

Spatial and temporal variability of absorption by dissolved material at a continental shelf

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Abstract. Optical properties of dissolved (colored dissolved organic material (CDOM)) and particulate matter and hydrographic measurements were obtained at the Mid-Atlantic Bight during the fall of 1996 and the spring of 1997 as part of the Coastal Mixing and Optics experiment. To assess the temporal and spatial variability, time series were obtained at one location and cross-shelf transects were carried out. On short timescales, variability in the vertical distribution of the dissolved fraction was mostly due to high-frequency internal waves. This variability was conservative, resulting in no changes on isopycnals. Over longer periods and episodically, CDOM variability was dominated by storms. The storms were associated with sediment resuspension events and were accompanied by an increase in the absorption by the dissolved materials. Data from spatial transects show that near the bottom, over the shelf, and in both spring and fall, increased particulate absorption and increased CDOM absorption co-occur. These data support the hypothesis that bottom sediments can act as a source of dissolved organic carbon during sediment resuspension events.

1. Introduction

Colored dissolved organic material (CDOM) absorption strongly impacts ocean color [Bricaud *et al.*, 1981; Carder *et al.*, 1989], especially in coastal regions where it is a major absorbing substance in the blue portion of the visible spectrum [Bukata *et al.*, 1995]. In order to invert reliably the remotely sensed ocean color to obtain the concentration of optically significant material, it is of major importance to determine CDOM distribution and its effect on ocean color. The spectral absorption by CDOM (here denoted by a_g) at the visible wavelengths can be described, to a high degree of accuracy, by a single exponential or a sum of two exponentials that decrease with increasing wavelength [Carder *et al.*, 1989; Jerlov, 1968; Roesler *et al.*, 1989]. As in previous studies, we use the term CDOM to denote colored material that passes through a 0.2 μm filter, regardless of its origin and chemical composition.

Terrestrial and oceanic sources and sinks contribute to the observed distribution of CDOM (also referred to as Gelbstoff, Gilvin, and yellow substance), in the world's oceans [Bricaud *et al.*, 1981; Carder *et al.*, 1989; Jerlov, 1968]. Terrestrial runoff is considered to be the main source of CDOM in coastal waters, resulting in a tight salinity CDOM relationship there. An additional source of CDOM comes from benthic flux; poorly oxygenated sediments in highly productive coastal areas have been observed to flux dissolved organic carbon (DOC) into the water column [Burdige and Homestead, 1994; Chen *et al.*, 1997]. Decomposition of particulate organic carbon is the primary source of the DOC released. Other potential sources for CDOM in the water column are its release as a byproduct of primary [Bricaud *et al.*, 1981; Twardowski, 1998] and secondary productivity [Nelson *et al.*, 1998]. The main known sink for CDOM is photooxidation [Miller, 1994; Vodacek *et al.*, 1997]. Bacterial metabolism and CDOM adsorption to sinking parti-

cles have also been suggested as sinks for CDOM [Thurman, 1985; M. Moran, personal communication, 1999].

The observed distribution of CDOM is complicated by physical advection and local mixing, which act to transport and erase the signatures associated with the above sources and sinks, respectively. The objective of this paper is to evaluate the contribution of these processes to the observed variability of CDOM on a continental shelf.

The data analyzed here were collected on the continental shelf at the Mid-Atlantic Bight. Hydrographic properties at the Mid-Atlantic Bight are strongly affected by estuarine sources at the land-sea boundary and by the Gulf Stream, its eastern boundary. The yearly mean circulation is predominantly along the shelf (westward), opposite to the direction of the Gulf Stream [Beardsley and Boicourt, 1981]. A density front is often found at the shelf break separating the cold and fresh shelf water from the saline and warm slope water offshore. Associated with this front is a geostrophic westward jet, with observed velocities of the order of 0.5 m s^{-1} [Barth *et al.*, 1998]. A weaker across-shore secondary circulation with vertical velocities of the order of 10 m d^{-1} associated with this front has been observed [Barth *et al.*, 1998]. This circulation is associated with the upwelling of sediment-rich bottom waters on the shore side of the front and downwelling chlorophyll-rich near-surface waters on the offshore side of the front.

Several studies have addressed the seasonal and spatial variability of surface CDOM in the Mid-Atlantic [DeGrandpre *et al.*, 1996; Vodacek *et al.*, 1997] and South Atlantic Bight [Nelson and Guarda, 1995]. These studies have concluded that the major source for CDOM absorption is riverine runoff, resulting in a strong seasonal variability and a strong linear relationship between increasing salinity and decreasing CDOM for each season (though the relationship varied between seasons). Photo-oxidation of CDOM resulted in lower levels of CDOM near the surface in the summer [Vodacek *et al.*, 1997]. These studies were mostly confined to the surface and used instrumentation that could not detect the low CDOM absorption

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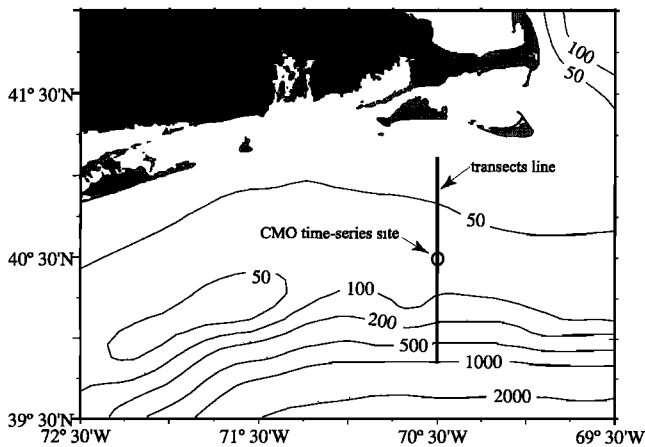


Figure 1. Study site of the Coastal Mixing and Optics experiment (CMO). The location of the time series station is indicated by an open circle, and the transect course is denoted by the bold line. Bottom depth is based on the ETOPO5 database.

signal in the visible range over the midshelf region (detection of UV absorption was possible since it is higher than in the visible). In this study we analyze CDOM absorption data at 440 nm collected at the Mid-Atlantic Bight that spans the whole water column and a period of a few weeks in the late summer and spring.

2. Methods

Data were collected during two cruises to the Mid-Atlantic Bight as part of the Coastal Mixing and Optics experiment (CMO) during August 17 to September 7, 1996 (denoted by CMOI), and April 26 to May 13, 1997 (CMOII). A time series station was occupied near 40.5°N, 70.5°W, and three across-shelf transects were performed, two in CMOI, before (August 17–18, 1996) and after (September 5–7, 1996) the time series and one after the time series for CMOII (May 12–13, 1997, Figure 1). *Sosik et al.* [this issue] and *Gardner et al.* [this issue] summarize the variability in optical and hydrographic properties during the time series.

Two WET Labs ac-9s were used to measure CDOM absorption, total absorption, and the absorption due to particles (by difference). To determine the contribution of dissolved materials to the total absorption coefficient, a 0.2 μm filter (Gelman Suporcap 100) was attached to the inlet of one ac-9. Both instruments were calibrated daily with optically pure water as a reference (Barnstead NANOpure) and corrected for temperature and salinity following *Pegau et al.* [1997]. The particulate absorption was corrected for scattering using method 3 (CMOI) and method 1 (CMOII) of *Zaneveld et al.* [1994]. Physical properties were measured on the same package with a SeaBird Electronics SBE-911 conductivity-temperature-depth (CTD) (a SBE-25 CTD was used after April 31, 1997). The data from the CTD and ac-9 were merged and binned to 1 m intervals.

The data were collected during daylight in sampling bursts (on average three per day) that lasted an average of 40 min (± 10 min) with an average of four casts per burst. In order to quantify the short-term variability in optical and physical properties the mean standard deviation and maximum standard deviation of bursts were computed for each depth. Daily means were computed by averaging the burst means. Data shallower

than 5 m were not used because of contamination by bubbles generated by the ship motion. The data analyzed here include 162 profiles (41 bursts) from CMOI before hurricane Edouard, 40 profiles (9 bursts) from CMOI after Edouard, and 136 (40 bursts) from CMOII.

During the analysis of the data the near-surface values of $a_g(676)$ were found to be of the order of -0.01 – 0.02 m^{-1} and decaying to ~ 0 at 10 m depth and below. Since we expect negligible absorption by CDOM at the infrared $a_g(676)$ was subtracted from the dissolved absorption at all wavelengths. This baseline offset removal procedure assumes that this depth-dependent error was not spectrally dependent. We have not been able to identify fully the source of this effect, but it appears to be related to changes in flow rate caused by the addition of the filter.

A noticeable difference in CDOM concentration was found between days 3 and 4 of CMOII, when the instrument measuring CDOM was changed. A vicarious correction was computed by matching the CDOM absorption along the 6° isotherms (~ 40 m depth) before and after the instrument change. The 6° isotherm was chosen because at this location neither surface nor bottom water mass intrusions were observed. The offset was found to be $+0.0095 \text{ m}^{-1}$ for the first 3 days. Similarly, a difference in salinity and density was observed between days 6 and 7 of CMOII when the CTDs were changed. The offsets were computed similarly to CDOM (salinity was $+0.05$ practical salinity units (psu), and density was $+0.03 \text{ kg m}^{-3}$ for the first 6 days). These offsets were added to the data. The adjustments were made to the shorter time record in each case. The offsets to the salinity and density make variations in the ancillary data more clear. Since these data are not used in calculations, it does not matter which period was adjusted. The offset to $a_g(440)$ was added to the data collected during the first 3 days because the spectral slope of the CDOM absorption during that time was inconsistent with the rest of the data collected. This suggests that the calibration error most likely occurred during the first 3 days. This temporal adjustment to the CDOM absorption was found to be spectrally dependent, but only the value at 440 nm is necessary for the discussion in this text.

The spectral slopes of a_g were found to be on average $\sim 0.018 \text{ nm}^{-1}$ (excluding the first 3 days of CMOII), within the range of published values [e.g., *Roesler et al.*, 1989] and observed by *DeGrandpre et al.* [1996] and *Vodacek et al.* [1997] in the Mid-Atlantic Bight, increasing our confidence in our calibration procedure. In order to estimate the effect of the subtraction of $a_g(676)$ on the vertical structure of $a_g(440)$ the corrected absorption data were compared to CDOM fluorescence measurements on the sampling platform (WET Labs Spectral Absorption and Fluorescence Instrument (SAFIRE), excitation/emission, 265 nm/460 nm) for randomly selected measurement profiles where both were available. The two independent measurements of CDOM concentration were found to be highly correlated (average $R^2 = 0.95$), increasing our confidence in our processing procedure.

For comparison with data collected previously in the South Atlantic and Mid-Atlantic Bights we include in our analysis data from *Nelson and Guarda* [1995], *DeGrandpre et al.* [1996], and *Vodacek et al.* [1997]. When absorption near 440 nm was not measured (first and last study), we extrapolated to 440 nm, assuming $a_g(440) = a_g(\lambda)e^{-0.018(440-\lambda)}$, on the basis of the value of the spectral slope (0.018 nm^{-1}) observed in these studies.

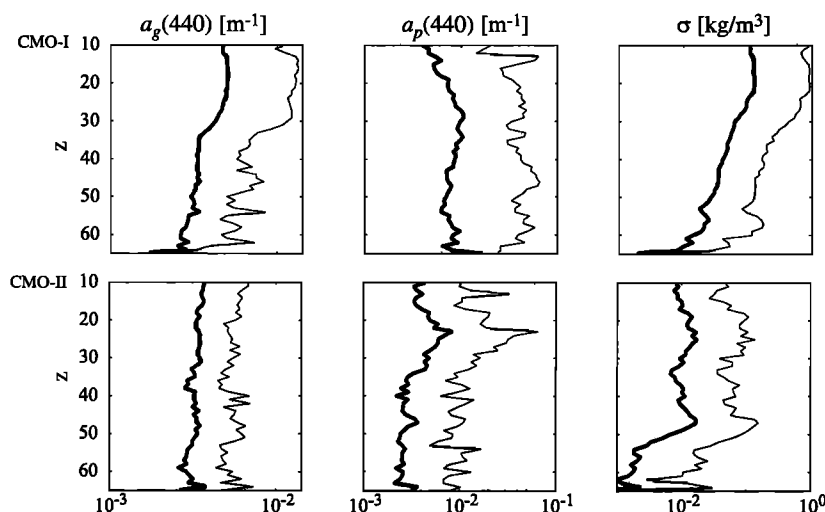


Figure 2. Mean (bold) and maximum of the standard deviation (over 40 min sampling bursts) of $a_g(440)$, $a_p(440)$, and densities for CMOI (prior to hurricane Edouard) and CMOII. The minimums were lower than the resolution of the instruments.

3. Results

The results are presented for different temporal and spatial sampling scales. We present the particulate fraction absorption at 440 nm, $a_p(440)$, for comparison, since together with $a_g(440)$ and the (almost) constant absorption of water, it constitutes the total absorption. *Sosik et al.* [this issue] discuss the main sources of variability in $a_p(440)$. Physical forcing, sinks, and sources near boundaries are expected to result in a variation of optical properties that depend on the physical distance from the boundary (z). In the interior, on the other hand, optical properties tend to stay constant along isopycnals. In order to separate the variability of optical properties at constant depth from that on constant isopycnal surfaces the variability of the optical properties as well as density are quantified at constant depths, and the covariance of density and optical properties is computed. Salinity is presented in order to compare it with the $a_g(440)$ distribution; in the simplest case, where the only source is riverine input of constant CDOM concentration, the two should inversely covary. Last, temperature is presented in order to assess changes in optical properties within water masses of constant hydrographic properties.

3.1. Temporal Variability

3.1.1. Short-term variability (40 min bursts sampling). When strong stratification is present (CMOI), CDOM variability (its standard deviation as a function of depth) correlates with the variability in density (Figure 2, correlation coefficient r of the standard deviation of all bursts, $r = 0.8$). This implies that on this timescale, CDOM behaves to a large extent conservatively and its variability is mostly due to isopycnal advection. The maximum in variability occurs at the pycnocline(s) during times of intense high-frequency internal wave activity associated with solitary wave packets [*Boyd et al.*, 1997; *Chang and Dickey*, this issue]. During CMOII, variability in CDOM is smaller than the instrument accuracy ($0.005 m^{-1}$, precision is $\sim 0.002 m^{-1}$), and the correlation between density and a_g is weak ($r = 0.18$). Higher variability near the bottom, where density is nearly constant, is suggestive of nonconservative processes and/or advection there. Particulate absorption a_p in both cruises is more variable than a_g . In CMOI, variability in

a_p correlates less with density ($r = 0.23$ for CMOI and $r = 0.31$ for CMOII). The short-term variability is higher, on average, in all properties in CMOI relative to CMOII (Figure 2).

3.1.2. Mesoscale variability. Over scales of 4–5 days the CMOI density and a_g exhibit wave-like variation (Plate 1) in the thermocline, indicating the potential presence of low-frequency Rossby or Kelvin waves associated with the shelf break front or the bottom topography. These waves cause vertical displacements of $O(5 m)$ at the pycnocline and can also be observed in the more evenly spaced CTD data set collected during the same cruise *Gardner et al.* [this issue] and in the current record of *Boyd et al.* [1997].

Intrusions of oceanic warm salty waters were observed during several occasions of both cruises. During CMOI, intrusions occurred on August 22, 25, and 27 and August 31 to September 1, 1999 (Plate 1). W. S. Pegau (Mixing of optical properties as evidenced in salinity intrusions observed over the continental shelf in the Middle Atlantic Bight, submitted to *Journal of Geophysical Research*, 2000, hereinafter referred to as Pegau et al., submitted manuscript, 2000) discuss intrusive features observed between August 25 and 27 associated with meandering of the shelf break front intruding at the base of the mixed layer and near the bottom. Within these intrusions, Pegau et al. (submitted manuscript, 2000) found CDOM mixed conservatively, while particulate absorption did not. In the spring, between May 4 and 6, a salty bottom intrusion is observed, and after May 7 a fresh water mass is observed in the upper 20 m. The salty bottom intrusion is associated with relatively low CDOM absorption, while the fresh surface intrusion is associated with higher values of CDOM.

3.1.3. Variability due to storms. Intense episodic storms (wind stress $> 0.4 N m^{-2}$) occurred during both cruises; during CMOI (September 2, 1996) the eye of hurricane Edouard passed 110 km from the time-series station while a series of spring storms took place during CMOII (April 27, 1997, May 4, 1997, and May 7, 1997). These storms have contributed to the variability in optical properties by vertically mixing gradients, reducing the physical stratification and resuspending sediments (Plate 1). Edouard reduced the near-surface gradients in CDOM while increasing the near-bottom gradients in partic-

ulate absorption (Plate 1). The spring storms caused mixing of the optical properties down to 20 m (Plate 1).

3.1.4. Seasonal variability. The vertically averaged CDOM value at the CMO site is decreased by $0.01 \pm 0.005 \text{ m}^{-1}$ from fall to spring. This difference is associated with the mean salinity during CMOI being, on average, 0.25 ± 0.06 psu fresher than during CMOII. During the spring, CDOM is less stratified than in the summer (Plate 1). The hydrographic and CDOM absorption properties of the waters denser than the shelf break front ($\sigma > 25.5$) and below the pycnocline are nearly constant throughout the year (Plate 2 and Figure 3).

3.2. Spatial Variability

3.2.1. Vertical structure of CDOM during the time series. Throughout both cruises, values of a_g monotonically increase with depth except for the last 4 days in CMOII where, near the surface, a low-salinity high- a_g water mass is present.

3.2.2. Variability in transects. The optical and hydrographic properties in the first transect are strongly stratified (Plate 2). Values of a_g above the shelf exhibit a subsurface maximum at depths of 40–60 m and a minimum near the surface. The bottom maximum in a_g near the 60 m isobath is associated with the 20–30% elevated particulate absorption a_p values.

The second transect, performed after the hurricane passage, shows little correlation between physical and optical properties. While the water column has restratified, intense resuspension of particles has taken place near the 60 m isobath. Vertical gradients of a_g are weak with bottom and surface maximum observed toward shore coincident with a maximum in a_p . Horizontal gradients in a_g following the hurricane are stronger than the gradients in the first transect.

The spring (CMOII) section exhibits low vertical stratification in both hydrography and optical properties. Values of a_g are higher both at the surface and bottom above the shelf (midwater minimum).

3.3. Salinity- a_g Relationship

In the case where the only CDOM source is riverine input, one would expect a_g to increase with decreasing salinity s as oceanic waters dilute the riverine input. Indeed, at the surface in the South Atlantic and Mid-Atlantic Bights a linear inverse relationship of salinity and a_g has been observed in previous studies [DeGranpre *et al.*, 1996; Nelson and Guarda, 1995; Vodacek *et al.*, 1997]; this is also the general trend observed in our spatial sections (Figure 3). By dividing the data into two seasons and adding the data of DeGranpre *et al.* [1996] and Vodacek *et al.* [1997] (collected 3 years earlier and downstream from the CMO site) we observe the following trends: (1) Variability in CDOM concentration within waters of given salinity is much higher in the late summer; twofold differences in CDOM absorption are found in waters with salinity from 31.5 to 32.3 psu in that time. (2) There is little variability in the deep waters beyond the shelf break front ($s > 32.3$) compared to the near-surface waters. The data of DeGranpre *et al.* [1996] and Vodacek *et al.* [1997] fit the trends observed in our data well, suggesting a consistency in the range of CDOM values over a 3 year timescale. (3) The CDOM absorption values from the fall, measured after the hurricane passage, obey a similar relationship with salinity as the spring data (approximate linear relationship $a_g(440) = -0.0157s + 0.58$). This relationship is different from that computed with the data taken in the fall prior to the hurricane passage ($a_g(440) = -0.032s +$

1.155 , computed without using the absorption values close to the surface, where photo-oxidation may be present).

The data of Nelson and Guarda, [1995, Figure 8] from the South Atlantic Bight have values of CDOM absorption at least a factor of 2 higher than those observed in the Mid-Atlantic Bight in the late summer and spring for the same salinity values (approximate linear relationship: $a_g(440) = -0.0727s + 2.618$). This may be due to (1) higher CDOM concentration in riverine inputs from south of the Mid-Atlantic Bight (e.g., from the Chesapeake Bay). (2) Accumulation of CDOM derived from in-water productivity and/or sediment-released CDOM into the southward flowing waters originating in the Mid-Atlantic Bight.

The correlation between salinity and CDOM absorption in the surface layer is season-dependent as observed in the referenced studies as well as here. At each depth horizon, a_g decreases and s increases with distance from shore. However, the observed relationship between s and a_g in the vertical during the time series station is, most frequently, opposite to the horizontal relation, with a_g increasing with increasing s (Plate 1).

4. Discussion

4.1. Role of Advection Versus Local Change

The short-term variability is higher in all properties in CMOI relative to CMOII. Some of this variability is associated with isopycnal advection due to higher stratification and associated internal wave activity (Plates 1 and 2). Other sources of short-term variability may be horizontal advection of horizontal gradients in absorption ($u \partial a_g / \partial x$) as well as variability due to local processes. The mean horizontal velocities during CMOI were of the order of 0.2 m s^{-1} (the upper 95% was 0.4 m s^{-1}) [Boyd *et al.*, 1997]. For a local change in CDOM absorption of the order of 0.01 m^{-1} over a 40 min interval to be totally due to horizontal advection by a 0.2 m s^{-1} current, the spatial gradient has to be of the order of 0.2 m^{-1} over 10 km. The maximum along-isopycnal CDOM gradients observed in the transects were of the order of 0.005 m^{-1} over 20 km. This is consistent with the vertical advection of isopycnals being the main cause for CDOM variability in CMOI, resulting in a high correlation between the variability in density and that in CDOM absorption during this time.

4.2. Storms and Seasonal Variability

The effect of a single storm can cause as much variability in CDOM absorption as is observed between seasons. Over the shelf the difference in values of a_g at the beginning and end of CMOI ($\Delta t \approx 3$ weeks) is larger than the difference in a_g between the end of CMOI and CMOII ($\Delta t \approx 8$ months, Plate 2 and Figure 3). Seasonal variability, in addition to winter vertical mixing, includes potential changes in $a_g - s$ in riverine sources and effects of seasonally modulated primary and secondary productivity. Our data are by no means adequate to resolve these processes.

4.3. Variability of CDOM in the Water off the Shelf Break Front

CDOM properties beyond the shelf slope front are found to vary little throughout the year (Figure 3), suggesting that processes affecting CDOM in these waters have timescales longer than O(6 months). It is interesting that a nearly linear rela-

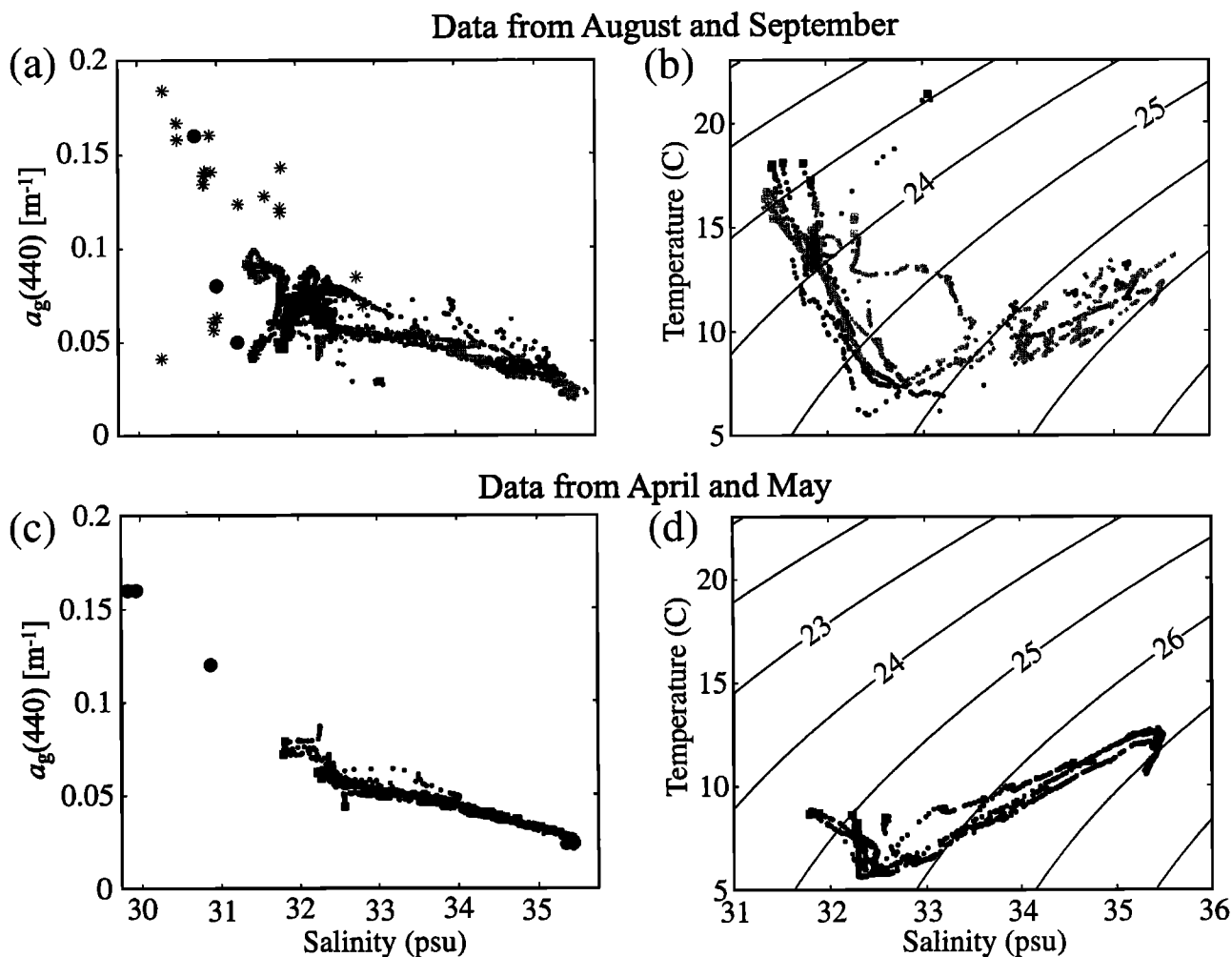


Figure 3. (a) and (b) The $a_g(440)$ -salinity and temperature-salinity diagrams compiled with the data collected during the summer-fall transect (August 17–18, 1996, solid dots) and the post-hurricane Edouard transect (September 5–7, 1996, shaded dots) and data collected 3 years earlier in the Mid-Atlantic Bight from *Vodacek et al.* [1997, Table 1] (extrapolating to 440 nm assuming $s = 0.018$ on the basis of *Vodacek et al.* [1997, Figure 7], denoted by stars) and by *DeGranpre et al.* [1996, Table 1] (and 442 nm absorption given by *Vodacek et al.* [1997, Figure 7], denoted by solid circles). (c) and (d) The data from the spring transect (May 12–13, 1997). Squares denote the 5 m data of each sampling station.

relationship still exists between salinity and CDOM within these waters despite their distance from riverine input.

4.4. Primary Productivity As Source for CDOM

Primary production over Georges Bank and the Mid-Atlantic Bight, where the CMO site is located, is nearly five times higher than the mean oceanic productivity [O'Reilly *et al.*, 1987]. Primary productivity is an important source of DOC at Georges Bank and the Mid-Atlantic Bight; on average, 14% of the primary production is released as DOC [O'Reilly *et al.*, 1987]. In our data there is no correlation between particulate and CDOM absorption, though on the basis of DOC budgets, phytoplankton is an important source. Even in the open ocean, where CDOM is believed to be mostly the result of primary production, no correlation has been found between biomass and CDOM [Bricaud *et al.*, 1981], suggesting that the other processes controlling CDOM distribution have a higher temporal frequency of variability, masking the contribution from this source.

4.5. Benthic Source

A back of the envelope calculation based on observed coastal benthic fluxes of DOC in Chesapeake bay ($2 \text{ mmol DOC m}^{-2} \text{ d}^{-1}$) [e.g., *Burdige and Homestead*, 1994] suggests a 440 nm absorption flux of the order of $0.01 \text{ m}^{-1} \text{ m}^{-2} \text{ d}^{-1}$ (assuming that half of DOC is CDOC and a specific absorption at 440 of $0.7 \text{ m}^{-1} (\text{mg L}^{-1})$ on the basis of *Blough et al.* [1993]). O'Reilly *et al.* [1987] found the annual primary production in the vicinity of the CMO site to be of the order of $210\text{--}450 \text{ g C m}^{-2}$ [O'Reilly *et al.*, 1987, Table 21.3]. Walsh *et al.* [1987] estimated that between 5 and 10% of the annual primary production is released as organic DOC from the sediment [O'Reilly *et al.*, 1987, Table 22.2]. These numbers suggest an absorption flux of the same order of magnitude as those observed by *Burdige and Homestead* [1994]. In order for the benthic flux to have a significant effect relative to the background values, near-bottom CDOM has to accumulate over a period of the order of a few weeks.

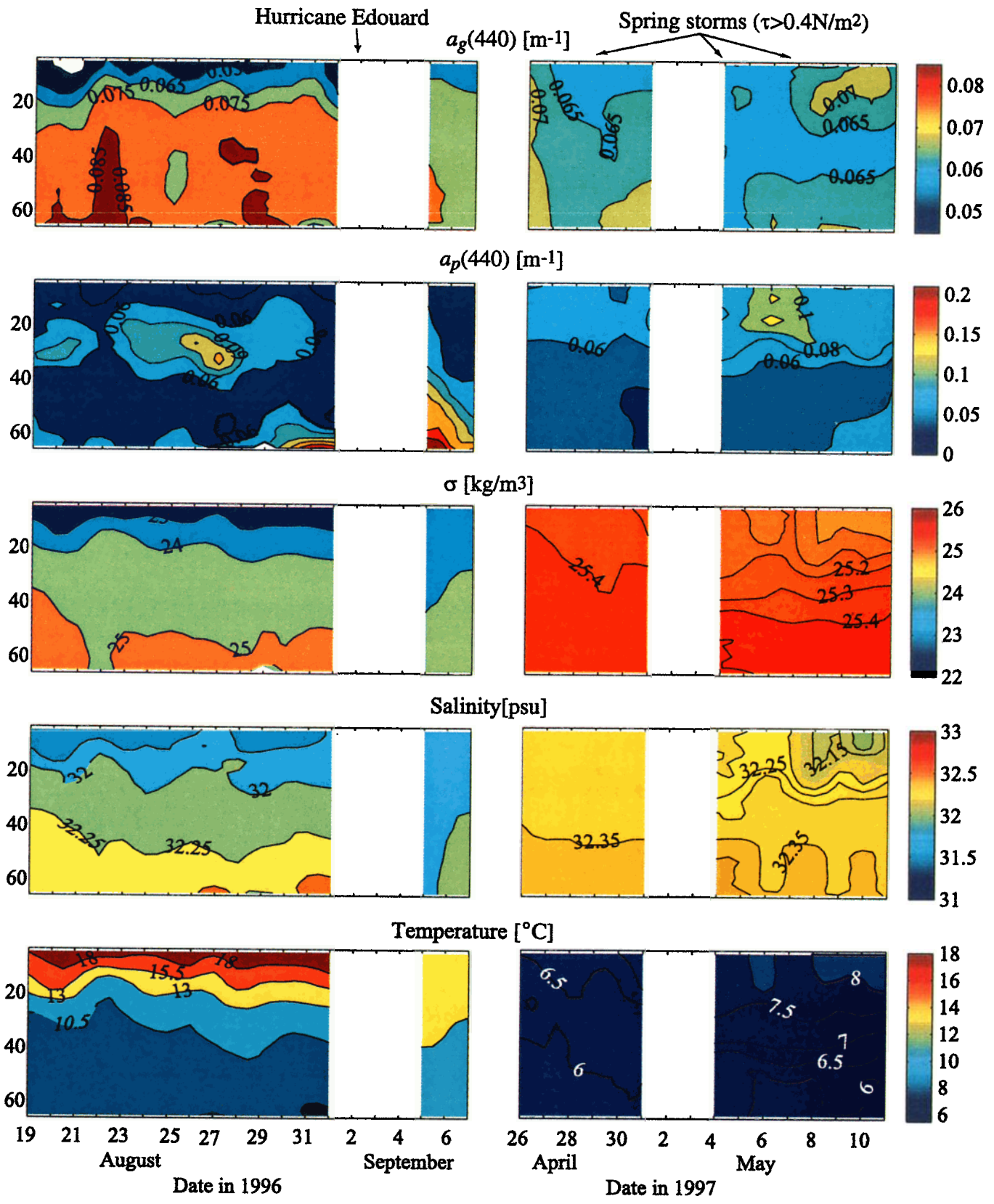


Plate 1. Contour plot of daily mean of $a_q(440)$, $a_p(440)$, salinity, and density at the time series station. Contour density is different for the two cruises because of a weaker stratification in CMOII. In both cruises, $a_q(440)$ increases near the bottom associated with bottom resuspension (higher $a_p(440)$) following storm passage.

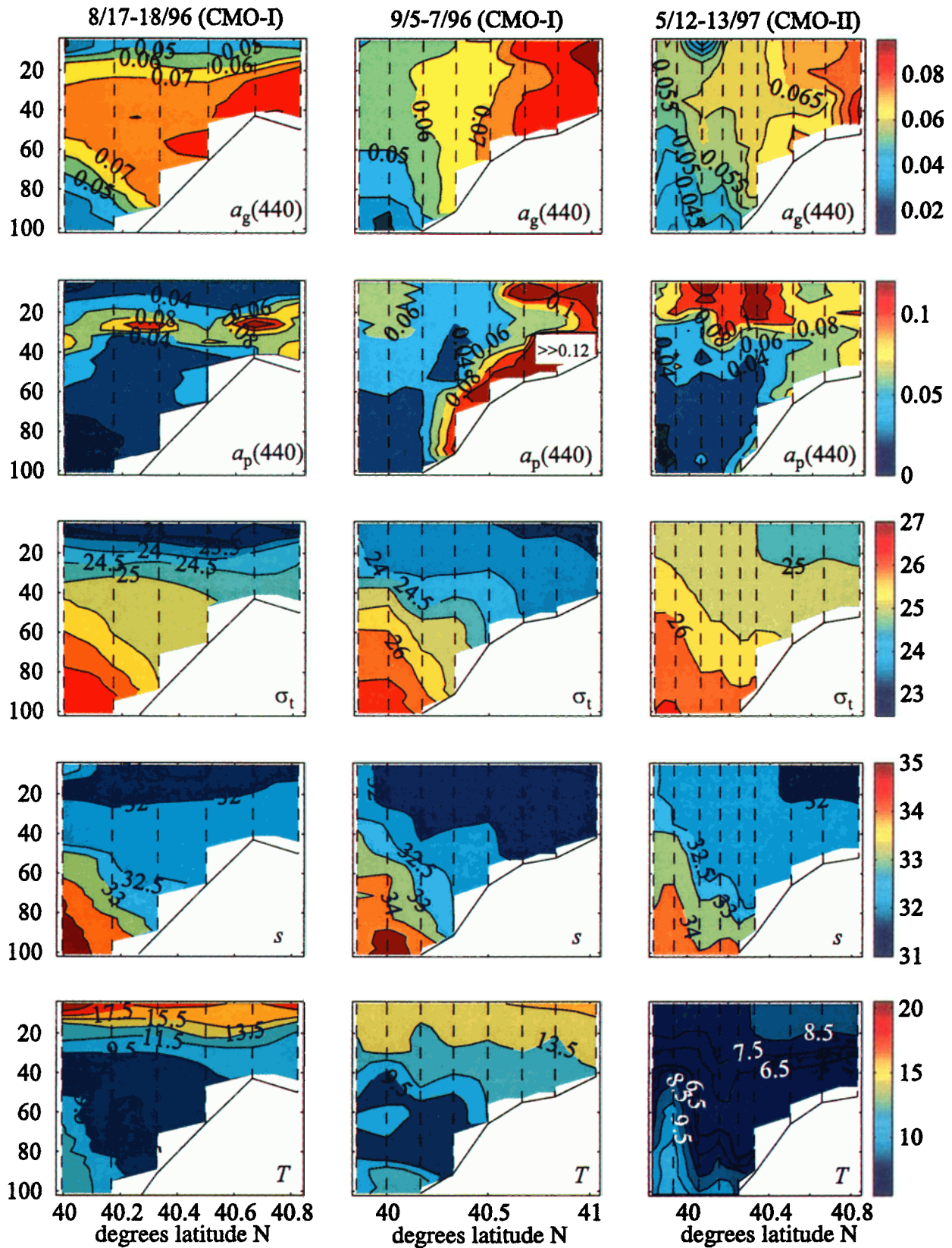


Plate 2. Contour plot of $a_g(440)$, $a_p(440)$, salinity, and density of three spatial transects. The bold black line indicates bottom depth at each sampling station. Dashed lines denote the location of the sampling stations. Notice the decrease in stratification following the hurricane passage (second transect) and spring transects compared to the late summer transect. Notice an elevated value of $a_g(440)$ near the bottom in all transects to the north of 40.5°N near the 60 m isobath.

While diffusive fluxes may be low, sudden stirring of the sediments may release water with very high concentration of CDOM. CDOM concentrations in the upper sediment of coastal waters have been found to be 5 times higher than those above waters (e.g., D. J. Burdige et al., *Fluorescent dissolved organic matter in marine sediment pore waters*, submitted to *Marine Chemistry*, 1999) while CDOM fluorescence in the upper meter of anoxic sediments has been observed to be 10–500 times higher than the overlying waters [Chen and Bada, 1994]. In all the transects we observe higher values of a_g on top of the shelf, in correlation with higher particulate values. In the last two transects a midwater minimum in CDOM absorption is observed on top of the shelf, uncorrelated with the hydrographic properties (Plate 2). A sedimentary source is consistent with such a pattern. Similarly, the strong gradient along isopycnals following the hurricane suggests that CDOM and particulate absorption have not mixed conservatively. Following the hurricane, a_g increased in the freshest waters ($s < 32$ psu), while it decreased in the saltier waters ($s > 32$ psu). This decrease in CDOM absorption may be due to vertical mixing of salty waters with the relatively CDOM-poor fresher water. The increase in CDOM of the freshest waters may be due to a benthic injection of CDOM into the waters on the shallow part of the shelf. This is also consistent with increasing bottom stress and elevated resuspension activity in shallower water caused by the wind and waves associated with the hurricane. Advection of a freshwater mass of a different CDOM-salinity relationship than that previously found on the shelf cannot be ruled out.

4.6. Photooxidation

Though we do not observe a direct reduction of surface a_g during the time series, photo-oxidation may have been present and is probably the main contribution to the trend of decreased CDOM in waters of decreased salinity observed above the shelf (Plate 1). The mean a_g distribution as a function of depth in the late summer could be the result of a balance of photo-oxidation in the mixed layer (ML) and a diffusive flux from lower in the water column (integrating the conservation equation over the ML):

$$0 = -H_{ML}\gamma a_g + K da_g/dz \text{ (at } z = H_{ML}\text{)},$$

where H_{ML} is the ML depth, γ is the ML-averaged photo-oxidation rate, and K is the eddy diffusivity. Taking $H_{ML} \approx 10$ m, $K \approx 2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ (on the basis of the in situ microstructure measurement of MacKinnon and Gregg (personal communication, 1998)), and the relative vertical gradient of CDOM across the ML base $a_g^{-1} da_g/dz \approx 0.2 \text{ m}^{-1}$ (Plate 1), the average photo-oxidation rate constant γ corresponds to a timescale (γ^{-1}) of the order of 1 month. Given that K varied by a factor of 5 near the ML base, this value should be interpreted as an order of magnitude estimate of the rate. This value is consistent with the estimated photo-oxidation rates of Nelson et al. [1998] and Vodacek et al. [1997]. We cannot, however, rule out the possibility that the surface reduction was due to the advection of lower CDOM waters, though this is unlikely given the general trend of decreasing CDOM with decreasing salinity observed in the time series (Plate 1). Photo-oxidation of a_g is a well-documented process and has been previously observed in the Mid-Atlantic Bight [Vodacek et al., 1997].

5. Conclusion

Our data set is unique in that it resolves the whole water column and includes both temporal and spatial information. These data, together with previous studies, suggest that the distribution of a_g is determined by a coastal riverine source, a shelf bottom source, and a photo-oxidative sink at the surface. Advection and diffusion by the background flow further modulates the distribution of CDOM absorption. There may also be an additional in-water source of CDOM associated with phytoplankton [Twardowski, 1998], which we did not observe in our data, though it may contribute to the different $a_g - s$ relationship observed farther downstream at the South Atlantic Bight [Nelson and Guarda, 1995]. This sink/source layout results in a spatial distribution of CDOM, which is decreasing away from shore (with increase in salinity) and increasing with depth at the shelf (also with increase in salinity).

Short-term variability in the vertical distribution of a_g was found to be mostly due to conservative processes consistent with the advection of isopycnals. Over periods of weeks and longer, sources and sinks of a_g cause a distribution that deviates from that of physical properties near the surface and above the shelf. Episodic storms are found to have an important role in the high-frequency variability in a_g through both redistribution and resuspension of bottom sediment.

Over the shelf, salinity and CDOM are found to have a different relationship depending on the seasons, as was found previously [DeGrandpre et al., 1996; Nelson and Guarda, 1995; Vodacek et al., 1997]. Beyond the shelf break front, subsurface a_g was found to behave in a conservative fashion for a period longer than 8 months (Plate 2 and Figure 3). Comparison of the (scarce) data obtained for this study and those of past studies over the Mid-Atlantic Bight shelf suggests that the seasonal cycle repeats itself over the years.

The variability in $a_g(440)$ is found to be significantly smaller than that in $a_p(440)$ on all timescales and space scales. However, the average magnitude of the dissolved absorption is similar to that of the particulate fraction at 440 nm, providing a similar contribution to the total absorption. This implies that high-frequency variability of ocean color in a given surface water mass is most likely due to variations in the particulate fraction.

Further study of the spectral shape (the exponential slope) of a_g is required to distinguish between marine and terrestrial sources and to determine whether the surface a_g has been photo-oxidized [e.g., Carder et al., 1989; Vodacek et al., 1997]. We do not have the spectral resolution to address this question fully with our data set.

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