Determination of soil organic C species using soft X-ray XANES: normalization & matrix effects

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Soil organic matter (SOM) storage and turnover are affected by the chemical nature and properties of its constituents, particularly the chemical forms of organic C. Synchrotron-based soft X-ray absorption near edge spectroscopy (XANES), probing the atomic and molecular structures of materials, is being used to provide information on the types of C functional groups (e.g., C=O, C-OH, R-COOH) in SOM [1]. This type of information is required to fully understand the global C cycle.

Normalization of C K-edge TEY and TFY data has always been a challenge due to the C contamination in soft X-ray beamlines, imparting features into the incident x-ray flux (i.e., Io). The mineral fraction of the soil also contributes to the TEY and TFY signal, in ways not fully understood. Hence, there is concerns that artefacts such as erroneous peaks and/or spectral distortions may be introduced into the C K-edge total electron yield (TEY) and total fluorescent yield (TFY) spectra during the normalization of the raw data and/or into the raw data from the matrix itself (e.g., adsorption saturation), particularly at low soil C content. Both of these could result in incorrect conclusions being reached. To date, no fundamental studies have been conducted that address normalization issues and matric effects in known systems as a function of organic C content, organic functionality and in different matrices.

At the SGM beamline, at the Canadian Light Source, we are studying model systems consisting of varying amounts (50 to <1% (w/w)) of an organic compound with different function groups (e.g., citric acid, phthalic acid, glucose, tannic acid) mixed with a soil constituent (e.g., Al hydroxide, kaolinite, montmorillonite, Fe hydroxide). The organic-matrix mixtures are deposited onto various substrates (e.g., Au coated Si wafers) and TEY and TFY spectra are collected under a variety of conditions such as in the presence and absence of a Ti filter and/or reducing radiation dose rates (C is susceptible to radiation damage at high radiation doze rates and/or in the presence of certain elements such as Cu [2]) by conducting fast scans (20sec) versus normal scans (1500sec). Determination of the appropriate Io using different detection methods such a photodiodes and the collection of TEY and TFY of a variety of substrates such as Au coated Si wafers and C-free matrixes are being explored to normalize the data. From this fundamental approach it is expected that a protocol will be developed that reduces the possibly that artefacts are introduced during the normalization process and/or during the collection of the raw data due to matric effects. Also, the study will provide insight into factors that affect the C detection limit of the soft X-ray. Moreover, this project is part of an initiative to make the SGM beamline a center for Soil Science studies.

[1] Gillespie (2011) Soil Biol. Biochem. **43**, 766-777.
[2] Yang (2011) Anal. Chem. **83**, 7856-7862.

Surface Complexation Models and their Practical Application

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Abstract

While surface complexation theory and models for the description of inorganic ion sorption on mineral surfaces have advanced continuously since the introduction and initial development of these models in the 1970s and 1980s (reviewed in [1]), so too has the practical application of the models. Deployment of surface complexation models to interpret and predict water-mineral partitioning of ions in geochemistry and engineering applications is challenging because of the complexity of these systems, the limitations of the models, the lack of surface complexation databases for all of the minerals of interest, and other factors. The substantial progress in application of surface spectroscopy methods and molecular modeling to increase understanding of the properties of mineral surfaces and the nature of their reactions with ions has been of limited usefulness in constraining surface complexation models [2,3] and has done little to advance their practical application. Of necessity, there is still widespread use of empirical isotherms and distribution coefficients (K_d) to describe and simulate ion sorption processes in field systems. However, surface complexation models have been applied in a variety of contexts to gain insight into the role of sorption reactions in governing the fate and transport of particular ions, and in governing overall system chemistry.

This talk will provide an overview of the development of surface complexation models, and the history of their practical application. Examples from modeling of ion transport in geochemical systems and from contaminant treatment and remediation will be described. The strengths and limitations of the models for practical applications will be examined. Some thoughts about developments needed to advance the practical application of surface complexation models will be offered. The divergence yet complementarity of surface complexation research focused on advancement of basic scientific understanding of mineral-water surface phenomena, and research motivated by practical applications will be discussed.

[1] Dzombak and Morel (1990). *Surface Complexation Modeling: Hydrous Ferric Oxide*, Wiley, New York.
[2] Lutzenkirchen (2006). *Surface Complexation Modeling*, Academic Press, Amsterdam (especially pp v-x).
[3] Karamalidis and Dzombak (2010) *Surface Complexation Modeling: Gibbsite*, Wiley, New York.