

The chemical composition of dissolved organic matter in seawater

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Oceanic dissolved organic matter (DOM) represents one of the largest dynamic reservoirs of carbon on Earth. At $\sim 10^{18}$ g carbon, DOM is of the same magnitude as the entire living vegetation on the Earth's continents, and larger than the atmospheric CO₂ pool (Hedges, 1992). As such, small changes in the cycling of DOM potentially have a significant impact on the global carbon cycle. However, the biological and geochemical mechanisms controlling this major carbon reservoir remain poorly understood. A principal reason for slow progress in DOM geochemistry is the difficulty in chemically characterizing this highly dilute (~ 1 ppm) and complex organic mixture. Total concentration measurement has been the principal method for DOM study. But even this approach remains controversial (Williams and Druffel, 1988), and cannot yield the detailed molecular-level information that can elucidate sources, fates, and mechanisms. Representative isolation of dissolved organics from the three orders of magnitude more concentrated salts in seawater has imposed a major barrier to obtaining molecular-level information.

Previous data on the chemical composition of DOM have come either from direct analysis of selected compound classes in seawater, or from using hydrophobic resins to isolate a chemically fractionated component. Only 1-15% of the total DOC pool can be accounted

for by these methods (Williams and Druffel, 1988), and isolated samples are not likely to be chemically representative of the entire DOM mixture. Chemical analyses of resin isolates in particular have contributed to a long-held perception that the bulk of DOM in the world's oceans is a refractory, high-molecular-weight humic-like substance with little dynamic role in biological cycling.

We have used tangential flow ultrafiltration as new approach to isolate a larger, more representative sample of seawater DOM. Large-volume seawater samples (~ 1000 l) were pre-filtered through a 0.2- μ m pore size cartridge to remove particulate organic carbon and living particles, and then ultrafiltered to concentrate components that are rejected by the 1000-dalton (~ 1 nm) nominal cutoff membrane. As a tool to study DOM, ultrafiltration has provided several distinct advantages over previous methods:

(1) It is capable of isolating a larger fraction of total DOM than any previous method. Typically better than 30% of the total DOM in surface waters can be recovered as a dry powder (Benner et al., 1992).

(2) It isolates organic compounds based primarily on size rather than chemistry. The isolation process takes place in the natural seawater matrix without alteration of pH or extreme changes in temperature. This allows

gentle collection of DOM samples that are more chemically representative of the true distribution of compound types in nature than has been previously been possible.

(3) Large volumes (> 1000 l) can readily be processed, yielding sufficient material (100–300 mg OC) to apply a variety of techniques in a comprehensive chemical investigation.

Past analyses of individual compound classes have taken a piecemeal approach: measuring individual compounds or compound classes and reported results as individual concentrations in water. Having large amounts of chemically representative ultrafiltered DOM allows powerful spectroscopic methods such as solid- and liquid-state NMR to be employed, as well as quantitative molecular-level analyses of major biochemical classes. Individual biochemical distributions can then be considered in relation to their quantitative contribution to the entire DOM mixture.

We have isolated ultrafiltered DOM samples (UDOM) from surface, oxygen minimum, and deep waters in a variety of oceanic environments including the North Pacific, Equatorial Pacific, Gulf of Mexico, and Sargasso Sea. A succession of chemical methods ranging from bulk elemental composition to molecular-level inventories are being applied to characterize the UDOM samples. We report here elemental compositions, ^{13}C NMR spectra, and individual neutral carbohydrate distributions for selected samples. Together these analyses reveal that seawater DOM is a biologically dynamic substance markedly different in composition from seawater humic materials isolated by conventional resin adsorption techniques.

CHN analyses of UDOM samples from the all the oceanic environments sampled yield atomic C/N ratios ranging from 13–15 in surface waters to 18–22 in deep samples. These values fall within the range of C/N ratios obtained from DOC and DON analyses of whole water samples obtained from similar environments (Hedges et al., 1993), and indicate that

ultrafiltration does not appreciably fractionate seawater DOM with respect to N-containing compounds. These values indicate that DOM is carbon rich relative to the Redfield value of 7 for fresh plankton material, yet is greatly different from typical C/N values of 35–45 obtained for marine humic isolates (Meyers-Schulte and Hedges, 1986).

Solid-state ^{13}C CPMAS NMR provides a broad view of the organic functional group distributions in the UDOM isolates. Fig. 1 shows spectra of UDOM samples isolated from surface and deep waters of the North Pacific (Benner et al., 1992) and Gulf of Mexico.

UDOM surface samples are uniformly characterized by a major peak at ~74 ppm, with significant area contributions by peaks centered around 30, 90 and 170 ppm (Fig. 1). The central resonances correspond to a major carbohydrate component (74 and 90 ppm), accounting for ~50% of total carbon, with the

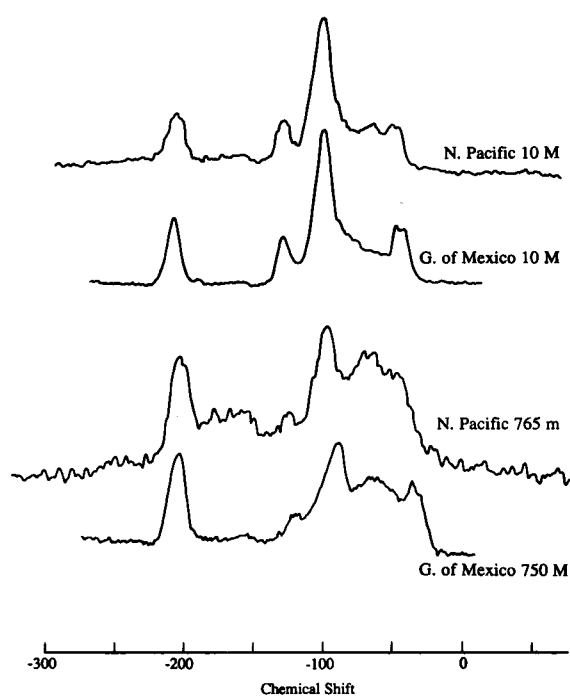


Fig 1. NMR traces of UDOM isolates from Gulf of Mexico and station ALOHA in North Pacific. Traces from similar depths at different stations are grouped together for comparison. (North Pacific NMR by P. Hatcher.)

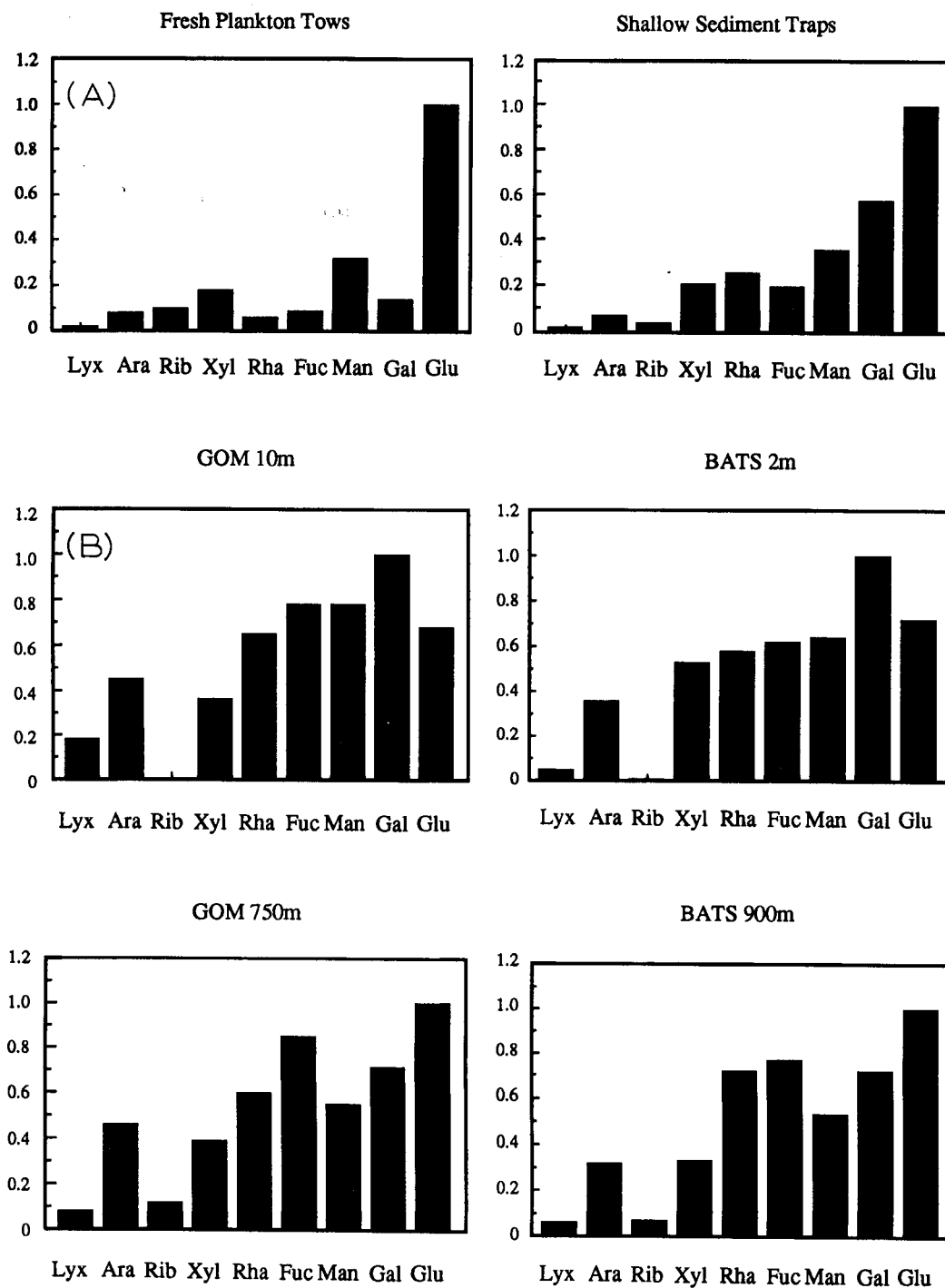


Fig 2. UDOM neutral sugar fingerprints: (A) average aldose fingerprints of some fresh plankton (Cowie and Hedges, 1984a, b; Hamilton and Hedges, 1987; Tanoue and Handa, 1987) and shallow sediment trap material (Cowie and Hedges, 1984a, b); (B) surface UDOM samples from Gulf of Mexico (GOM) and Sargasso Sea (BATS); (C) oxygen minima UDOM samples from the same sample locations.

balance largely derived from aliphatic and carboxylic acid carbon. The surface UDOM samples contain only minor portions of aromatic carbon. Deep samples yield spectra markedly different in appearance from their surface counterparts. The major difference is the attenuation of carbohydrate peaks at 74 and 90 ppm. Deep UDOM samples appear to be composed primarily of aliphatic and carboxylic acid carbon. The aromatic carbon content is larger, but remains a minor component of the total.

UDOM obtained from similar depths in the North Pacific and Gulf of Mexico yield almost identical spectra. The consistent differences between surface and deep UDOM spectra imply that the bulk of the change in DOC content between surface and deep water is due to degradation of the carbohydrate material which accounts for ~50% of surface UDOM samples. This pool of material represents an enormous carbon-rich substrate for biological respiration in the upper water column of the ocean, which likely is advected to and degraded in subsurface waters. Degradation of this higher-molecular-weight carbohydrate material is likely to be relatively slow with respect to the small compounds which may be cycled on time scales of hours or days in the upper ocean. The non-carbohydrate component of surface UDOM spectra is very similar to whole spectra from deep samples. The deeper material thus may be present throughout the ocean as a more refractory organic background, surviving multiple oceanic mixing cycles.

The nature of the carbohydrates in selected UDOM samples was investigated at the molecular-level by direct analysis of aldoses yielded by acid hydrolysis of dried samples (Cowie and Hedges, 1984a). Gulf of Mexico and Sargasso Sea surface samples yielded ~20 mg aldose per 100 mg OC and are especially enriched in galactose. Glucose, mannose, rhamnose, xylose and fucose also make substantial contributions. Lyxose is a minor com-

ponent of surface samples, and ribose is usually absent or below quantitation limits. In deep water samples, the total aldose yields per 100 mg OC decreased ~5-fold. While all the major contributing sugars in surface samples are still present at depth, glucose, fucose and rhamnose increase in relative abundance while galactose decreases. Ribose increases in absolute yield in deep UDOM samples and appears to have a source in the deeper water.

These neutral sugar distributions can be considered "fingerprints" of the types of polymeric carbohydrates actually present. When UDOM fingerprints are compared to carbohydrate distributions obtained from other natural materials, such as fresh plankton material or sediment trap samples, the neutral sugar composition shows distinct compositional differences (Fig. 2). Glucose, the major aldose hydrolysis product from plankton and sediment trap samples (Cowie and Hedges, 1984b; Ittekkot et al., 1984a, b; Tanoue and Handa, 1987) is relatively depleted in UDOM carbohydrate. By contrast, the usually minor deoxy sugars rhamnose and fucose, are major components of both surface and deep UDOM.

An outstanding feature in the carbohydrate data is their compositional consistency between different sampling locations (Fig. 2): the aldose fingerprints from similar depths in the Gulf of Mexico and Sargasso Sea are almost indistinguishable. This is consistent with NMR and elemental data, and implies that the chemical composition of the DOC pool may be relatively homogeneous throughout the ocean. This appears true both of the major labile carbohydrate fraction found in upper waters, as well as the more refractory material found at depth. The biogeochemical mechanisms responsible for maintaining the chemical uniformity of the seawater DOM reservoir are thus some of the most quantitatively important processes in the global carbon balance. Further work toward elucidating more comprehensive chemical structures in UDOM are likely to re-

sult in elucidation of some of the most abundant organic compounds on the Earth.

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