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# Assigning reactivities to individual molecules in marine dissolved organic matter

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Dissolved organic matter (DOM) in the ocean contains as much carbon as the earth atmosphere. This huge pool of energy- and nutrient-rich compounds provides an important base for microbial life in the water column. But only part of the DOM is rapidly turned over by microorganisms. A significant fraction of DOM resists rapid microbial degradation and accumulates in the oceans over thousands of years. We hypothesize that the molecular composition of this stable DOM is universal and that stable DOM can be traced by its characteristic molecular fingerprint.

We perform a long-term study of DOM composition in the open North Sea off Helgoland Island, which is carried out in close cooperation with the project MIMAS (Microbial Interactions in Marine Systems). The DOM pool in the North Sea is highly dynamic and influenced by a complex interplay of processes that produce, transform and degrade dissolved molecules. Most of these processes are mediated by microorganisms. The objective of our study is to link DOM composition with microbiological information obtained in the MIMAS core projects, and assign reactivities (on a relative scale) to individual compounds in DOM.

We present results covering an annual cycle (March 2009-April 2010), focussing on the molecular composition of bulk DOM. Ten-thousands of molecular formulae were identified in DOM by ultrahigh resolution mass spectrometry analysis (FT-ICR-MS, Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry). Differences in the molecular fingerprints of DOM reflect the highly dynamic nature of North Sea waters. Seasonal changes in the composition of DOM are dominated by phytoplankton blooms in spring and autumn as well as by sporadic intrusions of terrestrial runoff from the Southern German Bight. A detailed analysis of the relative abundances of individual molecules over time provided information on production and degradation of these molecules. We ranked the individual molecular formulae of DOM according to their stability in the water column on the time scale of an annual cycle. The molecular formulae of a ubiquitous DOM background signal were identified. This background was present in all samples and dominated during wintertime. The relative abundance of molecular formulae within this background pool was constant, confirming the refractory character of this compounds class. Because of its stability, the refractory DOM background of the North Sea should be globally present in the ocean. In support of this hypothesis, the majority of the molecular formulae identified in the background signal of the North Sea were also found in the deep ocean of the North Pacific, one of the oldest water masses worldwide. Only a small fraction of the molecules that turned over within the sampled year in the North Sea could be found in the North Pacific. Our results indicate that the molecular composition of refractory DOM in marine waters is universal and independent of its ultimate source.