CEAN MARGINS PROGRAM
Scientific Framework

ATMOSPHERE CLIMATE

Molecular

Global

OCEAN ECOLOGY

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DEPARTMENT OF ENERGY

OCEAN MARGINS PROGRAM

Water Column and Benthic Boundary Layer

Studies

SCIENTIFIC FRAMEWORK

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OCEAN MARGINS PROGRAM DESCRIPTION

The Department of Energy (DOE) has traditionally supported long-term interdisciplinary studies on the structure and function of coastal ocean systems as part of its concern for sustainable development and the dispersal and fate of energy-related materials (including CO_2) in the marine environment. The approach has been to conduct regional studies along the U.S. continental shelves, utilizing moored instrumentation, ship sampling, and remote sensing to measure watermass movements; spatial and temporal concentrations of chemical species and particles; biological productivity; zooplankton grazing and bacterial respiration; ecological dynamics; and biogeochemical fluxes of organic particles, nutrients, and dissolved organic carbon between estuarine systems, the shelf, and the interior ocean.

During FY 1992, the DOE restructured its regional coastal-ocean programs into a new Ocean Margins Program (OMP), to:

> Quantify the ecological and biogeochemical processes and mechanisms that affect the cycling, flux, and storage of carbon and other biogenic elements at the land/ocean interface;

> Define ocean-margin sources and sinks in global biogeochemical cycles, and;

> Determine whether continental shelves are quantitatively significant in removing carbon dioxide from the atmosphere and isolating it via burial in sediments or export to the interior ocean.

To achieve these objectives, the DOE has supported both process-oriented research to understand the physical, biogeochemical, plant, animal, and microbial mechanisms and interactions that affect the input, assimilation, and transformation of carbon in coastal waters and sediments; and the development of new instrumentation to obtain high frequency in-situ measurements of the environmental and biological factors affecting carbon fluxes in the ocean.

During FY 1993, the DOE launched a new molecular biology initiative within its Ocean Margins Program to provide a mechanistic understanding of the complex biological processes which mediate the carbon cycle in marine systems. Molecular biological techniques are being developed, adapted, and applied to determine how biological processes are regulated and controlled by genetic limitations and environmental variables. Research emphasis has been placed on

> (i)   molecular regulation of photosynthetic carbon reduction by phytoplankton,

> (ii) molecular diagnostic markers of bacterial growth, production, and nutrient limitations to growth, and (iii) molecular techniques for elucidating metabolic pathways.

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Currently, the DOE Ocean Margins Program supports more than 70 principal and co-principal investigators, spanning more than 30 academic institutions. Research funded by the Ocean Margins Program amounted to about $6.9M in FY 1994.

Planned Activities

During the past two years, OMP scientists have developed an integrated multidisciplinary science plan to quantify the physical and biogeochemical processes affecting carbon fluxes, nutrient cycles, and ecological dynamics along the ocean's margins. This document describes that science plan in some detail, including a rationale, component studies, and appropriate methodologies. It is best viewed as a living document into which new investigators and technologies can be woven into the larger fabric of the longterm goals of the Ocean Margins Program. Although this plan is generic in nature, it forms the scientific framework for melding the research summarized in this document into a field experimental program to assess the exchange of carbon and other biogenic elements between estuarine systems, the shelf, and the interior ocean. This field experimental program will be conducted in the coastal waters near Cape Hatteras, North Carolina, where carbon burial in sediments and carbon export (as either DOC or POC) into the interior ocean, are expected to be maximum.

Program Schedule

FY 1995:   Conduct an outside peer review of physical, biogeochemical, and biological research projects and award new competitive research grants to address the field experimental needs of OMP

FY 1995:   Initiate the field experimental phase of OMP at Cape Hatteras

FY 1996:   Conduct an outside peer review of molecular biological research projects and coordinate this mechanistic research with OMP field activities

FY 1996:   Make fully operational the field experimental phase of OMP

FY 1997:   Evaluate OMP's field and laboratory measurements and assess the role of the coastal ocean in the global flux of carbon

FY 1997:   Begin using OMP results to: (i) improve ocean-circulation, ocean-atmosphere-interaction, global-change, and global-carbon-cycle models, (ii) develop remote sensing algorithms for productivity in coastal areas, and (iii) plan the next phase of the OMP

FY 1998:   Initiate the next phase of OMP by identifying a new experimental location to confirm the representativeness of the Cape Hatteras results, or by addressing new policy-relevant issues in coastal science

Program Interfaces

The DOE Ocean Margins Program is fully integrated with the National Science and Technology Council's (NSTC) Committee on Environment and Natural Resources (CENR), as a focussed effort within the Subcommittee on Global Change Research and as a contributary effort within the Subcommittee on Water Resources and Coastal and Marine Environments. The OMP is the major U.S. integrated multidisciplinary research effort for understanding the ocean margin's role in the global carbon cycle. It is strongly linked with the JGOFS and GLOBEC Programs because there is compelling evidence that the input of nutrients to coastal areas from land-based sources (via rivers and the atmosphere) and from interior-ocean sources (via coastal upwelling and frontal exchange), cause as much as 30%-50% of the total primary production of the global ocean to occur along its margins. The OMP and its scientific researchers are also interacting with IGBP's LOICZ Program and several U.S. Agency programs concerned with quantifying the processes that affect the transport and fate of water, carbon, nutrients, biota, sediments, and pollutants in changing coastal environments, including EPA, MMS, NASA, NOAA, ONR, and NSF's Program on Coastal Ocean Processes.

Policy Payoffs

Research within the OMP is important for; (i) predicting the dispersal and biogeochemical fate of carbon, nutrients, and other biogenic elements in coastal waters, (ii) quantifying primary productivity and ecological dynamics (structure and function) in ocean-margin systems, and (iii) examining the impacts of nutrient loading and other pollutants from anthropogenic sources.

Quantitative information on the flux and fate of CO_2 and biogenic elements at the land/ocean interface is important for the IPCC and other integrated assessments of sources and sinks in the global carbon cycle. In addition, quantitative information on coastal processes underpins policy decisions on resource management in changing coastal areas.

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INTRODUCTION

It has been postulated that ocean margins are significant sinks for carbon on a global scale, however, there is little oceanographic data to support or refute this claim. Given this uncertain role in the cycle of atmospheric carbon dioxide, and the potential impact of man's activities in margin regions, it is important to obtain an improved understanding of the sources, sinks and fate of carbon in ocean margins in general. The U.S. Department of Energy's Ocean Margins Program is designing a field experiment in the vicinity of Cape Hatteras to quantitatively test the question of whether this region is a net source or sink for carbon, and at the same time develop a mechanistic understanding of the coastal carbon cycle which can be applied to other margin regions throughout the globe. To meet these objectives, the principal goals of the Ocean Margins Program are to:

- understand how the coastal ocean acts as a system, and as an interface between the continental land mass and its estuaries, and the open ocean;
- understand the biogeochemical and physical processes which transport and transform carbon within that system; and
- determine the net exchange of atmospheric CO_2 with the ocean at the continental margin.

To quantitatively constrain and understand the fate of carbon in ocean margin systems will require a concerted approach consisting of observations in the water column and at the sea floor. Processes in these two environments are governed and linked by physical processes. Exchanges between the water column and the sea floor occur in the benthic boundary layer (BBL). This implies the need for simultaneous observations of physical variables, e.g. gradients in current velocity and direction, together with chemical and biological variables in the water column and sea floor.

Recent advances in moored oceanographic sensors as well as the development of new biological and chemical techniques will permit use of novel approaches in studying the biogeochemistry of the continental shelf and slope system. In addition, satellite data will allow us to place our study off Cape Hatteras in a broader oceanographic context, as well as assist us in planning and interpreting our site specific studies. In light of these new tools, we have posed the following questions which can be answered within the context of the OMP water column studies:

- What controls primary production on ocean margins?
- What are the rates and mechanisms of transformation of organic carbon between dissolved, colloidal and particulate pools, and of total carbon between organic and inorganic pools?
- What is the source of carbon in the Cape Hatteras region?
- What is the fate and magnitude of carbon exported off the Hatteras shelf?
- Are episodic events important in determining the net flux of carbon in ocean margins?

- What are the physical forces which control carbon export off Hatteras?

In this document we describe in some detail the experimental approaches which will be used in the OMP to answer these questions. The experiment must address the exchanges and transformations of carbon in the coastal ocean, from bidirectional exchanges between the shelf system and atmospheric, terrestrial and marine sources, to long-term accumulation of carbon in sediments and the ocean interior. As such, this document is divided into an exchanges section, which addresses the processes that result in transport of carbon across internal or external boundaries of the coastal ocean, and a transformations section, which includes the biological, chemical and physical processes that alter the form of carbon within the coastal ocean.

Two complementary strategies will be applied to the problem of measuring carbon exchange and transformation processes. Semi-continuous measurements of some key parameters will be obtained from instrumented moorings equipped with automated, high-frequency measuring devices. Other biogeochemical parameters and process rates must be measured discontinuously from ships. The OMP field studies have been designed to bridge the gap between mooring- and ship-based measurement strategies.

The Ocean Margins Program will explicitly link instrumented moorings with comprehensive biological/chemical/physical cruises focused on characterization of the detailed workings of the carbon cycle. This linkage will include a concentration of ship-based sampling within a region bounded by mooring sites, with overlapping measurements acquired from both ships and moored instruments. For example, ship-based measurements of chlorophyll concentrations and photosynthesis rates are coupled with fast-repetition fluorometer (FRR) measurements of the same parameters, collected from both ships and moorings. Similarly, zooplankton biomass measurements based on net tows are coupled with biomass estimates based on the acoustic backscatter recorded by moored acoustic Doppler current profilers (ADCP).

Moored instruments also will acquire measurements of integrating parameters that represent the net result of complex biogeochemical processes best studied from ships. For example, oxygen concentration will be measured by both moored and ship-based instruments. Changes in oxygen saturation integrate the effects of biological processes that produce and consume oxygen. Time series data on oxygen concentration obtained from moored instruments will be related to ship-based measurements of these autotrophic and heterotrophic processes, including direct respirometry measurements. Sediment accumulations also integrate the net results of processes influencing carbon fluxes and provide an historical record for assessing temporal changes.

In addition to providing coverage over longer time scales than are sampled by cruises, moorings provide high resolution temporal data which can be used to understand the importance of episodic events on the margin carbon cycle. If episodic events are significant, then the margin carbon cycle may be especially sensitive to man-made perturbations which have not been considered in previous models.

Comprehensive field studies will be logistically constrained to detailed coverage over a relatively restricted spatial scale determined by the design of the mooring array. Such studies will require sampling in different seasonal conditions within a single year. In addition, as confidence is gained in many of the new techniques and instrumentation proposed here, repeat cruises or process specific studies should be conducted in following years. At the start of the

program, whole shelf cruises will be required which focus on measurements between George's Bank and Cape Hatteras. These studies will look for carbon sources using geochemical tracers, such as carbon and nitrogen isotopes and specific organic biomarkers, and further use these tracers to see the integrated signal of carbon transformation and fluxes throughout the NE shelf and slope region. In establishing and designing these studies, it is important to recognize that the variability of benthic and water column systems vary on different space and time scales and that the resulting study plan will reflect these differences. Whereas in general, the BBL has more intense spatial heterogeneity, greater temporal variability is observed in the water column.

The overall experimental design can be thought of as "nesting" various sampling modes over both temporal and spatial scales. Short-term studies of transformation processes are nested within long-term, continuous sampling of chemical, biological and physical parameters by moored instruments. Both moorings and process cruises are in turn nested within larger-scale surveys of the NE shelf as a whole, and the larger-scale surveys are nested within regional data acquired by remote sensing. Integrating parameters provide links and cross-relations across all spatial and temporal scales of the Ocean Margins experiment.

EXCHANGE STUDIES

I. OBJECTIVE

The purpose of the exchange studies is to quantify the horizontal (alongshore and cross-shelf) and vertical (air-sea, water column, benthic boundary layer, sediment column) fluxes of carbon, including dissolved and particulate forms of organic and inorganic carbon. These measurements will be linked to studies of the biological and biogeochemical processes that transform carbon in order to assess the net flux of carbon through this coastal ocean system.

II. COMPONENT STUDIES AND RATIONALE

A. Shelf/Estuaries Exchanges

In eastern North America, estuaries are the principle avenues of exchange of solutes and particles between the continents and the coastal ocean. To address the fate of carbon produced on the shelves, we must quantify the sign and magnitude of the carbon exchanges between the shelf and estuarine systems. Appropriate sampling of temperature, salinity, pCO_2, alkalinity, nutrients, organic carbon and nitrogen, terrestrial biomarkers, and pigments of the Chesapeake Bay would provide information about the estuarine-shelf exchange terms for carbon and nitrogen. In addition, assessment of sedimentary burial rates in conjunction with local carbon budget studies would constrain the long-term sequestration of shelf-derived carbon in the estuarine systems.

Alkalinity is a measure of ionic charge balance in seawater and river waters. River waters have alkalinity values markedly different form that of seawater (2300 μeq/kg), with some rivers having values up to three times that of normal seawater. Since pCO_2 in seawater depends on alkalinity as well as temperature and total CO_2 concentration, the spatial and temporal distribution of riverine water influences the areal distribution of the oceanic CO_2 flux.

Major estuaries (Hudson, Delaware, and Chesapeake) along the northeast coast of the US may contribute refractory dissolved organic matter (DOM) and particulate organic matter (POM) to the shelf that is subsequently exported by along shelf transport to Hatteras, or by cross shelf exchange. Indeed, mass balance calculations suggest that a significant fraction of refractory DOM in the deep ocean could be supplied by fluvial inputs. Terrestrial and marine sources of DOM have distinctive C and N isotopic values, and may be distinguished by characteristic biomarkers (e.g. lignin, cellulose, sterols, and certain aromatic compounds, etc). The recent introduction of compound-specific stable C isotope ratio GCMS analyses, and ^{14}C analyses provides a means for identifying source components of DOM at a more detailed level than has been previously possible. These approaches are helping to integrate data from molecular level studies with total (bulk) carbon analyses by using isotope and carbon mass balance and statistical treatments of whole sample pyrolysis or NMR techniques.

The qualitative influence of terrestrial organic matter on DOM and POM should be readily observed in molecular level studies of DOM composition. These analyses can be made on samples along a salinity gradient from the mouth of major estuarine systems to the shelf water. Quantitative evaluation of the terrestrial component of DOM and POM is more difficult, but may be attempted using a multiparameter approach.

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B. Lateral Fluxes - Cross-shelf and Shelf-slope Exchanges

Quantitative assessment of cross-shelf and shelf-slope exchanges will require determination of the transport of dissolved and particulate organic matter within the water column and benthic boundary layer. The quantitative distribution and particulate organic carbon (POC) content of suspended particles and particle aggregates will be measured across the shelf and upper slope. These data combined with information on water volume transport, near-bottom flow, and measured POC fluxes into sediment traps deployed in the slope region will be used to quantify the flux of particulate organic carbon from the shelf and across the slope. The deep water POC fluxes extrapolated from aggregate abundance profiles and measured by the sediment traps will be integrated with the benthic flux measurements to provide estimates of nutrient regeneration occurring at the sediment water interface. Off-shelf transport will also be indirectly estimated by assessing the deposition of shelf-produced organic matter on the adjacent continental slope and rise.

The BBL could be a conduit through which a significant quantity of POC is carried off continental shelves. Previous studies over the Middle Atlantic Bight (MAB) shelf have not resolved near-bottom flow or particulate concentration to the extent necessary for reasonable estimates of POC transport through the BBL. However, they have shown that shelf sediments of the MAB are mobilized by a number of processes. Those predominant over the shelf near Cape Hatteras are storm-induced flow (principally wave motions but also wind driven currents), internal waves and the Gulf Stream. Storm-induced currents are dominant in resuspending sediments over the inner and middle shelf, whereas internal waves and Gulf Stream currents are most important in mobilizing sediment at the shelf-edge and upper slope.

The flux of nutrients and dissolved inorganic carbon (DIC) will be estimated from automated sensor measurements, based on their correlation with proxy measurements such as dissolved O_2 saturation and pCO_2. Preliminary data from the Cape Hatteras region indicate that >95% of the variation in direct measurements of DIC can be predicted from measurements of temperature, salinity and oxygen. The required correlations can be determined during survey cruises, whereas the proxy measurements can be made continuously on moorings. If this approach works well, it will be possible to extend greatly the time scale and resolution with which nutrient and DIC fluxes can be estimated.

The loss of DOM generated in the shelf area and subsequently exported into the deep ocean basins may constitute a significant mechanism for the sequestering of anthropogenic carbon dioxide from the atmosphere. Thus, it is necessary to quantify changes in the dissolved organic carbon (DOC) pool on the shelf in order to fully characterize the carbon budget. This is especially important since the DOC pool is the second largest pool of exchangeable carbon in the oceans (could equal as much as 15% of the DIC), and the one whose magnitude is least well known in absolute terms. While dissolved organic nitrogen (DON) measurements cannot be used to accurately quantify the changes in the carbon pool, because the ratio of DOC/DON varies, changes in DON are useful to help characterize these transformations and to fully characterize the nitrogen budget. Biomarker analyses may also prove to be extremely useful in the DOC/DON pools to constrain sources and fluxes of the DOM.

C. Transport in Canyons

During the present interglacial period particulate organic carbon produced on the shelf can be intercepted by canyons as currents sweep material along the bottom. This carbon can be shunted quickly to deeper waters because daily internal tides cause flushing of the canyons which resuspends sediment in the upper canyon and moves it down and away from the canyon along isopycnal surfaces. Some of this material resettles down-canyon and some is moved out of the canyon and along the slope in the direction of prevailing currents. Little transport occurs along the deep canyon axis (>1000 m) except by the extremely rare turbidity currents.

While no large canyons incise the shelf in the OMP region, there is a large canyon (Norfolk Canyon) just north of the study area that could spew out sediments and organic carbon which could then accumulate along the slope in the study area. Through the use of moored current meters and optical sensors hydrodynamics and resuspension in the canyon axis can be studies. Optical instruments can be used to record resuspension of fine-grained sediments, but aggregates are not quantitatively sampled, and a large amount of transport within and away from canyons occurs in that form. To quantify the concentration gradients of both aggregates and suspended particles, a video imaging system for aggregates coupled with a CTD and optical sensors for suspended particles will be employed. It is unknown whether the small canyons and ravines on the slope in the OMP area cause focusing of internal tides and resuspension of bottom sediments as occurs in canyons. It is important to determine how far away from the slope the high concentrations of aggregates extend, because this determines how far downslope they may settle. This off-slope transport should also be related to the regions where ^{234}Th deficiencies have been measured down to 800 m, as the aggregates could be important in scavenging Th. Particular attention must be paid to dynamics of the bottom Ekman layer transport, bottom upwelling and downwelling as discussed elsewhere as these processes are important in moving carbon down the slope.

D. Alongshelf Transport

At Cape Hatteras, shelf water leaves the continental margin for the ocean interior. Associated with this advective transport is a carbon flux. A large proportion of this carbon is ultimately derived from the ocean interior upstream of Cape Hatteras, including but not limited to, the initial formation of shelf water masses. In order to determine the net entry of carbon into the oceanic carbon sink within the continental margin, it will be necessary to fully characterize the difference between advective inputs and outputs of carbon within the Cape Hatteras experimental region. The major advective transport is alongshelf. The magnitude of seasonal variability for all the relevant properties must be determined so that the seasonal changes in along- and cross-shelf gradients may be differentiated from the changes produced by processes occurring within the study area.

On a broader scale, the alongshelf transport of carbon can be measured for the entire Middle Atlantic Bight region. This is important for setting boundary conditions for the Hatteras studies as well as examining the potential for carbon export from the shelf as a whole. These alongshelf cruises should lead to a seasonal resolution of shelf dynamics matched to ongoing process work at Hatteras. The cruises will be broadly biogeochemical in nature, examining standing stocks and turnover of POM and DOM, as well as CO_2, oxygen and nutrient dynamics. In addition, the survey cruises will focus on biomarker characteristics

of organic matter from sources (estuaries, blooms, sediments) that may be advected into or exported from the Hatteras region. One or more cruises may incorporate detailed consideration of the cold pool, a band of cold bottom water on the outer shelf where patterns of carbon catabolism can be followed on a large scale over several months. This is a potentially unique natural experiment that nicely complements short-term process experiments being performed at Hatteras.

E. Vertical Transport (Sinking and Resuspension)

Among the least studied aspects of the carbon cycle are the *in situ* sinking rate of naturally occurring particles, the rates of release of dissolved organic matter from sinking particles, and the role of benthic resuspension in determining the character and quantity of carbon transported off the shelf.

Sinking rates determine whether particles generated in the neritic zone are deposited in the sediments of the continental margin. Rapidly sinking particles are retained on the shelf, whereas slower sinking particles are transported seaward. The particle spectrum will be sorted and differentially deposited as a function of the sinking speeds of the individual particles and the flow field of the water. Thus, fluxes and sinking speeds of particles, coupled with the flow field determine where deposition occurs on the continental margins.

Water entering the ocean's interior at Cape Hatteras has traveled over an extensive shallow continental shelf. In this region, the benthic boundary layer is frequently within the euphotic zone and often occupies a significant fraction of the total water column. Storm-driven resuspension of particles and pore water from the sediment is common. Thus, dissolved and particulate material in water exiting the shelf may be newly produced, or may have experienced biogeochemical transformation under both aerobic and anaerobic conditions, and by benthic as well as pelagic organisms. Unlike recently produced organic matter, this reworked material is unlikely to be oxidized in the ocean interior. The relative proportion of refractory DOC and POC leaving the shelf depends on processes occurring in the benthic boundary layer and on fluxes occurring at the sediment/water interface on inner and mid-shelf regions.

F. Burial

Burial in continental margin sediments is the dominant mechanism by which organic carbon is removed from the oceans. In the MAB, extremely high rates of organic carbon burial have been reported in the Chesapeake Bay estuary and in the continental slope depocenter at approximately 500-1000m water depth. Unlike open ocean systems where only a very small fraction of the deposited organic matter survive sediment diagenesis to be buried, margin systems may bury a significant (>50%) portion of the deposited materials.

Burial rates require knowledge of sediment accumulation rate and of the accumulation history of each location. The use of natural radionuclide and anthropogenically-derived tracers will play a key role in constraining deposition. Biomarker tracers, that may provide insight into the origin of the accumulating organic matter, will be used in conjunction with burial estimates to assess recent changes in burial patterns in the continental margin system.

G. Air/Sea Exchange

Carbon is also gained and lost via the air-sea exchange of CO_2. The CO_2 flux is dependent upon the difference in concentration between atmospheric and surface seawater pCO_2. Many factors contribute to pCO_2 variability in surface ocean waters. Mixed-layer heating and cooling, advective transport, air-sea exchange, biological respiration and photosynthesis, and chemical oxidation and dissolution all act to modulate pCO_2 over widely varying spatial and temporal scales. Within the Cape Hatteras region, surface water pCO_2 variability may be dominated by physical advection of alongshelf and Chesapeake Bay waters. By combining continuous mooring-based measurements of pCO_2 with periodic ship based measurements of other carbonate parameters (see below), we can begin to deconvolve the mechanisms controlling CO_2 gas exchange in the Cape Hatteras region.

III. METHODOLOGIES

A. Moorings and Remote Sensing

The mooring array is designed to answer questions regarding physical processes that affect the distribution of organic carbon within the system. Three cross-shelf transects of moorings (designated as mooring transects 1, 2 and 3 arranged from N to S, Fig. 1) were selected to address both cross- and along-shelf mass transports and the spatial variability in physical structures and dissolved and suspended material including DIC, POC and DOC. It was determined that a series of cross-shelf transects would better address questions regarding along-shelf transport, as opposed to an approach based on a "picket-fence" line of moorings following the shelf edge. The latter would be strongly influenced by the east-west movements of the shelf-edge front, and would not allow for along-shelf flow/exchange calculations. The location of these transects also allows us to examine the POC/DOC content of water influenced by Chesapeake Bay run-off (inner-shelf stations) and water which is unaffected by the Bay (outer-shelf stations). Mooring transect #1 is primarily influenced by the physical processes of the Middle Atlantic Bight, whereas transect #2 is located near the oceanic boundary between the Mid and Southern Atlantic Bights. The third transect is intended to monitor the near shore flows and exchanges that are known to occur.

Continuous time-series measurements of the horizontal flow fields together with temperature and salinity will provide the basis for calculating cross-shelf and along-shelf transports of volume, heat, and salt in the study area. Calculations of exchanges between the shelf and slope and between the Mid and South Atlantic Bights will be based on concentration differences between and along transects. From previously collected physical data sets, we know that between the northern transect and the middle transect, much of the shelf water will exit the shelf. Therefore, carbon export values may be calculated from POC/DOC measurements and time-series flow data taken along the transects.

A set of complementary and overlapping moored instruments will provide velocity and water property measurements throughout the water column. Instrumented bottom tripods will address bottom boundary layer processes. Meteorological buoys, with upper-ocean E-M current meters attached, will be used to quantify air-sea momentum and buoyancy exchanges in this meteorologically-complex domain. Coastal wind and sea level will be obtained from NODC.

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Acoustic Doppler Current Profilers (ADCP) will be used in high shear zones, with conventional taut wire moorings located in less complex regions and to compliment the ADCPs. Salinity, temperature, pressure, oxygen concentration, fluorescence, and particle concentration measurements will be made throughout the mooring array using in-situ CTD and oxygen sensors, fluorometers, transmissometers and turbidity sensors. Transmission profiles will provide temporal and spatial data sets on fine particle resuspension and advection events associated with storms.

An intensive investigation of particulate dynamics and transport within the BBL will be carried out as part of the OMP's moored instrument study. This effort will rely heavily on the use of the BASS tripod system. The standard form of this system includes a string of 8 thermistors, a CTD and a stack of 6 acoustic travel time current meters extending from 20 to 450 cm above the sea floor. To resolve suspended sediment concentrations, each BASS system used in the OMP will be equipped with Optical BackScatterance (OBS) sensors and transmissometers. The small size and streamlined shape of the OBS sensors will allow them to be located near each current meter without appreciable distortion of the flow. The combination of velocity from the current meters and sediment concentration estimates from the OBS will permit estimation of sediment flux through the bottom boundary layer, an operation not previously possible.

With the goal of estimating near-bottom POC fluxes, a subset of the BASS systems deployed in the OMP will be outfitted with fiber optic fluorometer arrays. Calibration of OBS and fluorometric measurements to POC will be made using simultaneous measures of organic matter from time-series water samplers. BASS units will be placed on both of the primary mooring lines of the OMP, with the heaviest concentration over the middle shelf to the shelf edge. Additional near-bottom velocity and optical particle sensors will be placed at several mooring locations not equipped with BASS tripods. The analysis of the data from these and the BASS instruments will initially focus on sediment and fluid dynamics over the Cape Hatteras region. Attention will be given to determine the extent that the various candidate resuspension and transport processes contribute to the export of particles from the shelf. The detail of the BASS measurements will allow us to study and better parameterize the operation of these mechanisms. Using the near-bottom fluorometer measurements together with relationships of suspended sediment to POC and DOC concentrations, determined in other aspects of the OMP, we will also examine the flux of carbon in the bottom boundary layer and attempt to assess its importance on the overall shelf carbon budget.

Satellite and aircraft sea surface temperature (AVHRR), ocean color (SeaWifs), ocean topography (Topex), synthetic and real aperture radar (SAR, RAR), surface sea state and wind (SSMI) will be obtained either in real time (AVHRR, SeaWifs) or directly from collaborating government agencies (NASA-JPL, ONR-NRL). The real-time satellite (AVHRR and SeaWifs) data will be used to guide shipboard surveys. Other satellite data will be utilized to identify shelf, slope and Gulf Stream-related features outside and inside the array and to determine the impact of these features on the enclosed region through correlation with direct contemporaneous measurements of velocity and particle concentration and flux.

The moorings will also be instrumented with pCO_2 sensors located at various depths in the water column. Continuous time-series measurements of pCO_2 made in combination with other physical, bio-optical, and oxygen measurements will provide a means for determining what factors control the flux of CO_2 across the air-sea interface. After deployment, the

mooring-based measurements will be combined with periodic ship surveys to obtain a regional map of CO_2 fluxes during the field year.

Sediment traps are to be placed on the moorings (6 total) deployed off the shelf in the deep-slope/rise region to quantify the vertical POC fluxes occurring in the offshore, organic carbon depocenters. Horizontal velocities are expected to be low in the deep-slope/rise region, and therefore in contrast to the shelf, trap biases for quantitative flux estimates are expected to be minimal. For the moorings located at the deep-slope carbon depocenter, two sediment traps per mooring are required. A trap at 500 m will be deployed to quantify POC fluxes and characterize sinking particulates; 500 m represents the base of a mid-water zone of POC regeneration, high biogenic particle production, and high marine aggregate density. A near-bottom trap will be deployed for the purpose of comparing deep-water geochemical fluxes to measured benthic fluxes, in order to estimate degree of lateral/advective input to the depocenter and calculate benthic remineralization rates. The exact location of the slope/rise, deep-water trap moorings will depend upon information acquired from benthic studies on the deep slope and rise.

B. Cruise-based Measurements

1. Water column hydrographic measurements

Time-series flow parameters (current meters, ADCPs), particle abundance (transmissometers), primary production (FRR fluorometer) and deep-water particulate fluxes (sediment traps) will be obtained from moorings. All other listed measurements in Table 1 must be obtained on cruises. Some of these are essential background data for transformation studies and are described in detail in the Transformation Studies section.

Repeated cruises in the near vicinity of the mooring transect lines are required in order to address the expected temporal variability. Sampling and measurements will be made throughout the water column at all stations (0-2000 m depth range). Samples will be obtained from standard CTD/rosette casts, as well as from a towed SeaSoar-style system. The bottle casts also will provide an opportunity to acquire additional samples for measurements not listed in this section (e.g. water samples for plankton taxonomy analyses). The ship cruises will also be used to investigate offshelf transport processes such as frontal eddies, filaments, and warm-ring and Gulf Stream interactions with the outer shelf. These special investigations will be carried out with a combination of standard hydrographic stations with which the entire suite of variables can be measured, and underway surveying using towed instruments. These specific studies will be directed toward processes of opportunity identified in realtime with satellite data transmitted to the ships.

i. Dissolved inorganic and organic carbon species

DIC represents the sum of three major CO_2 species present in seawater: $(CO_2)aq$, (HCO_3^-) and (CO_3^{2-}). The relative proportions of these species depend primarily on the alkalinity and temperature of the water. Changes in DIC concentration reflect the net amount of CO_2 gained or lost through air-sea gas exchange, calcium carbonate formation or dissolution, photosynthesis and respiration within the water column or underlying sediments, as well as mixing with waters of different DIC concentration. DIC is measured routinely with a

precision of about +/- 0.06% using a coulometric titration technique. The high precision attainable with this technique will allow it to be used in biological incubation experiments (which are described in the section on transformations) in addition to the routine water-column concentration measurements.

The pCO_2 of surface seawater will be determined using a continuous flow-through seawater-air equilibrator and infrared analyzer. Such an analysis system will be installed on ships to be used for both hydrographic transect cruises and buoy deployment/servicing cruises, in order to give improved temporal and spatial resolution. Preliminary measurements in the study area have revealed intensely undersaturated areas associated with waters discharging from the Chesapeake Bay (pCO_2 as low as 116 μatm, approximately 1/3 of the saturation value), making this increased resolution vital. Atmospheric CO_2 concentrations will be measured frequently (at least daily during the cruises) using the same infrared analyzers, to allow the air-sea pCO_2 differences to be calculated.

The pCO_2 in discrete samples of subsurface waters will be measured during all hydrographic transect cruises. pCO_2 is highly sensitive to changes in DIC concentration and can be measured with gas chromatographic techniques with a precision of +/- 0.2%. This allows smaller changes in DIC to be detected than can be done by measuring DIC directly. In addition, the measurement of DIC and pCO_2 on the same water samples fully determines the carbonate system, including the carbonate alkalinity and pH.

Methane is of interest as both an atmospheric "greenhouse" gas and as a contributor to organic carbon loss from the study area, being formed by microbial processes in sediments and released to the overlying water column, from which it can be lost to the atmosphere by gas exchange. Although not commonly measured, it can be determined with great sensitivity using the same gas chromatograph (equipped with flame ionization detector) used in the determination of discrete pCO_2, and thus the analysis is essentially "free" and does not require any additional time for sampling or analysis.

Alkalinity is a measure of the ionic charge balance in seawater and river waters. In seawater, it decreases primarily due to the formation of biogenic $CaCO_3$ within the water column and increases due to the its dissolution within the underlying sediments. In addition, river waters often have alkalinity values markedly different from seawater, with some rivers having values three times as high as normal seawater. Thus alkalinity measurements serve to estimate the amount of biogenic carbonate formation or dissolution which has affected a parcel of water, and as a tracer for river water. Also, since alkalinity strongly affects the relative proportions of the various inorganic carbon species, the pCO_2 and hence oceanic CO_2 sink/source area distributions are strongly influenced by these biological and mixing processes.

DOM is the largest reservoir of reactive carbon in shelf water. Concentrations of DOC probably average 80-90 μm, typical of oceanic surface waters. Periodic pulses of DOC to concentrations in excess of 120 μm may follow blooms in phytoplankton production. Such pulses have been occasionally observed, but need to be studied in further. DOC may be routinely measured by high temperature catalytic oxidation (HTCO). The measurement of DOC by HTCO has been intensively studied over the past few years. While there is now general agreement that the technique can yield highly precise and probably accurate values for DOC, care needs to be exercised to minimize problems with contamination, instrument blanks and analytical artifacts. DON can also be measured by high temperature methods. Methods for DON analyses have not undergone the intensive scrutiny and intercalibration that DOC

HTCO methods have, and making the intercomparability of data collected at different sites by different laboratories less clear.

Developments in continuous underway or synoptic sampling of DOM include fiber optic analysis of DOM fluorescence, and airborne oceanographic lidar fluorescence in the near UV. DOM concentrations are often linearly related to seawater absorbance, offering the possibility of remote sensing of DOM. However, algorithms are sensitive to the absorption/fluorescence properties of the water body, such that if estuarines make significant contributions to local DOM concentrations, DOM optical properties of the system need to be fully characterized in order to obtain reliable algorithms. Synoptic measurements of DOM are in the early stages of development, but are progressing rapidly. Some data from airborne oceanographic lidar may be useful in the OMP Hatteras study.

Large volume DOC isolation by ultrafiltration has made mg to g quantities of a colloidal fraction of the DOM available for detailed molecular level analyses. Chemical degradative and NMR studies have shown that approximately 50% of the > 1000 Dalton size fraction is composed of polysaccharides. Chromatographic techniques are currently under study which could further fractionate DOM by size or compound class, such that an even larger percentage of DOM may be characterized by chemical degradative and spectrometric techniques. In-source pyrolysis mass spectrometric analysis has been performed on a few samples of DOM isolated by ultrafiltration, and shows promise as a means for rapid characterization of protein, carbohydrate, and lipid fractions. In combination with on-line gas chromatography and isotope ratio mass spectrometry, this technique may allow us to better characterize the sources of DOM and follow changes in DOM composition along the shelf.

ii. Particles

POC has traditionally been measured or derived from particle mass measurements using nets (primarily collect zooplankton and large particles), water bottles (primarily phytoplankton and small particles), in-situ filtration of large volumes of water, or optical measurements of light scattering or attenuation. Optical methods provide the fastest and cheapest method of determining the distribution of total particles in the water column, but most of the optical signal is generated by the smallest particles, perhaps <20 μm. The small-particle mass has traditionally been thought to constitute most of the total mass of particles in the ocean, but recent measurements have shown that 10-50% of the particle mass is in aggregates >0.5 mm, so both large and small particles are significant in computing lateral fluxes off the shelf.

Large aggregates dominate the settling flux in the ocean and have received increased attention in studying biogeochemical cycles. Sampling these large particles for abundance and size distribution is difficult because traditional methods of determining particle concentration such as light transmission and particle analyzers do not sample a large enough volume of water to obtain statistically accurate data on aggregates. Water bottles can collect aggregates and other large particles (fecal pellets, etc.), but they can settle quickly (in minutes) below the bottle spigots or break up during extraction from the bottle.

In order to quantify the large particles, camera systems integrated with a CTD and transmissometer will simultaneously collect data on the distribution of suspended particles and aggregates along with the physical structure of the water column. Profiles and horizontal surveys of aggregate abundance allow for the identification of mid-water and benthic aggregate nepheloid layers which might be missed by sediment trap or pump sampling. Downslope

cascading by resuspension, advection and subsequent settling of aggregates may be a significant pathway for transport of carbon across the slope. Such a mechanism may explain any discrepancy between sediment oxygen demand and the export flux derived from overlying productivity.

The diel (24 hr) cycle is important in biological cycles, and many diel cycles have been observed in transmissometer data, aggregate abundance, mixed layer thickness and other biologically related parameters. Sampling will be planned to monitor changes on this important time scale.

In-situ particle settling velocities are needed to transform aggregate abundance data into aggregate fluxes. Particles produced on the shelf with high settling velocities are retained on the shelf, whereas slower sinking particles are more likely to be transported seaward. Thus settling velocities of particles, coupled with the flow field characteristics of the water determine where deposition occurs on the continental margin.

^{234}Th was one of the few tracers identified as being able to assist in quantifying particle export from the waters overlying the shelf in the vicinity of Cape Hatteras. This is due to ^{234}Th's relatively short half-life (24.1 days) and its non-specific particle reactivity. The activity distribution of ^{234}Th should reflect particle removal processes with time-scales on the order of days to many weeks. For longer time-scales (years to decades), the ^{210}Pb budget can be used in a similar manner, but need not be sampled as frequently. ^{234}Th and ^{210}Pb analyses are conducted conveniently on the same samples.

The ^{234}Th tracer technique has been successfully used in the open ocean to quantify export fluxes from the surface ocean. The major modification for the Oceans Margins Program would be to measure the advective fluxes by looking at concentration gradients and water velocities determined with moorings, as well as a sampling regime which minimized resuspended fluxes (by sampling surface waters in stratified waters over the outer shelf, and/or determining ^{234}Th resuspension fluxes by other techniques). Export fluxes of ^{234}Th would be compared to the sediment inventories of excess ^{234}Th to determine the amount of ^{234}Th (and hence particulate organic C) exiting the shelf. Once the ^{234}Th flux is determined, the ratio of organic C or N to ^{234}Th on particles (determined by analysis on filters) can be used to convert from ^{234}Th export to organic C and N particle export.

Suspended matter concentrations in shelf and slope water will be used as a master variable to predict organic carbon exchanges and rates from the continuous records from moored transmissometer. This approach is based on the following observations and model predictions: 1) particle concentration effects on ^{234}Th scavenging rate constants, particle removal rate constants, partition coefficients between particles, colloids and solution due to the coagulation of ^{234}Th containing colloids with particles ("colloidal pumping"); 2) the constant functionality of the partitioning between suspended particles, colloids COC>10kD and COC>1kD, and in many instances DOC; and 3) the similarity of the colloidal/dissolved ^{234}Th partitioning and COC/DOC partitioning. It will therefore be more important to measure ^{234}Th profiles along gradients of hydrodynamic biological and chemical conditions than to measure them along the real transit of a water parcel.

^{234}Th shows a deficiency with respect to its parent, ^{238}U, (i.e.,$[^{238}U]-[^{234}Th]>>0$) throughout the water column in slope waters 800-1500 m deep, indicating strong lateral

scavenging and/or exchange processes. It will therefore be important to define the "endpoints" outside the immediate study area where those boundary exchanges with time scales similar to the decay times of ^{234}Th, i.e., 35 days, will have subsided.

2. Benthic boundary layer - sediment measurements

Benthic environments provide both a temporary processing site and a final storage site for carbon sedimented from the water column. The coarse-grained nature of the shelf in the Hatteras region suggests that this area may not be important as a final storage site, but previous observations have shown rich benthic communities in the swales of sand ripple fields. These observations lead to the hypothesis that microenvironments may be important in processing deposited organic matter for some period of time, and then lose the carbon in a resuspension event associated with high-energy storms characteristic of this region.

The Hatteras region can be divided into a number of benthic provinces. These include:
- Shallow shelf of <15-25 m depth, characterized by the presence of benthic primary production in some seasons and frequent exposure to storm waves, topographically consisting of ridges and swales. Benthic primary production has been measured to depths exceeding 30 m in Onslow Bay. The maximum depth could be lower north of Cape Hatteras where there is probably more fine-grained, terrigenous material in the water column.
- Deeper shelf environments of 25-200 m depth, are characterized by the presense of heterotrophic organisms and topographically by ridges and swales. Slope depocenter is characterized by intense accumulations of organic matter at about 900 m, and perhaps areally more extensive regions of organic carbon accumulation at depths greater than typically seen in continental rises and slopes.
- Estuarine environments which have the potential to be a significant sink for shelf organic matter.
- Canyons that likely act as both an important conduit and perhaps also a significant processing zone for shelf-derived organic matter.

The first two of these environments would be studied as sites of deposition and benthic processing of organic matter. The slope depocenter is of interest primarily as a burial sink for shelf-derived organic matter and, through its metabolic activity, as a detector of the timing and extent of export from the shelf. The estuarine areas would be studied primarily for their potential role as burial sites for shelf-derived organic matter, leaving process-oriented studies for the many existing estuarine research groups. While export through canyons may be a major mechanism by which shelf-derived organic matter is transported to the deep sea, process studies within canyons are given a lower priority than the above studies. Processing of organic matter in canyons may be very different than at shelf locations.

The ridge and swale topography of the shelf provinces likely sets up a heterogeneity problem that will affect sampling. Fine-grained muds, and possibly organic matter, will preferentially accumulate in the swales; benthic responses may be similarly concentrated. It will therefore be necessary to assess the heterogeneity within the ridges and swales, and sample in either specific locations within this topography or in larger numbers to overcome the heterogeneity. Permanent benthic stations, revisited by submersible or ROV, would facilitate reproducible process studies. The temporal sampling strategy is predicated on assessing

event-related processes against a background of "normal", seasonally varying processes. Sampling would focus on the mid-winter storm events responsible for transport in the benthic boundary layer as well as instigation of blooms. The spring bloom may be responsible for a majority of the annual input to the benthos; the summer stratification period may represent a minimum input rate to the sea floor.

i. Fluxes across the sediment-water interface.

Studies of the exchange of nutrients and carbon across the sediment-water interface will play an important role in assessing carbon dynamics on the continental shelf and role of the ocean margin in sequestering carbon from the atmosphere. Significant exchange of nutrients and carbon may occur through the transport of dissolved, colloidal, or particulate materials across the sediment surface and may directly or indirectly influence many aspects of biogeochemical cycles on the shelf. These aspects include: nutrient inputs to shelf waters (via dissolved and particulate exchange processes); nutrient losses from the shelf system including burial and sedimentary denitrification; remineralization of organic matter; production of particulate organic matter through benthic primary, chemolithotrophic , or secondary production; and standing stock of water column particles.

In addition to these specific processes, sea floor flux studies can be used to constrain other processes that are important in determining the ultimate fate of shelf-derived organic matter. These include the mean particulate flux of organic matter to the sea floor, the export of particulate materials from the shelf, and the integrated net reaction rates in sediments including benthic primary production and respiration.

A variety of factors complicate studies of benthic exchange on continental shelves. For example: 1. A wide range of redox conditions are possible within a small geographic setting complicating the development of quantitative models relating the rates of diagenetic processes to benthic fluxes. 2. Shelf sediments contain abundant macrobenthic organisms that actively transport substrates and solutes through surface sediments. Since transport mechanisms are diverse and difficult to accurately parameterize, these activities also complicate the construction of models and the interpretation of results. 3. Many shelf regions are presently not accumulating sediments and are subject to sediment resuspension events. It is therefore difficult to assess particle input rates. 4. Because of frequent exposure to high current velocities and turbulent energies, many regions are depleted in fine-grained sediment particles and enriched in sands. Such sediments are difficult to core and sample for pore waters. Because of the high permeability of sandy sediments, hydrodynamic events may influence pore water solute transport. This may be the result of pumping due to wave action, enhanced dispersion rates caused by horizontal pressure gradients from waves, and/or wave-induced flow through vacant worm burrows. 5. Shelf sediments are exposed to a variety of temporally-varying conditions, inputs and forces. Examples include seasonal changes in sediment resuspension, particle flux, and temperature/metabolic rates. Temporal variability in sediment and pore water properties will be more extreme than in sheltered inshore environments or at slope depths; strategies for both sampling and interpretation must take this into account.

Innovative techniques will be required to measure benthic fluxes in this environment. For example, to include wave induced near-bottom turbulence and benthic photosynthesis, clear flexible chambers may be used. The measurements will be interpreted in the context of BBL physics, biological community structure, and water column input events.

Attempts should be made to investigate integrative parameters which can be used to map net fluxes. For example, to what extent does sedimentary chlorophyll concentration serve as a flux measure for metabolizable organic matter? Is the technology for measuring dissolved oxygen concentration sufficiently refined to assess apparent sedimentary oxygen utilization by measuring oxygen deficits in the overlying benthic boundary layer, as a means of mapping benthic metabolism over large areas?

ii. Sediment accumulation and mixing rates

Continental margins are regions of the oceans where rates of sediment accumulation and carbon burial are high, reflecting sediment and nutrient inputs from adjacent landmasses. Moreover, modern inputs of nutrients to the coastal ocean may be elevated by human activities, potentially increasing the modern rate of carbon burial above the long-term average. We can directly address the role of the continental margin in drawing down present atmospheric CO_2 by determining modern rates of carbon burial in margin sediments. To also recognize possible global change we must provide an historical context for the modern burial rates by extending determinations of carbon burial rates thousands of years into the past.

Particle-associated radionuclide tracers are used for determination of rates of sediment accumulation; combined with measurements of carbon concentrations, sediment accumulation rates yield carbon burial rates. Natural excess ^{210}Pb and weapons-fallout nuclides (Pu, ^{137}Cs) provide information on rates of sediment accumulation and mixing for the past 100 years. ^{14}C itself is used to determine accumulation rates over longer time-scales. To assess the impact of carbon burial on atmospheric CO_2 it is necessary to determine the burial rates of both organic and inorganic ($CaCO_3$) carbon.

Determination of sediment accumulation rates from sediment tracer profiles rests upon a number of assumptions as to sources of the radionuclide tracers and processes of tracer transport within the sediment column. At a minimum, tracer transport by physical or biological mixing must be separated from tracer transport due to sediment accumulation. Various models, involving multiple tracers of different, but overlapping, time-scales (half-lives or input histories), have been used successfully with tracer profiles of simple shape. Using these conventional models, complex tracer profiles are often simply left uninterpreted. A new procedure applicable to both simple and complex radionuclide tracer profiles has been designed. The procedure combines inverse numerical techniques with predictive models to separate effects of variable tracer strength and variable sediment accumulation rate in complex profiles. The numerical algorithm can be used to derive accumulation rates from different tracer profiles in the same core. This method will be used with radionuclide data (at least ^{210}Pb, fallout Pu, ^{14}C) to determine time variation in accumulation rates in sediment cores from shelf-rise environments off Cape Hatteras. Relative to conventional methods of interpretation, improved spatial and temporal resolution in sediment accumulation is anticipated.

The rate and style of particle transport within deposits has a major influence on decomposition pathways, recycling patterns, and storage of reaction products. Particle reworking by macrobenthos dominates particle transport in most subtidal sediments underlying oxygenated waters. Bioturbation rates should be measured using a variety of tracers including ^{234}Th, ^{7}Be, chloropigment profiles, and injected luminophores. This has the dual purpose of potentially evaluating changes in decomposition patterns in relation to bioturbation and

comparing the agreement and resolution provided by different tracers in the examination of mixing processes.

Sedimentary environments where sediment mixing caused by both biological and physical processes is occurring will also be analyzed using numerical models. The bioturbation signature will be separated from the radioisotope data profiles using two isotope profiles for a single core.

The rate and style of particle transport within deposits have a major influence on decomposition pathways, recycling patterns, and storage of reaction products. Particle reworking by macrobenthos dominates particle transport in most subtidal sediment underlying oxygenated waters. These activities depend on the types and abundances of animals. Biological community structure, including species composition, abundances, sizes and functional groupings can vary significantly both spatially and seasonally in shelf environments and may be correlated with seabed topography. Erosion of "ridge" areas by storms removes organic matter and disturbs the benthic community. These regions are dominated by fossorid and interstitial feeding macrofauna and tubiculous polychaetes which are typical early colonizers. Depressions or swales that may be located a few hundred meters away are less frequently disturbed and are the foci for organic matter deposition. Dense populations of deposit feeding tubiculous amphipods and burrowing polychaetes, typical of higher-order successional stage communities, dominate swales. The characterization of benthic communities in our study will be used largely for interpreting transport processes in radionuclide distribution, pore water profiles, and solid phase diagenetic reactions. The relative importance of biological and physical processes is essential for understanding the dynamics of the shelf and slope environments. Macrobenthos will also be measured as one component of biomass cycling representing in situ synthesis of new carbon from planktonic inputs.

While the measurements described above will provide much information concerning the deposition, resuspension, transformation, dissolution and burial of particles on the shelf and adjacent areas, morphological features of the sea floor may significantly influence the carbon dynamics of a particular location. For example, ridge and swale structures on the shelf may concentrate or focus the deposition of fresh organic materials into the topographically low areas. This would, in turn, intensify metabolic and diagenetic processes in these regions relative to the surrounding higher locations. Depending on the horizontal scale of such features, significant variability of benthic processes may result. Similarly, on the slope, canyons may serve as major conduits for the off-shelf transport of particulate materials and away from canyons, slope morphology suggests that mass wasting is an important down-slope transport process.

To understand and interpret the results of mechanistic and process studies described in the previous sections, it will be necessary to assess sediment morphology and type distributions on the shelf and slope. Broad surveys using side-scan and 3.5 KHz sonar should be used to identify the scales of horizontal variability. Sampling at specific, known locations using ROV's or submersibles will be required to relate sediment types and processes to the larger-scale morphologic features. Attempts should be made to resolve sediment properties such as grain size and water content, as these properties may serve as correlative measures for organic matter content or biotic communities.

iii. Near-bottom velocity, shear, and suspended particle concentrations

Near-bottom flow and shear is the physical cause of transport and erosion of sediment. In boundary layer flow, the velocity decreases from the free-stream value far above the boundary to zero at the surface. The shear in velocity generates turbulence which in turn transports momentum to the boundary; viscosity is not a significant effect in rough boundary layers. The stress which the flow exerts on the sediment can be estimated from velocity profiles, from correlation of velocity fluctuations (Reynolds stress), or from turbulent kinetic energy. In wave-dominated flows, flows where the velocity reverses or approaches zero each half wave period, the velocity profile is the most reliable estimate of bottom stress and the spectrum of turbulent kinetic energy is a measure of wave energy and stress.

When the stress exceeds the shear strength of the sediment, material is eroded. Conversely, if turbulence levels are high, material in suspension will not be redeposited. When material is suspended, the mean flow transports it. The flux of sediment is the vertical integral of the vector velocity at each height times the sediment concentration. Since both the velocity and sediment concentration vary with height, it is necessary to measure both at enough heights to resolve the variability and to bracket the boundary layer. BASS tripods measure vector velocities at 2 Hz and optical backscatter at 6 heights from 30 cm to 5 meters above bottom which provides the flow and shear measurements plus the particle concentration (with POC calibration of the sediments responsible for the optical signals) necessary for the POC flux.

To understand the relationship between the forces that influence shelf-water dynamics and sediment transport events, the fundamental principles governing flow in the BBL must be understood. Recent studies indicate that previously accepted concepts about the dynamics and structure of the BBL, such as Ekman transport and bottom friction, may be invalid on the continental margin. Velocity and density profiles in the BBL may be markedly different from those predicted by classical concepts. Modelling efforts are currently underway to assess how previously neglected processes or properties (e.g. across-shelf variations in currents, bottom slope, hydrography) may affect these conclusions. Direct assessment of velocity and density profiles in the continental shelf BBL will be needed to evaluate the accuracy of the model calculations.

Hydrography studies in the OMP must extend close enough to the bottom to resolve the BBL. The overlying water column structure strongly influences conditions within the BBL, and is in turn influenced by it. For example, the frictional stress exerted on the slope/margin bottom depends not only on condition above the BBL (the current, the surface wave field, and the internal wave field), it also strongly depends on the lateral density variation in the BBL which in turn result from diabatic motions unique to the BBL. A simple diagnostic of the effects of lateral density variation in the BBL on the bottom shear stress can be inferred by examining the variation of BBL thickness along sections. It is important to recognize that the most likely region in the world's ocean where the bottom shear stress is greatly reduced due to lateral BBL density variations is on the upper continental margin. Thus it is critical that hydrographic surveys extending seaward of the shelf break resolve the BBL.

TABLE 1. Partial list of salient property measurements.

Physical:
- Temperature, Salinity
- Currents
- Turbulence/Shear
- Bottom Stress
- Wind Stress
- Air-Sea Interaction

Optics:
- PAR
- Spectral irradiance
- Transmission
- In vivo fluorescence
- Fast-Repetition Rate Fluorometry
- Multi-spectral transmission
- Ocean color/AVHRR

Biological:
- Abundance, biomass, taxonomic composition, size, biovolume, physiological state (as appropriate) of:
  - Bacteria
  - Autotrophic organisms (benthic microflora and pelagic phytoplankton)
  - Protozoans (pelagic and benthic)
  - Metazoans (pelagic and benthic)
  - Macrobenthic organisms
  - Viruses

Chemical:
- Dissolved:
  - DOC/DON
  - COC
  - DOC fluorescence
  - Oxygen
  - Nitrogen gas (total gas tension)
  - nutrients (nitrate, phosphate, silicate, ammonia, nitrite, urea)
  - DIC
  - pCO_2 continuous and discrete sampling
  - Alkalinity
  - Biomarkers
  - Stable and radioisotopes (^{14}C, ^{13}C, ^{15}N)
  - Particle-reactive radio-tracers
  - Water-mass and mixing tracers (e.g. Freons)
- Particles (suspended and sinking):
  - Particulate metal carbonates
  - Pigments
  - Biomarkers
  - Stable and radio-isotopes (^{14}C, ^{13}C, ^{15}N)
  - Particle-reactive tracers (Th isotopes)
  - Total suspended material
  - Particulate metal carbonate
  - Aggregates

TRANSFORMATION STUDIES

I. OBJECTIVE

The Ocean Margins Program will employ an integrated set of measurements designed to address the major transformations of carbon, often from a number of different perspectives. The purpose is to evaluate the rates of these transformations as they occur in the coastal waters of the Cape Hatteras study region. By coupling these studies with measurements from broad shelf survey cruises, we will be able to assess the potential and mechanisms for long-term removal of carbon from the atmosphere to the ocean in this ocean margin system.

II. COMPONENT STUDIES AND RATIONALE

A. Primary Production

Primary production, the transformation of DIC to POC, is a key transformation and the most important mechanism by which carbon dioxide enters the pool of particulate organic matter. New primary production in the shelf system is constrained by nutrient supply rates from shelf/slope and shelf/estuary exchange processes, atmospheric deposition, and benthic and water column supply processes. Considerable seasonal variations in phytoplankton carbon characterize shelf waters of the U.S. east coast, the most prominent being the spring phytoplankton bloom. The physical oceanography of these waters is believed to be largely responsible for this variability, by determining the residence time of nutrients and resulting phytoplankton within the euphotic zone. Short residence times, on the order of days-weeks, provide ample time for phytoplankton growth, but only grazers with explosive growth potential (e.g. protozoan and gelatinous metazoan zooplankton) develop quickly enough to consume such blooms. In the absence of such rapid grazing responses, substantial portions of phytoplankton carbon may sediment or cascade off the outer shelf. Longer residence times of weeks-months allows POC to be cycled and transformed, for example via bacterial activity and zooplankton grazing, prior to being removed from the water column by deposition or advection. Since the euphotic zone may extend to the seafloor at certain locations and times of the year, benthic primary production and nutrient dynamics may contribute and influence the integrated shelf DIC to POC transformation rate. The net loss or gain of carbon in the coastal ocean is determined by the balance of these transformation processes.

Although it is critically important to understand the rates of carbon fixation and subsequent transformations, it is equally important to assess the composition of the phytoplankton community. It has often been observed that blooms of larger cells, such as diatoms, can lead to significant export of intact cells to the underlying sediments, while blooms of smaller organisms can lead to cycling of carbon within the microbial food web. In addition, blooms of coccolithophorids export carbonate from the upper water column to the sediments. Thus it is important to determine the relative importance of each component of the phytoplankton to the community primary production.

Optical measurements can be used to infer temporal and spatial patterns in pigments, particulates and primary production and provide increased vertical resolution of water column biological properties. Discrete measurements of biomass can be extrapolated on the basis of in

vivo fluorescence and transmissometry measurements. Using active fluorescence, it is possible to derive rates of phytoplankton photosynthesis. Depth-resolved time series information about the irradiance field and pigment biomass can be used to support primary production models. This time-series capability will allow the identification of episodic high-productivity events. Inadequate sampling of such events can lead to underestimation of regional primary production. Since primary production over the continental margins is both high and more variable than in the open ocean, there is a clear need for high- resolution temporal and spatial information.

B. Respiration

Photosynthesis and respiratory metabolism of organic matter are major determinants of the vertical distribution of carbon in the ocean. The gradients of organic and inorganic carbon created by these two processes in turn affect the exchange rates of CO_2 between the ocean and the atmosphere. The rate of respiration of organic matter in the water column also regulates the supply of organic matter to the ocean's interior ("biological pumping") and ultimately the benthos. While much research has focused on the production of organic matter, there are still surprisingly few direct measurements of respiration rates in the ocean. Much of the difficulty associated with measuring respiration in the ocean has been due to a lack of precision in determining the small changes in the concentration of dissolved oxygen or CO_2 in samples over short periods time. Using commercially available automatic titrators with potentiometric end point determination it is now possible to accurately and precisely determine small changes (<1 $\mu M/h$) in dissolved oxygen. Likewise, small changes (1 μM) in DIC can now be routinely detected by coulometry. In either case, the measurements will reflect the net respiratory activity of the community.

The net flux of carbon dioxide across the air-sea interface is most strongly affected by the net transformation of carbon between inorganic and organic forms. Therefore, it will be important to make robust, long-term estimates of net community production and respiration in the water column, BBL and sediments. Such transformations are likely to be episodic and temporally variable, and continuous measurements and/or tracer measurements will therefore be required. In the Ocean Margins Program, we will take advantage of the heavily instrumented moorings and new technologies, especially in applying a multiple tracer approach based on in-situ measurements of pO_2, pN_2, and pCO_2.

C. Heterotrophic Bacterial Production

Bacterial turnover and metabolic activity are now generally accepted as crucial and often dominant processes which drive major biological and biogeochemical cycles, ranging from the direct importance of bacteria as a food resource, to a critical role in global carbon and nitrogen budgets and the production and consumption of greenhouse gases. It has become increasingly evident that a large fraction (commonly 20-50%) of oceanic and freshwater primary production cycles through bacterioplankton. Bacteria are primarily responsible for recapture of DOC into particulate form, which can then re-enter pelagic and marine food webs. Bacteria are frequently the initial, and sometimes the primary route of nutrient and energy cycling in aquatic sediments. As a result of these activities, bacteria mediate much of the oxygen

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consumption and most of the carbon remineralization in marine waters and sediment. Assessments of the role of microbes in transforming and remineralizing organic matter have become a necessary and integral part of any system-level study of the fate of organic matter.

The measurement of bacterial production is a powerful approach for estimating the contributions of heterotrophic bacteria to overall metabolism in ecosystems. The supply of bacterial biomass potentially available to grazers can be determined from rates of bacterial production. Bacterial production, almost by definition, represents a net conversion rate of DOC to POC. Combined with estimates of the average growth efficiency of the bacterial community, production rates can be used to calculate the total utilization of DOC and consumption of oxygen by bacteria. The validity of these estimates is dependent on how well bacterial growth efficiency is known, and can be checked by comparing bacterial production to direct measurements of respiration (thereby estimating growth efficiency). In addition, rates of bacterial production can be used as a sensitive indicator of the response of bacteria to spatial and temporal fluctuations in environmental conditions.

At present, most bacterial processes are measured as community averages, with essentially no characterization of the internal structure of bacterial communities or the dynamics of individual species. Because of these limitations, it is possible to measure the average process rate but difficult to gain a mechanistic understanding of the factors which control bacterial processes. Unmeasured changes in community composition can invalidate predictions of the response of bacteria to a particular stimulus, unless the response is uniform across the community. Differential responses of species within the community are masked when all measurements are community averages.

New methodologies developed in the OMP are directed toward providing assessments of the response of specific bacteria, for example to variations in the concentration or form of DOC derived from phytoplankton. Based on standard molecular biology techniques, these methods target individual taxa, focus on single-cell measurements, are incubation-free, and are relatively economical in terms of sampling and processing time.

D. Geochemical Tracers of Organic Matter Transformations

A geochemical approach can be used to quantify the transformation rates between dissolved, colloidal and particulate forms of organic carbon occurring near Cape Hatteras. One approach is to examine the cycling of dissolved, colloidal and particulate forms of organic carbon by analyzing size-fractionated samples for isotopes of thorium and carbon. Knowledge of the time-scales of transformation and the sources of organic carbon is important to establish the degree to which organic carbon is buried in shelf sediments or exported by advection to the open ocean.

It is important to note that interactions between colloids, small particles and sinking aggregates are complex and mediated by a combination of biological (primary production, respiration, bacterial production, zooplankton grazing and production) and abiological (adsorption, aggregation, disaggregation) processes. The proposed geochemical work will provide information on the abiologically controlled transformation rates, which are, in turn, intimately related to physical and biological processes. Together with direct information on the biologically controlled transformation rates, the Th isotopic results will provide a comprehensive understanding of the time scales of organic carbon transformation. By using

the particle-reactive thorium isotopes as natural "clocks," the geochemical approach provides an independent method to quantify transformations.

Almost every water parcel in a vertical water column profile on the slope will have, at some recent point in time, been in contact with sediments and associated nepheloid layers. Therefore, we expect to encounter resuspended or diagenetically altered POC and DOC at any depth in the water column of the shelf or slope. In order to distinguish the terrestrial, water column or benthic sources of DOC and POC, we will rely on the following tracers: 1) biomarkers (e.g., loliolides originating mostly from sediments, vs phytoplankton pigments such as fucoxanthin or zeaxanthin, or lignin phenols from riverine sources), 2) radioactive and stable isotopes (e.g., variations in $^{228}Ra/^{226}Ra$ in the water due to recent diffusion out of margin sediments, variations in $\delta^{15}N$ due to different nitrogen pathways, variations in $\delta^{13}C$ due to different carbon sources, variations in ^{14}C due to recent bomb $^{14}CO_2$ uptake, old CO_2 from upwelled deep water sources, or mixing with older forms of carbon).

The compositional relationship between DOM, small particles, and aggregates can be investigated by an analysis of constituent biomarkers. Biomarker analyses do not explicitly yield transformation rates, however they may serve to help identify major transformation pathways and place mass balance constraints on competing transformation reactions. Biomarker analyses also provide a knowledge of composition that is useful in designing experimental systems to study the formation and fate of different carbon pools, both in the laboratory and in the field. It is now widely recognized that analyses at the macromolecular level may provide important and often unique information that is not attainable from traditional biomarker analyses, as well as serve to integrate molecular level analyses with bulk chemical properties. New developments in spectrometric methods (mass, nuclear magnetic resonance, and infrared spectrometry) along with advances in chromatographic separation of high molecular weight compounds, have made macromolecular analyses on complex samples such as DOM and aggregates possible. Preliminary analyses have only recently been made for DOM and small particles. To the best of our knowledge, no such analyses have been reported for aggregates. Such studies may contribute significantly to our understanding of organic matter transformations.

E. Zooplankton Grazing and Production

The primary importance of zooplankton, in terms of potential long-term removal of carbon from the ocean-atmosphere system, lies in the transformation of carbon from one form to another by means of their growth and grazing activities. To the extent that any of these transformations have, on the community level, a significant net positive or negative effect, the fate of the carbon in the planktonic system will be affected. For example, if protozoan grazers feed primarily on particulate materials, excrete primarily dissolved and colloidal compounds, and possess an average gross growth efficiency (body carbon produced/carbon ingested) of 40%, they will function as net transformers of POC (food) into DOC and colloidal organic carbon (COC, waste products). Furthermore, if the primary fate of these protozoan grazers is to be eaten by larger organisms, an additional effect will be the transformation of POC into fewer, larger, and more mobile packages.

The division of grazer-produced organic carbon into POC, COC and DOC, and the size distribution of the POC component, will determine whether that carbon will tend to remain in

the upper water column indefinitely (i.e. through recycling) or be removed to deeper waters and sediments. Carbon in zooplanktonic biomass will tend to move through the food web and, ultimately, be recycled as respiratory DIC. Large detrital particles such as the fecal material of copepods and salps may sink rapidly to deep waters and underlying sediments. Smaller detrital particles may remain in the upper water column via breakdown and subsequent utilization by bacteria or direct ingestion by protozoan zooplanktonic grazers. Alternatively, these smaller particulates, as well as COC, may be scavenged by sinking organic materials such as 'marine snow'. This division will depend on the relative abundance and activities of bacteria, protozooplanktonic grazers, and marine snow particles and their producers. The fate of DOC is less clear. If bacterial uptake is sufficiently slow, much of it may move via diffusion and advection into the deep ocean, where it may ultimately enter a detrital food web largely isolated from the food web of near-surface waters. Much of the carbon entering the deep-sea may be deposited as either fecal material or animal carcasses on the sea floor.

Previous research has shown that organisms in the 0.5 - 20 μm size range are responsible for the bulk of both carbon fixation and respiration in shelf systems. However very little is known, either qualitatively or quantitatively, of the fate of these cells in pelagic food webs. It is generally believed that these nanoplankton are ingested primarily by protozoan zooplankton. The relative importance of microbial food webs vs metazoan food webs in marine systems determines to a large extent the proportion of fixed carbon which will be respired or converted to non-sinking dissolved or colloidal organic matter, compared to the fixed carbon (as fecal pellets or decaying phytoplankton debris) which will either sink out from the euphotic zone or be transported elsewhere on the shelf. At present, the question of what proportion of the carbon contained in <20 μm-sized cells is recycled, channeled to metazoan food webs, or transported from the pelagial, is an open question. The issue is complex, since various categories of pico- and nanoplanktonic organisms could have dramatically different fates.

The abundant occurrence of both protozoan and metazoan zooplankton in shelf waters implies a close coupling between production and consumption in the water column. Approximate rates of ingestion of pelagic tunicates calculated from *in situ* growth rates, can range from <100% to >600% of their body carbon per day, depending on the type and concentration of food. That explains their potential of controlling phytoplankton as well as protozoa. When a large proportion of primary production is consumed by quickly responding zooplankton, less material should be available for sedimentation or export. Yet, there is limited evidence of deposits of organic carbon in slope sediments, and phytoplankton blooms themselves are offered as evidence of trophic decoupling, presumably between metazooplankton and larger size classes of phytoplankton. These conflicting hypotheses underscore our inadequate understanding of the relative importance of small and large phytoplankton in ocean margins, the roles of protozoan and metazoan grazers in regulating their dynamics, the temporal and spatial heterogeneity of these processes, and their relationship to particle export.

F. Production of DOC

Dissolved organic carbon is a potentially important reservoir of organic carbon that has been nearly ignored in budgets of carbon flux and storage in marine ecosystems. Like POC, DOC is not a homogenous pool of organic matter, but a heterogenous pool of materials with variable reactivity. Included in the pool of DOC on continental margins are small molecular

weight compounds that are likely to be biologically labile and high molecular weight compounds that may be biologically labile, but may also be nearly completely refractory or labile to only a few oxidative processes. In the latter case, oxidation may be incomplete, and may occur under unique environmental conditions or require the participation of specific groups of organisms.

Several processes are likely to produce pulses of DOC in continental shelf waters. Phytoplankton are likely to make significant contributions to DOC pools when nutrient limited at the end of blooms, or when experiencing other kinds of environmental stress. New techniques being developed as part of the OMP program will permit rapid evaluation of the metabolic state of bloom-forming phytoplankton in the water column and will greatly facilitate identification of water masses in which release of photosynthate by phytoplankton is a potentially important source of DOC.

Much of the DOC released by phytoplankton will be biologically labile. Thus, it is important to evaluate rates of bacterial transformation of recently produced DOC to POM, CO_2, and refractory organic compounds. These rates will depend on the species of phytoplankton associated with the blooms, and the taxonomic identity of bacteria in the water column. OMP research in molecular ecology is designed to provide species-specific determinations of bacterial growth rates, and species-specific determinations of phytoplankton physiological state. Additional pulses of DOC may originate with the bacterial pool of POM when epidemics of viral infection occur.

Zooplankton feeding may also produce pulses of DOC, either directly through inefficient grazing, direct excretion, or by production of fecal material from which DOC is leached. A major gap in our ability to budget the transformation of carbon by zooplankton is the lack of a technique for the determination of DOC production by zooplankton. Several approaches to this problem are in developmental stages for use during the major field season.

Storms are episodic events that are responsible for pulses of DOC input to the water column from sediment pore waters. Benthic resuspension associated during storms is also a mechanism for moving particles that will leach DOC into the water column. Because of the large expanse of shallow continental shelf that acts as a "drainage" for export from the OMP at Cape Hatteras, there is a large reservoir of geochemically old, highly refractile DOC in the pore water of the sediments on the shelf. The flux of this material from the continental shelf to a permanent sink in the ocean's interior will be determined by the lability of the DOC introduced to the water column by benthic resuspension, and the frequency of resuspension events.

G. Transformations of Detrital POC

The fate of carbon in the shelf and slope system will depend on the extent of remineralization, removal by lateral exports, and burial in underlying sediments after biological incorporation. Most of the photic zone production is recycled within the water column. Besides considering grazing as a sink for phytoplankton carbon, it is worth considering it as a source of degradation for materials sinking from the photic zone, particularly as aggregates or snow particles. Zooplankton can utilize detrital "snow" particles as food in at least two ways: by ingestion of entire particles, including attached bacteria, phytoplankton, micro- and meso-zooplankton; or by selective ingestion of specific components of the particles. Methods to

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measure ingestion of small copepods associated with snow particles with the objective of quantifying the total impact of these processes on the degradation of sinking particles in the depths immediately beneath the photic zone are being developed.

H. Mineral Dissolution and Precipitation Reactions Rates

One of the commonly overlooked components of benthic carbon cycles in shelf sediments is the formation and dissolution of $CaCO_3$. At a global scale, $CaCO_3$ is more important than organic carbon as a burial mechanism for carbon. A variety of studies have demonstrated extensive dissolution of sedimentary carbonates in shelf depth environments despite supersaturated overlying waters.

The decomposition of organic matter or oxidation of anaerobic metabolites drives dissolution. Substantial, and perhaps the greatest, dissolution apparently occurs during the spring bloom recruitment which is timed to the spring bloom delivery of carbon to the bottom. The recruitment of benthos, including shell-bearing bivalves, is often greatest during spring bloom periods in this type of environment. The dynamics of recruitment and loss of small carbonate-bearing species of benthic forams and bivalves must be assessed during the spring bloom period. Patterns of live/dead/total abundances during this time should allow estimates of net dissolution or precipitation of benthic carbonate. This information will be factored into the interpretation of the time dependent CO_2/O_2 flux balances. Other mineral groups that may play an important role in the interpretation of the cycling of organic carbon in the BBL include sulfide and iron and manganese oxide minerals.

III. METHODOLOGY

Most measurements of carbon transformation in aquatic systems cannot, at this time, be made remotely. The exceptions are primary production and total community respiration, for which the capability for moored-instrument measurements is under development (FRR fluorometer and oxygen sensors). Therefore shipboard work is essential for this component of the OMP program. Because transformation studies tend to require lengthy experiments by numerous investigators, a few, relatively intensive investigations of representative inner, mid and outer shelf stations are indicated. The number of investigators involved in making transformation measurements (approximately 50) requires the use of two ships; we anticipate that one of these will be "cold", (no radioisotopes on board) for natural abundance work.

Transformation studies should be conducted during seasons that are expected to represent key periods of biological, chemical and physical activity: Dec/Jan (coldest temperatures, formation and transport of bottom nepheloid layer); Feb/Mar (strongest storm effects, spring bloom); May/June (beginning of water column stratification); Aug/Sep (highest water temperatures, strong stratification, potentially high rates of microbial activity). Each cruise should combine limited transport sampling, using tow-yo (e.g. SeaSoar) mapping, with water-column and sea floor sampling at closely- spaced stations along transects coordinated with the mooring array. The transect mapping data will be used to provide a larger-scale, high-resolution framework for both planning and interpreting transect data, and will be supported by real-time acquisition of remote sensing data (e.g. SeaWifs and AVHRR images). Cruise

schedules should remain flexible enough to incorporate segments dedicated to intensive, experimental studies at selected locations, or for responding to unique sampling opportunities such as repeated sampling of discrete eddies. These complementary objectives require cruises of ca. 15-20 days duration at minimum.

Information collected semi-continuously by moored instruments will be used to extrapolate transformation rate measurements to expanded temporal scales. This extrapolation has proved difficult in the past, but is essential. Therefore, in the OMP experiment, transformation cruises will be tightly coupled to deployment of new in-situ measurement technologies.

In order to understand the transformation of carbon among its various pools, a suite of measurements must be obtained that describe the oceanographic setting. These accompanying measurements must be made at the same time as more process-oriented transformations are monitored, and thus must be obtained on all transformation cruises. In particular, nutrients exercise a fundamental control over carbon cycling. The transformation of DIC to and from organic carbon will occur in conjunction with transformation of nutrients, and seasonal nutrient signals are tracers of production and respiration processes. Field measurements of a broad suite of nutrients are vital, both to characterize vertical and lateral fluxes from hydrographic surveys (and potentially from moorings), and to support experiments conducted to determine transformation rates of carbon. Thus, measurements of nitrate, phosphate, silicate, ammonia, nitrite and urea concentrations through the euphotic zone are needed on all transformation cruises.

A. Primary Production

Primary production will be assayed via $^{14}CO_2$ uptake for samples obtained at various depths throughout the photic zone using temperature and light quality/quantity-controlled deck incubators. These measurements will be conducted at selected stations. Because the euphotic zone may extend to the sea floor, benthic primary production rates must also be determined. At stations representing the inner shelf, middle shelf and shelf /slope boundary, process studies will be conducted on consecutive days. In each of these experiments, phytoplankton carbon specific growth rates and carbon biomass will be determined using ^{14}C labeling of photosynthetic pigments. In some cases, post-incubation size-fractionation experiments will be conducted to determine production, growth rates and biomass of specific size ranges.

In addition, primary production will be modeled by determining photosynthesis-irradiance parameters (P-I; alpha and P_{max}). Using this approach, P-I parameters can be considered in conjunction with mooring-sensed chlorophyll distributions in the study region and measurement of incident irradiance, to estimate the production of organic carbon in the study region, both at specific process study sites and for the region as a whole.

Measurements of primary productivity will also be made using the Fast Repetition Rate (FRR) fluorometer. This will allow estimation of primary productivity over the entire shelf from synoptic FRR measurements, and from the moored FRR measurements. Another goal is to identify the factors limiting primary productivity on the continental shelf, and to design molecular probes indicative of in-situ growth limitation. The study requires two FRR fluorometers, one operating in a profiling mode (interfaced to a CTD), and another being operated aboard a ship. The profiling instrument will provide real-time measurements of

primary productivity and the basic photosynthetic parameters (absorption cross section, turnover time of photosynthesis, and photoconversion efficiency photosynthesis). The estimates of primary productivity and photosynthetic parameters will be related to ^{14}C-based measurements. The deck FRR fluorometer will be used in conjunction with immunological investigations to study the effects of nutrient limitation and light regime on the photosynthetic parameters of phytoplankton. The photosynthetic parameters will be related to nutrient-pigment data acquired over the same spatial and temporal scale. The immunological measurements will be done using fluorescently tagged antibodies on preserved phytoplankton samples and will be analyzed by microscopy.

Over a much larger scale, satellite images establish the distribution of chlorophyll, which when coupled with irradiance measurements can be used to infer the broad-scale distribution of primary production. However, over continental shelves with high concentrations of chlorophyll and dissolved organic matter, standard reflectance algorithms used to derive chlorophyll from satellite-based measurements are notoriously inaccurate. Ground truth verification and development of satellite algorithms for estimating pigment biomass and primary production is therefore critical for the Ocean Margins Program. It can be achieved using moored, vertically-resolving optical sensors that provide near-surface and subsurface information. Satellite remote sensing and in-situ (mooring-based) measurements are complementary: as well as providing ground-truth, the latter can cover periods during which satellites cannot "see" the sea-surface (e.g. at night, periods of cloud cover) as well as providing essential depth resolution; the former provides the areal coverage that would be prohibitively expensive to obtain with moored instrumentation.

B. Respiration

Water-column respiration rates will be determined from direct measurements of oxygen consumption in seawater samples using a high-precision automatic titration system with a potentiometric detector during relatively short-term (2-12 h) bottle incubations. In conjunction with direct measurements of oxygen consumption, measurements of total CO_2 will also be made using coulometry. This high-precision method (ca. 1 μM C) is capable of making direct measurements of carbon mineralization and thereby provides an independent assessment of respiration. These complementary measurements will provide an estimate of total POC and DOC remineralization rates in the water column.

Dissolved oxygen is one of the few chemical parameters that can currently be measured *in situ* from long-term moorings. Recently, a sensor has been developed to measure total dissolved gas tension, and an in-situ pCO_2 sensor is currently under development. Total dissolved gas tension measurements (from moorings) combined with oxygen measurements allows the partial pressure of nitrogen gas (pN_2) to be calculated. Combination of pN_2, pO_2 and pCO_2 time-series data permits the physical processes affecting pO_2 and pCO_2 to be quantified (e.g. air-sea gas exchange and mixing) and therefore permits direct estimation of bulk rates of net community production and respiration from moored chemical sensor time-series data. Note that neither pO_2 nor pCO_2 measurements alone can fully characterize the biological transformations of carbon because of the potentially complicating effects of alkalinity changes arising from biological calcification and river inputs. These measurements are therefore complementary: pO_2 changes reflect soft-tissue formation and degradation,

whereas pCO_2 is also affected by biocalcification and dissolution of calcium carbonate.

Because of the shallow nature of shelf systems, a significant proportion of the respiratory oxidation of organic carbon may occur in bottom sediments. Pore water concentrations are sensitive indicators of metabolic reactions occurring in sediments. Reactions that do not produce measurable variations in the chemistry of the solid phase often produce easily observable signals in the pore waters. As such, pore water concentration measurements and complementary reaction rate incubation experiments are necessary to identify the diagenetic processes and reactions that determine the fate of organic materials deposited on the continental shelf sea floor. Furthermore, diffusive and non-diffusive exchange rates of solutes across the sediment-water interface are directly proportional to the concentration difference between the pore waters and overlying bottom waters. Studies of sea floor exchange rates and processes therefore require pore water concentration measurements.

Initial measurements will focus on redox sensitive species that are known to participate in the oxidation of organic matter, nutrients, and carbon system parameters. The measured down-core variations in concentrations will be interpreted in terms of the solid phase chemistry, known metabolic and inorganic reactions, and in the context of transport - reaction models. These studies should identify the dominant reactions influencing pore water composition and constrain the relative rates at which the transport processes and reactions are occurring. Incubations of sediment samples will provide direct measures of reaction rates permitting total transport and exchange rates to be estimated. These can then be compared to those estimated by other strategies in the program.

C. Organic Carbon Preservation

To understand and quantify the sequestration of organic carbon in continental shelf systems, the properties and processes that retard remineralization and promote preservation must also be identified. Characterization of the solid phase will provide measurements necessary to interpret process studies such as organic decay and carbon burial, and provide indicators of the sources of carbon in the sediment. These characterizations will form the bulk of measurements to be made in extensive surveys, and will also be performed at the more intensively studied sites focusing on transformations.

Organic matter will be characterized in terms of total concentrations (TOC, TN) and measurement of labile subfractions that fuel benthic metabolic activity (e.g., enzymatically hydrolyzable compounds). Extensive work on biomarkers will seek to identify the sources of organic matter to the sediment; this work will be supplemented by bulk and compound-specific stable isotope measurements. Characterization of the refractory macromolecular materials will help clarify reasons for survival of organic matter during burial. Analysis of metal oxide and sulfur concentrations will provide evidence for the dynamics of metabolic oxidants and products.

Calcium carbonate concentrations will be measured to assess the importance of this form of carbon in both seasonally varying processes and long-term burial. Other mineralogical studies will allow interpretation of the origin of the sediments and diagenetic reactions that are associated with metabolic activities.

The organic matter-grain size relationships that define monolayer-equivalent concentrations need to be measured on cores used to determine shelf-slope burial rates.

Measures of specific surface area and organic carbon will allow testing of the hypothesis that organic matter burial in this region is controlled completely by the supply of mineral surface area to the depocenters. In other words, the correlation often found between sedimentation rate and organic carbon burial is indicative of a direct control of organic matter preservation by mineral surfaces. Presence of organic carbon concentrations above the monolayer-equivalent level (e.g., at the 900 m depocenter site) would provide an indicator of abnormally high input of organic matter to a site; normally such high concentrations are found only in high-productivity estuarine areas. Interpretation of organic carbon concentrations in the context of grain size will also allow determination of organic carbon loading extends to greater water depths along the slope off of Cape Hatteras relative to slopes farther north.

Measurement of the amount of enzymatically hydrolyzable organic compounds provides a direct measure of labile organic matter that fuels benthic communities. Current methods are capable of assessing enzymatically digestible amino acids. Methods that measure analogous fractions of lipids are under development. These analytical approaches could be extended to obtain the stable isotope composition of the labile fractions of organic matter. This approach would provide a higher signal:noise ratio for the presence of organic matter from isotopically distinct sources, one which is not confounded by the presence of older organic matter whose source signal may have been obscured.

The analysis of specific biomarker compounds may help identify the sources of organic matter, the phases (particulate, dissolved, colloidal) that are important in transporting organic matter and the reactivity, composition and age of the organic matter. Certain compounds, particulately the pigment and lipid compounds, but to some extent the sugars and amino acids, are only found in taxonomically restricted sets of organisms. "Molecular markers" can broadly differentiate between terrestrial and marine organic matter. Such lipid markers include sterols, hydrocarbons, lignins and fatty acids. Biopolymeric markers for source materials are also being recognized. These terrestrial/marine source markers are useful in determining whether organic matter in particles or sediments is from water column primary production or from a terrestrial source.

Biomarkers can also be used to determine the rates and transformation pathways of biological and chemical processes such as food web dynamics, remineralization processes, and exchange between particulate, colloidal, and dissolved pools. Moreover, a new level of information is now available through stable carbon isotopic composition of these individual biomarkers. Much higher resolution of the source of the organic matter is potentially available from these compound specific isotope measurements. In addition to the source, the age of individual components can now be addressed by radiocarbon measurements.

D. Bacterial Production

Of the various methods available to measure bacterial production, [^{3}H]- thymidine incorporation has become the most widely used. This method estimates the rate of bacterial DNA synthesis and consequently the rate of cell division. Some of the assumptions of the thymidine method have been extensively tested with positive results in marine and freshwater environments, while other assumptions remain untested or are disputed. The latter include the specificity of thymidine for DNA, the best way to convert incorporation rates to bacterial production values, and whether thymidine is a reliable predictor of growth rate for all, or only

some marine bacteria. Modifications to the methodology overcome or circumvent some of these problems, but uncertainty remains. Consequently, additional and independent indicators of bacterial growth are needed. Leucine incorporation into protein has been used as a measure of protein synthesis and bacterial biomass production, and is rapidly becoming a standard method. A second alternative measurement is the use of dilution culturing, in which unfiltered seawater is mixed with filtered seawater. This procedure decreases the efficiency of grazing by microzooplankton in proportion to the dilution factor. By measuring the growth of bacteria at various dilutions, it is possible to extrapolate to the theoretical condition of bacterial growth in the complete absence of grazing. The primary disadvantage is that the incubations are lengthy and subsequent analyses are labor-intensive, so that dilution culturing can only be used for a small subset of all possible stations and depths sampled. Simultaneous measurements of different combinations of these independent indices have been used successfully in marine environments, and are proposed for studies of bacterial growth and production in the ocean margin program.

In addition to the above-described methods for determining bacterial production, an entirely new approach using ribosomal RNA content and rRNA-specific oligonucleotide probes will be used to estimate protein synthetic capacity and growth. Data from culture studies with marine bacteria suggest that rRNA content measurements may estimate the community-average growth rates as well as more conventional methods. Furthermore, the methodology can be taxon-specific and cell-specific. At the species-specific level, rRNA content measurements appear to be near-perfect predictors of growth rate when the rRNA-growth relationship is determined empirically. The frequency distribution of rRNA among cells is the frequency distribution of protein synthetic capacity and under appropriate conditions can be interpreted as the frequency distribution of growth rate. Prior to the field year, DNA hybridization methods will be employed to identify a subset of bacteria that dominate biomass and abundance in coastal water and sediment of the study area. Probes specific to these dominants will be constructed and used to establish empirical RNA-growth rate relationships for these bacteria in axenic or mixed-community "natural" cultures (it is easier, but not necessary to isolate the bacteria in axenic cultures). The goal is to develop and apply the capability to evaluate the population dynamics of these dominant bacterial taxa in response to changes in environmental conditions. It is important to recognize that a significant portion of the microbial activity occurs in the bottom sediments. Because of uncertainties related to tracer adsorption onto sediment surfaces, interference by particles in optical microscopy, and steep and easily disturbed chemical and biological stratification, determining microbial activities and metabolic rates in sediments represents a particularly difficult challenge. Chemical flux incubations must be employed in conjunction with the more problematic tracer-based biomass production techniques to quantitatively constrain the role of the sediment microbial community in the shelf carbon cycle.

During the OMP field year, bacterial abundance and production will be determined routinely in water and sediment samples recovered along transects of the study area during four seasonal cruises. Rates of DNA and protein synthesis, and rRNA content, will be measured as independent indicators of bacterial production. A broad spatial coverage of the study area, including vertical profiles, will be obtained so that estimates of heterotrophic bacterial carbon production and mineralization can be compared with estimates of primary

production, community respiration, nutrient and DOC concentrations, microzooplankton abundance and grazing rates, and other parameters that describe the links between bacteria and other trophic levels.

E. Geochemical Tracers of Organic Matter Transformations

A multiple natural isotopic tracer approach using ^{12}C, ^{13}C, ^{14}C, ^{234}Th, ^{228}Th, and ^{230}Th on each of the different organic carbon classes will be employed to provide concomitant information on turnover rates, sources and potential sinks of organic carbon. Information on specific biomarkers (lignin, carbohydrates) will be needed as these compounds will help investigators determine the sources and transformations of carbon. Pigment and lipid biomarker analyses provide semi-quantitative estimates of classes of phytoplankton, bacteria, zooplankton and terrestrial organic matter. Stable isotope (^{13}C and ^{15}N) analysis will be useful in distinguishing source terms along the shelf and in tracking their decomposition and dispersal.

The naturally occurring radioactive Th isotopes, ^{234}Th (t1/2 = 24.1 y) and ^{228}Th (t1/2 = 1.91 years) and ^{230}Th (t1/2 = 75,000 years) have been identified as excellent tracers for quantifying rates and mechanisms of transformation between the various size classes. The distribution of all three Th isotopes in the oceans is constrained by a balance between supply from soluble parent nuclides, radioactive decay and removal ("scavenging") from the water column onto suspended and sinking particulate matter. By using measurements of $^{234}Th/^{238}U$, $^{228}Th/^{228}Ra$ and $^{230}Th/^{234}U$ disequilibria in dissolved, colloidal and particulate fractions and existing box models, it is possible to calculate transformation rates between the various size classes.

Bomb ^{14}C in surface waters imprints newly-produced biomass with a unique "future-age" radiocarbon signature. Sediments which accumulate only or predominantly modern biodetritus should yield future ^{14}C ages ($\delta^{14}C > 0$) in surface layers. In fact, while examples of this sort have been found in extreme nearshore settings, $\delta^{14}C > 0$ is rare in surficial sediments from open-ocean settings. Finite ^{14}C ages ($\delta^{14}C < 0$) in surface sediments result from rapid loss of the bomb ^{14}C signal by two mechanisms: (i) remineralization of fresh biodetritus in the water column and surface sediments; and (ii) mixing with older organic matter in the sediment column.

Despite the dearth of clear examples of bomb ^{14}C in shelf and slope sediments, surveys of ^{14}C in surficial sediments remain important to the question of storage of modern carbon on the continental margin. In the first place, geographic coverage of such measurements is very limited globally, especially on margins not distinguished by exceptional productivity or rapid sediment accumulation. Limited data on the Atlantic continental margin of the United States show sediment accumulation and transport to be laterally heterogeneous.

For the Mid-Atlantic Bight at least, this heterogeneity extends to ^{14}C in surface sediments. We need more observations of ^{14}C in surface sediments along sediment dispersal pathways before we can conclude that the bomb signal is absent from the sediments. Indeed, at present we need more such observations before we can intelligently plan a sampling program to search for modern biodetritus ($\delta^{14}C > 0$) in a designated field area.

Measurements of ^{14}C in surface sediments of the continental margin help to constrain maximum storage of modern biodetritus, whether or not unambiguous modern ^{14}C ($\delta^{14}C > 0$)

is discovered. By combining ^{14}C determinations with other tracers of modern particle input (excess ^{210}Pb and weapons-fallout) historical variations in carbon accumulation can be assessed.

The ^{14}C signature in the different size classes also can be used to assess the relative average ages of organic carbon, and to provide information on the sources of carbon (e.g. carbon fixed on the shelf vs. older oceanic carbon). Other biomarker compounds, such as lignin, are unambiguous source indicators which can provide estimates of contributions by terrestrial carbon.

F. Consumer Biomass Production and Grazing

In the water column, these studies can be divided conveniently into studies of proto- and metazoan zooplankton. Each of these requires different sampling and measurement techniques. In the sediments, studies of biomass production by consumers must include macrobenthic organisms in addition to protozoans and metazoans.

The overall goal of the protozooplankton studies (specifically phagotrophic flagellates and ciliates < 200 μm in size) is to assess grazing impact of protozooplankton on picoplankton and nanoplankton-sized prey, including heterotrophic bacteria, coccoid cyanobacteria, and < 20 μm algal cells. A large part of this research will involve development and testing of new methods of determining protists grazing on various types of prey, and comparing the new methods with more established techniques. Seawater dilution and size fractionation techniques will be used to measure rates of protozooplankton growth and grazing. A state-of-the-art color imaging system as well as direct microscopic techniques will be used to identify and enumerate the various components of the protozooplankton community, and determine their carbon biomass. To better couple the above taxonomic and rate process approaches to protozooplankton research, HPLC separation of phytoplankton pigments will be used in conjunction with the seawater dilution technique and microscopic examination of the protozooplankton community. Using this approach community functional response curves (i.e. grazing pressure as a function of phytoplankton concentration) will be obtained for individual phytoplankton taxa, and this information will be coupled with data on grazer community composition.

The goal is to develop a predictive capability concerning the potential grazing impact of individual taxa, and biomass levels of protozooplankton. Current techniques for the measurement of protozooplankton grazing are labor-intensive and generally require lengthy incubations. Thus, developing a predictive capability is critical to overcoming the difficulty of obtaining synoptic measurements of protozooplankton grazing over a sizeable geographic area.

Methods in development include quantitative measurements of the rates of substrate hydrolysis by a suite of phagotrophic protistan digestive enzymes which relate to in situ rates of bacterivory and herbivory. The suite currently includes acid lysozyme (an indicator of bacterivory) and a- and b-glucosidases (indicators of herbivory). The assays can be performed as cell-free assays for determination of community-level fluxes and as intracellular assays for determination of specific trophic pathways.

Metazoan zooplankton are a major link between primary production and large-bodied predators and the main producers of fecal material that settles to the seabed. To quantify the transformation of carbon by these grazers, we must specify both their biomass, its fluctuation in response to physical forcing, and the rates at which they process carbon. The biomass of

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the larger metazooplankton will be determined by moored and ship-mounted acoustic Doppler current profilers recording backscatter intensity, with backscatter intensity and seasonal variability in species composition verified by net tows. Investigation of transformations of organic matter which potentially store and transfer carbon from one season to another (i.e., lipid synthesis and mobilization) and investigation of growth rates (i.e., egg production) will be used to develop size-specific, species-specific, and season-specific algorithms. Water column rates of grazing and growth, and their seasonal variability and fluctuation in response to physical forcing, will be obtained by combining acoustic estimates of biomass with algorithms derived from measured rates of transformation.

Grazing rates of calanoid copepods, including copepodid stages and adult females, will be quantified through shipboard experiments, using bottle incubations with hand-sorted specimens. The planned approach is indirect as it uses growth over 24 hours to estimate the ingested amount through back calculation. Auto- and heterotrophic cells are considered as being the main food source. Combining these ingestion estimates with abundance and distribution data will result in an estimate of grazing of the copepod community. Research will also be directed to develop methods to (a) obtain time-series of the abundance and distribution of gelatinous zooplankton and small metazooplankton by way of an optical zooplankton counter, and (b) obtain real-world feeding rates.

G. Production of DOC

Molecular tools for determining the physiological state of individual phytoplankton cells are under development, using phytoplankton cultures representative of major bloom-forming taxa from the Atlantic and Pacific continental shelf environments to correlate the mean and variance of cell health parameters with rates of DOC production and sinking rates. Cell health markers under development include photosynthetic activity by autoradiography, lipid content using the fluorescent stain Nile Red, and cell viability using the fluorogenic esterase substrate Calcein-AM in combination with DNA detection using ethidium homodimer, a nuclear stain which does not penetrate the cell membrane of intact cells.

In field studies, major taxa of large phytoplankton (> 10 μm) will be identified that contribute directly to sedimentary flux off the shelf. The dominant phytoplankton identified in water column samples (vertical net tows and samples from discrete depths) will be compared with their contribution to material in 500 m sediment traps. These water column samples will be collected throughout the year, with highest temporal resolution during the period of the spring bloom, and will also provide a basis for evaluating the shelf-wide importance of taxa which are dominant at study sites selected for intensive biological sampling (eg. characterization of DOC production and cell health). The health of cells in populations of these taxa will be evaluated using molecular probes, during different periods of the year and at different locations on the shelf, to quantify the flux of primary photosynthate from phytoplankton into pools of DOC.

A method will be developed for the measurement of DOC production during grazing. The proposed method would decouple DOC production from bacterial uptake by preconcentrating zooplankton of various size fractions, then adding increasing amounts of the concentrate to natural water samples to yield a concentration series. Bottles would be sampled at the beginning and end of an incubation period. The net changes in DOC concentration,

extrapolated to natural zooplankton abundance, should indicate levels of DOC production by these grazers in the absence of bacterial uptake. Because small changes (<5 μM C) in DOC cannot accurately be measured in the face of large background concentrations of naturally-occurring DOC, total dissolved carbohydrate concentration (via an improved MBTH assay) will be measured as a proxy for DOC. Total dissolved carbohydrates have recently been shown to comprise a sizeable fraction of total DOC in oligotrophic waters and, as carbohydrates are a significant biochemical component of bacteria, phytoplankton, and zooplankton, these compounds are expected to be a major by-product of grazing.

H. Production and Transformations of Detrital POC

An *in situ* collector will be used to obtain sinking aggregates and pellets. The instrument will consist of a gentle suction collector operated by a pump, and the collections can be made to depths of several 100 m. Using this visually guided system, relatively undisturbed, larger particles (>1 mm) will be collected from the water column for shipboard rate measurements of associated processes. Transformations of carbon and various nutrient elements (N, Si, P) from particles into dissolved organic and inorganic pools will be measured in conjunction with other components in the project. The incubated particles and their associated communities will be contrasted with particles collected by traps, to assure these incubated particles represent "typical" sinking material in the study area.

The vertical export of particulate organic carbon from the euphotic zone will be measured at three selected sites in the Cape Hatteras region. These stations will be the same as the inner shelf, middle shelf and shelf /slope boundary process stations described herein. Measurements of export will be accomplished using free-floating MULTITRAP design sediment traps placed below the photic zone and at another selected depth beneath the photic zone. Each deployment will be for 48 hours in duration and will include both formalin preserved traps and screened (333 μm mesh) unpreserved traps so that we may address the degree to which POC is exported to the shelf sediments. Traps will also be included to look for the vertical export of phytoplankton pigments and nuclides, especially Pu) we can estimate maximal bomb ^{14}C in bulk samples of finite age (δ^{14}C < 0).

Ocean Margins Program Mooring Array
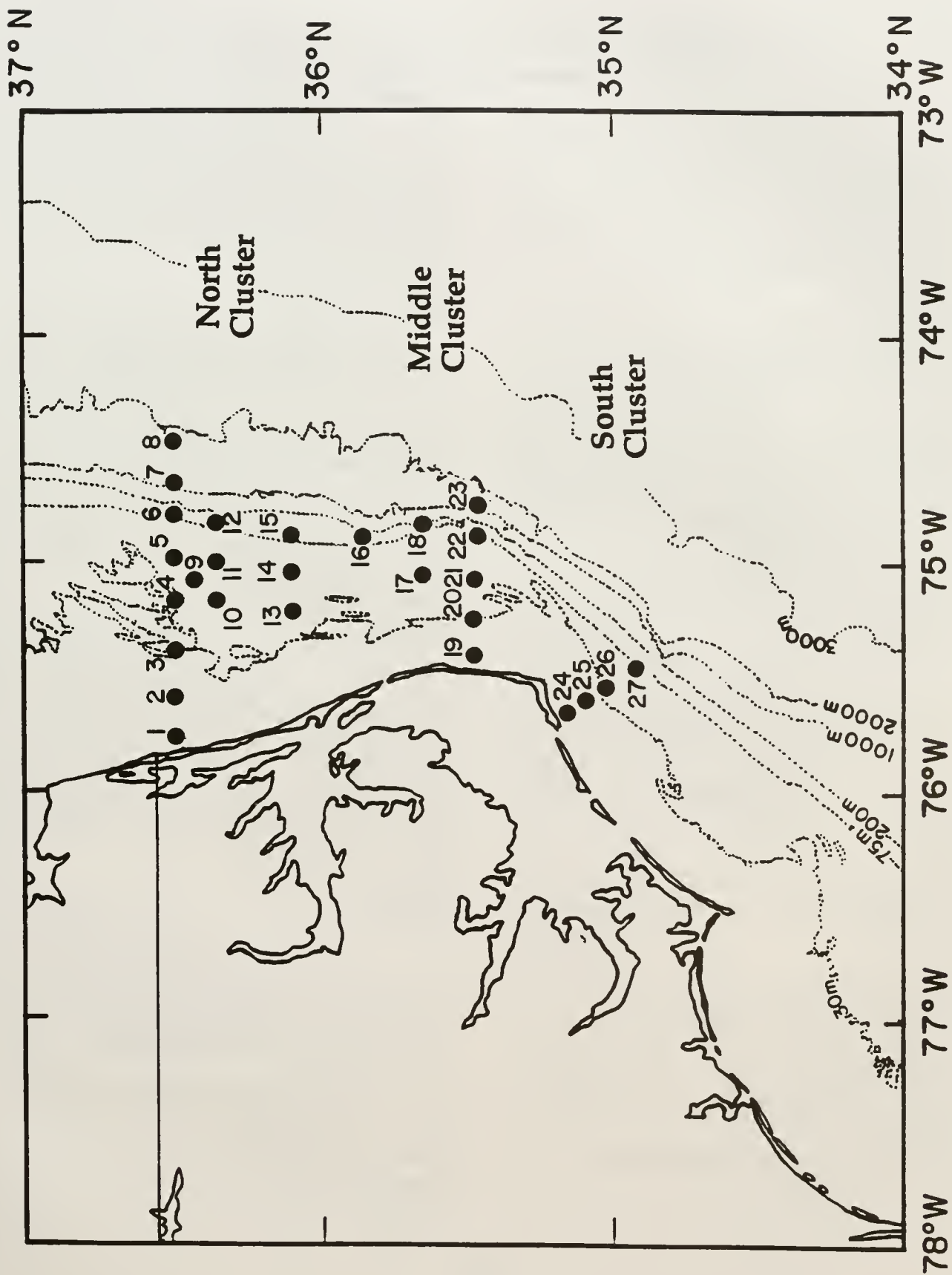
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