PROBING MOLECULAR-LEVEL TRANSFORMATIONS OF DISSOLVED ORGANIC MATTER: INSIGHTS ON PHOTOCHEMICAL DEGRADATION AND PROTOZOAN MODIFICATION OF DOM FROM ELECTROSPRAY IONIZATION FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY


Introduction

Molecular-level characterization of natural organic matter (NOM) has been elusive due to the inherent complexity of natural organic mixtures and to the fact that individual components are often polar and macromolecular. Electrospray ionization (ESI) is a “soft” ionization technique that ionizes polar compounds from aqueous solution prior to injection into a mass spectrometer. The highest resolution and mass accuracy of compounds within NOM have been achieved when ESI is combined with an ultrahigh-resolution mass spectrometer such as the Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS). With this technique, individual molecules within a variety of natural organic mixtures can be detected and their elemental composition can be determined. At low mass-to-charge (m/z) ratio, the resolution is high enough to assign exact molecular formulas allowing specific components of these mixtures to be identified. In addition to molecular identification, we can now use ESI FT-ICR MS to examine molecular-level changes in different organic mixtures as a function of relevant geo-processes, such as microbial alterations and photochemistry. Here we present the results from the application of ESI FT-ICR MS to two geochemical questions: (1) the effect of photoirradiation on the molecular composition of fulvic acids and (2) the role of protozoan grazers in the modification of DOM in aquatic systems.1

Results and Discussion

The Figure shows the visually striking effect of irradiation on Suwanee River fulvic acid. Negative ion mode ESI FT-ICR mass spectra were acquired for SRFA samples before and after photo-bleaching. For example, at m/z 413, every other peak is missing from the irradiated sample! Furthermore, the peaks that have been removed differ from one another by multiples of 0.036 Da, the difference between CH4 and O, likely from replacement of a methyl group by an aldehyde or ketone: \( \text{RCH}_2\text{CH}_3 \) versus \( \text{RCHO} \). That kind of information is available only from ultrahigh-resolution mass analysis.

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References