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Graphical resolution of Humic structures

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Advanced techniques have been recently used to obtain information on Natural Organic Matter (NOM). However, the current knowledge of the chemical structure of humic substances (HS) is still incomplete. These substances appear to be too complex mixtures of charged organic molecules, and their characterization remains one of the most stimulating challenges in modern environmental science. Knowledge of the chemical composition of NOM is of great importance for the definition of soil and water properties because it has a significant impact on the understanding of numerous molecular and global-scale processes.

This study aims to apply two-dimensional graphical methods to resolve homologous series in mass spectra of humic extracts (Suwannee River, Nordic Aquatic and Soil) obtained using FT-ICR / MS (Thermo LTQ FT, 7 Tesla) in negative ionization mode. Electrospray ionization (ESI) coupled with ultra-high resolution mass spectrometry offered by Fourier transformed ion cyclotron resonance (FT-ICR / MS) has emerged with great promise as it can provide an overview of the NOM composition and details on a molecular scale. NOM's very high-resolution FT-ICR spectra can be extremely complicated. These spectra usually contain many peaks at each nominal mass and thousands of peaks across the entire spectrum. Each peak can represent a chemically distinct compound. This complexity poses an analytical challenge to the study of spectra for structural interpretation. Two-dimensional graphing methods, such as Kendrick and van Krevelen graphs, have been successfully applied to very high-resolution mass spectra, allowing peaks to be sorted into complicated spectra from their homologous relatives across the mass range.

In van Krevelen plots, ionic signals corresponding to structural similarities between homologous series of compounds involved in the loss or gain of functional groups are found on straight lines. We identified many interesting homologous regions and compared the three humic standards with each other. Finally, we recognized the structural relationships of the homologous series obtained through Kendrick graphs.

The results showed homologous series in the Suwannee River and Nordic Aquatic samples compared to the soil-extracted samples (soil-FA and soil-HA). In particular, homologous series signals related to methylation/demethylation, hydrogenation/dehydrogenation, hydration/dehydration, and oxidation/reduction processes were lower in the soil-FA van Krevelen diagrams. On the contrary, the differences were not so evident in all the homologous series for the soil-HA samples.