

# INHERENT WATER OPTICAL PROPERTIES AT THE CARIBBEAN TIME SERIES STATION (CaTS)

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## ABSTRACT

The temporal variability of the inherent water optical properties at the Caribbean Time Series (CaTS) station was evaluated with three years of data. The absorption coefficient of total particles ( $a_p$ ), detritus, ( $a_d$ ), and phytoplankton ( $a_{ph}$ ) were measured with an integrating sphere attached to a spectroradiometer using the filter pad method. The absorption coefficient of the colored dissolved organic matter ( $a_g$ ) was determined using a double-beam spectrophotometer. Profiles of the backscattering coefficient ( $b_b$ ) were obtained with a HydroScat-6 sensor. The analyses show a large, wavelength-dependent, variability in the total absorption coefficient ( $a_t$ ) as determined by the sum of  $a_p$ ,  $a_g$ , and  $a_w$  (pure water absorption coefficient). Although these are oceanic waters, it was found that  $a_g$  is an important component of  $a_t$  in the blue and green wavelengths. The maximum values of  $b_b$  were measured at the blue wavelengths down to 200 meters. A clear  $b_b$  peak at green wavelengths was detected in the same depths of the deep chlorophyll maximum during several months. Large variability was also found for the  $b_b/a_t$  ratio at different wavelengths, but in all cases, the values were less than one. The correlation between bio-optical properties was poor in months where the chlorophyll-a concentrations were lower than  $0.1 \mu\text{g l}^{-1}$ . Multi-year time series recorded at CaTS depict seasonal variations in the inherent optical properties of near-surface waters that are associated to seasonal events, like the intrusion of the Orinoco River. Such variability is responsible for low accuracy in the estimation of chlorophyll-a using the current bio-optical algorithms.

## INTRODUCTION

Accurate estimates of phytoplankton chlorophyll-a are still difficult to obtain in tropical oceans because of the large variability in the inherent and apparent optical properties. Clear waters with high penetration of light are characteristic of most tropical regions. However in some areas, like the Caribbean Sea, seasonal events affect the light field in the water column (Farmer et al., 1993 and Hochman et al., 1994). This induces variations in phytoplankton responses at different local and regional scales (Bidigare et al., 1993; Gilbes et al., 1996; Smith and Demaster, 1996). These spatial and temporal variations of bio-optical properties make the interpretation of remote sensing data very difficult. Therefore, we need to measure these variations at local and regional scales in order to find appropriate remote sensing techniques that could be used at global scale.

Since 1994, the Department of Marine Sciences of the University of Puerto Rico at Mayagüez (UPRM) has maintained a time series station denoted Caribbean Time Series (CaTS) at  $17^{\circ}38' \text{ N } 67^{\circ} \text{ W}$ . CaTS is approximately 28 nautical miles off the southwestern coast of Puerto Rico and provides an observing station for researchers

interested in the magnitude and periodicity of basin-scale phenomena affecting the bio-optics and biogeochemistry of regional waters. The research has focused on the characterization and understanding of seasonal and inter-annual variability of near-surface features in the Northeastern Caribbean Basin as affected by seasonal riverine intrusions and human-induced changes. The long-term goal is to characterize the expression and modulation of processes related to biological productivity and carbon cycle in these waters. As part of the routine sampling at CaTS, the Bio-Optical Oceanography Group of UPRM has been measuring the bio-optical properties to better understand their variability and to develop site-specific bio-optical algorithms for the Eastern Caribbean Sea. Here, we discuss the temporal variability of the inherent water optical properties and provide preliminary interpretations of the results. We expect that the outcome of our research will help to improve the accuracy of the ocean color products from current and future satellite sensors.

## MATERIALS AND METHODS

Data were collected during monthly cruises to the CaTS station from January 1997 to March 2000. Total particulate absorption spectra,  $a_p(\lambda)$ , for samples collected on Whatman GF/F glass-fiber filters were measured with a LI-COR integrating sphere attached to a GER 1500 portable spectroradiometer using the method developed by Mitchell and Kiefer (1984) and the optical-path elongation factor  $\beta$  from Bricaud and Stramski (1990). Methanol-extractable pigments were removed by slowly passing hot methanol through the filter pad (Roesler et al., 1989). The absorption spectrum of this pad was measured to determine the detritus absorption coefficient,  $a_d(\lambda)$ . The difference between the particulate and detritus spectra, before and after the methanol extraction, was considered the "in vivo" phytoplankton absorption,  $a_{ph}(\lambda)$ . Optical absorption spectra of the colored dissolved organic matter,  $a_g(\lambda)$ , were determined with a Perkin Elmer double-beam spectrophotometer following the method described by Bricaud et al. (1981). Profiles of the backscattering coefficient,  $b_b(\lambda)$ , at six wavelengths (442, 470, 510, 589, 620, and 671 nm) were measured with the HydroScat-6 sensor (from Hobi Labs). The methodology of these measurements and determination of the  $b_b(\lambda)$  is described in detail in Maffione and Dana (1997). The backscattering coefficient of suspended particles,  $b_{sp}(\lambda)$ , was calculated by subtracting from the measured  $b_b(\lambda)$  the backscattering coefficient of pure seawater,  $b_w(\lambda)$ , as determined by Smith and Baker (1981). Concentrations of phytoplankton Chlorophyll-a (Chl-a) were obtained using the fluorometric method developed by Welschmeyer (1994), in which no acidification is necessary for pheopigments correction. Profiles of Chl-a were also obtained using a WET Labs fluorometer that was calibrated with extracted samples of Chl-a.

## RESULTS AND DISCUSSION

The largest temporal variability of the inherent water optical properties at CaTS was detected in the blue region of the spectrum (Figure 1). Statistical analyses of selected wavelengths show that  $a_g$  mean values, along with their variability, were higher than  $a_p$  mean values (Table 1). This demonstrates that even in these oceanic waters  $a_g$  is an important component of the total absorption in the blue and green wavelengths. The

highest  $a_g$  values were found during October of 1998 and 1999 (Figure 1). That is the time when the intrusion of the Orinoco River into the Eastern Caribbean Sea is large (Müller-Karger et al., 1989) and could reach the region of CaTS. The lowest  $a_g$  values were found during March of 2000, the same time when the Orinoco River discharge is low. In that month, the  $b_b$  values were also high at blue wavelengths, which is characteristic of clear oceanic waters. The two years of  $a_g$  data support the idea of the tremendous effect of the Orinoco River in the bio-optical properties of Caribbean waters as closed as 28 nautical miles off the southwestern coast of Puerto Rico.

The variability of the inherent water optical properties is normally associated to the variations of biological components, like phytoplankton. At CaTS, the multi-year time series showed seasonal and inter-annual variations in near surface waters of phytoplankton biomass (Figure 2). Chl-a concentrations ranged from 0.01 to 0.33  $\mu\text{g l}^{-1}$  with a mean value of 0.13  $\mu\text{g l}^{-1}$  (Std. Dev.=0.08  $\mu\text{g l}^{-1}$ ). Traditionally, these waters have been classified as oligotrophic (Beers et al., 1968; Corredor, 1979). However, new evidence, especially from remote sensing data, demonstrates that the Eastern Caribbean can also have mesotrophic conditions (Müller-Karger et al., 1989; Gilbes et al., In preparation). Our time series of Chl-a show several peaks along the year that could be related to those seasonal events (Figure 2). For instance, distinctive peaks were detected during spring and summer, when the Caribbean coasts of South America experience strong upwelling and there is intrusion of the Amazon River into the Eastern Caribbean. The discharge of the Orinoco River may also affect the Chl-a concentrations in CaTS during fall. However, September and October of 1999 showed the lowest concentrations of Chl-a. Ocean color data from the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) show that the intrusion of the Orinoco River do not reach the CaTS location in the same way every year (Figure 3). The imagery shows the formation of filaments and eddies, which produced a large regional variability in the bio-optical properties. Since CaTS is only one spot in the entire region and we sampled it only once per month, the variability of the measured parameters is highly affected by the location of these filaments and eddies in a specific time.

Photosynthetic pigments, like Chl-a, absorb light and provoke large optical variability in the surface waters of the open ocean. A good understanding of such variability is necessary for the development of better bio-optical algorithms. Several researchers are taken the absorption coefficient of phytoplankton,  $a_{ph}$ , as function of Chl-a concentration. However, absorption by phytoplankton varies widely in space and time due to pigment composition and species dominance. In CaTS, a weak relationship was found between  $a_{ph}(675)$  and Chl-a when all the data was used (Figure 4A). However, the same relationship improved ( $r^2=0.8$ ) when data from months with Chl-a values greater than 0.1  $\mu\text{g l}^{-1}$  were only used (Figure 4B). This suggests that either our filter pad method for  $a_{ph}$  determination is not good for waters with very low Chl-a or this relationship does not occur below concentrations of 0.1  $\mu\text{g l}^{-1}$ . If the datum of December 98 is also eliminated the  $r^2$  goes up to 0.92, but it is not clear what happened in that month.

Suspended organic particles, like Phytoplankton, can affect the backscattering coefficient ( $b_b$ ) at specific wavelengths. Stramski et al. (1998) showed good correlation between the backscattering coefficient of suspended particles ( $b_{bp}$ ) and the concentration of Chl-a plus pheopigments. In a more recent article, they also describe how  $b_{bp}$  is well

correlated with the particulate organic carbon (Stramski et al., 1999). In CaTS, we have been measuring  $b_b$  with the same instrument than Stramski and colleagues, the HydroScat-6, but we lack of POC and pheopigments measurements. Nevertheless, we tried to correlate  $b_{bp}$  and Chl-a in our waters. The correlation between these two parameters was poor at the surface waters (Figure 5). This could suggest that small phytoplankton cells are affecting  $b_b$  but they are not collected in the filter. If that is the case, we are also underestimating the concentration of Chl-a. We are now planning to evaluate the role of small phytoplankton in the optical properties of these waters. It is also possible that we have large noise in the data, and therefore high variability, due to the small signal produce by these low concentrations of phytoplankton. The high correlation presented by Stramski et al. (1998) included points with high Chl-a concentrations, but the data suggest that they could have similar low correlation if only low values are used. Another possibility could be the error introduced by the attenuation correction in the  $b_b$  measurements. However, in our case that error should be negligible because these are clear oceanic waters with small particles and the correction provided by Maffione and Dana (1997) should be adequate. Besides the lack of correlation between  $b_b$  and Chl-a in surface waters, down in the water column other interesting features can be identified. At several months, we detected a clear  $b_b$  peak at green wavelengths very close to the depth of the deep Chl-a maximum (Figure 6). The  $b_b$  and Chl-a peaks are not exactly in the same depth, perhaps because the depth sensors were not inter-calibrated.

The data suggest a large, wavelength-dependent, temporal variability in the total absorption coefficient,  $a_t(\lambda)$  as determined by the sum of  $a_p(\lambda)$ ,  $a_g(\lambda)$ , and  $a_w(\lambda)$ . They also demonstrate that  $b_b(\lambda)$  is variable in time at CaTS. These two inherent optical properties,  $a_t(\lambda)$  and  $b_b(\lambda)$ , are responsible for changes in remote sensing reflectance,  $R_{rs}(\lambda)$ , the apparent optical property used in most recent bio-optical algorithms. Therefore, in order to develop good regional algorithms is necessary to better understand the changes in the  $b_b(\lambda)$  and  $a_t(\lambda)$  ratio. We found high variability in this ratio, especially in the blue wavelengths, but no clear trend was identified (Figure 7). It is hard to explain the temporal trend of  $b_b(\lambda)/a_t(\lambda)$  because of missing data in the current time series. Perhaps future samplings will provide more data and we will get a better idea of the changes in these inherent water optical properties. This will allow us to develop accurate bio-optical algorithms for the Caribbean region.

## CONCLUSIONS

The Caribbean Time Series station shows the highest temporal variability in the inherent water optical properties at the blue wavelengths. This variability is highly affected by the impact of seasonal events, which provoke that the colored dissolved organic matter plays an important role in the optical properties of the station. We found no correlation between bio-optical parameters in conditions below the  $0.1 \mu\text{g Chl-a l}^{-1}$ . More data are necessary in order to evaluate the source of this variability and lack of correlation. At deep Chlorophyll maximum is possible to detect a clear peak of  $b_b(\lambda)$  in green wavelengths, demonstrating the effect of phytoplankton cells over the backscattering coefficient.

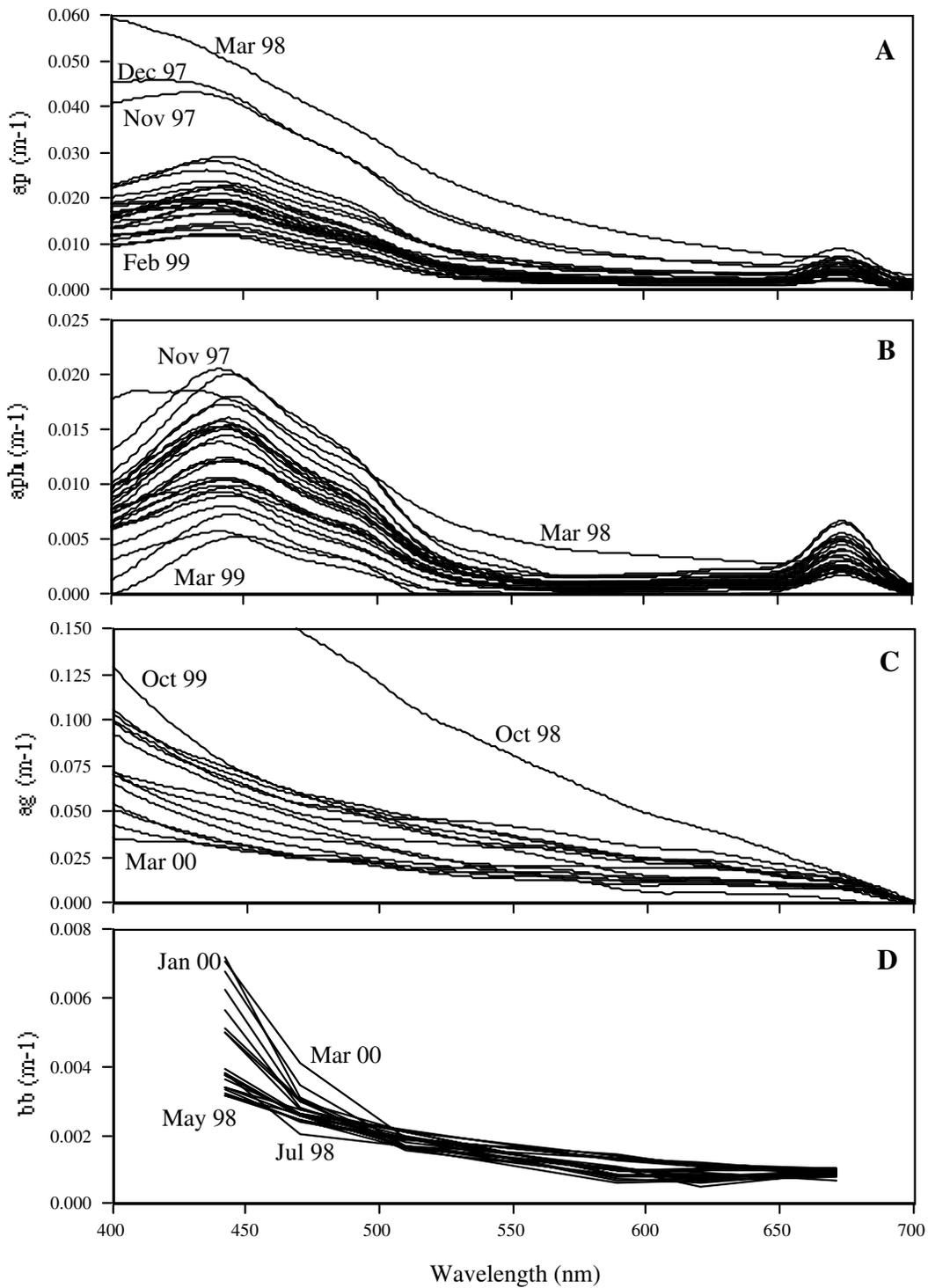
## ACKNOWLEDGMENTS

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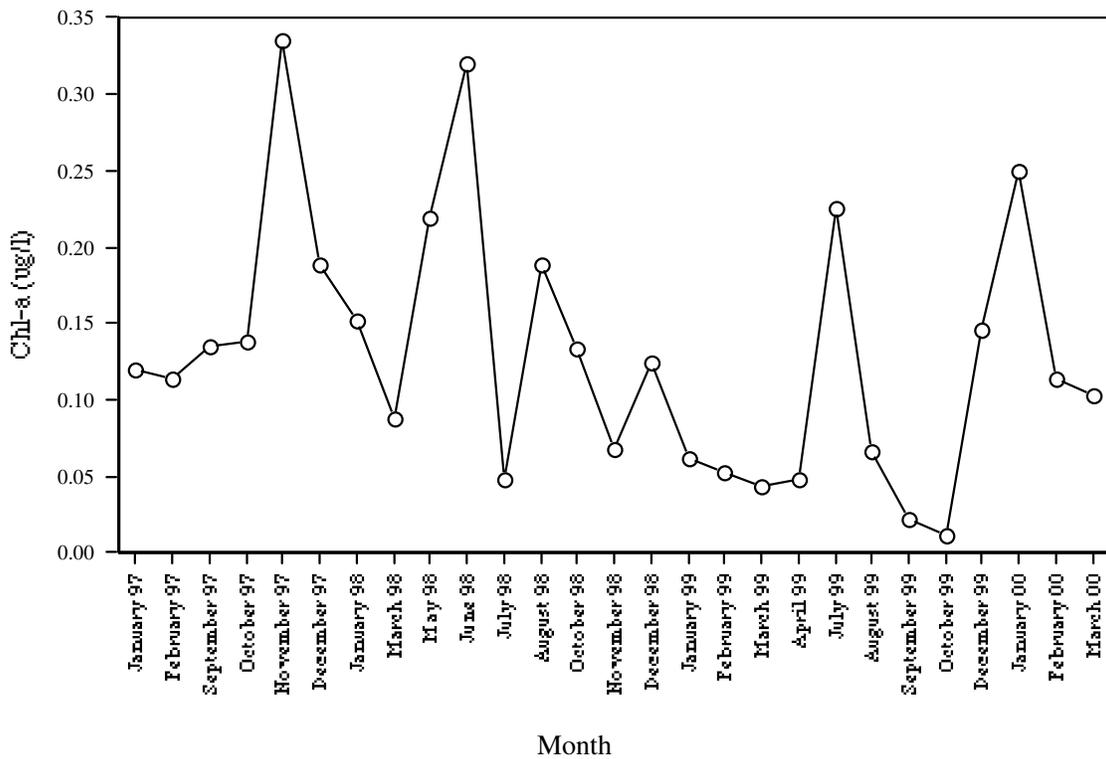
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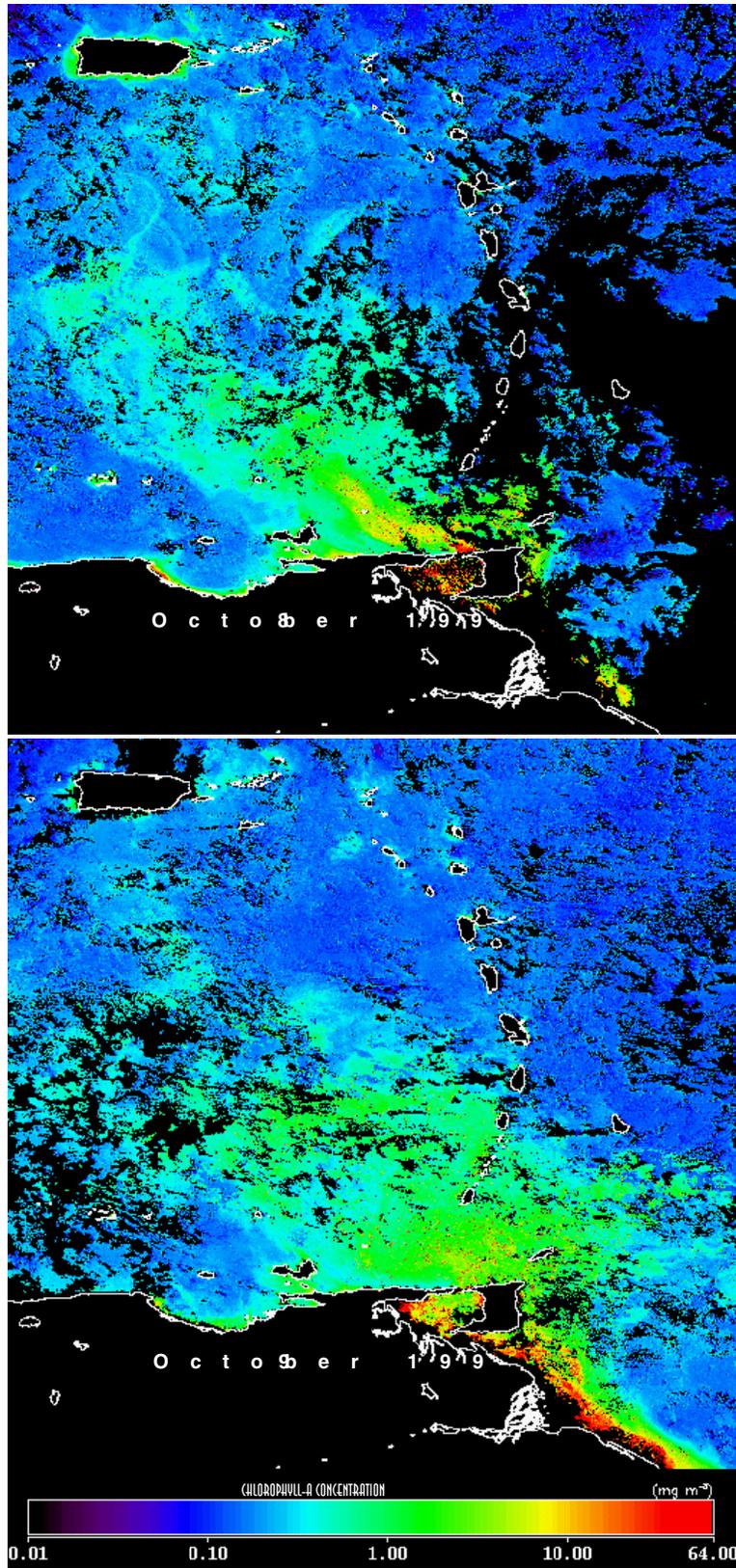
**Figure 1. Temporal variability of the absorption coefficient of particles (A), phytoplankton (B), colored dissolved organic matter (C), and the optical backscattering coefficient (D) at surface waters of the Caribbean Time Series (CaTS) station.**

**Table 1. Statistical variability of the absorption coefficient of particles ( $a_p$ ), colored dissolved organic matter ( $a_g$ ), and backscattering ( $b_b$ ) at selected wavelengths in surface waters of the Caribbean Time Series (CaTS) station.**

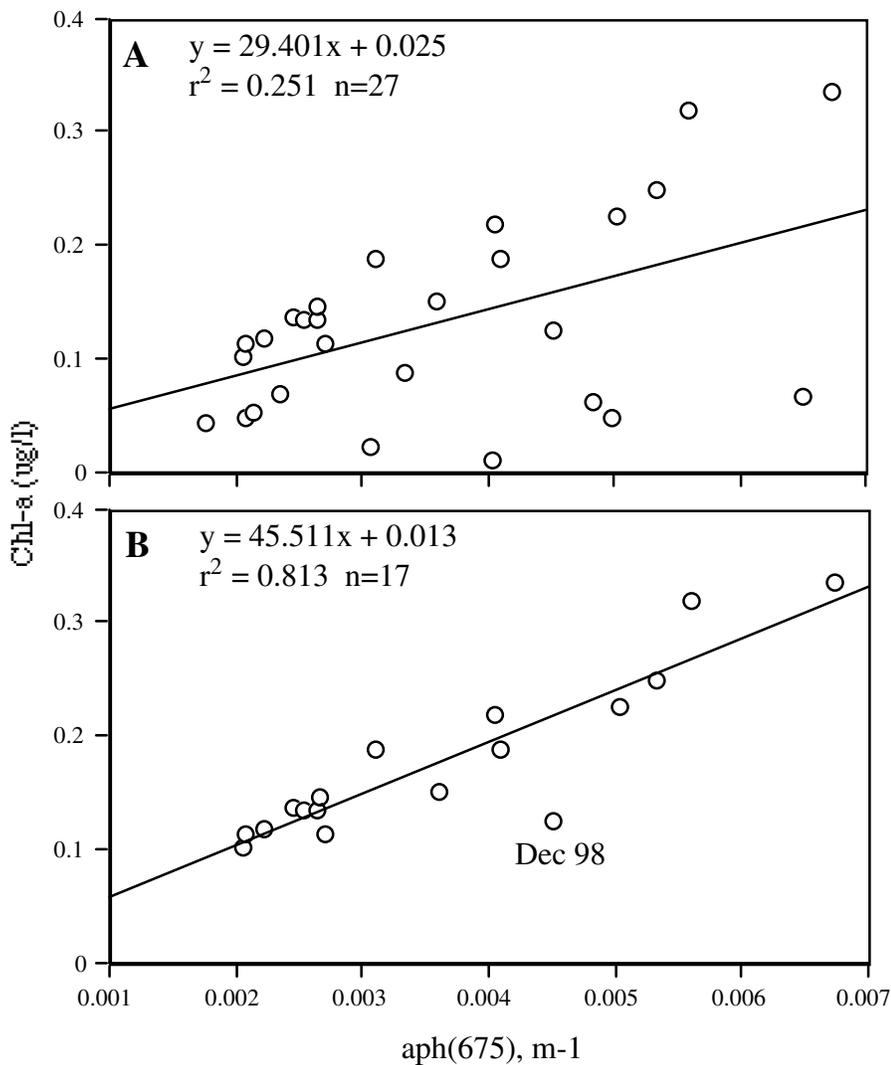
Parameter	Samples (n)	Mean	Std. Dev.	Minimum	Maximum
$a_p(443)$	27	0.0221	0.0094	0.0118	0.0504
$a_p(555)$	27	0.0044	0.0036	0.0016	0.0178
$a_p(671)$	27	0.0044	0.0018	0.0021	0.0089
$a_g(412)$	16	0.0776	0.0452	0.0341	0.2240
$a_g(443)$	16	0.0595	0.0360	0.0298	0.1787
$a_g(555)$	16	0.0276	0.0159	0.0128	0.0772
$a_g(671)$	16	0.0107	0.0036	0.0023	0.0169
$b_b(442)$	20	0.0045	0.0014	0.0031	0.0072
$b_b(589)$	20	0.0010	0.0003	0.0006	0.0015
$b_b(671)$	20	0.0009	0.0001	0.0007	0.0010



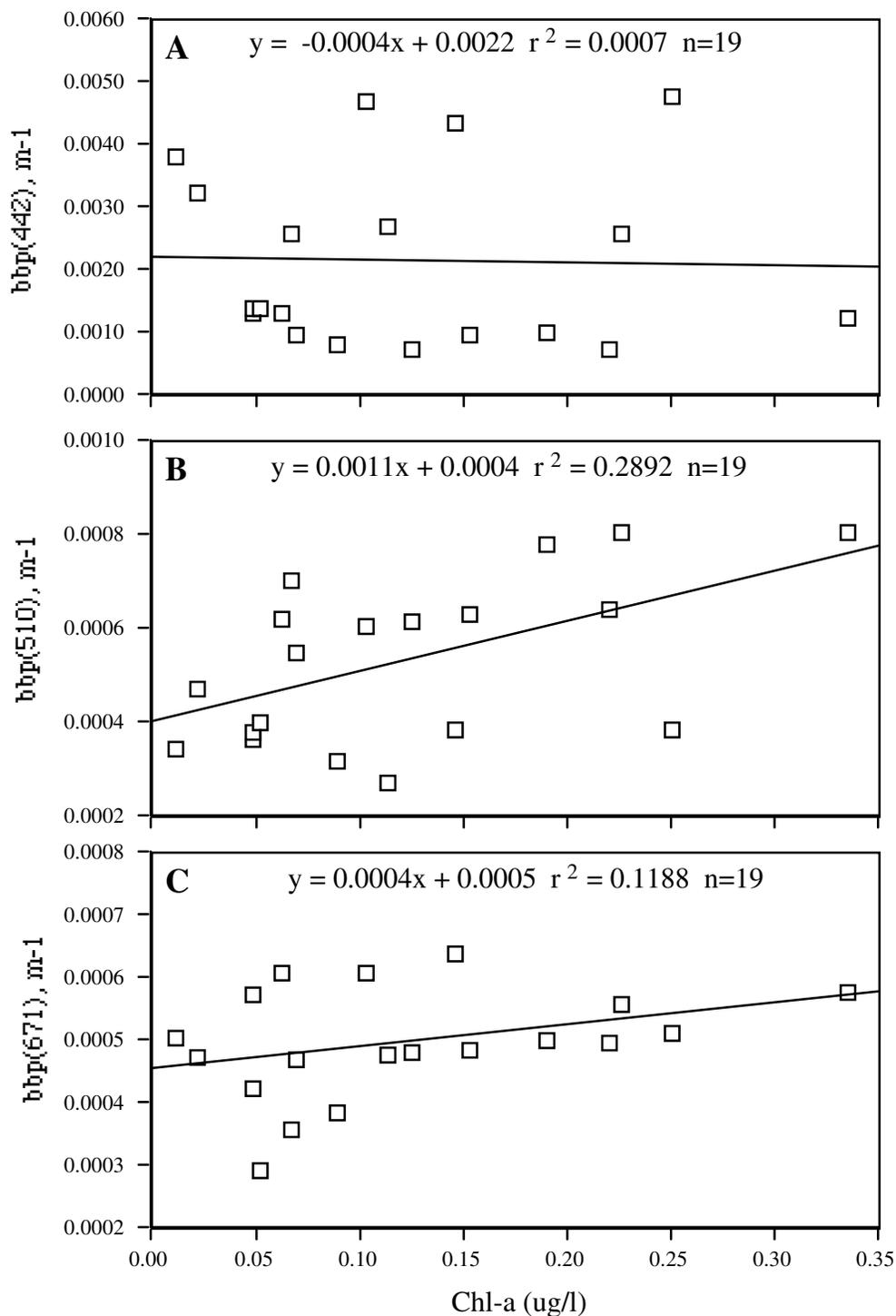
**Figure 2. Temporal variability of Chlorophyll-a concentrations in surface waters of the Caribbean Time Series (CaTS) station.**



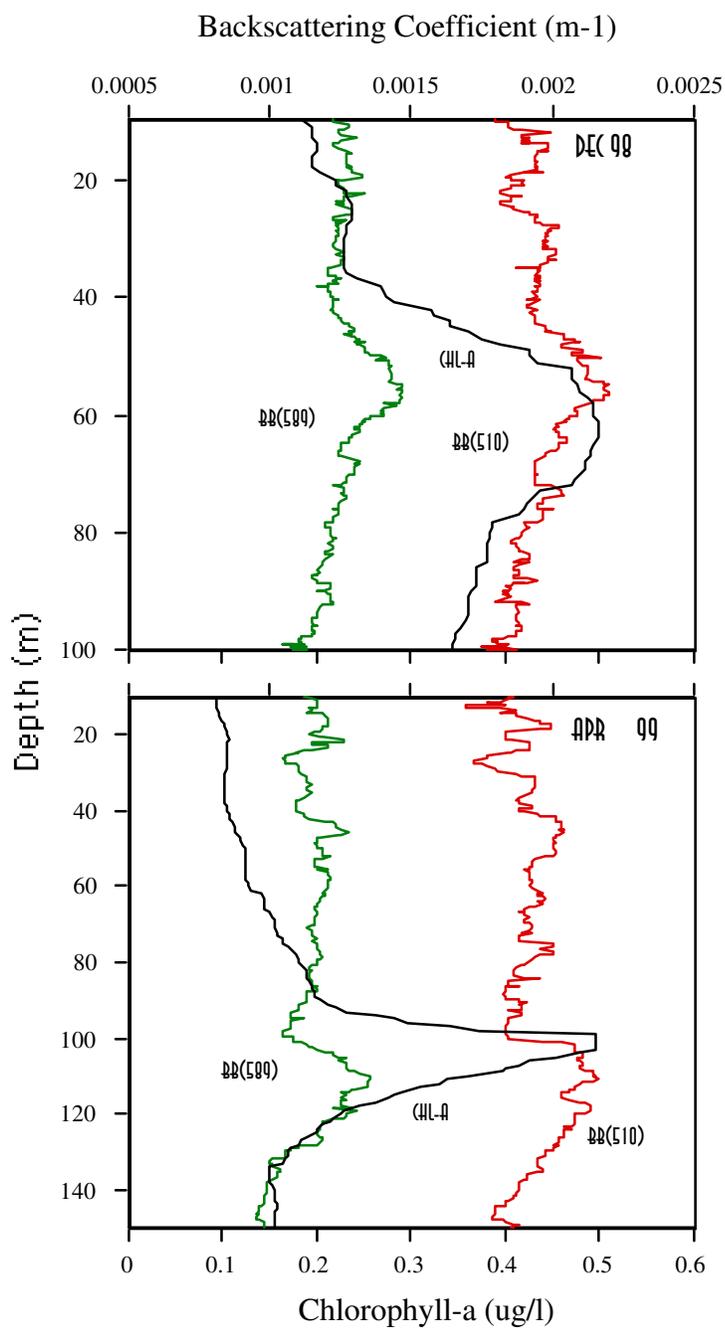
*Figure 3. Mean composite images of SeaWiFS for October 1998 and 1999.*



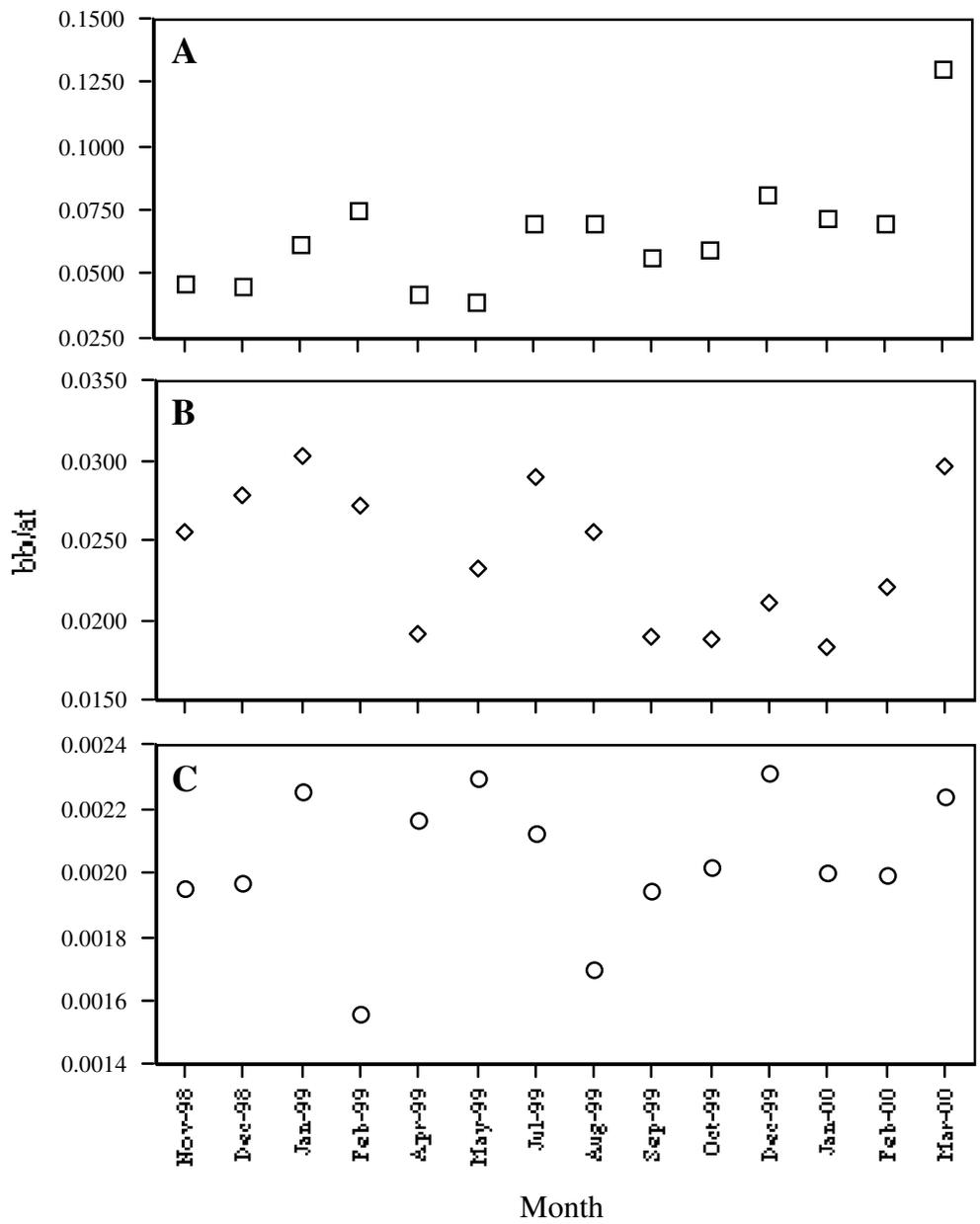
**Figure 4. Relationship in surface waters between the absorption coefficient of phytoplankton (aph) at 675 nm and Chlorophyll-a concentration using the entire data set (A) and only data points greater than 0.1 ug/l of Chlorophyll-a (B). The solid line represents the best-fit linear regression to the data, with the equation,  $r^2$ , and n values given in each panel. By eliminating the point of December 98 in lower panel (B) the  $r^2$  is equal to 0.92.**



**Figure 5. Relationship in surface waters between Chlorophyll-a concentration and the backscattering coefficient of suspended particles ( $b_{bp}$ ) at 442 nm (A), 510 nm (B), and 671 nm (C). The solid line represents the best-fit linear regression to the data, with the equation,  $r^2$ , and  $n$  values given in each panel.**



**Figure 6. Profiles of Chlorophyll-a and backscattering coefficient at two wavelengths (510 and 589 nm) during December 98 (upper panel) and April 99 (lower panel). Notice the good correlation between the peaks at the deep Chlorophyll maximum.**



**Figure 7. Ratio of backscattering coefficient ( $b_b$ ) and total absorption coefficient ( $a_t$ ) in surface waters of the Caribbean Time Series (CaTS) station at three different wavelegths: 442 nm (A), 510 nm (B), and 671 nm (C).**