The Department of Energy - Ocean Margins Program

Final Report

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Transformation Rates and Fate of Dissolved, Colloidal and Particulate
Forms of Organic Carbon in Ocean Margins

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INTRODUCTION

The goal of our proposal was to develop new sampling and analytical techniques which could be used to understand the transformation rates and mechanisms of exchange between dissolved, colloidal, small particle and large particle size classes of organic carbon in ocean margins. To meet this goal, we focused on the development of cross-flow filtration (CFF) for the isolation of colloidal material from the dissolved phase in seawater. In addition, we tested and optimized high sensitivity techniques for the measurement of thorium isotopes using thermal ionization mass spectrometry (TIMS) and carbon isotopes using accelerator mass spectrometry (AMS) and stable C mass spectrometric techniques. Many of these techniques were pioneered by the PI's assembled for this original DOE study.

In this final report, we highlight some of these new sampling and analytical developments as well as preliminary results from our first DOE cruise this past April. The report is broken down into 4 sections, namely 1) colloidal sampling strategies, 2) TIMS analytical developments, 3) carbon isotopic measurements and 4) results from the *R/V Columbus Iselin* cruise. For more detailed discussion of our findings, we have included as an appendix to this final report manuscripts which have been published or will be submitted during this funding cycle.

1) COLLOIDAL SAMPLING STRATEGIES

At the start of this proposal in early 1992, the first studies using cross-flow filtration (CFF) for the isolation of colloids from seawater had only recently been published (Moran and Moore, 1989; Whitehouse *et al.*, 1990; Moran, 1991). The basic principal of CFF is that fluid flows tangential as well as perpendicular to the filter, thus allowing material smaller than the nominal pore size to pass through the membrane, while large solutes flow across the membrane and recirculate back into the feed reservoir. Typically, 0.2-1 μm prefiltration separates out the larger particles from the colloidal pool, and a CFF membrane cut-off in the range of 1,000 to 10,000 NMW is used to separate the colloidal material from the "truly" dissolved material.

We tested and used three different types of CFF systems during this grant period. The emphasis was to design a system that was compatible for both trace level organic and radionuclide/trace metal analysis. The primary results thus far come from two commercially available CFF units manufactured by Amicon (Bauer) and Osmonics (Buesseler and Moran). In these systems, the samples are collected either with a surface hose or by clean Niskin or Go-Flo bottles and processed at sea. The third basic style, which is still under development for this proposal, is a custom designed in-situ CFF. With this unit, a standard Osmonics polysulfone CFF membrane is coupled to an existing battery-powered in-situ pump, such that samples can be prefiltered and CFF processed in-situ, thus eliminating potential artifacts related to pressure, temperature and/or handling and blanks. The in-situ unit required the design and development of unique microprocessor controlled valves and flow meters, as well as novel plumbing and sample collection reservoirs.

The results presented below on the distribution of carbon and thorium isotopes (see Results from *R/V Columbus Iselin* cruise and attached manuscripts) have been obtained using our on deck CFF systems. We have confidence that we have solved earlier concerns related to compatibility issues for C isotopes and thorium analyses. The in-situ system has yet to work well in the field, however, primarily due to mechanical problems (sticky valves) and a design flaw in the flow meter at low permeate velocities. Most importantly, the in-situ CFF blank for ^{230}Th and ^{232}Th is unacceptably high, when considering the sample size (30 liters) and the level of these isotopes in seawater (10^6 - 10^7 atoms/liter for ^{230}Th). By the end of this DOE grant cycle we are confident we can solve these issues with minor modifications to the in-situ CFF pumps, and we are fortunate to have ship time in the spring of 1995 using other funding sources (NSF grant to Buesseler/Moran) when these modifications can be tested. The final choice of a single CFF system for the work proposed in our renewal program, will await results from the Colloid "Cookout", an intercalibration exercise that is now underway.

Colloid "Cookout":

Cross-flow filtration is acknowledged to be the only operational technique which can easily separate colloids from other particulate and dissolved species in >10 liter sized seawater samples. To fully utilize CFF, it became apparent early on in this proposal cycle, that an intercomparison of the various CFF systems was required in our field. Evidence for the need of an intercomparison between

different CFF systems can be found in some of the early marine colloid data. For example, using the radionuclide ^{234}Th as a particle-reactive tracer of marine colloid residence times, the group of P. Santschi *et al.* has found both high colloidal ^{234}Th abundance's (up to 55% of the total) and large adsorptive losses to their CFF system in the Gulf of Mexico and in recent MAB cruises. This in contrast to much lower ^{234}Th colloid abundance's (<20%) and sorptive losses (<2%) experienced by Moran and Buesseler in both Atlantic coastal margin and open ocean sites (many of these results are described below). It remains, therefore, an open question whether or not these differences reflect real site-to-site variations, or differences in the operational CFF techniques employed. Another example of the apparent variability in CFF data are the suggested large differences between the ^{14}C ages of DOC and COC. Some, but not all groups, have found the ^{14}C age to be sensitive to whether or not a 1,000 or 10,000 NMW CFF cut-off is used. Finally, even within a single CFF system, variations in DOC permeate concentration have been documented with time, during the several hours or more it typically takes to process 10's of liters of seawater through a CFF membrane.

To address some of these important issues, one of the PI's (KOB), sought and was awarded supplemental funds from DOE, NSF, and ONR to organize a colloid inter-comparison exercise, the "Colloid Cookout". This was viewed as a pilot experiment to gather the main oceanographic labs using CFF at one place and time, to subsample and analyze common aliquots from a variety of different or similar CFF systems. The first Cookout took place during the first week in August 1994 in Woods Hole. Roughly 20 scientists from 12 labs used over 17 different cross flow filtration systems produced by 6 different manufacturers in the intercomparison. Local Buzzards Bay water was prefiltered through a 0.2 μm filter and supplied to each group from a common reservoir (1500 liters total). The samples were then separated into a filtrate and retentate sample, defined most commonly by a new 1,000 NMW CFF membrane (donated by 4 different CFF manufacturers), and approximately 1000 samples were collected for analysis in this manner. In close to real time, we were all able to look at the performance of the systems with respect to DOC, Al, and absorbance/fluorescence data, and subsequent results for DON, nutrients, trace metals, radionuclides and specific organic compounds should be completed within the coming months.

The details of the intercomparison will take some time to collect and digest, but it became clear quite early on that the systems all have varying operational characteristics, and no one system was "right" or "wrong" for all of the tests that were conducted. Problems were seen with respect to both blanks and sorptive losses of organic material and particle reactive metals. The results have been compiled and returned to the PI's, and a preliminary discussion of the data awaits the fall AGU meeting in San Francisco, and our second gathering in January, 1995, in Hawaii where we will conduct further intercomparison work and hold a short meeting. The goal has always been to have the group submit a series of papers to Marine Chemistry to alert the community to our findings, and perhaps schedule a special session at an appropriate meeting to show case our efforts.

Until the data are finalized and the group meets again in Hawaii, it is inappropriate in this single DOE final report to comment on any specific results. As mentioned above, most of the participants left the Woods Hole intercomparison with a much clearer understanding of the basic operational similarities and differences of the CFF systems and their affect on the measured bulk DOC/COC and particle reactive metal concentrations in each phase. Operationally, the CFF systems differ in many ways, including: the wetted materials used in construction; the type of recirculation pump used; the transmembrane pressure; overall concentration factors employed in concentrating the bulk COC; operating temperatures; and in the widely varying processing times. Each of these factors may affect the quality and quantity of the colloidal matter which is isolated.

In the end, the participants in the Colloid Cookout learned more in the 5 days we worked together, than we would have learned individually conducting many years of lab and field CFF studies. There is no reason to suspect at this juncture, that the systematics of CFF cannot be understood, and simple tests suggested to document the integrity of each application of CFF technology to marine sciences. The recent attention to colloids in oceanography reflects a scientific interest to better understand the role of sub-micron particles in biogeochemical cycles.

2) THERMAL IONIZATION MASS SPECTROMETRY

One of the goals of this proposal was to use the thorium isotopes as tracers of particle and colloid residence times in ocean margins samples. Initially, a single isotope, ^{234}Th ($t_{1/2} = 24.1$ days) was used in these studies, as its activity is relatively simple to measure on samples of 20-40 liters using low level beta counting procedures (see, for example, Moran and Buesseler, 1993a, attached, and discussion of spring DOE cruise). Using a second thorium isotope, however, allows us the potential to model both forward and reverse rates of reaction between dissolved, colloidal and particulate phases. The focus of this recent DOE effort has been the application of thermal ionization mass spectrometry for the measurement of ^{230}Th and ^{232}Th in sea water (in collaboration with R. L. Edwards-U of Minn.). ^{230}Th ($t_{1/2} = 75,000$ yrs.) is particularly useful, as like ^{234}Th , it has a constant production rate from a soluble uranium parent, ^{234}U . Given its long half-life, however, the activity of ^{230}Th is extremely low, requiring the collection of 1000's of liters of seawater for its analysis by traditional radiochemical procedures. Using TIMS, in contrast, we have been able to develop techniques during this funding cycle to routinely and reproducibly measure total ^{230}Th and ^{232}Th concentrations on volumes as small as 0.5 liters.

The details of our TIMS procedures are described in an attached manuscript which has been submitted to GCA. In short, there were two main issues which needed to be addressed. First, the Finnigan 262Q Mass spectrometer which is used by Drs. Edwards and Hoff at the University of Minnesota for this study, needed to be installed, tested and optimized for ultra low level thorium measurements. Some of the specialized characteristics of this machine include ion-counting capabilities, the lack of detectable reflected beams, low dark noise of the multipliers, and high abundance sensitivity. Secondly, careful attention to blanks is a prerequisite to any ^{230}Th work, as total sample concentrations are on the order of 10^6 - 10^7 atoms per liter (i.e. $^{230}\text{Th} = 10^{-15}$ g/l range). Controlling blanks therefore is a major factor in all aspects of sample collection (at-sea), sample extraction and purification (at WHOI), and sample mounting and introduction to the mass spectrometer (at U of Minn.). The careful attention to blanks continues to be a very important aspect of our TIMS work, and we currently have a analytical/chemistry blank of 10 ± 5 pg for ^{232}Th and 0.06 ± 0.03 fg for ^{230}Th , which is 2-3 orders of magnitude lower than any other reported values. The total blank which we achieve in the field though our CFF system is only slightly higher (15 pg for ^{232}Th and 0.1 fg for ^{230}Th). This blank is checked regularly with every CFF deployment by passing our cleanest water through the CFF system and analyzing it as a sample. In a separate experiment, we documented the accuracy of our blank corrections by analyzing volume aliquots of 4, 2, 1, and 0.5 liter of seawater collected at two depths at Bermuda (see Hoff *et al.*, 1994; attached). To our knowledge, this is the first documentation of a reproducible ^{230}Th and ^{232}Th isotopic measurements in seawater at these levels (1.4 to 11.7 fg of ^{230}Th and 60.9 to 537.6 pg of ^{232}Th).

In addition to the TIMS data to be discussed below from our CFF samples, we have also analyzed several 2 liter total and filtered samples from the water column off of Bermuda (Hoff *et al.*, 1994) and in the Norwegian Sea (Moran *et al.*, 1994). While not directly related to this DOE project report, the consistency of this data and absolute calibration against radiochemical results obtained from >1000 liter samples, attests to the quality of our TIMS procedures. To fully utilize ^{230}Th in studies of colloids and particle cycling, we feel that it is imperative to demonstrate such high sensitivity in order to avoid the need for large volume sampling, and the tedious and potentially unreliable nature of large volume CFF work. We were fortunate that for the purposes of this DOE proposal, the contributions by the U of Minn. group could be directly supported by NSF funds, without which none of this developmental TIMS work would have been possible.

3) CARBON ISOTOPIC MEASUREMENTS

Another of the goals of this and our other on-going work is to elucidate some of the reasons for the observed differences and similarities in carbon isotopic composition (especially ^{14}C) between the various forms of organic carbon in the oceans. Recent advances in the isolation and identification of marine DOC components have aided in our understanding of its composition, but it still remains largely uncharacterized (>60-80%) with respect to its molecular and molecular-isotopic makeup. Both isotopic and molecular evidence points to the vast majority of this pool as being autochthonous in origin, most likely originating from euphotic zone production. The old (4000-6000 yrs BP) apparent ages reported

for marine DOC (Williams and Druffel, 1987; Bauer *et al.*, 1992) indicate that at least a major proportion of the DOC cycles on very long time scales and ages *in situ* during deep water transit (Bauer *et al.*, 1992; Druffel *et al.*, 1992). However, a pool of recently produced, "young" DOC has also been deduced to exist in the mixed layer (Druffel *et al.*, 1992) that itself appears to be comprised of at least two dynamically distinct sub-pools.

Several methods have been used with varying degrees of success to isolate and concentrate "representative" DOC from ocean waters. Hydrophobic resins were initially used to isolate from 25-80% of the organic matter dissolved in marine and other natural waters, including seawater (Thurman and Malcolm, 1981). These resins have been subsequently found to potentially bias the sample towards more hydrophobic organic matter, and it has since been proposed that methodologies such as cross-flow filtration do a better job of isolating and concentrating a representative form of DOC (Benner *et al.*, 1992) method used to fractionate or otherwise separate the DOC pool from a given sample of water into its component parts, the $\Delta^{14}\text{C}$ signatures are remarkably similar. Humic materials separated using XAD resins (Druffel *et al.*, 1992), colloidal organic carbon (COC; 1000 kD - 0.2 μm) using cross-flow filtration (Bauer *et al.*, 1994), bulk DOC isolated by UV or high-temperature catalytic oxidations (Bauer *et al.*, 1992), all reveal highly ^{14}C -depleted DOC with old "apparent" ^{14}C ages. In fact, our initial results show that $\Delta^{14}\text{C}$ of colloidal and small particulate DOC (1000 kD - 0.2 μm) are identical to the bulk DOC (Fig. 1). While other studies have indicated that differences exist in the $\Delta^{14}\text{C}$ values of various size classes of COC, these results are difficult or impossible to interpret in the absence of concomitant bulk measurements of the $\Delta^{14}\text{C}$ of the bulk DOC pool.

From measurements of $\Delta^{14}\text{C}$ in suspended particulate organic carbon (POC), we have found that the degree of depletion in $\Delta^{14}\text{C}$ is much greater with increasing depth in deep ocean sites than that expected on the basis of suspended POC residence times or if the POC contained recently derived surface components. We have postulated that a significant part of the lowering of $\Delta^{14}\text{C}$ during this time may be due to lower overall DIC $\Delta^{14}\text{C}$ values that accompany enhanced upwelling at one of our sites off the coast of California during summer. It is also possible that adsorption of low $\Delta^{14}\text{C}$ DOC and/or COC onto the POC, could cause lower overall $\Delta^{14}\text{C}$ signatures of the suspended POC. Adsorption of even small quantities of colloidal or truly dissolved organic carbon would cause a significant lowering of $\Delta^{14}\text{C}$ of the suspended POC. Likewise, recent evidence exists for DOC and POC $\Delta^{14}\text{C}$ signatures from our slope stations in the Middle Atlantic Bight (MAB; see R/V *Columbus Iselin* cruise results below), that the reverse may also be true, that is, that solubilization of POC with disparate $\Delta^{14}\text{C}$ may produce DOC with anomalously shifted $\Delta^{14}\text{C}$ signatures.

From similarities in the $\Delta^{14}\text{C}$ profiles of DOC and DIC in the open ocean, we have postulated that DOC in the main thermocline contains significant quantities of bomb ^{14}C ; however, separate ^{14}C analyses of younger components of the DOC have not yet been achieved. Most of the labile DOC is believed to have originated from POC produced in the surface during photosynthesis and then recycled. Within the labile DOC and POC fractions are identifiable compounds (amino acids/proteins [THAA], polysaccharides [TCHO], and lipids) that comprise ~10-20% and ~50-80% of the total organic carbon, respectively. Separate $\Delta^{14}\text{C}$ analyses of specific organic constituents of POC from our site in the eastern north Pacific have revealed significant differences in the turnover rates of specific forms of organic matter falling to the seafloor (Druffel *et al.*, 1994).

4) RESULTS FROM R/V COLUMBUS ISELIN CRUISE

We participated in a DOE funded cruise aboard the R/V *Columbus Iselin* cruise conducted April 18 to May 1, 1994, which covered the shelf and slope region between Woods Hole and Cape Hatteras. Our goal was to test in the field some of our new cross-flow filtration sampling gear and apply AMS and TIMS technology to the sample analyses in order to obtain the full suite of carbon and thorium isotopic measurements on size fractionated samples. Our sampling strategy was broken down into three main sample types. One set of surface water samples was collected from 6 transects at up to 3 stations from an in-line seawater system. These samples were analyzed for dissolved, particulate and total ^{234}Th and the organic C/ ^{234}Th ratio on particles in order to obtain a first order estimate of particulate organic C flux from the surface waters of the MAB. Secondly, along 3 of the 7 cross shelf transects, we sampled using CFF at two locations—surface waters only at a mid shelf site, and a more complete profile over the slope from surface to deep waters (0-1500m max., n=3-6 depths). At each of these sites, we used

multiple CFF systems (Amicon, Bauer and Druffel; Osmonics in-situ and deck systems, Buesseler and Moran) and exchanged samples for a full suite of isotopic analyses. Finally, samples for carbon isotopic composition of POC and DIC were taken along each of the 7 cross-shelf transects at an inner, mid and outer shelf station.

The oceanographic setting during this study period was as follows: focusing on the outermost end of the MAB transects, from T-S data it is evident that Gulf Stream waters impinged on the shelf/slope at the southernmost transect (Fig. 2). Supporting data show nutrient depletion and elevated suspended particulate matter concentrations ($\sim 200 \mu\text{g/l}$) in surface waters at all stations (Fig. 3). Also, from salinity, and the clear relationship between DOC and salinity, the nearshore sites and surface waters across the shelf south of the Delaware and Chesapeake Bay were clearly impacted by fresh water runoff from these water sheds.

Thorium-234 Regional Pattern and POC Flux:

Figure 4a shows the cruise track and ^{234}Th activity distribution in surface waters measured on our cruise. There is a broad trend of lower ^{234}Th activities near shore, increasing activities off shore along each transect, as well as a general decrease in ^{234}Th activity from N to S, as water travels along the shelf and ^{234}Th is progressively removed from MAB waters. The exact opposite trend was found for DOC (Fig. 4b — preliminary data courtesy of B. Chen and D. Repeta). Both sets of data point to the importance of near shore waters as both a source of DOC (and likely COC), and a reactive sink for particle-reactive elements such as ^{234}Th (lower ^{234}Th indicates a higher net particle flux). While these ideas are not new, neither of these trends has been shown on this scale for the MAB region or any other coastal margin. Using these data one can begin to make quantitative inferences regarding POC and DOC fluxes from this region. An example of the POC flux estimate is provide below, and DOC flux estimates for the entire MAB region are being undertaken by Repeta *et al.*

Thorium-234 ($t_{1/2} = 24.1$ days) is a useful tracer of particle dynamics in the oceans due to its non-selective particle reactivity and its known production and decay rates in seawater. Mathematically, the ^{234}Th particle flux can be shown to be estimated from the disequilibrium between the soluble ^{238}U parent, and the observed ^{234}Th activity in a given parcel of water (assuming steady-state and negligible advective and diffusive fluxes — see for example Buesseler *et al.*, 1992, 1994a for a more detailed analysis of these assumptions). Using this relationship, one can calculate the particulate ^{234}Th flux from surface waters given the data shown in Fig. 4a. For illustrative purposes, we use a mean ^{234}Th activity of 1.24 dpm/kg ($n=16$) to calculate a net vertical flux of $540 \text{ dpm m}^{-2} \text{ d}^{-1}$ out of the upper 15 m for the MAB region. In fact, site and area adjusted fluxes could be calculated from this same data set.

In previous studies (Buesseler *et al.*, 1992) we have also shown that by using the empirical ratio of ^{234}Th to organic C, one can convert from the calculated ^{234}Th flux, to an estimate of POC flux (and by analogy, PON flux). The only assumption here is that the particles which are carrying organic C are also carrying ^{234}Th , and that the particles we collect represent at least in their POC/ ^{234}Th ratio, the sinking particle pool. In a coastal setting, we also restrict this analyses to surface waters, where resuspended sediments provide a negligible source of ^{234}Th to the water column. Using our own measurements of ^{234}Th and POC on GFF filters, we find a mean POC/ ^{234}Th ratio of $19 \pm 6 \mu\text{mole C/dpm}$. Using this approach, we would therefor calculate a mean POC flux on the order of $10 \text{ mmole C m}^{-2} \text{ d}^{-1}$. This represents a net export flux of POC of about 15-20% of annual primary production rates for this region. There are a number of details which would need to be included in a more rigorous application of this ^{234}Th approach for estimating POC budgets, and we hope to focus in on these in our renewal proposal. We will need to examine the seasonal dynamics of the $^{234}\text{Th}/^{238}\text{U}$ disequilibria, and use non-steady state modeling as well as consider advective components in the ^{234}Th budget. Also, variations in the C/ ^{234}Th ratio will need to be examined based upon particle size and type (Moran *et al.*, 1993). In addition, we plan to pursue additional radioactive tracers, including cosmogenic P and Be isotopes, to further constrain the POC and particulate nutrient budgets off of Cape Hatteras in 1996.

Returning to the ^{234}Th data, the general shape of each of the total ^{234}Th vertical profiles (Fig. 4a) is typical of much of the ocean, with low values in surface waters and activities near secular equilibrium with ^{238}U at depth. When examined in more detail, there is a slight excess of ^{234}Th over ^{238}U at 300m and 750m at stations 46 and 55 near Cape Hatteras ($^{234}\text{Th}/^{238}\text{U} = 1.14 \pm 0.02$ (mean $\pm$ sd),

n=4). Excesses of ^{234}Th are only found if the intensity of surface scavenging is high, and the flux of exported particulate matter and its sub-surface remineralization rate are greater than any local supply and loss terms. Given the large aerial extent of the observed ^{234}Th deficit over the shelf (Fig. 4a), there is the possibility that some of the excess ^{234}Th activity in mid slope waters is balanced by lateral inputs of ^{234}Th which was scavenged from shallower waters, and then transported cross shelf with the resuspended particulates. The precision and accuracy of these deep water total ^{234}Th values should not be in question, as samples were collected on this DOE cruise for intercalibration with a discrete batch processing mode which uses thorium yield monitors, and our Mn adsorber technique, both of which used radiochemical purification and low level beta counting in the final analysis. The overall uncertainty in the calibration of our beta counting procedures in addition to counting error, has been shown to be $\pm 2\%$ in both surface and deep waters (Buesseler *et al.*, 1994b).

Cross-Flow Filtration Studies - Thorium Isotope Results:

For this final report, we discuss our ^{234}Th data and a selected set of TIMS analyses. Final TIMS data will be available within 6 months and carbon isotopic analyses on a different CFF system are reported in a separate section of this report. Carbon isotopic analyses and ht-DOC/DON concentration measurements on the same aliquots as the thorium samples will be completed by the end of this grant period.

Thorium data are reported for the particulate (defined by a $1\ \mu\text{m}$ nucleopore filter), colloidal ($<1\ \mu\text{m}$ and $>1,000\ \text{NMW}$ cut-off), filtrate ($<1,000\ \text{NMW}$) and total sample (collected separately) at stations 16, 46, and 55 (see Fig. 4 for locations). CFF samples were either collected directly via a sampling hose (surface waters) or Niskin bottles. An independent sample for total ^{234}Th and TIMS analyses (^{230}Th and ^{232}Th) was also taken at each site. Thorium data are reported here for our deck mounted CFF unit only, which uses an OSMONICS spiral wound $1,000\ \text{NMW}$ polysulphone membrane. Samples were concentrated by factors of 5-8, and total volumes of 20-30 liters were processed in approximately 4 hours. In addition, at the end of each CFF run, separate Q-water samples were run as blanks, and Seastar $0.5\ \text{N HCl}$ was used to both clean the CFF unit between samples, and as a check for sorptive losses of thorium to the CFF membrane or plumbing. Consistently low sorptive losses of $<1\text{-}5\%$ were found. The blank for ^{234}Th is at background for low-level beta counting, and only $15\ \text{pg}$ for ^{232}Th and $0.1\ \text{fg}$ for ^{230}Th . This extremely low handling and analytical blank for the TIMS samples was achieved after considerable effort was spent in measuring both field and lab blanks, and quantifying all sources of contamination (Hoff *et al.*, 1994). This low blank allows us the unique possibility to work on this suite of thorium isotopes using comparatively small sample sizes (20-30 liters vs. >1000 liters for other CFF systems and analytical procedures). ^{232}Th , while measured simultaneously with ^{230}Th by TIMS, is less useful for our studies, as its primary input source is via atmospheric deposition, and therefore its scavenging rate cannot be determined directly by measuring its water column activity profile.

Overall, we find relatively low colloidal ^{234}Th activities at all sites and depths; $f_c = 1\text{-}22\%$ (colloidal/total activity) (Fig. 5). This is consistent with our previous studies in Buzzards Bay, the Gulf of Maine, and at Bermuda (Moran and Buesseler, 1992, 1993a) and can be explained by the equilibrium like partitioning of thorium between available particulate and colloidal surfaces. The ^{230}Th data from station 55 represent the first of their kind in oceanography (Fig. 6a). At all depths, the ^{230}Th activity of the colloidal fraction is smaller than the particulate or dissolved fractions. Particulate and dissolved ^{230}Th both increase between 300m and 1500m, constant with earlier studies. This increase is attributed to continued input of ^{230}Th to the water column from ^{234}U decay, accompanied by vertical scavenging and exchange between sinking and suspended particles (Bacon and Anderson, 1982). We find particulate ^{230}Th activities which range from 13-52% of the total activity (f_p = particulate/total activity), and colloidal activities are much lower, with f_p for ^{230}Th ranging from 1-26%. With a longer half-life, f_p and f_c are expected to be greater for ^{230}Th than ^{234}Th , and this is also seen (see modeling section below).

We are striving in the future to achieve a closer mass balance between the sum of the CFF fractions and the independent total samples. This is a generic problem with all CFF systems (see "Colloid Cookout"). For ^{234}Th , we find that the mass balance using CFF is generally $\pm 10\%$, but there are still some problems, particularly at station 55 deep waters and in surface waters in general

(compare solid circle and diamond in Fig. 5). Totals for ^{230}Th and CFF fractions agree quite well at three depths (surface, 300m and 1500m), but only one station (Sta. 55) has been completed. The problem with achieving a good mass balance in surface waters we attribute in part to greater natural variability. On this cruise, we found that replicate surface water ^{234}Th activities collected within a 4 hour period differed by as much as 10%. These variations were found to vary with salinity changes of 1 ppt or more, which reflected the sampling of different water masses at a single physical location. In the modeling section below, we focus on the station 55 data from 300m, due to the combined quality of the ^{230}Th and ^{234}Th data and the tight mass balance which was achieved for both isotopes at this depth (Fig. 6a). Under separate funding, we are also addressing the issue of CFF mass balances by obtaining many replicate samples at a single deep water site, and then sampling the totals and CFF fractions as a time-series for ^{230}Th , ^{232}Th , ^{234}Th and ht-DOC and Al analyses.

Using the single isotope, ^{234}Th , and a scavenging model such as outlined in Fig. 6b, we can make a first order estimate of particulate and colloidal residence times. For 300m at station 55, one calculates a net residence time of 6.7 days for both colloidal and particulate ^{234}Th , and a much longer, 136 day residence time for dissolved ^{234}Th . Using a second thorium isotope, namely ^{230}Th , one can set up the same type of box model and simultaneously solve for both forward and reverse rate constants. Using the notation in Fig. 6b, and the combined ^{230}Th and ^{234}Th data from this same sample, one calculates a corresponding turnover times for uptake ($1/k_1$), release ($1/k_1$), colloidal aggregation ($1/k_2$) and particle disaggregation ($1/k_2$) of 64, 5, 4, and 8 days, respectively. These rates imply that once a colloid is formed, the turnover of this pool is on the order of several days before it is either aggregated into a larger particulate phase, or broken down and returned to the "truly" dissolved phase.

Carbon Isotope Results - Spatial Distributions, Sources and Residence Times

During the Spring 1994 OMP Geochemistry cruise samples were collected for determinations of pool sizes and carbon isotopic compositions (^{14}C and ^{13}C) of bulk DOC, POC and DIC. Of the six cross-shelf transects that were made during the cruise, three were sampled for DOC, COC, POC, and DIC measurements (Fig. 4). In addition, several stations were also sampled for concomitant measurements of both carbon and thorium isotopes in colloidal organic matter. To date, all DOC samples have been analyzed, approximately one-third of the POC and DIC samples have been analyzed for $\Delta^{14}\text{C}$, and the remainder, as well as all of the COC samples, are currently awaiting analysis by Accelerator Mass Spectrometry (AMS). The 3 transects that were chosen for carbon isotopic distributions were: a) transect 3, located off the eastern end of Long Island (away from the influence of the Chesapeake and Delaware Bays), b) transect 6, between Chesapeake and Delaware Bays, and c) transect 8, off Cape Hatteras. These specific transects were chosen to provide the range of geographic and estuarine input conditions needed to establish the ranges in isotopic signatures for each of the carbon pools. On each transect, samples were collected from surface (5 m) and near bottom depths in shelf waters wherever possible. In slope waters, samples were collected from four depths, each representing different lateral distances from the slope. The specific goals of this aspect of the cruise were: 1) to evaluate potential source terms and turnover times for DOC of continental shelf and slope waters of the MAB, 2) to evaluate the isotopic composition of DOC relative to that of the POC and DIC and 3) to compare the isotopic composition and turnover times of MAB shelf and slope DOC to that of the interior North Atlantic (Sargasso Sea).

Figure 7 illustrates a comparison of all available DOC data derived from both ultra-violet (UV) and high-temperature catalytic (HTC) oxidations of seawater samples as part of the carbon isotopic component of this cruise. UV oxidations were performed on all samples (650 ml volumes) in the laboratory for oxidation of DOC for isotopic analyses; HTC oxidations were performed on small volume injections of samples while underway at sea. As can be seen, while relatively good agreement was obtained between the different analyses, and the results agreed in a positive fashion. However, it may also be noted that the majority of HTC-derived values lie above the 1:1 line of correspondence. Recently it has been shown by Peltzer (1994) that agreement between these two methods (i.e., UV and HTC) is excellent and essentially indistinguishable if adequate care is taken in evaluating the blank system blank component of the HTC measurement. The UV oxidation method introduces an insignificant blank and therefore is the basis for comparison. These results therefore indicate that the

HTC blank must be more carefully monitored while performing at-sea, discrete injection measurements of DOC concentrations.

Concentrations of DOC determined by UV oxidation of large volume samples plotted as a function of sample salinity (Fig. 8) exhibit, with the exception of several stations on southernmost transect 8, an excellent inverse relationship and are indicative of the conservative mixing of freshwater/riverine/estuarine and shelf- and open ocean-derived DOC. One of the major implications from this is that, in most cases DOC from riverine and Chesapeake Bay watershed sources are not labile forms of carbon for either Bay or MAB shelf microheterotrophic populations. While this relationship has been previously observed for regions of estuarine mixing, this is the first evidence of freshwater end-member material persisting in seaward regions of shelf waters. Stations 55, 58 and 62 from southern transect 8 all show significant departure from the conservative mixing line, and the DOC concentrations at these sites are indicative of the input of one or more forms of DOC to the water column. These sources could include exchanges with sediments and porewaters, atmospheric inputs or submarine hydrocarbon seeps.

Similar to the DOC vs. salinity relationship, $\delta^{13}\text{C}$ values of DOC from MAB waters (Fig. 9) indicate that lighter, ^{13}C -depleted organic matter persists in certain regions of the shelf. Values are invariably lighter in $\delta^{13}\text{C}$ of shallow, lower salinity shelf waters compared to deeper shelf waters (Fig. 9, top and middle panels) and indicate a contribution of ca. 5-10% terrestrial material to shelf waters assuming that marine DOC is $\sim 21\text{‰}$. There is also a noticeable presence and/or persistence of this material in slope waters of the southern-most transect 8 near the Cape Hatteras region (Fig. 9, bottom panel). The $\delta^{13}\text{C}$ of DOC from all samples shows a strong negative relationship with DOC concentration (Fig. 10), indicating that as the concentration of DOC varies as a function of salinity, the $\delta^{13}\text{C}$ of DOC also varies as a function of DOC concentration and freshwater vs. marine sources. The greater amount of scatter in $\delta^{13}\text{C}$ values at lower DOC concentrations (Fig. 10) is a result of samples collected from southern transect 8 and is indicative of a broader range of isotopically variant DOC sources to the water column there.

The $\Delta^{14}\text{C}$ values of DOC collected in the MAB also showed spatial differences as a function of both station and depth (Fig. 11). The most ^{14}C -enriched values were found for surface, lower salinity waters of the central and southern inner and middle shelf (Fig. 11, top and middle panels). The average apparent radiocarbon age of this ^{14}C -enriched DOC is approximately 500-700 years B.P. The DOC from deeper, higher salinity shelf waters was always more depleted in ^{14}C (i.e., more negative $\Delta^{14}\text{C}$ values). MAB deep slope waters contained the lowest $\Delta^{14}\text{C}$ values (Fig. 11, bottom panel), resembling values seen previously for deep open ocean regions. Interestingly, surface slope waters from central transect 6 were significantly enriched in ^{14}C , and this pattern persisted to the deepest waters of the slope here. The highly ^{14}C -depleted DOC in southern transect 8 surface (5 m) waters are the lowest $\Delta^{14}\text{C}$ values ever observed for surface water DOC. The $\Delta^{14}\text{C}$ of DOC also showed a relatively strong negative relationship with $\delta^{13}\text{C}$ (Fig. 12) indicating that ^{13}C -enriched material derived from terrestrial and freshwater sources also contributed the majority of ^{14}C -enriched DOC to MAB shelf and slope waters. Similar to the $\delta^{13}\text{C}$ vs. DOC relationship, the greater variability in $\delta^{13}\text{C}$ values at very low $\Delta^{14}\text{C}$ values are a result of the greater variability in the source terms for DOC in southern transect 8 waters ($\sim 450\text{‰}$).

When $\Delta^{14}\text{C}$ values for DOC collected from slope waters are compared to previously determined values from the Sargasso Sea (Bauer *et al.*, 1992), a surprising pattern is observed (Fig. 13). In mid-depth slope waters we find that the $\Delta^{14}\text{C}$ of DOC is much more highly depleted (by $\sim 125\text{‰}$ or ~ 1500 years) than in the interior ocean. These values converge at both shallower and greater depths, indicating that an older, more ^{14}C -depleted source of DOC is being injected to shelf waters at mid-depths. Thus, the MAB may be a source of both younger, ^{14}C -enriched (from shelf waters) as well as older, ^{14}C -depleted (from slope waters) DOC to the interior ocean. While we are relatively certain of the source of the ^{14}C -enriched DOC to shelf waters (i.e., terrestrial and/or riverine material), we are less certain of the source of ^{14}C -depleted DOC to southern transect and slope waters. An examination of the $\Delta^{14}\text{C}$ values of POC from some of these samples (Appendix 1) indicates strong ^{14}C -depletion of the POC in slope waters, but especially so in southern transect 8 slope waters. In fact, these are the most highly ^{14}C -depleted values for water-column POC ever observed. This must be related to the resuspension of organic material from shelf and slope sediments and its transport and persistence in even

shallow (5 m, Sta. 55) slope waters, since $\Delta^{14}\text{C}$ values of DIC are typically of other well-mixed surface waters (Appendix 1). In addition to POC, DOC derived from porewaters could also be mixed with water column DOC as sediments are eroded. Whatever the exact mechanism is shown to be, it is apparent that this material has a significant effect on the DOC content and $\Delta^{14}\text{C}$ values in southern MAB waters close to the Cape Hatteras region.

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Fig. 1 . Values of $\Delta^{14}\text{C}$ for total dissolved organic carbon (dashed line) , colloidal organic carbon (filled diamonds) and suspended particulate organic carbon (open squares) at a site in the eastern north Pacific.

Fig. 2 Vertical profiles of temperature and salinity at the slope water stations during the MAB alongshore cruise.

Fig. 3 Vertical profiles of suspended particulate matter and dissolved nutrients at the slope water stations during the MAB alongshore cruise.

Fig. 4 Transects on the 1994 DOE-OMP alongshelf cruise (transects 3, 6, 8 refer to transects for C isotopic distributions only —see text): a) Total ^{234}Th (dpm kg⁻¹) in surface waters and in vertical profiles in the slope water stations; b) DOC in the surface waters (µM).

Fig. 5 Vertical profiles of size-fractionated ^{234}Th at the slope water stations during the MAB alongshore cruise.

A

B

Fig. 6 a) Vertical profiles of size-fractionated ^{230}Th at slope water station 55 during the MAB alongshore cruise. b) Box model of the Th-based particle cycling model for the interaction between dissolved, colloidal, small particle, and large particle size classes.

Figure 7. Comparison of DOC concentrations of samples collected for $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ analyses as measured by two at-sea high temperature catalytic (htc) oxidation units and laboratory ultraviolet (uv) oxidation of seawater from Spring 1994 OMP Geochemistry Cruise to MAB.

DOC_{uv} vs Salinity

Figure 8. DOC concentration as a function of salinity for all samples analyzed. The 4 points lying above the mixing curve were all shallow samples (<40m depth) from southern transect 8, and indicate that there exists an additional source of DOC to the water column besides that contained in the marine and freshwater end-members.

Figure 9. Values of $\delta^{13}\text{C}$ of DOC from inner and mid-shelf and slope stations. Note changes in depth and $\delta^{13}\text{C}$ scales.

$\delta^{13}\text{C}$ -DOC vs DOC Concentration

Figure 11 Values of $\Delta^{14}\text{C}$ of DOC from inner and mid-shelf and slope stations. Note changes in depth and $\Delta^{14}\text{C}$ scales. Central transect 6 waters had most consistently ^{14}C -enriched (i.e., youngest) DOC, especially in surface and shallow waters.

Figure 12. In MAB shelf and slope waters, the $\Delta^{14}\text{C}$ signature of DOC appears to co-vary to a limited extent with its $\delta^{13}\text{C}$ signature. This indicates that a significant proportion of the $\Delta^{14}\text{C}$ signature is determined by inputs of DOC that are presumably derived from different sources (i.e., terrestrial vs. marine) having differentiable $\delta^{13}\text{C}$ signatures. The large amount of variation in $\delta^{13}\text{C}$ at low $\Delta^{14}\text{C}$ values is due to samples from southern transect 8.

Comparison of MAB Slope Water and Sargasso Sea $\Delta^{14}\text{C}$ -DOC

Figure 13. Comparison of $\Delta^{14}\text{C}$ of DOC from Middle Atlantic Bight shelf and slope waters (present study) and from the Sargasso Sea (previously determined by Bauer et al. [1992]).

Appendix 1. $\Delta^{14}\text{C}$ Results To-Date for DIC and POC.

<u>Transect</u>	<u>Stn</u>	<u>Sample depth (m)</u>	<u>$\Delta^{14}\text{C-DIC}(\text{‰})^a$</u>	<u>$\Delta^{14}\text{C-POC}(\text{‰})^a$</u>
3	10	5	NA	+3.6
		25	NA	NA
3	12	5	NA	NA
		50	NA	NA
3	16	5	NA	NA
		300	NA	NA
		750	NA	NA
		1000	NA	NA
6	40	5	NA	NA
6	42	5	+54.4	NA
		15	+32.6	NA
6	46	5	+48.2	+7.5
		300	-23.2	-256.5
		750	NA	NA
		1000	-49.7	-266.9
8	62	5	NA	NA
8	58	5	+63.2	+47.0
		40	+44.6	-53.2
8	55	5	+80.2	-97.1
		300	NA	-437.8
		750	NA	NA
		1000	NA	-499.6

^aaverage precision ($\pm 1\sigma$) of $\Delta^{14}\text{C}$ values is $\sim \pm 8\text{‰}$

NA - data not yet available, analysis pending