

CHEMICAL CHARACTERIZATION OF DOC AND POC IN SEAWATER: DO PARTICLES PUMP DOC TO THE DEEP OCEAN?

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Abstract

In order to highlight the mechanisms that link the oceanic DOM and POM pools, we studied the chemical structure of: a) surface active POM (foam), produced after bubbling of algal-derived DOM and b) aggregate and sinking POM collected from the surface and the deep ocean. ¹H-NMR spectra and molecular level analysis of foam samples resemble those of oceanic high molecular weight (HMW) DOM, showing an important contribution from polysaccharides, along with contributions from lipids, proteins and acetate. Furthermore, bulk and molecular analysis of aggregate and sediment trap material showed that there are two distinct classes of polysaccharides in these samples, the insoluble and soluble ones, which can be distinguished by their neutral sugar composition. The results of our study put additional evidence to two hypothesis: 1) physical removal by macroaggregates could control HMW DOM concentrations in surface seawater and 2) hydrolytic cleavage and release of HMW DOM from sinking macroaggregates might be of importance for the introduction of newly produced DOM to the deep ocean.

Introduction

The deep ocean inventory of dissolved organic carbon (DOC) is approximately 550 GT, comprising one of the Earth's largest carbon reservoirs. Despite its potential significance, many of the basic chemical and dynamic processes that collectively determine the cycling of DOC in the ocean are still poorly understood. Chemical characterization of high molecular weight (HMW) DOC, recovered by ultrafiltration, showed that a large fraction of DOC is a structurally well-defined class of acylated polysaccharides (APS) (1,2).

A possible mechanism for the removal of APS from the euphotic zone is coagulation or adsorption onto settling particles. Previous studies have shown that transparent exopolymer particles (TEP) can be formed from extracellular polysaccharides, which are considered to control the formation of marine snow during diatom blooms (3,4). In order to investigate this mechanism, we focused on the chemical characterization of particulate material produced both naturally and artificially after bubble-stripping of DOM. Two different types of surface-active material have been analyzed: i) particulate material (foam) produced after bubbling of HMW DOM (isolated from an algae culture) and ii) natural foam samples, collected from an enclosed coastal marine site (Salt Pond, Woods Hole, U.S.A.).

Methods and Materials

Foam samples, culture DOM and residual (bubble-stripped) samples were chemically characterized by proton-nuclear magnetic resonance spectroscopy (¹H-NMR), elemental analysis, spectrophotometry (bulk carbohydrate and transparent exopolymer particle concentrations) and molecular level analysis (monosaccharides) (5).

Results and Discussion

¹H-NMR and molecular level analysis revealed that both mechanically and naturally-produced particles are rich in polysaccharides. ¹H-NMR spectra showed that the major resonance in both natural and artificial foam is from polysaccharides (3-4 p.p.m (CHOH), and 1.3 p.p.m (CH₃)). Resonances for low-molecular weight, non-acetate lipids were present at 0.9 p.p.m (CH₃) and 1.3 p.p.m (CH₂), for acetate at 2.0 p.p.m (CH₃COO/N) and for proteins between 2.8-1.5 p.p.m. Proton-NMR spectra revealed that there are strong similarities in the chemical structure of seawater HMW DOC and surface-active particulate material.

Both naturally and artificially produced HMW DOM and foam samples have similar monosaccharide distribution pattern. Galactose was observed to be the most abundant sugar, with mannose, fucose, rhamnose, xylose and glucose being relatively less abundant, and arabinose being the least abundant monosaccharide. Foam samples were enriched in deoxysugars (fucose and rhamnose) and galactose, and were depleted in glucose compared to the HMW DOM. Our results show that POM with similar chemical characteristics to HMW DOM can be produced from algal-derived DOM.

One possible mechanism by which APS may be introduced to the deep ocean is hydrolytic cleavage and release from settling macroaggregates. In order to assess the importance of this mechanism, a second series of experiments has been carried out. Marine aggregates collected during a diatom bloom from Buzzards Bay (Woods Hole, USA), and settling particles collected by sediment traps in the Arabian Sea and the Southern Ocean were chemically characterized. Samples were extracted with 100 mM Na₂EDTA solution in order to separate a

'soluble' carbohydrate fraction, which is associated with the particulate matter.

Neutral monosaccharides in total particulate samples and the 'soluble' Na₂EDTA extract showed different sugar distribution patterns. In the former, glucose was the most abundant sugar (79%), with a low contribution from galactose (7%) and mannose (5%) and with a minor contribution from the rest of the sugars (3%). In the 'soluble' extract, glucose and galactose were found more abundant (34% and 24 %, respectively), with mannose (15%), fucose (9%), rhamnose (9%), xylose (6%) and arabinose (1%) contributing less. The former distribution resembles that of marine POM, while the latter is similar to that of foam and seawater HMW DOM. These results imply that soluble and insoluble polysaccharides are two distinct classes of particulate organic matter, and can be distinguished by their neutral sugar composition.

In accordance with our results, radiocarbon measurements support the hypothesis that newly-produced DOM is introduced to the deep ocean. APS isolated from the deep ocean DOM have a young radiocarbon age (Repeta *et al.*, in preparation), while deep-sea total DOM yields very old apparent ages (4000-6000) (6). Moreover, experiments with laboratory-produced soluble polysaccharides suggest that they can spontaneously form microgels and larger aggregates in seawater (7). Further research is needed in order to highlight the DOC pumping through settling particles and the implications of this phenomenon on the estimation of carbon budgets in the ocean.

References

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