatic, (6) nitrate, (7) aliphatic.



**Figure 2:** C *K*-edge XANES electron yield spectra and major transitions for rhizosphere and bulk soils from the Elstow and Melfort sites. Numbered resonance assignments are (1) quinone, (2) aromatic, (3) aromatic C-N, (4) phenolic, (5) carboxylic, (6) carbohydrate, (7) carbonate.

Figures 1 and 2 show N and C *K*-edge spectra, respectively. Assignments for nitrogen functionality were based on extensive characterization of N-containing compounds by our group [2]. Carbon functionalities were assigned based on spectra published previously [3,4].

## Discussion

**N-spectra:** The influence of rhizosphere processes on the types and amounts of N is dependant on the initial source soil. Rhizosphere generated on soil from the Elstow site shows nitroaromatic functionality. Evidence exists for the incorporation of nitrite ( $\text{NO}_2^-$ ) into aromatic and phenolic structures [5], representing one possible route of N incorporation into organic matter [6] and a potential pathway for nitrous oxide ( $\text{N}_2\text{O}$ ) production in soils [5]. The nitroaromatic functionality was not expressed in rhizosphere soil generated from the Melfort site, but was present in lesser amounts in the bulk soils from both sites.

Pyrrolic and pyrazolic/nitrile functionalities were evident in the spectra for bulk soils but were decreased in both rhizosphere soils, indicating degradation or transformation of these functionalities. All soils showed strong signals for amide N, which is consistent with Shulten & Schnitzer's [7] contention that amide-N is the predominant form of organic N in soils. This was, however, less evident in the Elstow rhizosphere, indicating increased degradation of amide-N in lighter textured soils.

**C-Spectra:** Carbon functionalities revealed fewer rhizosphere associated patterns. Aromatic functionality decreases in rhizosphere from the Elstow site, and remained unchanged between bulk and rhizosphere in the Melfort soil. It is possible that nitrosation of aromatic compounds, as observed in the N-XANES spectrum, resulted in a decrease in the aromatic signal. Carboxylic functionality conversely, remained unchanged between the Elstow soils, and increased in the Melfort rhizosphere.

## Conclusion

Carbon and nitrogen *K*-edge XANES are powerful tools that can be used to investigate the functionality of whole soils with minimal sample preparation. In this study, we show that rhizosphere soil generated from bulk soil was soil specific. The observation of nitroaromatic compounds indicates unique N cycling in some soils, which warrants further investigation.

The use of C and N XANES is currently being paired with analytical pyrolysis and advanced mass spectrometry to offer a detailed, and complementary, analysis of organic compounds in the rhizosphere and bulk soils.

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