

In Situ Carbon Speciation of Soil Organic Matter – Application of X-Ray Absorption Spectro-microscopy

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Abstract No. Sche7642

Beamline(s): X1A

Introduction: Soil organic matter (SOM) plays a crucial role in terrestrial ecosystems, e.g. as sorbent and carrier of plant nutrients and organic and inorganic pollutants, or as an important sink in the global carbon cycle. In spite of its importance, the chemical structure and morphology of SOM is insufficiently understood¹. While established methods have made substantial contributions to the bulk chemical characterization of SOM, C1s microscopy and microspectroscopy offers several advantages compared to other methods. Samples can be measured in water and without chemical pretreatments, which allows investigating soil organic matter hydrated and in association with soil minerals, i.e. in its most common natural state in soil. Furthermore, spectroscopy can be conducted with submicrometer resolution, which enables to measure the chemical structure of SOM in dependence of morphology.

Methods and Materials: We used the outboard scanning transmission x-ray microscope at NSLS beamline X-1A. About 1 μm thin films of suspensions were investigated using a wet cell with silicon nitride windows². The two topsoils investigated were a strongly humified A-horizon under oak forest and a partly decomposed O-horizon under pine forest, both from Long Island. Colloidal suspensions were collected after shaking 1 g of soil in 500 mL D.I. water for 5 minutes. C1s NEXAFS spectra of reference compounds were measured in suspension after sorption onto ferrihydrite gel particles (pH 5).

Results: Features in the NEXAFS spectra of reference compounds could be correlated to their functional groups (aromatic, phenolic, carboxyl) (**Figure 1**). Band positions agree well with those from a spectral library established using EELS³, which was used to define band ranges for alkyl and carbonyl groups.

The NEXAFS spectra of particles from the A-horizon show pronounced peaks at spectral locations consistent with aromatic and carboxyl groups (**Figure 2, left**). A shoulder on the low-energy wing of the carboxyl band could be fitted with a band at 288.4 eV indicative of alkyl groups. The spectrum of Aldrich humic acid shown for comparison has a weaker aromatic band, a stronger carboxyl band, and a weak phenolic band. All spectra of the A-horizon were similar to each other, indicating a similar set of functional groups.

The spectra of particles from the O-horizon are different from those of the A-horizon (**Figure 2, right**). The aromatic band is less pronounced, and a weak carbonyl band appears on the right wing of the carboxyl band. Weak phenolic bands are 1 eV lower in energy compared to the references. The spectra show a much higher variability than those of the A-horizon, consistent with a smaller degree of degradation of source materials with various chemical compositions.

Acknowledgments: We would like to thank the x-ray microscopy group at SUNY Stony Brook for assistance.

References: ¹J. Buffle and G.G. Leppard, "Characterization of aquatic colloids and macromolecules. 2. Key role of physical structure on analytical results," *Environ. Sci. Technol.*, **29**, 2176, 1995. ² U. Neuhäusler, C. Jacobsen, D. Schulze, D. Stott and S. Abend, "A specimen chamber for soft X-ray spectromicroscopy on aqueous and liquid samples," *J. Synchrotron Rad.*, **7**, 110, 2000. ³ A.P. Hitchcock and D.C. Mancini, "Bibliography and database of inner-shell excitation-spectra of gas-phase atoms and molecules," *J. Electron Spectr. Rel. Phenomena*, **67**, 1, 1994.

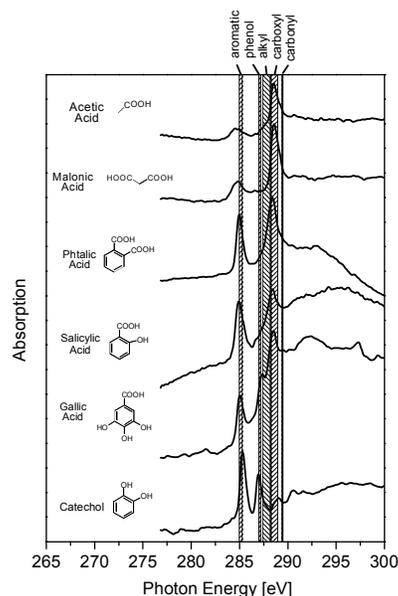


Figure 1. C1s NEXAFS of reference compounds sorbed onto ferrihydrite.

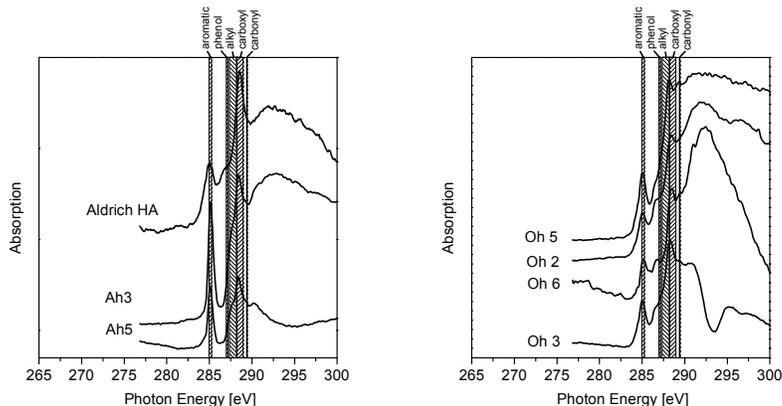


Figure 2. C1s NEXAFS of topsoil A (left) and O (right).