ULTRAHIGH RESOLUTION MASS SPECTROMETRY OF DISSOLVED ORGANIC MATTER IN ESTUARIES

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Introduction

Electrospray ionization combined with high-field Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) can now identify individual compounds in complex dissolved organic matter (DOM) mixtures. This ultrahigh resolution (UHR) technique generates large databases of chemical formulas for individual samples which can be searched for specific compounds and compound classes or integrated across the entire dataset to summarize the molecular characteristics of DOM (e.g. aromaticity, elemental ratios, degree of unsaturation). Here we demonstrate how UHR MS data can define the molecular changes that accompany terrestrial DOM as it moves from its fresh water sources through estuaries and into the coastal zone. Specific examples included are microbial alteration of riverine DOM as it percolates through coastal sands, and photochemical processes that change fluorescence signatures.

Materials and Methods

Sampling. For irradiation experiments, 2 L water samples were collected from the Black River (salinity 0) and Cape Fear River Estuary (salinity 13) in North Carolina. One liter from each sample was irradiated for 21 h using a 1000 W solar simulator, while one liter of the same water sample was stored in the dark at 4 °C (dark controls). In the sand filtration experiment, one of two 50 cm columns was filled with sterile sediment (combusted for 8 h at 500 °C) and another was filled with natural sediment. Water collected from the St. Marks river estuary 50 miles east of our St. George Island study site that had a DOC concentration of 615 µM was pumped for 48 h through the columns. Samples were collected in 500 ml glass bottles at the entry, and then the exit of each column (1 natural and 1 sterile). It took approximately 10 h to collect each.

DOM Extraction. Prior to mass spectrometric analyses, sample solutions were acidified to pH 2 and extracted using Varian Mega Bond Elut PPL solid-phase extraction (SPE) cartridges filled with 1 g of the PPL resin. The cartridges were activated with methanol and rinsed with 20 mL acidified Mill-Q water (pH 2). After the sample solution had passed through the SPE cartridge, the remaining salts were washed off with acidified Mill-Q water and the cartridge vacuum dried prior to the elution of the adsorbed dissolved organic matter (DOM) using 10 mL HPLC-grade methanol.

ESI-FT-ICR-MS Analysis. All samples were all analyzed using the 9.4 Tesla FT-ICR mass spectrometer at the National High Magnetic Field Laboratory (NHMFL), Tallahassee, Florida, USA. A spectrum of ions present in one DOM sample can contain several thousand peaks. A particularly useful method to interpret the data is to create van Krevelen diagrams, which are effective for visualizing large numbers of exact molecular formulae. A Van Krevelen plot consists of elemental ratios of hydrogen to carbon (H/C) (y-axis) for each formula identified plotted against the oxygen to carbon (O/C) ratios (x-axis) of the same formula.

Results and Discussion

Photochemically-induced changes in the EEM fluorescence of DOM. An EEM fluorescence spectrum provides a three dimensional plot which can be used to distinguish fluorescent compound groups which show distinct differences in their excitation and emission maxima. Figure 3 suggests that the decrease in specific classes of the EEM fluorescence (humic-like A-peak and fulvic-like C-peak) are quite different in these samples. The marked changes in optical properties after exposure to simulated sunlight appear to be due to the original molecular composition of the DOM (Figure 4).

Figure 1: Ultrahigh resolution (9.4 Tesla) FT-ICR Mass Spectrometer at the National High Magnetic Field Laboratory. The use of this instrument to describe the molecular composition of DOM mixtures has been described in several previous publications.

Figure 2: This experiment tested whether filtration of DOM (derived from river water) at realistic flushing velocities through a sediment layer, comparable in thickness to the flushed sediment surface layer at the study site, causes degradation of the DOM. Fifty cm long sediment columns were used to test the hypothesis that a fraction of the DOM is degraded while passing through natural marine sediment. See poster by Huettel et al. for additional information regarding these experiments.

Figure 3: Absolute changes in the EEM fluorescence intensities arising from 21 h solar irradiation in the Black River (left) and Cape Fear Estuary (right) samples.

Figure 4: van Krevelen diagrams summarizing molecular formulas of the (a) Black River and (b) Cape Fear Estuary DOM samples.

Figure 5: van Krevelen diagrams of DOM before and after passage through sand columns. Left; formulas lost; Right; formulas that appear.

Acknowledgements

Mass spectra were obtained at the National High-Field FT-ICR Mass Spectrometry Facility (NSF CHE-99-09502) at the National High Magnetic Field Laboratory in Tallahassee, FL. Financial support was provided by NOAA (NA05OAR4311162) and NSF (OCE-0726754).