

Molecular Investigation of Natural Organic Molecules and Their Complexes Using Soft X-rays

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The chemical states of organic molecules in aqueous solutions and at the mineral-water interfaces modify a variety of environmental processes. The functional group chemistry (type and concentration of functional groups, and their protonation and metal/mineral-surface complexation) is one of the critical parameters that influences these reactions. While several spectroscopic methods (NMR, vibrational, electron spectroscopy) can be used for its direct examination, characterisation of natural organic molecules is often difficult because of their heterogeneity, and because of the presence of molecules or ions that interfere with the spectral signatures of molecule of interest. Recent studies have indicated that element- and group-specific X-ray spectroscopy studies can be conducted to examine the chemistry of different functional groups in simple and complex organic macromolecules in heterogeneous matrices. We have been developing soft X-ray spectroscopy methods to characterise the functional group chemistry of simple and organic macromolecules in aqueous solutions and at the interfaces.

Using these methods, we are examining the functional group chemistry of simple model organic molecules (e.g. carboxylic, amino acids), model macromolecules (e.g. siderophores and their derivatives) and isolated humic substances using the core hole transitions at the C-, N-, O, P-, S-, and Cl K-absorption edges. Our studies suggest that classes of different moieties (e.g. carboxyl, carbonyl) can be examined directly using these methods. We find that electronic transitions are also sensitive to protonation and metal complexation of different functional groups, and the X-ray spectra can provide such information. We are complementing the soft X-ray spectroscopy studies with the hard X-ray absorption spectroscopy studies (EXAFS) at the metal K-absorption edges (in the case of metal-organic complexes), and the vibrational spectroscopy studies. A detailed discussion of the soft X-ray spectroscopy methods, and a summary of their application in studying organic molecule chemistry in aqueous solutions will be presented.

Probing the Coordination Chemistry of Natural Organo-Cl Compounds Using Soft X-rays

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Organo-Cl compounds have been used extensively for years in agricultural and industrial applications. Because of their long residence time in the environment, these compounds threaten to contaminate aquatic and soil systems. On the other hand, several living organisms were found to produce organo-Cl compounds using enzymatic processes and inorganic-Cl in soils and aquatic systems. Although experimental evidence for the occurrence of small chain chlorinated alkanes in soil and marine systems exists, direct probing of the persistent, stable, less-volatile organo-Cl compounds and their macromolecules has been very difficult or impossible. We are using the *in-situ* synchrotron based spectroscopic methods for examining the chemical forms of Cl in soil and aqueous organic molecules, and the biogeochemical processes involved in their formation.

Previous X-ray spectroscopy studies (NEXAFS & EXAFS) suggest that the 1s core hole transitions of Cl are sensitive to the oxidation state and local coordination around Cl. Using these methods we examined a series of inorganic chlorides (e.g. Cl-metal complexes), aliphatic-Cl, and aromatic-Cl compounds with Cl in different coordination environment. The near-edge X-ray absorption fine structure (NEXAFS) spectroscopy studies suggest that the energy transitions of 1s to unoccupied and partly occupied molecular orbitals shift as a function of Cl local coordination environment. Our studies suggest that the absorption edges of aliphatic-Cl compounds are at a lower energy when compared to the aromatic-Cl compounds. In addition, increases in the number of Cl atoms in aliphatic molecule tends to shift the absorption edge to a lower energy. The extended X-ray absorption fine structure (EXAFS) spectroscopy studies are also useful in the identification of Cl local coordination environment and complement the Cl-NEXAFS studies. Using this information obtained on a series of model compounds, we examined the coordination environment of Cl in fresh and weathered plant material. A summary of these studies and the nature of chlorination reactions and their influence on Cl- and C-cycle in the environment will be presented.

Improved understanding on the geochemistry of natural organo-Cl compounds is useful for the evaluation of the toxicity of both natural and man-made organo-Cl compounds, and to take remedial strategies for the treatment of chlorinated hydrocarbons in contaminated systems.