

Bacterial origin of a major fraction of refractory marine dissolved organic nitrogen

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The enormous pool of fixed nitrogen bound in organic forms is one of the most important, but least understood, major biogeochemical reservoirs. In systems as diverse as temperate forests, desert streams and the open sea it is the 'leak' of nitrogen bound in organic forms not rapidly remineralized that maintains the defining condition of nutrient limitation (Jackson and Williams 1985).

In the sea, most organic nitrogen resides in subsurface waters in dissolved nitrogenous material (DON) not readily identified by conventional biochemical techniques. Persisting over multiple ocean mixing cycles, such substances have been assumed to consist largely of structurally complex products of common biochemicals often termed 'geomolecules.' This abiotic mechanism has long constituted a central theory for organic matter preservation in many environments. This abstract brings together recent evidence from ^{15}N CPMAS NMR and amino acid enantiomeric ratios suggesting that at least in oceanic DON this model is largely inaccurate, and instead that specific nitrogenous biopolymers survive relatively intact over long time scales.

Results and discussion

Ultrafiltered dissolved organic matter (UDOM) was isolated from surface and deep waters in three ocean basins. Natural abundance ^{15}N CPMAS NMR spectra were obtained on a Bruker AF-300 spectrometer, following the parameters determined by Knicker *et al.* (1993). Amino acid hydrolysis was conducted and individual D and L amino acids were quantified as pentafluoropropyl isopropyl esters.

The ^{15}N CPMAS spectra of samples (Fig. 1) from all depths are characterized by a single peak centered near 260 ppm, corresponding mainly to the chemical shift range for amide nitrogen. Although the line width of the center band is similar in the surface

samples, width and range of the 260 ppm resonance increases somewhat in deep water. Apart from the main peak, no other signals can be unambiguously identified in any sample. This suggests that nearly all UDOM nitrogen at all depths is present as biosynthesized amides.

Because 60–80% of organic nitrogen in biomass or marine particles is recoverable as hydrolyzable amino acids (Cowie and Hedges, 1992), peptides would be expected to make up the majority of this

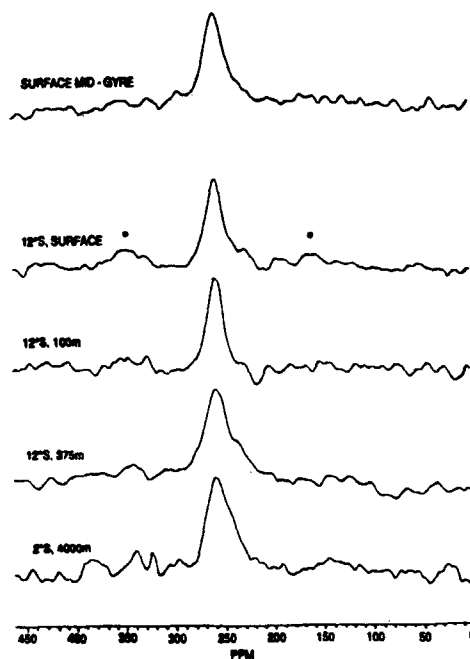


FIG. 1. Natural abundance ^{15}N CPMAS Spectra for Pacific UDOM.

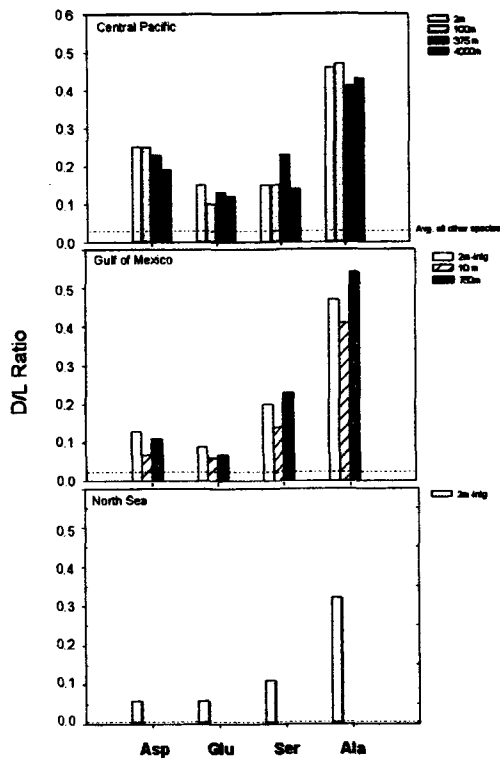


FIG. 2. Amino Acid D/L Ratios in oceanic UDOM.

amide, especially in upper ocean waters. However, only a minor (10–20%) percentage of total nitrogen can be recovered as hydrolyzable amino acids from any UDOM isolate (McCarthy *et al.*, 1996). This result indicates that most of the nitrogen in UDOM is either hydrolysis resistant or some other amide-containing macromolecule.

Amino acid enantiomeric ratios provide one clear part of the answer. Alanine (Ala), aspartic acid (Asp), glutamic acid (Glu), and serine (Ser) consistently have D/L ratios far above blank levels (Fig. 2). Ala shows the most dramatic enrichment, with D/L ratios

near 0.5, while Asp, Glu and Ser ratios generally fall between 0.2–0.4. The magnitude and pattern of these D/L enrichments is inconsistent with abiotic generation. Instead the enantiomeric patterns which characterize UDOM thus closely match those characteristic of bacterial peptidoglycans. These observations suggest that relatively intact peptidoglycan remnants derived from bacterial cell-walls constitute a major source of the unidentified and relatively refractory DON in the ocean.

Conclusions

Our data indicate that the majority of the slowly cycling dissolved organic nitrogen in the ocean is derived from amide biomolecules that have undergone little fundamental chemical alteration. The high D/L amino acid ratios strongly suggest that a substantial fraction of this material originates in bacterial cell-wall biopolymers, and that accumulation and environmental persistence of such substances may be strongly related to intrinsic structural properties. It is unlikely that these observations have relevance only to the oceanic water column, and there has been considerable recent interest in the role of bacterial products in organic matter preservation in sediments and soils (Parkes, *et al.*, 1994). Our results, representative of an environment without factors such as anoxia, burial, or interactions with mineral surfaces, may provide a particularly unobstructed view of widespread processes.

References

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