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High field NMR Spectroscopy and FTICR Mass Spectrometry: Powerful Discovery Tools for the Characterization of Marine Dissolved Organic Matter

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High-field NMR and FTMS of SPE-derived marine dissolved organic matter (SPE-DOM) from the South Atlantic Ocean provided molecular level information of complex unknowns with unprecedented coverage of carbon and resolution. SPE-DOM represented major oceanic regimes of general significance: 5 m (near surface photic zone), 48 m (fluorescence maximum), 200 m (upper mesopelagic zone) and 5446 m (30 m above ground).

1H NMR spectra showed rather smooth bulk NMR envelopes with a few percent of visibly resolved signatures. 1H NMR spectra of SPE-DOM indicated considerable variance in abundance for all major chemical environments. Two-dimensional NMR spectra of SPE-DOM displayed exceptional resolution. JRES (sensitive but limited resolution), COSY (highly resolved) and HMBC NMR (informative but limited S/N ratio) spectra depicted resolved molecular signatures in excess of a certain minimum abundance. COSY cross peaks were most diverse for sample FMAX and conformed to >1,500 molecules present.

Classical methyl groups terminating aliphatic chains represented only $\sim$ 15 % of total methyl in all marine DOM investigated; 2 % of methyl was bound to olefinic carbon. Methyl ethers were abundant in surface marine DOM, and the chemical diversity of carbohydrates was larger than that of freshwater and soil DOM.

TOCSY and HSQC cross peaks enabled unprecedented depiction of sp2-hybridized carbon chemical environments in marine SPE-DOM with discrimination of isolated and conjugated olefins as well as [U+F061],[U+F062]-unsaturated double bonds. Olefinic protons were more abundant than aromatic protons; relative HSQC cross peak integrals indicated more abundant olefinic carbon than aromatic carbon in all marine DOM as well. Furan, pyrrol and thiophene derivatives were marginal. Benzene derivatives and phenols as well as six-membered nitrogen heterocycles were prominent. Various key polycyclic aromatic hydrocarbon substructures suggested the presence of thermogenic organic matter (TMOC) in marine DOM at all water depths.

Eventually, olefinic unsaturation in marine DOM will be more directly traceable to ultimate biogenic precursors than aromatic unsaturation. The conformity of key NMR signatures suggests the presence of a numerous set of identical molecules throughout the entire ocean column even if the investigated water masses belonged to different oceanic regimes and currents.

High field (12 T) negative electrospray ionization FTICR mass spectra showed abundant CHO, CHNO, CHOS and CHNOS molecular series with slightly increasing numbers of mass peaks and average mass from surface to bottom SPE-DOM. The proportion of CHO and CHNO molecular series increased from surface to depth whereas CHOS and especially CHNOS molecular series markedly declined. The exhaustive characterization of complex unknowns in marine DOM will enable a meaningful assessment of individual marine biogeosignatures which carry the holistic memory of the oceanic water masses.

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