SPATIAL AND TEMPORAL VARIATION OF CHROMOPHORIC DISSOLVED ORGANIC MATTER ABSORPTION IN THE CARIBBEAN

By

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ABSTRACT

Spatial and temporal variation of Chromophoric Dissolved Organic Matter (CDOM) absorption was studied in the course of diverse research cruises through the Caribbean region. CDOM absorption and spectral slopes showed marked seasonal and spatial variability. Temporal trends showed maximum mean surface CDOM absorption and spectral slopes during summer. The spatial analysis showed highest absorption values in the Gulf of Paria. Values remained relatively high along the Orinoco River Plume throughout the Eastern Caribbean. High values were also found along the edges of a cyclonic eddy with entrained Orinoco River Plume waters. Values outside of the plume were found to be low. Differences found on spectral slopes point to spatial-temporal differences in water mass sources in the Caribbean. Mesoscale eddies affect the spatial and temporal distribution of CDOM by advection of the Amazon and Orinoco River plumes into the Eastern Caribbean basin creating complex mosaics of optically clear and optically dense waters.

RESUMEN

Se estudiaron las variaciones espaciotemporales de la absorción de materia orgánica disuelta coloreada (MODC) durante diversos cruceros de investigación a través de la región del Caribe. Tanto la absorción como las pendientes espectrales mostraron marcada variabilidad estacional y espacial. Las tendencias temporales mostraron un máximo de absorción promedio de MODC durante el verano en superficie. El análisis espacial mostró valores máximos de absorción en el Golfo de Paria. Los valores se mantuvieron relativamente altos a lo largo de la pluma de descarga del Río Orinoco en todo el Caribe Oriental. También se encontraron valores altos a lo largo de los bordes de un remolino ciclónico que arrastraba aguas de la pluma del río Orinoco. Se encontraron valores bajos fuera de la pluma. Diferencias encontradas en las pendientes espectrales apuntan a diferencias espaciotemporales en la naturaleza de las fuentes de masas de agua en el Caribe. Los remolinos de mesoescala afectan la distribución especial y temporal de MODC por advección de las plumas de los ríos Amazonas y Orinoco a la cuenca del Caribe Oriental creando complejos mosaicos de aguas ópticamente claras con aguas ópticamente densas.

For teaching me to never give up,
and to live as if each day was the last.
for always believing in me and motivating me
to fulfill my dreams. Thanks Dad

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"It is good to have an end to journey toward; but it is the journey that matters, in the end" Ursula K. LeGuin

"*To get through the hardest journey we need take only one step at a time, but we must keep on stepping*" Chinese Proverb

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1. Introduction

1.1 Motivation

Chromophoric Dissolved Organic Matter (CDOM) is a chemically complex material which can be found in natural waters. It is produced by the decay of plant and algal matter and is frequently refractory to microbial decomposition. It is photochemically reactive, being destroyed when exposed to solar radiation, forming a variety of intermediates and products (Coble, 2007).

In waters influenced by river input, CDOM can compromise the determination of phytoplankton biomass from satellite measurements (Blough and Del Vecchio, 2002). It is frequently the major light absorbing constituent of the DOM pool in natural waters, absorbing not only visible light, but also UV-A and UV-B. Furthermore, it contributes significantly to the attenuation of photosynthetically available radiation (PAR).

The profound effect of CDOM on the optical character of marine waters is especially important for remote sensing applications since it can affect the accuracy of chlorophyll determinations through satellite imagery. The objective of this study is to document the effect of CDOM on the optical properties of near-surface Caribbean waters. For this purpose we characterized range and spatial and temporal variability of its absorption spectrum in the visible range.

1.2 Background

In order to determine the amount of CDOM in a sample, its optical properties or parameters derived from them are frequently used. One of the optical properties usually measured to characterize CDOM is its absorption. Absorption spectra typically decrease exponentially with increasing wavelength. These spectra have been typically fit to the expression:

$$a_{CDOM}(\lambda) = a_{CDOM}(\lambda_0)\exp^{-S(\lambda-\lambda 0)} \quad \textbf{1.1}$$

Where $a_{CDOM}(\lambda)$ and $a_{CDOM}(\lambda_0)$ represent the absorption coefficients at a given wavelength and a reference wavelength, respectively, and S represents the spectral slope. The absorption coefficients are calculated by a relation between the absorbance, the pathlength and a conversion factor from log to natural log, which can be found on the Methods section (Eq. 2.1). As shown above, the spectral slope parameter is derived from absorption, which has proven to be useful in remote sensing applications of ocean color (Coble, 2007). This parameter characterizes the spectral dependence of the CDOM absorption coefficient, providing information about the origin of the CDOM chromophores. It can vary due to CDOM source, but can also be affected by alterations to the material (Blough and Del Vecchio, 2002). Spectral slopes are usually lower for freshwater and coastal environments and higher in oligotrophic waters. These differences might be due to the shift in CDOM source, but photobleaching could also play an important role (Coble, 2007). Photochemical bleaching has been shown to account for spectral slope gradients observed from coastal to offshore waters (Vodacek et al., 1997; Blough and Del Vecchio, 2002).

1.3 Literature Review

Transport by rivers of terrestrially derived chromophoric dissolved organic matter represents an important source of organic carbon to the oceans. This injection of CDOM could alter the optical and photochemical properties of marine waters in the region of outflow (Blough et al., 1993).

The magnitude of CDOM absorption varies considerably along salinity gradients, it can range from over 15 m^{-1} for some coastal and fresh waters to less than 0.1 m^{-1} for surface oligotrophic seawaters, when measured at 355 nm. (Blough and Del Vecchio, 2002). For coastal waters strongly influenced by river discharge, CDOM absorption frequently dominates the total light absorption not only in the UV region, but also in the blue wavelengths overlapping with a portion of the phytoplankton absorption spectrum (Blough and Del Vecchio, 2002).

Significant levels of terrestrial CDOM can get transported beyond coastal areas, extending well offshore for regions experiencing large freshwater inputs (Blough and Del Vecchio, 2002). The eastern Caribbean is an example of such regions, presenting relatively high levels of CDOM absorption (a_{CDOM} 355 ~ 0.6 m^{-1}) during the Orinoco River high flow period (Blough et al., 1993; Del Castillo et al., 1999). Major rivers such as the Orinoco and Amazon can have a significant impact on the optical properties of ocean waters over extensive geographical areas, by seasonal injection of CDOM. (Müller-Karger et al., 1989; Blough et al., 1993; Hochman et al., 1994; Del Castillo et al., 1999).

1.4 Objectives

The main objective of this study was to determine the spatial and temporal variation of CDOM abundance due to freshwater inputs in the NE Caribbean by the two major South American rivers, the Amazon and the Orinoco. The study was designed to characterize CDOM in these waters and to assess the effect of mixing and photoptical changes on the optical properties of this material. A further objective was to assess the contribution of CDOM absorption to the attenuation of photosynthetically active radiation k_d (PAR).

These goals were achieved by analyzing absorption and fluorescence of discreet water samples collected from monthly cruises to the Caribbean Time Series (CaTS) station and research cruises carried throughout the Caribbean basin.

2. Materials and Methods

2.1 Sample Collection

Water samples were collected from Niskin-type Ocean Test Equipment Teflon lined bottles mounted on an SBE 32 rosette at 0, 10, 25, 50, 75, 100, 125, 150 and 200 meters. Samples were drained to acid washed fluorinated polypropylene bottles and stored refrigerated until analysis. Samples were filtered with pre-combusted and sample rinsed Whatman GF/F filters either before analysis or directly from the Niskin bottle. The definition of CDOM is operational, depending on the method used to separate between the dissolved and particulate fractions, usually regarded as organic substances that absorb light in the UV and visible portion that pass through a submicrometer filter (Nelson and Siegel, 2002). Even though 0.2 μm filters are more commonly used for this purpose, GF/F filters (0.7 μm) are widely used for several oceanographic and optical measurements on pigment absorption (Ferrari, 2000).

2.1.1 Caribbean Time Series (CaTS)

The Caribbean Time Series (CaTS) station is located at 17°38' N, 67 °W, about 23 nautical miles off the southwestern coast of Puerto Rico, and is occupied monthly by the Department of Marine Sciences of the University of Puerto Rico, Mayagüez Campus. CaTS provides an observing station for researchers interested in the characterization of physical, chemical, and biological variability of upper ocean features and asses the optics and biogeochemistry of regional waters (Corredor and Morell, 2001). Samples were collected during separate monthly cruises on board the R/V Chapman coinciding with the Orinoco River different flow periods; the dates of the cruises can be seen below (Table 2.1).

TABLE 2.1 Dates of samples taken on CaTS cruises.

Year	Date	FI	a_{CDOM}
2003	August 19	X	X
	September 9	X	
	November 4	X	X
	December 9	X	X
2004	April 13	X	X
	May 4		X
	July 8	X	X
	August 3	X	X
	September 22	X	X
	October 29	X	X
	November 23	X	X
	December14		X
2005	January 18	X	X
	February 16		X
	April 28		X
	June 9		X
	August 15		X

2.1.2 Caribbean Vorticity Experiment Cruises (CaVortEx)

Four cruises were undertaken as part of an ONR funded project titled "Characterization of Caribbean Sea Mesoscale Eddies" in order to describe the structure of mesoscale eddies situated in the Caribbean Sea. The first three cruises were performed on board of the R/V Chapman from the University of Puerto Rico and the last one on board the R/V Pelican from the Louisiana Universities Marine Consortium (LUMCON). Table 2.2 presents a summary of CaVortEx stations where water samples for CDOM measurements were collected and their respective position.

TABLE 2.2 Coordinates of CaVortEx Cruises Stations

	CaVortEx I		**CaVortEx II**		**CaVortEx III**		**CaVortEx IV**	
Stations	**Latitude (N)**	**Longitude (W)**	**Latitude (N)**	**Longitude (W)**	**Latitude (N)**	**Longitude (W)**	**Latitude (N)**	**Longitude (W)**
CAV 1	15.874	-67.920	16.176	-67.262	-	-	15.566	-74.301
CAV 2	13.834	-67.835	16.630	-66.387	17.340	-67.850	16.000	-74.292
CAV 3	14.833	-67.833	16.420	-66.833	-	-	16.105	-74.497
CAV 4	16.083	-67.833	17.000	-65.667	17.000	-67.240	16.621	-74.512
CAV 5	15.541	-68.847	16.801	-66.050	16.980	-67.480	17.068	-74.501
CAV 6	15.302	-68.355	17.200	-65.300	17.000	-67.700	17.567	-74.500
CAV 7	-	-	17.417	-64.867	16.750	-67.700	17.842	-75.252
CAV 8	-	-	-	-	17.250	-67.700	-	-

2.2 Absorption spectroscopy

Absorption spectra were obtained using a Shimadzu UV 1601 double-beam spectrophotometer with 10 cm quartz cells. Measurements were made against air between 280 to 700 nm at 0.5 nm intervals. Each sample was scanned three times and the resulting spectra were averaged to reduce noise and yield a more robust spectrum (Conmy et al., 2004). B & J Brand High Purity Water for Spectroscopy use was also scanned and subtracted from the averaged spectra. Data were then corrected for baseline fluctuation and scattering by subtracting from each wavelength the measured absorption at 700 nm (Bricaud et al., 1981). Figure 2.1 presents an example of the spectrum correction performed before the absorption coefficient calculation.

Absorbance values were converted to absorption coefficients using the equation:

$$a(\lambda) = 2.303\ A\ (\lambda)\ /\ r \qquad \textbf{2.1}$$

Where, A is the absorbance at a given wavelength, and r is the pathlength in meters.

The absorption coefficients at 355, 412 and 443 nm were used as an index for CDOM abundance. Spectral slope coefficients (S) were calculated for the range of 320-650 by fitting each spectrum to the following equation:

$$a_{CDOM}(\lambda) = a_{CDOM}(\lambda_0)\exp^{-S(\lambda-\lambda_0)} \qquad \textbf{2.2}$$

We used 412 nm as the reference wavelength (λ_0). The non-linear regression was carried out in the Origin 6.0 software (Microcal Software, Inc. 1999)

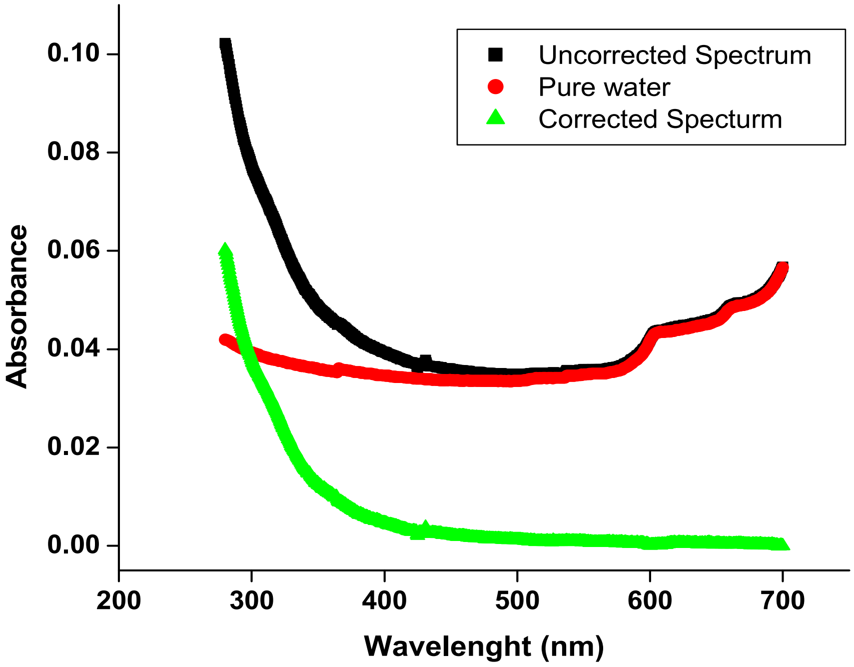

Figure 2.1 Example of absorbance spectrum correction.

2.3 Fluorescence spectroscopy

Fluorescence spectroscopy was performed with a Hitachi F-2000 fluorescence scanning spectrophotometer. Sample emission was scanned from 350-600 nm upon excitation at a wavelength of 350 nm. The resulting spectra were normalized to the water-Raman intensity of the blank after being corrected by the sample Raman intensity.

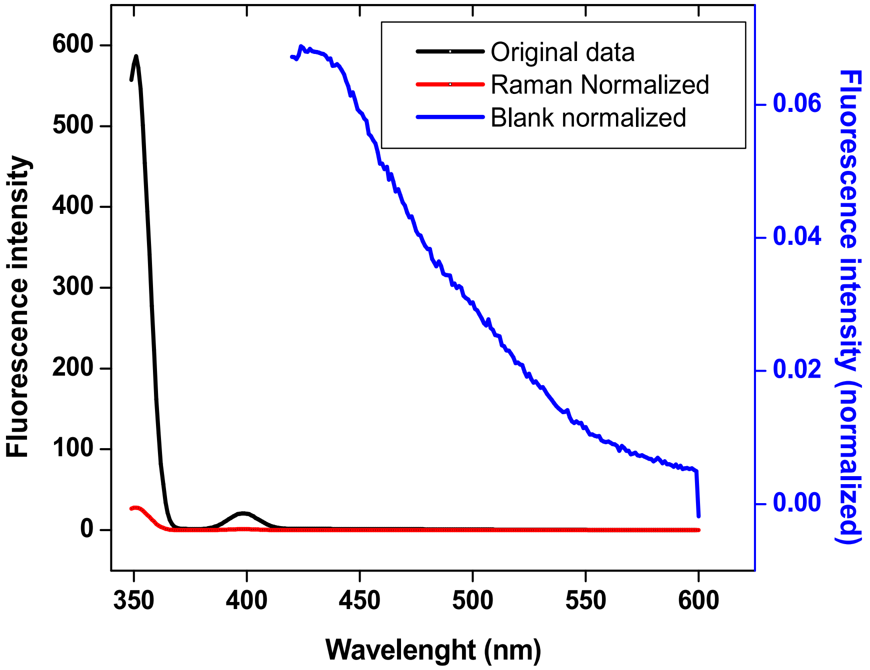

Figure 2.2 Example of a fluorescence spectrum correction
The black line represents a raw spectrum, the red line represents a spectrum after being normalized to its Raman peak and the blue line represents the fluorescence intensity normalized to the Raman peak of the blank.

3. Results

3.1 Temporal Variations at Caribbean Time Series Station

3.1.1 CDOM range

Temporal variability of CDOM absorption was characterized by quasi-monthly sampling at the Caribbean Time Series Station (CaTS) from August 2003-August 2005. For this sampling period, the value of the CDOM absorption coefficient at 355 nm in surface waters was found to vary from 0.037 to 0.27 m^{-1}, with a mean value of 0.094 m^{-1}. The variability of the CDOM absorption was found to decrease with depth, with an average range of 0.22 m^{-1} in the mixed layer. Below the mixed layer, the average range was found to be 0.11 m^{-1}, a two-fold decrease. The highest mean and median CDOM absorption coefficients were found between 75 and 150 meters, not at the surface (Table 3.1).

TABLE 3.1 Descriptive statistics of CDOM absorption at 355nm

Depth (m)	Mean	Minimum	Maximum	Range	Median	St dev	St Err
0	0.0939	0.0368	0.2660	0.2291	0.0793	0.0562	0.0141
10	0.0849	0.0073	0.2430	0.2357	0.0808	0.0534	0.0134
25	0.0902	0.0361	0.2276	0.1915	0.0795	0.0481	0.0124
50	0.0931	0.0407	0.1796	0.1389	0.0887	0.0390	0.0101
75	0.0984	0.0560	0.1551	0.0990	0.1048	0.0310	0.0080
100	0.0983	0.0599	0.1647	0.1048	0.0971	0.0277	0.0074
125	0.1018	0.0553	0.1739	0.1186	0.1040	0.0314	0.0084
150	0.1059	0.0576	0.1570	0.0994	0.1098	0.0310	0.0083
200	0.0954	0.0507	0.1420	0.0914	0.0986	0.0271	0.0072

The corresponding value of the spectral slope of the coefficient ranged from 0.0127 to 0.0259 nm^{-1}, and the mean value was 0.0182 nm^{-1}. The maximum range for the spectral slope was found at 50 m, and the minimum was found at 75 m. The highest mean and median slopes were found at the surface, and values tended to decrease with depth (Table 3.2).

TABLE 3.2 Descriptive statistics of the spectral slope

Depth (m)	Mean	Minimum	Maximum	Range	Median	St dev	St Err
0	0.0182	0.0127	0.0259	0.0132	0.0184	0.0040	0.0010
10	0.0171	0.0102	0.0297	0.0196	0.0158	0.0047	0.0012
25	0.0164	0.0106	0.0225	0.0119	0.0154	0.0033	0.0008
50	0.0173	0.0119	0.0405	0.0286	0.0150	0.0071	0.0018
75	0.0146	0.0109	0.0194	0.0084	0.0152	0.0028	0.0007
100	0.0135	0.0098	0.0227	0.0129	0.0122	0.0036	0.0010
125	0.0126	0.0078	0.0178	0.0099	0.0123	0.0027	0.0007
150	0.0130	0.0088	0.0248	0.0161	0.0119	0.0041	0.0011
200	0.0119	0.0071	0.0208	0.0138	0.0112	0.0034	0.0009

Although CaTS is located well offshore (23 nautical miles from the coast and 3000m depth) the spectral slope values were generally similar to those found in coastal waters influenced by river input, which usually range from 0.013 to 0.018 nm^{-1} (Blough and Del Vecchio, 2002). Odriozola et al. (2007) found that the range of S values increased at salinities above 30, indicating an alteration of the composition of the CDOM as the Orinoco River Plume underwent mixing with Caribbean surface water.

3.1.2 Seasonal patterns of variability

3.1.2.1 Surface

CDOM absorption in the mixed layer (0-25m) at CaTS presents lower values during winter and spring, and higher values during summer and autumn (Fig. 3.1). The maximum surface absorption for the sampling period was observed during July 2004. This maximum coincides with previous satellite observations of the CDOM absorption coefficient of the area covered by the Amazon River Plume, in which the peak of CDOM absorption was found to lag the Amazon's hydrograph by one month (Hu et al., 2004). These results suggest that the Eastern Caribbean region is seasonally influenced by both the Amazon and Orinoco Rivers, since the high values in summer and autumn coincide with the rivers peak discharge seasons.

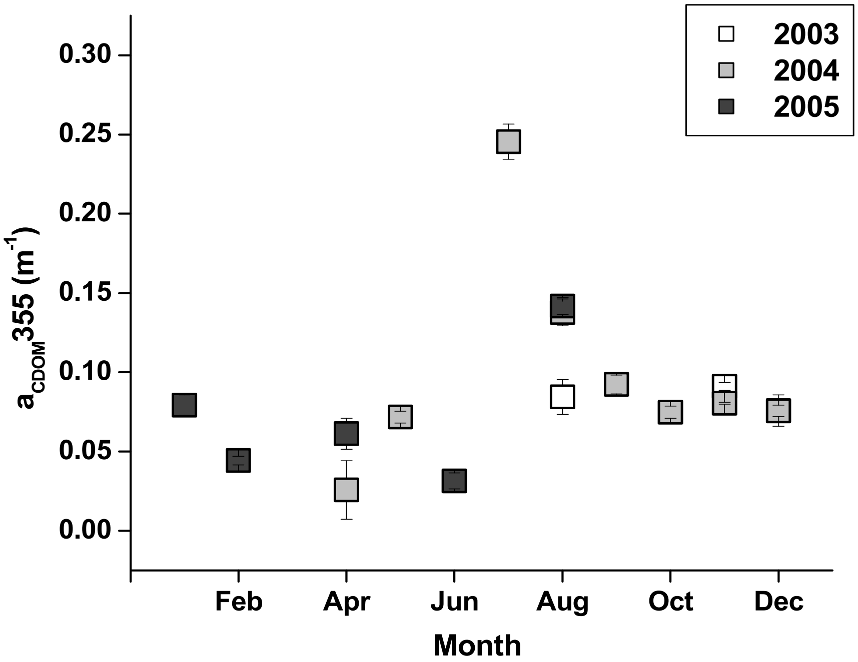

Figure 3.1 Mixed layer average of CDOM absorption coefficients at 355 nm at CaTS from August 2003-August 2005.

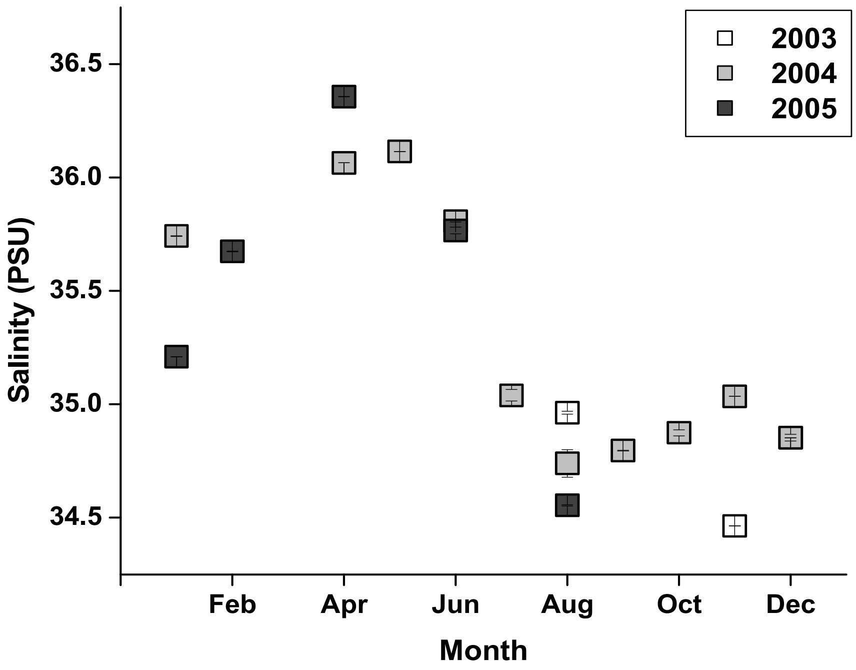

Figure 3.2 Mixed layer average salinities at CaTS from August 2003-August 2005.

The near surface salinity at CaTS also presented a seasonal pattern, being higher during the first half of the year and lower on the latter half (Fig. 3.2). These low salinity values coincide with the high CDOM absorption values, providing additional evidence for an allochtonous source of this material.

3.1.2.2 Subsurface

Vertical distribution of CDOM at CaTS tracks surface values, presenting also maximum values during summer and autumn, with decreasing values during winter and spring on the water column upper 75 m. Below this depth, summer values remain higher, but the average absorption for autumn samples falls below the values found during winter (Fig. 3.3). During spring we found the lowest CDOM values at most depths, only at the surface and 75m was this trend not followed. The lowest values were found during winter.

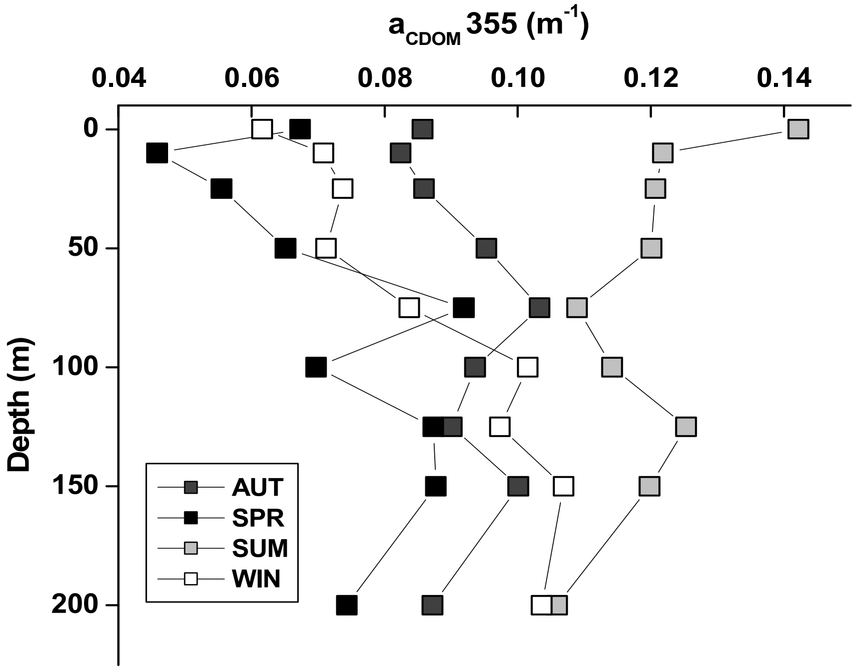

Figure 3.3 Mean CDOM absorption coefficient at 355nm by season

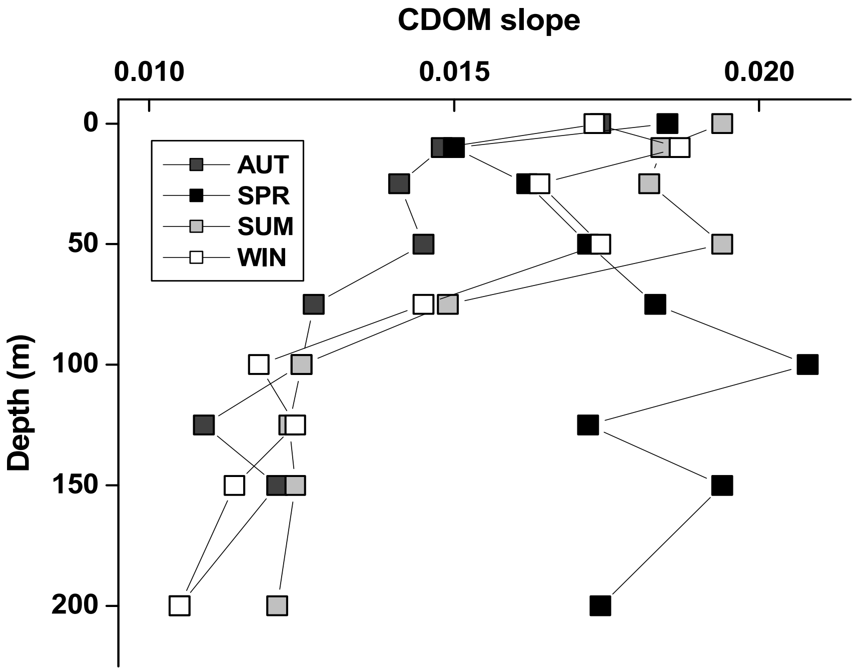

Figure 3.4 Mean CDOM slope by season

Temporal variability of CDOM slope (S) displays a seasonal pattern, with lower surface (0m) values during autumn and winter, and higher values during summer and spring. Below this depth down to 50m, autumn CDOM slopes are lower while summer values are generally above those of the other seasons. Below 75m, the slopes for summer, winter and autumn samples follow a similar trend, generally decreasing with depth (Fig. 3.4). It is remarkable that around the same depths, values remain high during spring.

3.2 Spatial Variability

Spatial variability of CDOM was characterized throughout the eastern Caribbean and extended into the northwestern Caribbean while characterizing mesoscale eddies. These data were also compared with previously obtained data (provided by Prof. Julio Morell) during cruises to the Orinoco River Plume. The value of the absorption coefficient of CDOM at 355 nm in surface waters was found to vary from 0.0353 to 5.557 m^{-1}, with a mean value of 0.77 m^{-1}. The corresponding value of the spectral slope of the coefficient ranged from 0.00819 to 0.0235 nm^{-1}, and the mean value was 0.0162 nm^{-1}.

The highest values were found in the Gulf of Paria, near the mouth of the Orinoco River. Values remained relatively high along the Orinoco River Plume throughout the Eastern Caribbean (area marked as ORI 3 & 4). High values were also found at the northern and southern edge of a cyclonic eddy that had entrained Orinoco River Plume waters (CAV I). Values outside of the plume were found to be low, sometimes below detection limits (a_{CDOM} below 0.046 m^{-1}) (Fig. 3.5).

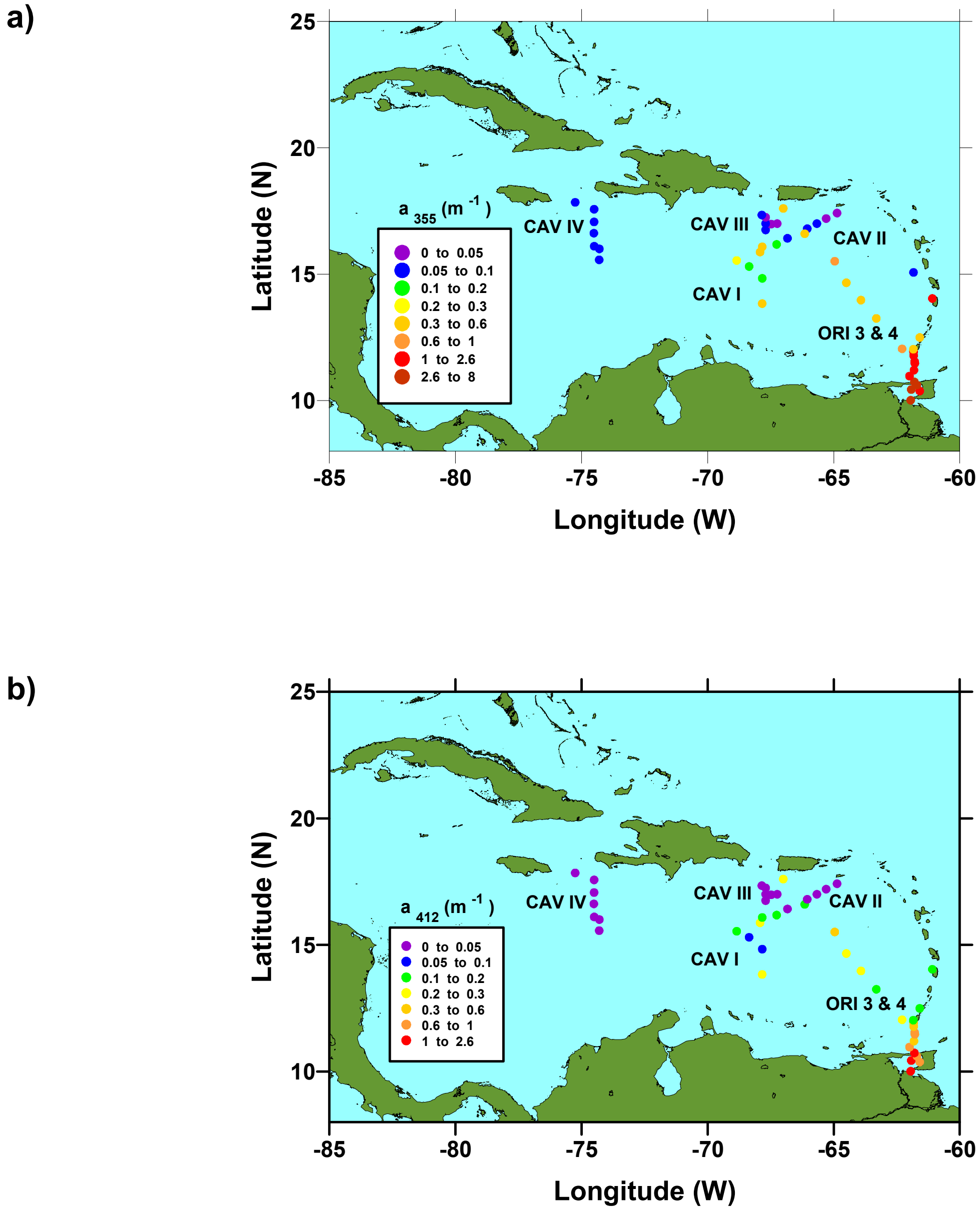

Figure 3.5 Spatial distributions of surface (0m) CDOM absorption coefficients at a) 355 nm and b) 412 nm

For analytical purposes, we assessed spatial variability of CDOM slopes along geographic coordinates comparing readings across the latitudinal range 12-18 ºN and the longitude range 63-76 ºW (Fig 3.6 and 3.7). CDOM slopes varied greatly with latitude, usually ranging from 0.008 to 0.024 nm^{-1}. This variability decreased at latitudes below 14 ºN, ranging from 0.008 to 0.016 nm^{-1}(Fig. 3.6)

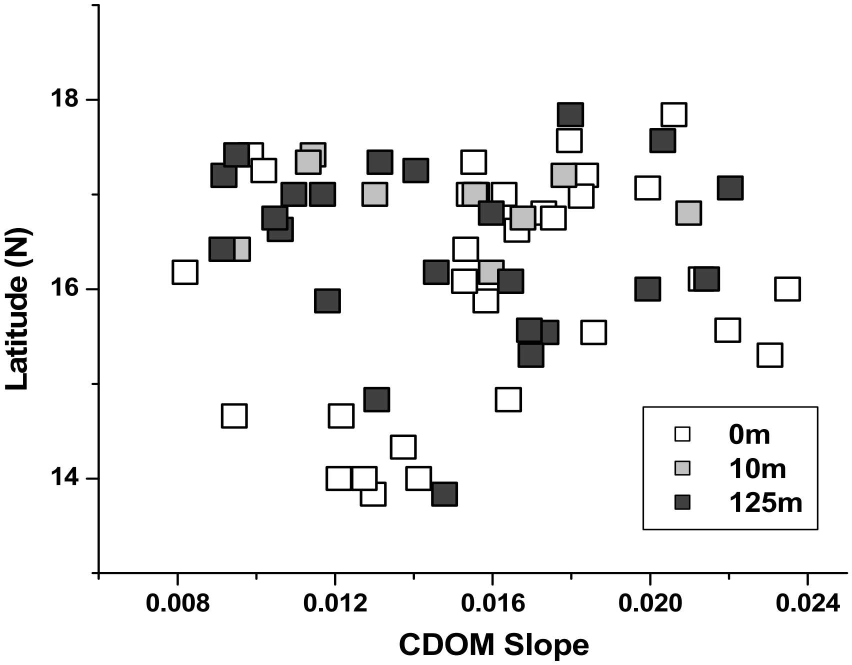

Figure 3.6 Latitudinal plot of the CDOM slope at depths 0, 10 and 125m

In terms of longitude, slopes also showed high variation in the eastern Caribbean ranging from 0.008 to 0.023 nm^{-1}. Values west of 74 ºW showed also a decrease in variability, but in this case the slopes tended to be higher. The CDOM slope range for the westernmost stations was 0.016 to 0.024 nm^{-1} (Fig. 3.7).

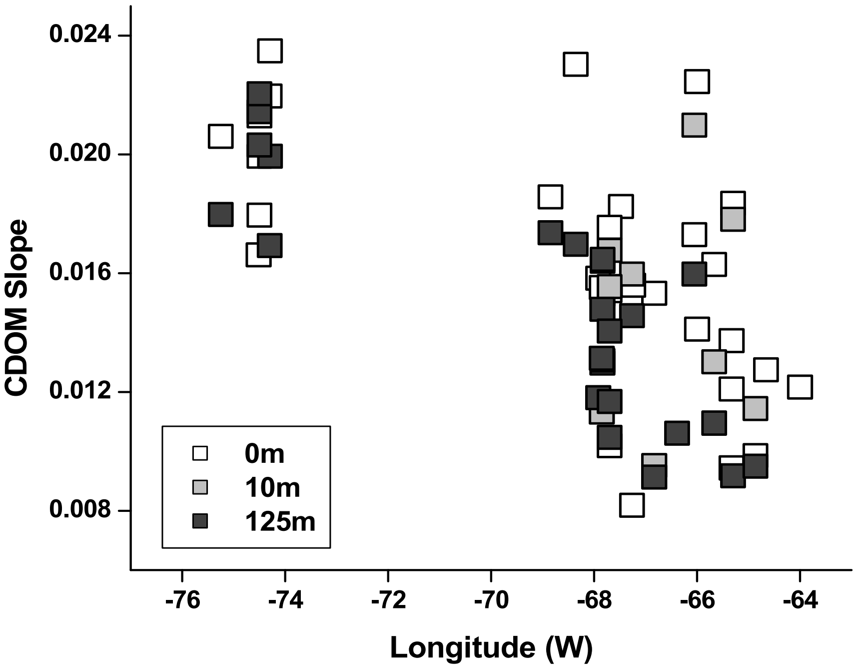

Figure 3.7 Longitudinal plot of the CDOM slope at depths 0, 10 and 125m

These differences in slope variability point to spatial-temporal differences in water mass sources in the Caribbean Sea. We find lower slope values, indicative of terrestrial CDOM influence, at the southernmost stations and higher slope values, indicative of aged oceanic CDOM at the westernmost stations.

3.2.1. Variability due to mesoscale eddies

At least 4-6 mesoscale eddies traverse the Eastern Caribbean basin each year (Murphy et al, 1999; Richardson, 2005), affecting the distribution of optical properties in the region. They can do so by promoting water mass mixing and also by advection of river plume waters (Corredor, et al., 2004; Canals Silander, 2005). Optical properties of Caribbean mesoscale eddies were characterized as part of the Caribbean Vorticity Experiment (CaVortEx) cruises.

The first mesoscale eddy characterized had a cyclonic rotation and had entrained Orinoco River Plume waters. This feature was studied during August 2003, which is the peak discharge period for the Orinoco River. The edges of the eddy had high CDOM absorption concurrent with a riverine origin, whereas the eddy core had more oceanic characteristics (Fig. 3.8a).

The optical characteristics of a cyclonic-anticyclonic eddy pair were studied during June 2004. There was evidence for upwelling and downwelling of CDOM, seemingly of autochthonous origin, on the cyclone and anticyclone side, respectively (Fig. 3.8b).

The third feature studied was not sufficiently coherent to be classified as an eddy, but later on developed into an anticyclonic eddy. This anticyclone was studied in February 2005. Low absorptions values were found throughout the eddy (Fig. 3.8c).

The fourth eddy was an anticyclonic eddy, which also presented low absorptions values (Fig. 3.8d). This feature was studied during March 2005. The low absorption values of the last two features might be due to seasonal variation.

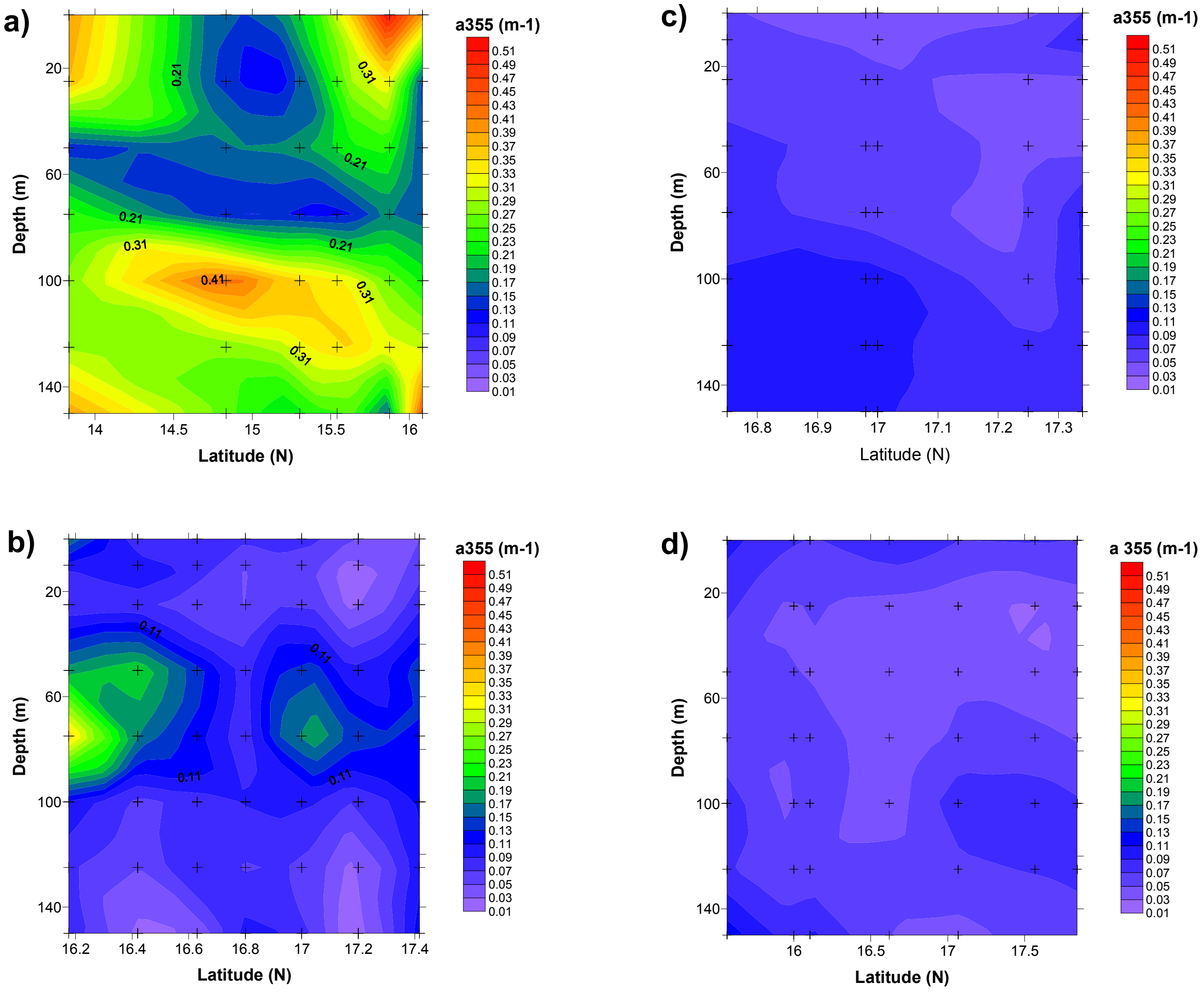

Figure 3.8 Contour plots showing a meridional cross-section of the CDOM absorption coefficient at 355 nm for: a) a cyclonic eddy, b) an eddy pair, c) a developing anticyclone and d) an anticyclonic eddy

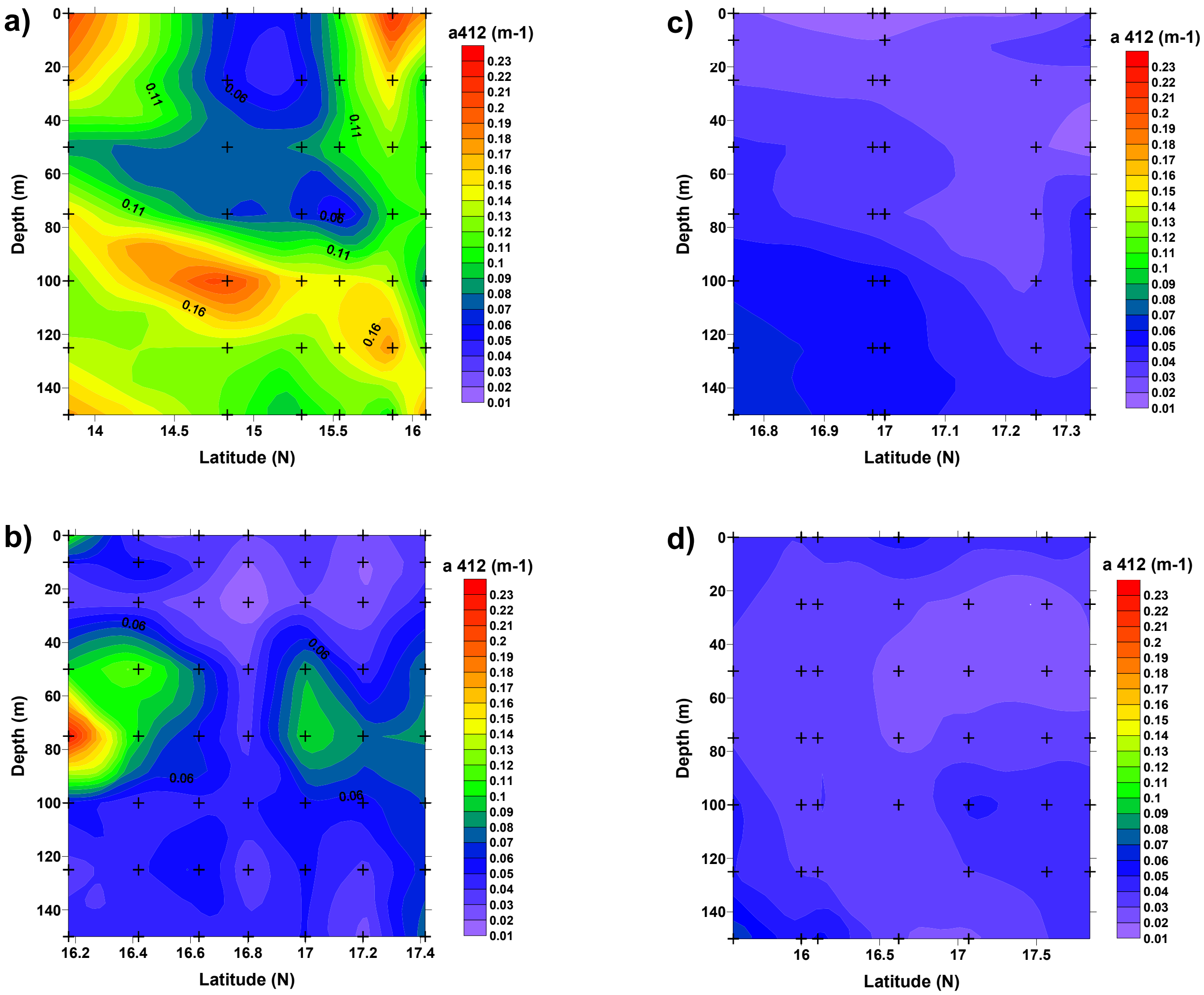

Figure 3.9 Contour plots showing a meridional cross-section of the CDOM absorption coefficient at 412 nm for a) a cyclonic eddy, b) an eddy pair, c) a developing anticyclone and d) an anticyclonic eddy

4. Discussion

4.1 Temporal Variation

CDOM absorption and spectral slopes showed marked seasonal variability. These variations can be due to differences in CDOM sources and alteration of the material. Carder et al. (1989) found that changes in the proportion of humic to fulvic acids can cause variation in spectral slopes. Other possible causes for these changes include alteration of CDOM by photobleaching (Del Castillo et al., 1999) and CDOM production through biological processes (Nelson and Siegel, 2002).

The time series contour plot of CDOM absorption reveals what appears to be either vertical displacement through time of CDOM from surface waters to deeper waters down to 200 meters or subsurface CDOM production by the microbial community (Fig. 4.1). Since these high values are found below the deep chlorophyll maximum and no evidence is available for subduction of surface waters, the latter hypothesis is more likely.

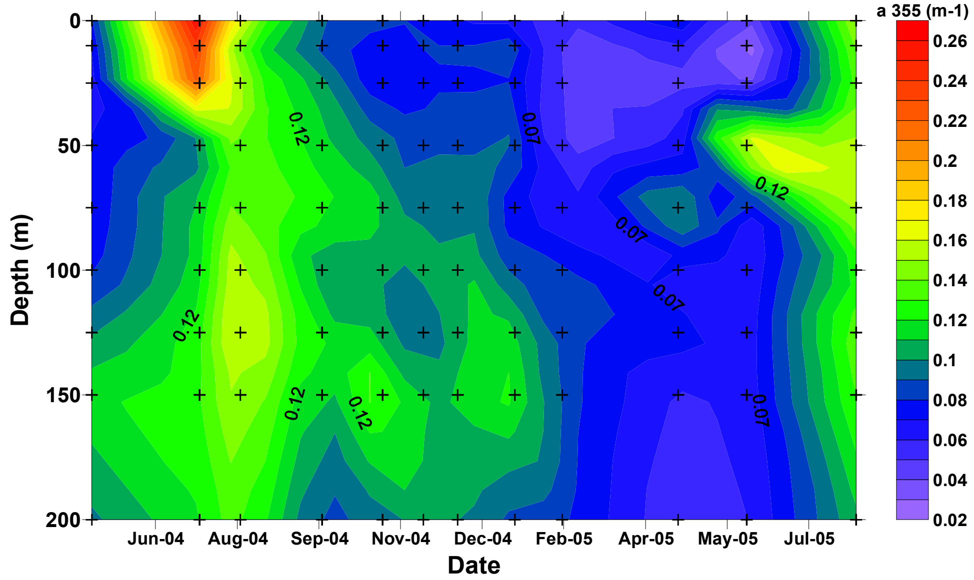

Figure 4.1 Contour plot of CDOM absorption coefficient at 355 nm for CaTS cruises May 2004-August 2005

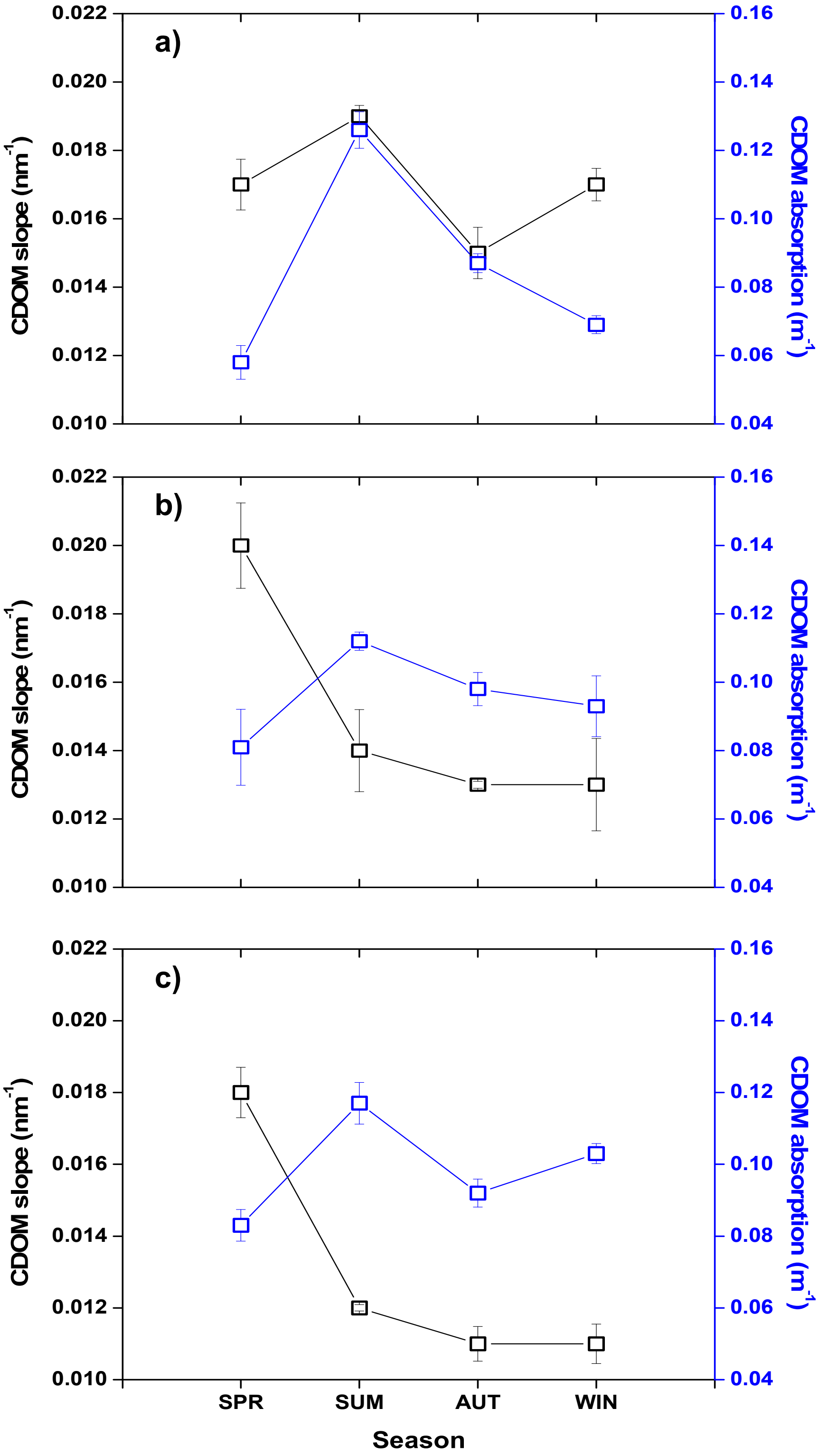

Figure 4.2 Seasonal variations of CDOM slope and absorption averaged by depth layers a) 0-50 meters b) 75-100 meters and c) 125-200 meters.

Comparison of temporal trends of a_{CDOM} and S shows that the maximum mean surface CDOM absorptions coincide with the highest mean surface slopes; both found during the summer (Fig 4.2a). The high a_{CDOM} suggests an allochtonous source, and the high slope suggests photoxidative removal of the material (Vodacek et al., 1997). We hypothesize that this surface maximum during summer is due to the influence of the Amazon River Plume during this season.

Chérubin and Richardson (2007) analyzed salinity maps for the Caribbean region and found seasonal variations of the freshwater plumes originated from the discharge of the Amazon and Orinoco Rivers. They found that the Amazon plume extends towards the Caribbean during the first half of the year, during the latter half there appeared to be advection of the plume by the NBC retroflection. Even after the advection, some remnant plume remained northwest of the retroflection. This remnant of the Amazon plume merged with the Orinoco River plume during August, when the Orinoco presents its peak discharge. This has been previously observed after analyzing ocean color imagery (Müller-Karger et al., 1988; Müller-Karger et al. 1989; Hu et al. 2004). Also, the formation of NBC rings that detach from the retroflection with Amazon plume waters has been found to transport these waters to the Caribbean (Fratantoni and Glickson, 2002).

During autumn, the Orinoco River plume appears to dominate the region. The Amazon River water must travel almost 2000 km in order to reach the Caribbean Sea (Chérubin and Richardson, 2007). Therefore, the CDOM present in its plume would be exposed to solar radiation for a longer period of time. This would explain the high slopes observed during summer, which could indicate significant photodegradation of the material. On the other hand, the Orinoco River plume must travel only 200 km, arriving faster to the Caribbean region (Chérubin and Richardson, 2007). Consequently, CDOM present on the plume would be less exposed to solar radiation so its spectral slope would be expected to be lower than CDOM that has undergone significant photobleaching. These differences in residence time might explain why the surface spectral slopes are lower during autumn.

In subsurface samples, the CDOM slopes values follow a similar trend during most seasons. It is remarkable that S values are higher in subsurface samples during spring, while the CDOM absorption is lowest during this season. Oceanic samples usually have low CDOM absorption and high spectral slopes. We chose two representative stations for oceanic sources to the east and to the north of CaTS. The eastern station was station 2 (6.17 ºN, 40.41 ºW) during a cruise through the Atlantic Ocean (AEROSE), in which a_{CDOM} 355 was found to be low (0.060 m^{-1}) and the slope was high (0.022 nm^{-1}). Similar trends have been observed to the north at the Bermuda Atlantic Time-series Study (31.67 ºN, 64.17 ºW), with average absorption values of 0.088 m^{-1} and average spectral slopes of 0.025 nm^{-1} during spring (Nelson et al., 1998 as cited in Blough and Del Vecchio, 2002).

The seasonal differences observed in both absorption and spectral slopes at CaTS suggest diverse sources of CDOM for the Eastern Caribbean basin. This could be due to changes on circulation patterns and water mass formations.

4.2 Covariability of surface absorption to fluorescence

A moderate correlation (r^2=0.43) is observed when comparing near surface a_{CDOM} to the normalized fluorescence intensity (plot not shown). A strong correlation (r^2=0.73) arises when comparing the fluorescence peak wavelengths with the absorption values for surface samples (Fig 4.3). This strong correlation indicates a terrestrial origin of the higher absorption values. Marine humic-like materials present emission maxima towards the shorter wavelengths, whereas terrestrial humic-like materials display its emission maxima at longer wavelengths due to their increased aromatic chemical nature and higher molecular weight (Coble, 2007).

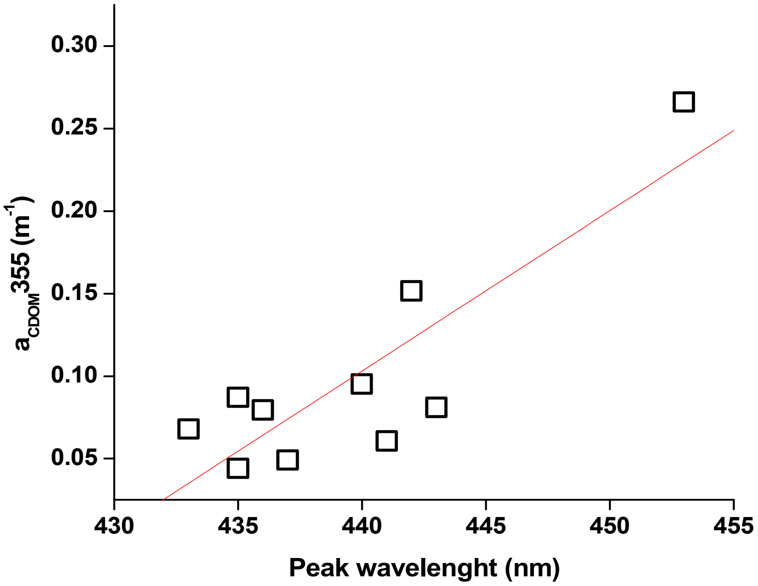

Figure 4.3 Plot of surface a_{CDOM} 355 as a function of fluorescence peak wavelength
The relationship is expressed by the linear function
a_{CDOM} 355 = 0.00972 (Peak λ) - 4.17233 (r^2= 0.73; n= 10)

4.3 Covariability of surface measurements to salinity

The relationship between a_{CDOM} and salinity at CaTS suggests non conservative behavior (Fig. 4.4). Since salinity is typically a conservative constituent of water, examining the relationship between this parameter and the CDOM absorption can help us assess whether it is behaving conservatively or not (Stedmond and Markager, 2003). When CDOM behaves conservatively there is a linear inverse correlation between absorption and salinity, which indicate that only dilution is important during the mixing of different water masses (Stedmond and Markager, 2003). Deviations from this mixing line can occur as a result of in situ CDOM production and/or removal processes (Twardowski and Donaghay, 2001). Such deviations have been previously reported for the Orinoco River Plume (Blough et al., 1993; Del Castillo et al., 1999; Morell and Corredor, 2001; Odriozola et al., 2007).

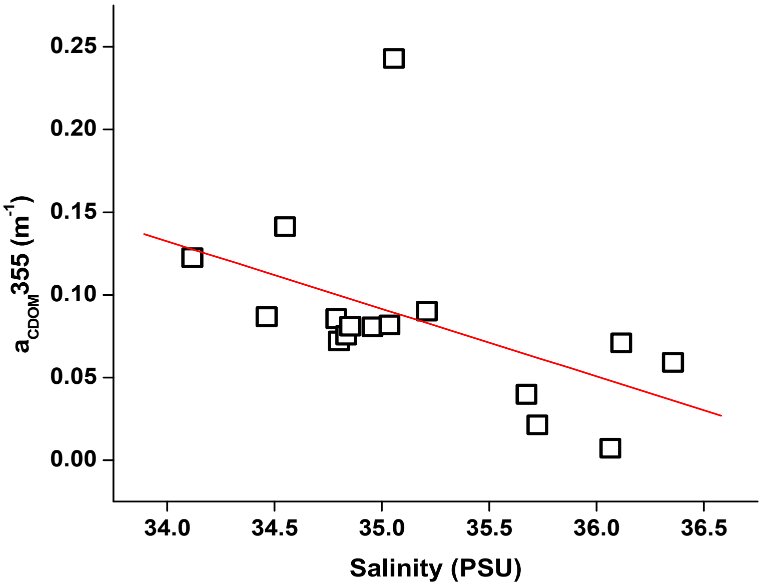

Figure 4.4 Plot of surface a_{CDOM} 355 as a function of salinity at CaTS The relationship is expressed by the linear function a_{CDOM} 355 = 1.52121 (Salinity) - 0.04085 (r^2= 0.24; n= 16)

This finding of non-conservative behavior combined with the observed slopes and fluorescence measurements is consistent with our hypothesis that the CDOM that reaches the Northeastern Caribbean region during summer has a terrestrial origin and goes through significant photodegradation.

On the other hand, the samples around the Caribbean presented a trend similar to previous studies for the Orinoco River plume (Blough et al., 1993; Del Castillo et al., 1999), with a linear relationship between a_{CDOM} and salinity (Fig 4.5).

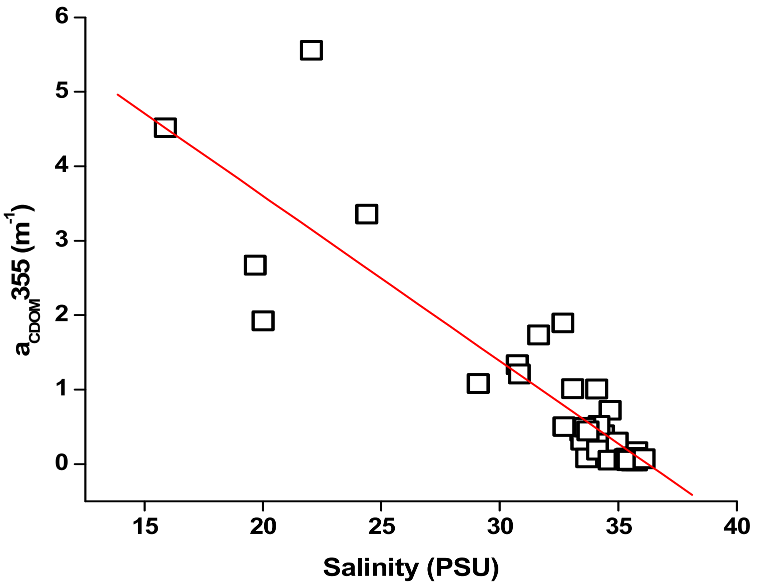

Figure 4.5 Plot of surface a_{CDOM} 355 nm as function of salinity for the Caribbean The relationship is expressed by the linear function
a_{CDOM} 355 = -0.22181 (Salinity) + 8.03955 (r^2= 0.78; n= 40)

When comparing salinity and spectral slopes we find typical results for both the Caribbean and CaTS samples; presenting low and fairly constant slopes at lower salinity (Fig. 4.6). At salinities above 30 spectral slopes increase rapidly and present higher variability, as concentration of marine CDOM begins to reach those of the diluted freshwater CDOM (Coble, 2007). Previous studies have found a similar relationship for areas influenced by freshwater inputs (Blough et al., 1993, Del Castillo et al., 1999, Conmy et al., 2004).

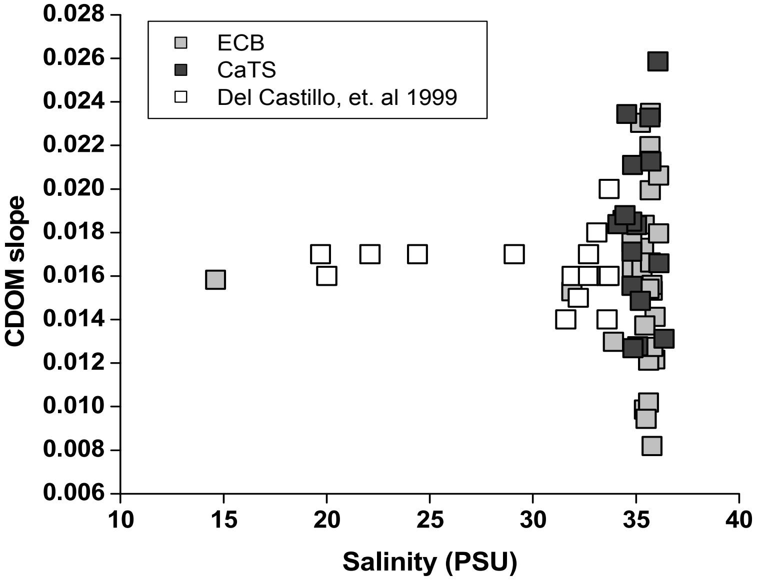

Figure 4.6 Plot of surface Salinity vs. CDOM slope for samples through out the Eastern Caribbean Basin (ECB) and CaTS

4.4 Spatial Variation

4.4.1 North-South Variation

The value of the absorption coefficient of CDOM at 355 nm in surface waters was found to vary from 0.0353 to 0.445 m^{-1} in the northern part of the Caribbean around 17º N. To the south, the values ranged from 1.894 to 5.557 m^{-1} around 10º N.

There is a North-South gradient of CDOM with higher values on the southernmost samples indicating the influence of the Orinoco River Plume. The lowest CDOM values were found above 16º N (Fig. 4.7).

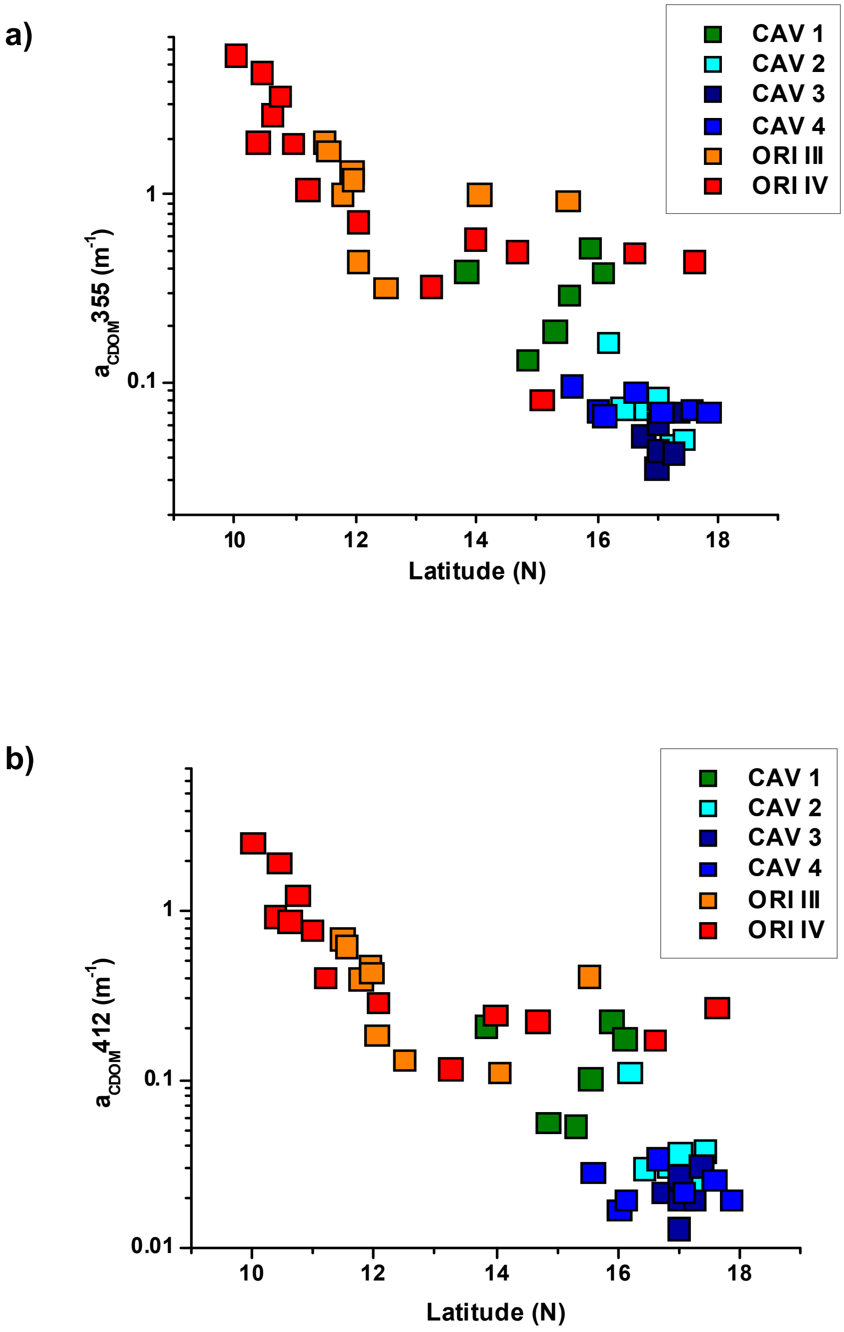

Figure 4.7 Latitudinal plots of surface (0m) CDOM absorption coefficients at a) 355 nm and b) 412 nm

4.4.2 East-West Variation

The value of the absorption coefficient of CDOM at 355 nm at surface waters was found to vary from 0.0817 to 5.557 m^{-1} at the eastern part of the Caribbean around 61º W. At the west, the values ranged from 0.0668 to 0.0967 m^{-1} around 74º W.

Variation of the CDOM absorption coefficient with longitude was high, except for the westernmost samples, in which the absorption was found to be below 0.1 m^{-1} (Fig. 4.8). This concurs with the variation observed on the spectral slopes. The high spectral slopes and low CDOM suggest an oceanic origin for these waters.

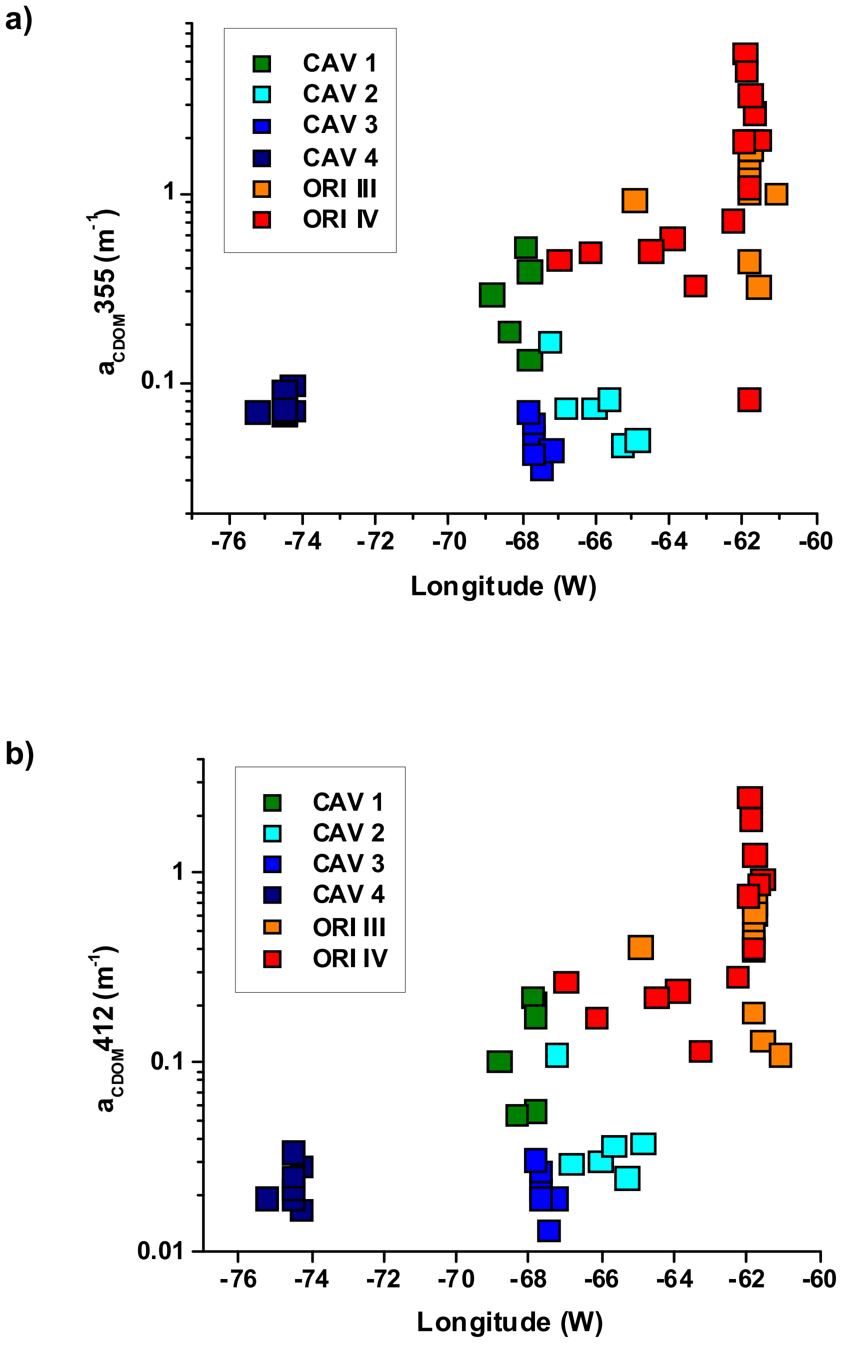

Figure 4.8 Longitudinal plots of surface (0m) CDOM absorption coefficients at a) 355 nm and b) 412 nm

4.5 Contribution to the attenuation of photosynthetically active radiation

There is a strong linear relationship (r^2= 0.86) between CDOM absorption and the vertical attenuation coefficient at 412 nm (Fig. 4.9). This provides further evidence that absorption at lower wavelengths is mainly due to CDOM, as has been previously stated (Blough et al., 1993, Del Castillo et al., 1999).

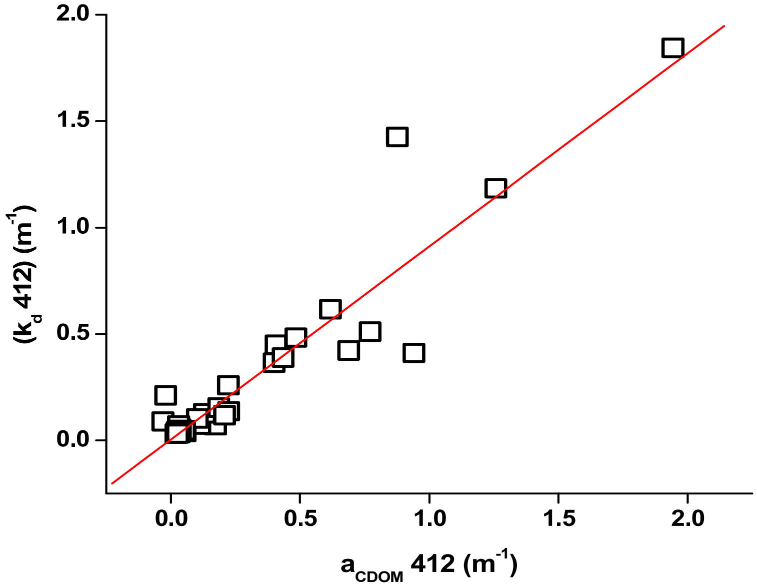

Figure 4.9 Plot of surface a_{CDOM} 412 vs. K_d 412
The relationship between them is expressed by the linear function
K_d 412 = 0.9071 (a_{CDOM} 412) + 0.00424 (r^2= 0.86; n= 35)

Assuming absorption of other substances to be negligible, we analyzed the percentage contribution of phytoplankton and CDOM to total light absorption in the water column. We computed in vivo phytoplankton absorption using a formulation of the chlorophyll-specific absorption $a_{\phi}(\lambda)$ (Bricaud et al., 2004):

$$a\phi\ (440) = 0.0654\ [\text{Chl a}]^{0.728} \quad \mathbf{3.1}$$

CDOM dominates light absorption at most depths throughout the year, most notably during the summer. Only during spring and winter does phytoplankton equals or dominates light absorption at certain depths (Fig 4.10). This again denotes the significant role of South American Rivers in modulating the optical properties of Eastern Caribbean waters.

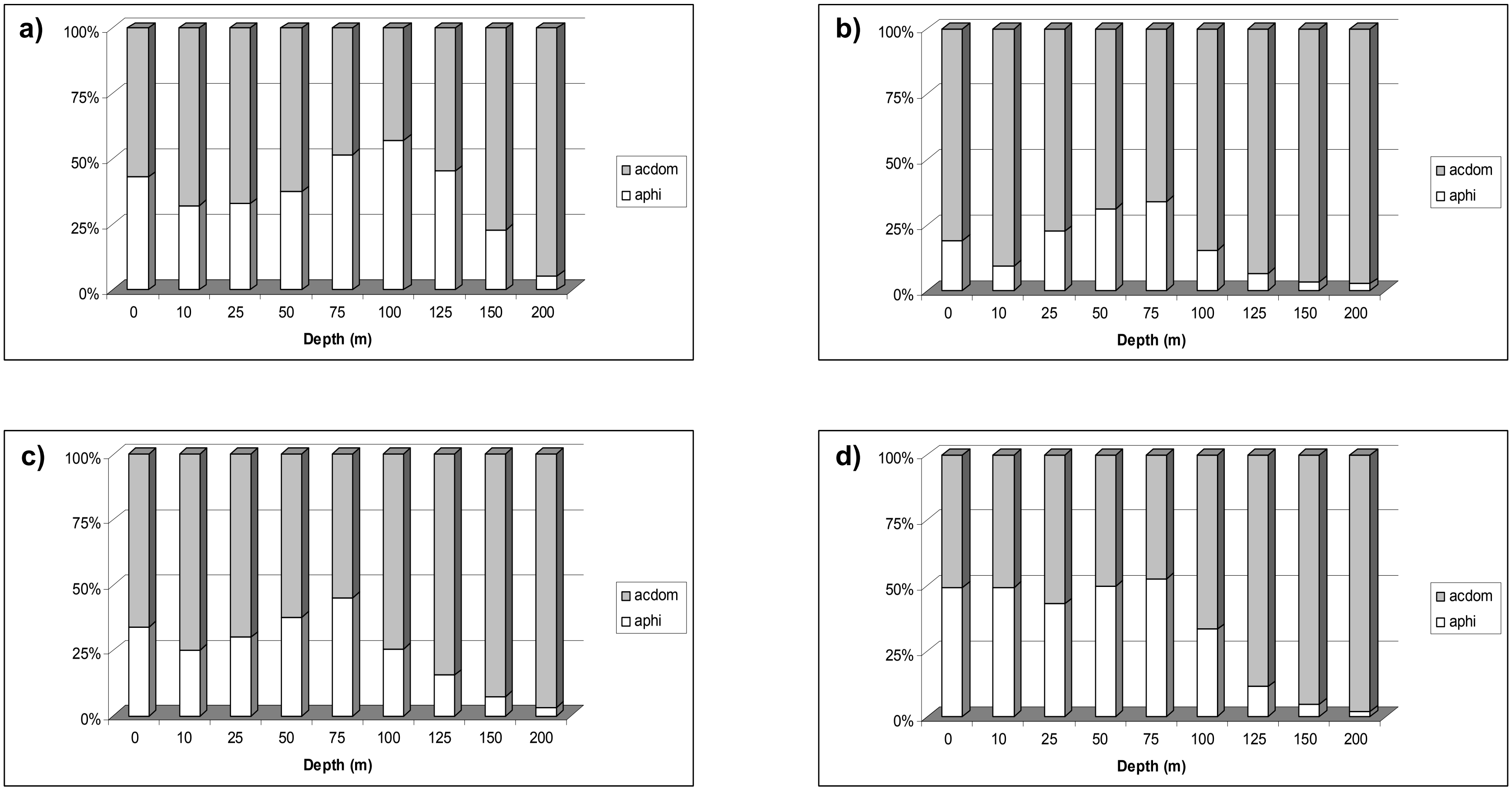

Figure 4.10 Percentage contribution of a_{CDOM} 440 and aϕ 440 to total absorption in the water column at the northeast Caribbean during a) spring b) summer c) autumn and d) winter

5. Conclusions

1. In surface and near surface waters, light attenuation at shorter wavelengths is mainly due to absorption by chromophoric dissolved organic matter (CDOM) transported in the Orinoco and Amazon River plumes during autumn and summer.
2. In subsurface waters CDOM still contributes significantly to the total absorption when contrasted with phytoplankton absorption.
3. Mesoscale eddies affect the spatial and temporal distribution of CDOM by advection of the Amazon and Orinoco River plumes into the Eastern Caribbean basin creating complex mosaics of optically clear and optically dense waters.
4. CDOM that reaches the NE Caribbean during summer present higher absorption and spectral slopes than that found later in the year. During autumn, CDOM absorptions are relatively high although lower than summer. The higher slopes indicate photodegradation of the material, pointing towards predominance of older, Amazon River plume waters in summer followed by the intrusion of Orinoco River plume water in the fall.
5. Although we did not sample the western Caribbean as intensively, CDOM loads of surface waters in that region appear to be lower and less influenced by continental runoff.

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