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FINAL REPORT

Export and Molecular Level Characterization of Dissolved and Particulate Organic Matter from the Mid-Atlantic Bight

DE-FG02-92ER61428

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with subcontract to Robert F. Chen

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As part of the OMP field program, Dr. Repeta served as chief scientist on two whole shelf cruises to survey the MAB, one in late winter/ spring (February/March 1996) and one in summer (July/August, 1996). Our field program surveyed the shelf under two very different biogeochemical regimes. In the late winter/spring, river discharge and primary productivity are maximal. The water column is well mixed, relatively fresh, and has high standing stocks of nutrients and biomass. In summer, both primary production and river discharge decrease. A strong pycnocline develops that restricts the freshwater inputs to a very shallow surface layer, and isolates surface water from colder deep water (cold pool). Our objective was to inventory dissolved and particulate forms of carbon (and to the extent possible, nitrogen) in order to establish spatial gradients and seasonal patterns of elemental distribution and flux on a much wider area of the shelf than accounted for by the moored array. We proposed to use geochemical tracers that integrate over longer spatial and temporal scales to supplement C cycling studies conducted by the benthic, water column processes and moored array teams of OMP.

Samples were collected along seven transects perpendicular to the coast with stations located every 5-10 miles (6-8 stations per transect). Samples were also collected up the Delaware estuary to 0 ppt, and in the Chesapeake estuary. A total of 55 stations were occupied between Nantucket Island and Cape Hatteras. At each station, samples were collected for discrete measurements of DOC (R. Chen, UMass), DIC (D. Wallace, BNL), oxygen (D. Wallace, BNL), DOM fluorescence (R. Chen, UMass), phytoplankton pigments (D. Repeta, WHOI), POC/PON (Repeta; Falkowski, BNL), and nutrients (Wallace, BNL). Large volume samples were also collected at in shore, midshelf, and offshore stations on each transect for DOC/DIC compositional (Repeta/Eglinton, WHOI) and isotopic (Bauer VIMS; E. Druffel, UC Irvine) analyses, and microbial incubation experiments (Hopkinson, MBL). Continuous underway measurements were made for pCO₂ (D. Chipman, LDEO), primary productivity by FFR (Falkowski/Kolber, BNL), and chlorophyll fluorescence. Overflights were made of the cruise track by NASA -P3 Airborne Oceanographic Lidar (F. Hoge, R. Swift). Finally as part of our standard CTD package used to collect hydrographic data for modeling (described below), we deployed and calibrated a DOM fluorometer to provide much greater coverage of DOC distributions on the shelf.

Between 80-90% of the standing stock of organic carbon on the shelf is dissolved. We performed over 1600 analyses of DOC as part of our shelf surveys, and our analyses show

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clear spatial and temporal trends (Fig. 1). At all times of year DOC concentrations along the entire shelf are elevated relative to open ocean water (typically 70-80 μM), with some shelf stations having DOC in excess of 200 μM . Steep gradients in DOC are observed between inshore (high DOC) and offshore (lower DOC) stations, and from south (high DOC) to north (lower DOC). There is also an increase in average surface water DOC concentration from spring (average 92 μM) to summer (average 103 μM) due primarily to stratification and isolation of fresh water at the surface, although total water column inventories have not been determined and may not track surface water values.

Our DOC measurements are being incorporated into a 3 dimensional model of shelf circulation developed by B. Vetrano and T. Hopkins at NCSU (Raleigh) which incorporates hydrographic data collected on our cruises. The model is designed to quantify the transport of DOC down and off the shelf. Preliminary results suggest a high flux of DOC across the shelf in early spring, while in summer transport is dominated by alongshelf processes. Annually integrated fluxes range from 3-30 MTC/year, in agreement with our previous estimates using simple box model calculations. We anticipate we will be able to refine our estimates using higher resolution data in future runs of the model.

The accumulation of DOC along the trajectory of shelf water movement suggests that in-situ production or import of DOC from the continental margin exceeds remineralization in this environment. Elevated DOC inventories on the shelf may result from persistently high rates coastal primary productivity, or from the import of DOC by adjacent rivers, groundwater, and surface run-off. Preliminary evidence suggest both elevated in-situ production and continental inputs play approximately equal roles. DOC along the shelf is highly correlated with salinity and CDOM fluorescence. Within specific transects correlation coefficients are > 0.9 . For the entire shelf, the correlation is somewhat weaker, but still significant ($r > 0.7$). A compilation of USGS data for major river discharge along the shelf, as well as DOC concentrations suggest that up to 50% of the DOC added to the MAB may originate from freshwater inputs. This value is considered to be a lower estimate, as it does not consider groundwater discharge or direct run-off.

In addition to our study of DOC distribution in shelf waters, we have been actively investigating the chemical structure, sources, and sinks for DOC. This work is the basis of the Ph.D. thesis of Ms. Lihini Aluwihare, to be completed in December of 1998. Our OMP supported study has led to the hypothesis that a major fraction of marine dissolved organic matter is a family of structurally well defined acyl heteropolysaccharides synthesized by marine algae (Aluwihare et al., 1997; Aluwihare and Repeta, 1998). The biopolymer is present in all surface and deep ocean waters. Chemical analyses of size fractionated dissolved organic matter shows a uniform composition throughout the 1-10kD size fraction (Repeta et al., 1998a) characteristic of a true biopolymer, and recent studies have shown the polymer to be present in freshwater rivers and lakes (Repeta et al., 1998b).

With the aid of the above grant we have also pioneered the development of new methods to trace the sources and cycling of organic matter in the marine system. In particular

we have focussed upon two different approaches that address specific aspects of carbon cycling.

A major emphasis has been the development of methodology to measure the radiocarbon content of individual organic compounds present in dissolved and particulate organic matter (Eglinton et al., 1996). This involves the use of preparative capillary gas chromatography to isolate pure compounds from complex mixtures such as those encountered in the marine system, together with optimization of techniques for processing and analyzing the small amounts of sample available for AMS ^{14}C measurement. We established the method using a suite of reference materials of known ^{14}C age, and that contained compounds of the type that are encountered in marine samples. We showed that the isolated compounds faithfully recorded the radiocarbon content of their parent material, and that a precision for ^{14}C of $\pm 25\%$ is readily attainable (Eglinton et al., 1996). We have subsequently continued to improve on this level precision.

The development of this molecular radiocarbon approach has stimulated a great deal of interest and prompted research in a variety of directions. Of greatest pertinence to the goals of the OMP is our further refinement of this approach for the measurement of terrestrial marker compounds in the dissolved pool. Specifically we adapted methodologies for hydrolysis, derivatization and isolation of lignin-derived phenols from ultrafiltered DOM samples so that their radiocarbon contents could be determined (McNichol et al., 1998). Using this approach, we measured phenol ^{14}C contents in DOC-rich riverine and salt marsh waters from the eastern seaboard of the US (Ertel, McNichol and Eglinton, unpublished results). We found that there was a spread in ^{14}C ages for different phenols, but in general the ^{14}C contents reflected biomass that had been synthesized after the injection of ^{14}C from atomic weapons testing into the atmosphere (i.e. post-1960 AD). Thus this terrigenous fraction of DOM is modern in origin, and can be used as an isotopic end member in mass balance calculations to place constraints upon the proportions of dissolved (and particulate) OM exported the shelf that derive from autochthonous and allochthonous sources.

We are currently still processing UDOM samples from selected locations along the MAB and will report the results of the molecular ^{14}C analyses of terrestrial and other compounds once our data set is complete. We are also completing molecular ^{14}C studies of the organic carbon-rich sediments that form a lens on the shelf-slope break around Cape Hatteras. The focus of this work is to examine the ages (and hence sources) organic matter that are sequestered in this reservoir in order to further constrain the fate of carbon fixed on the MAB. A second major aspect of the work we have undertaken involves the use of direct temperature-resolved mass spectrometry (DT-MS) to examine compositional aspects of dissolved and particulate organic matter in the water column. For these analyses we organized and participated in several cruises to Georges Bank and the MAB. Samples were collected on up to 8 different shore-perpendicular transects along the MAB. Pumping and cross-flow filtration was used to recover colloidal and particulate matter from surface and deeper waters. Particulate matter was separated into large ($>53\text{ }\mu\text{m}$ "sinking") and small (>2 and $<53\text{ }\mu\text{m}$ "suspended") fractions prior to analysis by DT-MS. Colloidal matter was

concentrated and desalted by ultrafiltration and diafiltration respectively prior to analysis. Most samples analyzed to date were collected during March 1996.

DT-MS is a useful technique because it allows molecular-level information to be derived for a broad range of compound classes (lipids and biopolymers) from very small sample sizes (a few micrograms of carbon). Our goal has been to relate compositional variations in different organic matter phases to physicochemical and biological properties, so that the cycling of organic matter on the MAB can be understood at a molecular level. In this way we hope to ultimately be able to predict how the fate (i.e. subduction/burial versus remineralization) of different input materials responds to changing oceanographic conditions (anthropogenically driven or otherwise).

Statistical analysis of mass spectral data for particulate organic matter collected throughout the MAB revealed compositional differences between size classes (Minor et al., 1997). Although different particle types share many similar compositional features (i.e. they both contain proteins, polysaccharides, lipids etc.), it is the relative proportion of these biochemicals that differs in a systematic fashion. For example, small ("suspended") POM is enriched in constituents that imply a higher proportion of phytoplankton biomass relative to large POM. There are other more subtle differences (e.g., variations in chain lengths of fatty acids, proportions of hexose vs pentose-based polysaccharides) that are exposed when the mass spectra are subject to statistical data reduction (multivariate analysis). Using this information we have a better grasp for the types of organic matter that are likely to be removed by vertical transport and participate in benthic processes, and of chemical transformations in the suspended pool. Moreover, as part of separate NSF-funded research we have investigated compositional heterogeneity within the suspended particle size class. Specifically, in the latter we have separated particles according to their chlorophyll content using flow cytometry and have noted marked differences between these classes.

While the most of the variability in particle composition is in relation to size, there are also significant variations within a particle class that vary with location (Minor and Eglinton, 1998). Both small and large-sized particles exhibited compositional characteristics that were related to oceanic regime (i.e., shelf, shelf-edge and slope waters). For example, shelf-derived large particle POM was enriched zooplankton biomass, whereas the same particle class from the slope exhibited chemical characteristics consistent with phytodetritus. In contrast, while small ("suspended") POM also displayed across shelf compositional variations, in this case indicating phytoplankton biomass was concentrated at the shelf-edge (relative to equivalent particle sizes from mid-shelf and slope stations), there was also a marked alongshelf gradient in composition. Correlation of the chemical properties observed with other parameters revealed several statistically significant relationships. In particular, the ratio of phytoplankton to total particles (determined by flow cytometry) was strongly coupled to compositional trends in the large particle pool, while along shelf variations in phosphate suggested that the parallel trend in suspended POM was a reflection of the varying stages of the spring bloom at different locations along the MAB.

DT-MS of colloidal organic matter was performed under a range of conditions. The most comprehensive data sets were acquired using ammonia chemical ionization (NH_3 CI). In addition the structural elucidation of colloidal OM the goals were to examine genetic relationships and cycling between dissolved and particulate pools. DT-MS results support previous investigations that imply a significant fraction of colloidal ($> 1\text{kD}$) OM is composed of polysaccharides. Mass spectral fragments of neutral sugars (normal, deoxy- and methylated aldoses), N-acetyl amino sugars and, possibly, acidic sugars were detected (Boon et al., 1998). The methylated and N-acetyl amino sugars are taken to imply bacterial contributions to UDOM. An additional aspect of the DT-MS data is the separation of components according to their thermal lability, and two distinct components of UDOM were recognized in this way. The relative proportions of these components were found to vary as a function of location and depth, implying either source or reactivity control on their abundance. A final observation was the detection of some similar sugar components in detrital fractions of POM, suggesting a link between these two fractions.

We believe these DT-MS studies represent one of the first attempts to directly correlate detailed compositional aspects of organic matter with physicochemical and biological properties of a water mass. Although it is important to bear in mind that the results obtained reflect only a temporal snap shot of the MAB, this approach provides valuable insights into the relationships and cycling of organic matter on continental shelf systems.

March 1996

August 1996

Figure 1) DOC concentrations (μm) in surface water of the MAB

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