Comprehensive Chemical Characterization Of Marine Dissolved Organic Matter Using Efficient Isolation Coupled To Advanced Analytical Techniques

Dissolved organic matter (DOM), operationally defined as the fraction passing through a 0.1-0.45 µm filter, plays major roles in oceanic and global biogeochemical processes. It accounts for >90% of the organic carbon in the oceans, making it one of the Earth's largest active carbon pools (~700 Pg C), approximately equal to atmospheric CO2. Consequently, any minor changes in DOM dynamics can impact the Earth's carbon-cycle. Despite its importance, the cycling and chemical composition of marine DOM are poorly constrained, with any net shifts largely obscured by analytical limitations. Recent analytical breakthroughs, especially advanced nuclear magnetic resonance (NMR) spectroscopy involving spectral editing and multidimensional techniques and ultra-high resolution Fourier transform ion cyclotron mass spectrometry (FT-ICR MS) have the potential to bring a major fraction of marine DOM within our analytical window, thus greatly facilitating the reading of DOM's "molecular messages". Despite the great promise of these techniques, if DOM isolation procedures result in an altered, biased or contaminated sample, then the usefulness of the results will be, at best, limited. The most promising improvement in DOM isolation to date appears to be reverse osmosis coupled with electrodialysis (RO/ED), which we have shown to isolate up to 95% of marine DOM, compared to ~10-40% for previous techniques. We propose to combine this major breakthrough in marine DOM isolation with the unparalleled power of ultra-high resolution FT-ICR MS and advanced NMR spectroscopy, to gain major new insights into the composition of marine DOM and the biogeochemical processes controlling its composition. The main goals of this exploratory stage of the proposed study are to: (1) characterize bio-refractory DOM that dominates the marine DOM pool especially in the deep sea; (2) characterize newly produced DOM in an upwelling region; (3) characterize semi-biolabile and photobleached DOM that accumulates in oligotrophic, subtropical gyre surface waters; and (4) compare RO/ED isolated DOM to the original sample and to DOM isolated using ultrafiltration and solid-phase extraction (e.g., XAD and C18).

Intellectual Merit: Determining the detailed composition and structure of DOM offers unparalleled rewards, for, if the usefulness of a set of tracers is defined by their informational richness, it is apparent that the molecules within the DOM pool, diverse as they are in source, reactivity and history represent a unique set of biogeochemical tracers capable of providing important insights into the origins of their parent waters and the diagenetic alterations that have occurred within those waters during transport. The prospect of mining this vast store of information led John Hedges to comment that "the future of oceanographic research belongs in large part to those who can learn to read these molecular messages". During the course of the study we intend to chemically characterize biolabile, semi-biolabile, and biorefractory DOM in order to shed light, not only upon the structures of these compounds, but also the reasons for their varying reactivities and distributions in the global ocean. This study will also evaluate the relative contribution of terrestrial organics to the total marine DOM pool (e.g., black carbon and lignin) to address the ongoing debate concerning the fate of terrestrial matter and the ultimate sources and fates of DOM in the oceans.

The overarching goal of our study is to determine the detailed chemical composition and structures of marine DOM, laying the foundations for a significantly improved understanding of marine biogeochemistry.