



Dissolved organic matter in the ocean: recalcitrant or simply too diverse for bio-degradation?

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The amount of carbon in the dissolved organic matter (DOM) pool in the ocean is estimated to be 700 Pg C, whereas the particulate marine organic carbon accounts only for about 30 Pg C. Dissolved organic carbon (DOC) is almost as much as the amount of carbon in atmospheric CO₂ (~800 Pg) or terrestrial biomass (~610 Pg). The majority of DOC in the ocean has an average age of 4000 to 6000 years. Thus, DOM must be extremely resistant against biotic and abiotic degradation and remineralization and/or unusable for microorganisms. However, the mechanisms of generation of recalcitrant DOM are still unclear. DOM is produced by primary producers, is actively released or originates from a huge variety of biological and chemical processes. This originally labile DOM is transformed to semi-labile and finally to recalcitrant DOM. These transformations proceed on time scales of days to month and probably over very long periods of time.

Without knowledge on molecular structures it is impossible to discern why DOM is so resistant against biotic and abiotic decomposition. Tools for the chemical characterization of DOM in the ocean are limited, and thus, the molecular structure of marine DOM remains largely unknown. The present molecular level determination of DOM in seawater is essentially restricted to carbohydrates, amino acids, lipids and aminosugars. These compounds represent less than 10% of the open ocean DOC, and because they are usually determined after considerable chemical treatment the chemical structure they are embedded is also unknown. Other data on molecular level characterization are obtained by the combination of analytical techniques with various methods of isolation and fractionation of DOM such as solid phase extraction and ultrafiltration. However, it has to be considered that only a method-dependent fraction can be isolated from the total DOM. In the past few years, Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) enabled to determine the molecular elemental composition of thousands of DOM molecules. For the first time collision induced dissociation FT-ICR-MS was used to study fragmentation pathways of single isolated masses. Mainly stepwise losses of CO₂ and H₂O were observed for all precursor masses. Therefore, it can be concluded that similar structures (carboxyl and hydroxyl groups) are ubiquitously present in DOM. Most molecules are highly oxygenated which implies that they are not per se stable and should be utilizable by microorganisms. The extremely low concentration and complex composition may be important properties that DOM appears to be recalcitrant and is not or only slowly utilized by microorganisms. It might be not profitable for bacteria to degrade these molecules because they have no energetic advantages. However, the common view is that biotic and abiotic processes exist that make organic material recalcitrant and thus unattractive for microbial degradation. A close co-operation with microbiology is indispensable to understand the cycling of DOM. It is crucial to identify sources and transformation processes as well as molecular structures of DOM as detailed as possible to assess the impact of DOM on global carbon cycles.