

RESOLVING UNRESOLVED COMPLEX MIXTURES: CHARACTERISTICS OF NATURAL ORGANIC MATTER DETERMINED BY ULTRAHIGH RESOLUTION MASS SPECTROMETRY

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Recent progress in the field of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) resulted in new and extensive insights in the molecular composition of natural organic matter (e.g. (Koch *et al.*, 2005; Kujawinski *et al.*, 2004; Stenson *et al.*, 2003)). In this work, we focus on the marine dissolved organic matter (DOM) which represents one of the largest active pools of organic carbon in the global carbon cycle. Its amount (700×10^{15} g C) is comparable to that of carbon in atmospheric CO₂ (750×10^{15} g C) and 30-times larger than all carbon in marine animals, plants, bacteria and marine organic particles combined ($\sim 25 \times 10^{15}$ g C). Despite the importance of DOM, the proportion of deep-sea dissolved organic carbon (DOC) that can be characterized with conventional methods on the molecular level is marginal. The lack of molecular information prevents detailed characterization of the exact sources, availability to organisms, transformation and preservation mechanisms, binding to minerals and heavy metals and the role of DOC in the global carbon cycle.

Especially the enormous resolution power of >200000 of modern FT-ICR-MS and the precise mass accuracy of up to 200 ppb allowed mass based separation of thousands of ions in the spectra and resulted in new insights into the molecular composition of marine DOM. We can assign thousands of molecular formulas which are suitable to distinguish between sources and degradation processes. Although every molecular formula can represent a multitude of chemical structures, FT-ICR-MS data can also provide structural information. The aromaticity index AI (Koch & Dittmar, 2006) is a conservative tool to identify aromatic or polyaromatic structures in a molecule and is solely based on the determination of the exact mass and the molecular formula. A new liquid-chromatography method allowed a polarity based separation of DOM molecules and to reduce the complexity of the FT-ICR-MS spectra. On the basis of this method, ions of different molecular elemental composition can be separated (Figure 1) and even dissolved nitrogen and sulphur compounds can be identified.

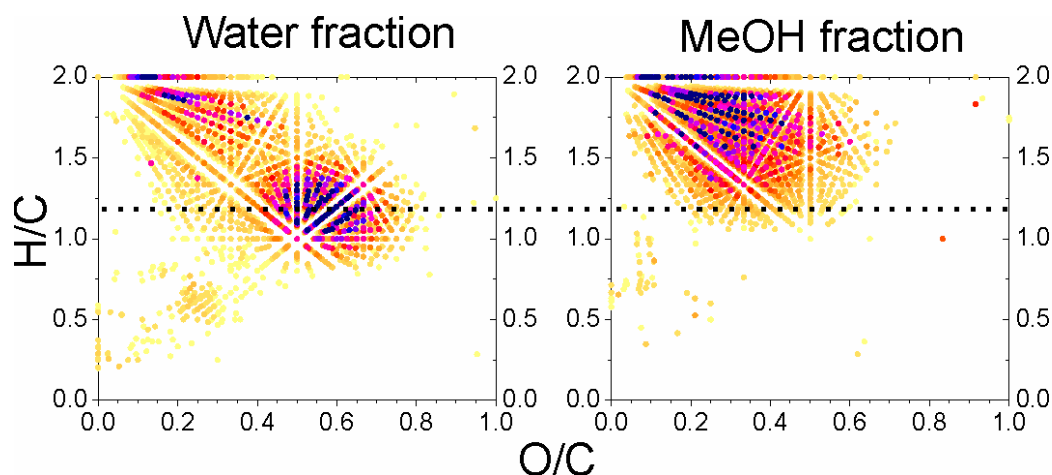


Figure 1. Molecular element ratios from an ESI-FT-ICR-MS analysis for a polar (left) and a less polar (right) chromatographic fraction of a marine DOM sample. Chromatographic separation and preparative enrichment was performed on an HPLC-system using an RP18-column and a H₂O/methanol gradient. Decreasing polarity results in lower O/C and higher H/C ratios and shifts the ions to the upper left corner of the plot. The colours represent peak intensity.

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