



**PARTNERSHIP AWARDS FOR INNOVATIVE AND UNIQUE EDUCATION  
AND RESEARCH PROJECTS**

**NASA GRANT NAG13-99029**

**DEVELOPMENT AND VALIDATION OF BIO-OPTICAL ALGORITHMS  
IN COASTAL WATERS**

**FINAL REPORT  
(1999-2002)**

**SUBMITTED TO**

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## INDEX

I. COVER PAGE .....	1
II. INDEX .....	2
III. PROJECT SUMMARY .....	3
IV. INTRODUCTION .....	3
V. MATERIALS AND METHODS .....	4
A. Bio-Optical Rosette .....	4
B. Sampling in Mayagüez Bay .....	5
C. Bio-Optical Measurements .....	6
VI. RESULTS AND DISCUSION .....	6
A. Bio-Optical Variability .....	6
B. Validation of Bio-Optical Algorithms .....	12
C. Primary Production Experiments .....	15
VII. GENERAL CONCLUSIONS .....	16
VIII. METRICS .....	17
A. Students Participation .....	17
B. Publications and Meeting Presentations .....	18
C. New Collaborations and Proposals .....	18
IX. CITED LITERATURE .....	18
X. APPENDIX ONE: Bio-Optical Rosette .....	20
XI. APPENDIX TWO: Marcos Rosado's Paper .....	21

## PROJECT SUMMARY

Several years ago a joint effort between researchers from the NASA-Stennis Space Center and the University of Puerto Rico at Mayagüez intended to use remote sensing for a better understanding of the land-sea interactions of Mayagüez Bay; a semi-enclosed bay in the western coast of Puerto Rico. However, the complexity of the bay's optical properties and certain limitations of the technology at that time made it very difficult. Recently improved methods and instruments have been used in this bay, allowing a better understanding of such bio-optical variability. A new sampling design with twenty-four stations was performed. Inherent and apparent water optical properties were measured using the NASA ocean optics protocols for validation of satellite ocean color sensors. A custom-made rosette with several optical instruments helped to provide more detailed analyses of the bio-optical properties. In addition, water quality parameters were measured. Our results show that large spatial and temporal variability of the bio-optical properties in Mayagüez Bay are generated by changes in rivers discharge and anthropogenic activities. The new efforts clearly show that current bio-optical algorithms do not work in this bay. Therefore, new algorithms are now in development. The efforts of this project are finally providing the crucial steps for better application of remote sensing in the western coast of Puerto Rico.

## INTRODUCTION

The application of remote sensing in coastal environments has been difficult because of the optical complexity of these waters (Carder et al., 1989). Seasonal river discharge and land run-off increase the concentration of phytoplankton biomass along with colored dissolved organic matter and suspended sediments. Therefore, the conventional bio-optical algorithms, which apply the band-ratio technique and assume that variations in ocean color are determined solely by phytoplankton pigments, do not work properly.

Typical atmospheric correction algorithms may also suffer from serious deficiencies when they are applied in coastal areas (Arnone et al., 1998). They assume that the water reflectance is negligible in the red and near-infrared wavelengths (Gordon et al., 1983). This assumption is valid for open ocean waters but it is not for waters that contain inorganic suspended matter, which strongly scatters light at those wavelengths. In shallow waters, bottom reflectance also affects the optical signal and it must be considered (Lee et al., 1994).

It is clear that good estimates of water quality parameter, like phytoplankton biomass, in coastal waters cannot be obtained using the conventional algorithms. A new approach is required where all sources responsible for the optical variability are considered in the interpretation of the remote sensing signal. Inverse modeling of the reflectance curve is an alternate approach that has been suggested for coastal remote sensing (Gould and Arnone, 1997). In this procedure, the different spectral contributors of the light field are separated and their effects in the remote sensing reflectance are evaluated (Lee et al., 1994).

In Puerto Rico, a large effort has been done for several years in order to better understand the bio-optical properties of Mayagüez Bay. This semi-enclosed bay in the west coast of Puerto Rico suffers spatial and temporal variations in phytoplankton pigments and suspended sediments due to seasonal discharge of local rivers (Gilbes et al., 1996). Several years ago a joint project with researchers from NASA-Stennis Space Center and the University of Puerto Rico at Mayagüez

intended to use remote sensing for a better understanding of the land-sea interface in this bay (Otero et al., 1992). However, the complexity of bay's optical properties and certain limitations of the technology at that time made it very difficult. Most recently new methods and instruments have been used, allowing a better study of the bio-optical properties of Mayagüez Bay. Such studies demonstrate that large spatial and temporal variability of bay's optical properties makes very difficult to apply conventional bio-optical algorithms. The available data demonstrate that improved algorithms and different remote sensing techniques are necessary for this coastal region.

This final report is a summary of the most recent NASA project in Mayagüez Bay which helps to continue the efforts that started several years ago toward the application of remote sensing for land-sea interface studies.

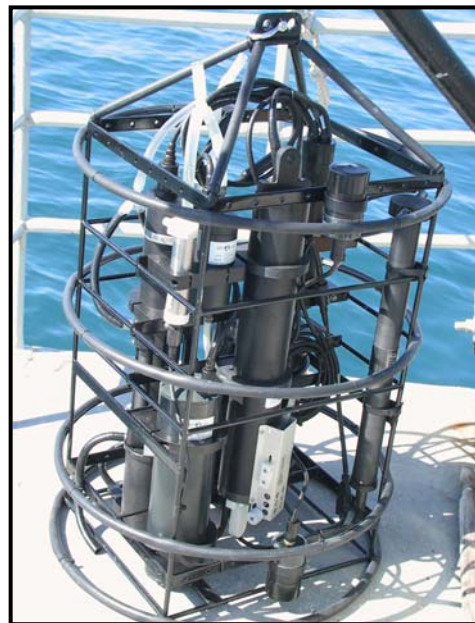
The main goal of the project was to improve the remote sensing techniques for a better estimation of water quality parameters in coastal waters. In order to accomplish this goal, the specific objectives were:

1. Evaluate the spatial and temporal variability of the bio-optical properties.
2. Correlate water quality parameters and bio-optical properties.
3. Perform inverse modeling of the remote sensing reflectance curves.
4. Develop bio-optical algorithms for Mayagüez Bay.
5. Cross-validate our results with the efforts in coastal waters of the Gulf of Mexico.

## **MATERIALS AND METHODS**

### **Bio-Optical Rosette**

One the main activity of the collaboration between NASA-SSC and UPRM through this project has been the development of similar bio-optical rosettes. After a careful design of the optical rosette, the purchase order to Wet Labs Inc. was issued in March 2000. They build several optical instruments along with a custom made frame to deploy them. As stated in the proposal, the purchased instruments were similar to those purchased by Dr. Richard Miller: an AC-9, a WETStar fluorometer, a WETPak 20 rechargeable battery pack, and a Mpak-3 Data Logger. Wet Labs delivered the instruments and the deployment cage by the end of April 2000. The design and construction of the rosette took a while but the final product is excellent. Figure 1 shows a photo of the rosette as it is finished. The SBE-19 CTD and the HydroScat-6 were already purchased and they were sent to the factory for checkout and calibration. After their arrival in May, they were mounted on the deployment cage and the whole optical rosette was ready for testing. A preliminary test was performed during the end of May to understand how the instruments work



**Figure 1: Bio-Optical Rosette at UPRM.**

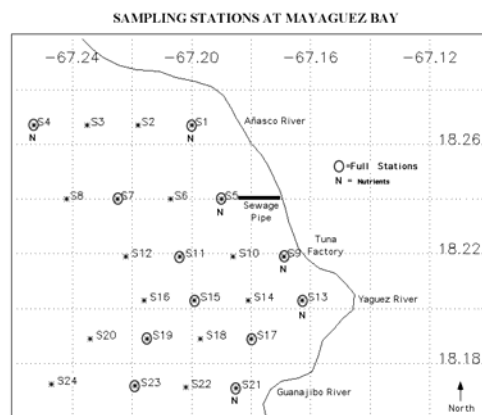
and to get familiar with the software. The rosette was fully tested for the first time during two cruises to the Caribbean Sea in June 2000. The purpose of the first cruise called CARATLAN was to characterize the geochemical and bio-optical gradients in near surface waters between the mesotrophic waters of the east central Caribbean Sea and the profoundly oligotrophic waters of the adjacent Atlantic Ocean. During the second cruise called PRIDE, bio-optical measurements were taken to validate MODIS data for measuring the Sahara Dust. The rosette was used in Mayagüez Bay for the first time in July 2000. Since then several cruises has been performed and many bio-optical data has been collected.

### Sampling in Mayagüez Bay

During October of 1999, Dr. Richard Miller and Dr. Greg Booth from NASA Stennis Space Center came to Puerto Rico to participate in a bio-optical sampling of Mayagüez Bay. Eleven stations were sampled during two days and the inherent and apparent optical properties were measured. The optical rosette assembled by Dr. Miller was used for the first time in the Bay, collecting very important data. All data were processed, compiled, and sent to Dr. Miller for inter-comparison and they were incorporated in Marcos Rosado's thesis.

In February 2000, another cruise to Mayagüez Bay was carried out and six stations were sampled. Inherent and apparent optical properties were also measured. Dr. Carlos Del Castillo from University of South Florida (now at NASA-Stennis Space Center) participated in this cruise. The data were used for teaching purposes in our remote sensing class and they were added to the database.

During July of 2000, we performed the first and most complete bio-optical sampling of Mayagüez Bay from inshore to offshore waters, covering the Añasco, Yagüez, and Guanajibo rivers, and the regions affected by the dumping of the Tuna factory and the sewage pipe. Figure 2 shows the location of the stations. Twenty-four (24) stations were sampled with the new optical rosette, in which 12 stations (indicated with a circle in the figure) had ancillary data. The ancillary data collected at those 12 stations were chlorophyll-a, nutrients, total suspended sediments, absorption of particles and colored dissolved organic matter, remote sensing reflectance with the GER-1500, secchi measurements, and wind speed. The new sampling design demonstrated to be very appropriate, therefore further samplings at the same stations were carry out during April 2001, October 2001, February 2002, and August 2002.



**Figure 2: Sampling stations at Mayagüez Bay as determined by the latest design.**

## Bio-Optical Measurements

The bio-optical rosette with several instruments was used at selected stations to measure profiles of different water properties. A CTD (Seabird SBE-19 with pump) measured temperature and salinity. A small fluorometer (Model WetStar from Wet Labs) measured chlorophyll fluorescence. The spectral transmittance,  $c(\lambda)$ , and spectral adsorption,  $a(\lambda)$ , were measured over nine wavelengths with the AC-9 meter (from Wet Labs). The backscattering coefficient,  $b_b(\lambda)$ , at six wavelengths was measured with the HydroScat-6 (from Hobi Labs). Upwelling radiance,  $L_u(0^-, \lambda)$ , and downwelling irradiance,  $E_d(0^-, \lambda)$ , were obtained using a submersible radiometer (Model OCR-200 from Satlantic).  $L_u(0^-, \lambda)$  and  $E_d(0^-, \lambda)$  values were used to calculate the diffuse attenuation coefficient (K). Water-leaving radiance,  $L_w(\lambda)$ , and the above-surface downwelling irradiance,  $E_d(0^+, \lambda)$ , were measured using the GER 1500 portable spectroradiometer.  $R_{rs}(\lambda)$  was calculated from the ratio between  $L_w(\lambda)$  and  $E_d(0^+, \lambda)$ .

The optical measurements from the profilers were compared with water samples measurements collected at several depths. Concentration of phytoplankton chlorophyll-a was obtained using the standard fluorometric method (Yentsch and Menzel, 1963). Total particulate absorption spectra,  $a_p(\lambda)$ , for samples collected on Whatman GF/F glass-fiber filters were measured with an 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, is considered to be the *in vivo* phytoplankton absorption,  $a_{ph}(\lambda)$ . Optical absorption spectra of the colored dissolved organic matter,  $a_g(\lambda)$ , was determined with a Perkin Elmer double-beam spectrophotometer following the method described by Bricaud et al. (1981).

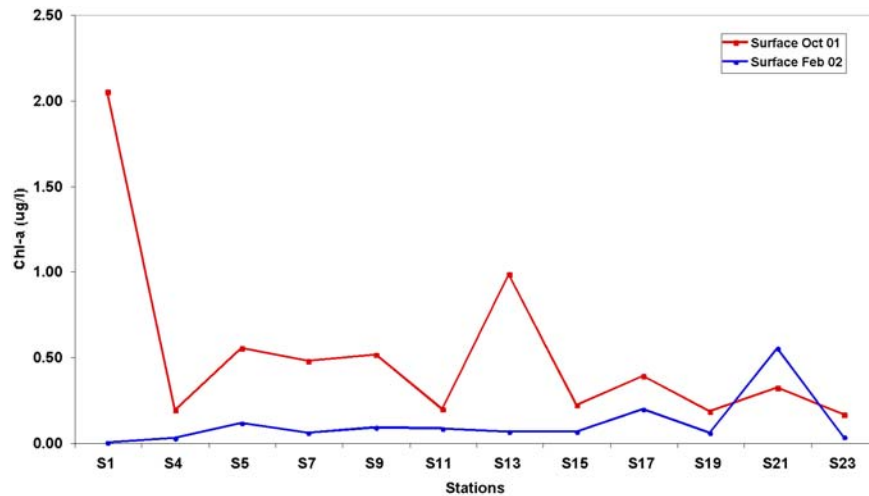
## RESULTS AND DISCUSION

### Bio-Optical Variability

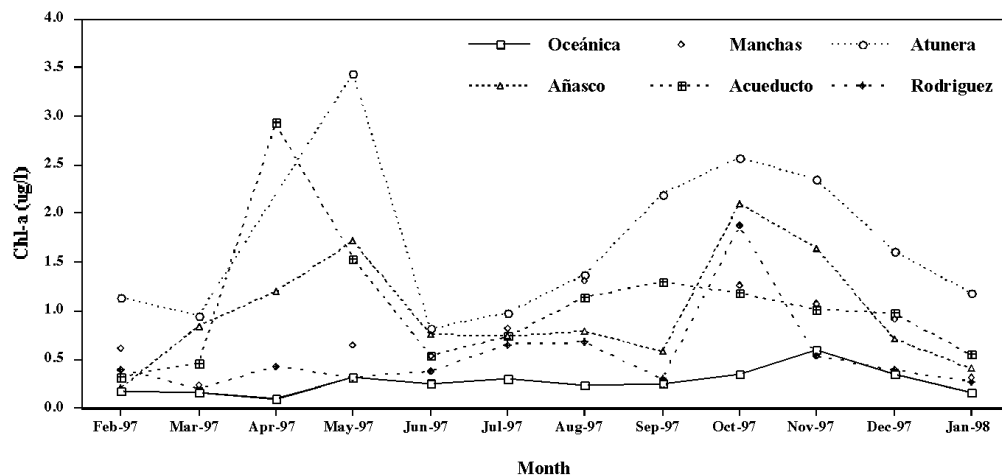
Mayagüez Bay is a highly dynamic environment that shows large spatial and temporal variability of bio-optical properties. Trends in Chl-a concentrations measured in this bay during recent years are similar to those measured in the past by Gilbes et al. (1996). A clear Chl-a peak in October (Figure 3) is due to the high river discharge during the rainy season that goes from August to November. Stations 1, 13, and 21 are the closest to the rivers mouth and they show the higher concentrations of Chl-a.

In addition to the October peak, time series measurements show another peak in April or May at some stations, which is more difficult to explain (Figure 4). The weak correlation between Chl-a and rivers discharge suggest that other factors may also play an important role in the phytoplankton dynamics during times of low river discharge. These factors may include anthropogenic activities,

wind-driven organic matter resuspension and internal waves. Figure 4 shows that along the sampled year the station called Atunera maintained the higher concentration of Chl-a. This station is located in an area where a tuna factory is dumping material. The data clearly show the effect of such dumping in the bio-optical properties of the bay.



**Figure 3: Chlorophyll-a concentrations in surface waters of Mayagüez Bay.**

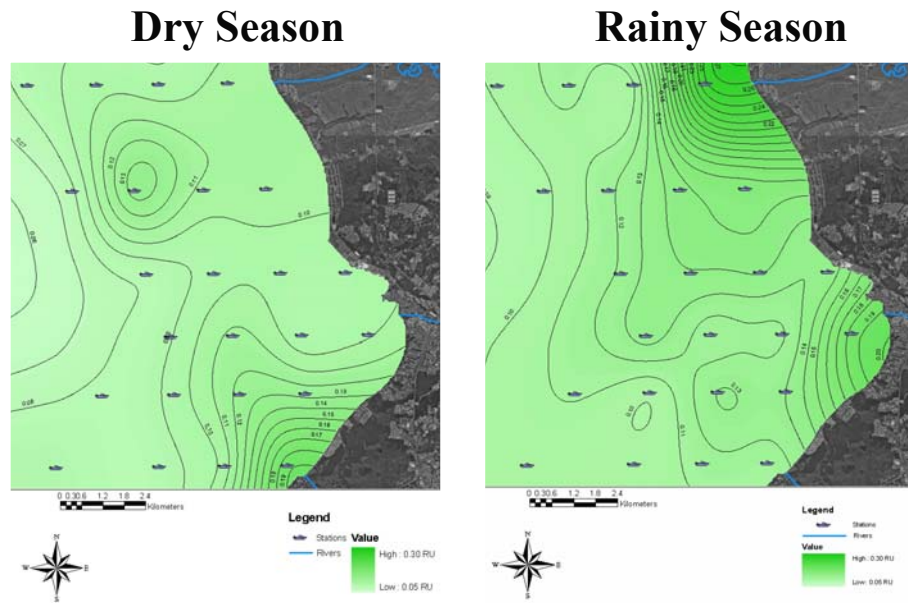


**Figure 4: Time series of Chlorophyll-a concentrations at Mayagüez Bay.**

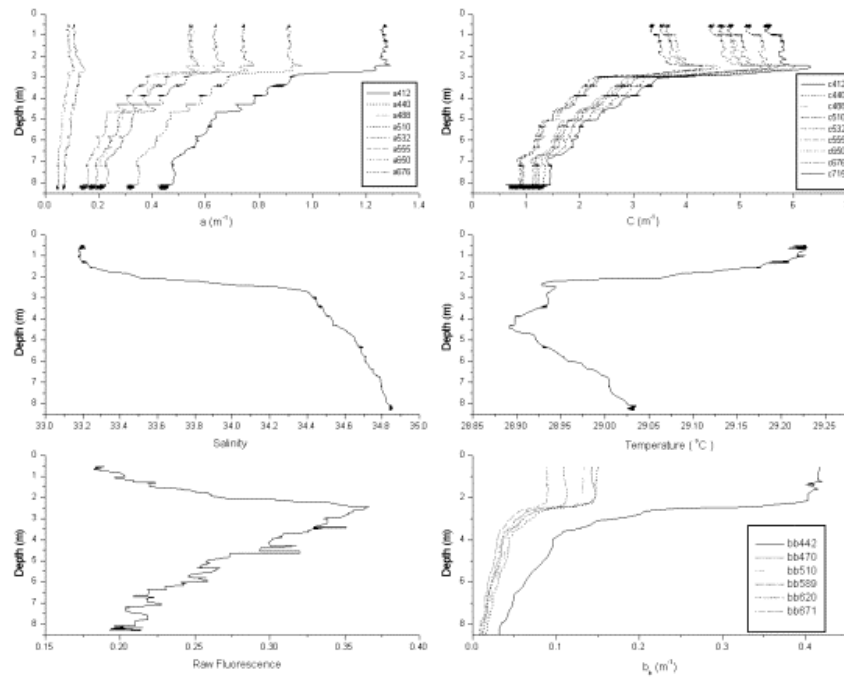
The effect of river discharge on the bio-optical properties of Mayagüez Bay is perhaps more clearly recognize with the data collected by the bio-optical rosette. For example, a contour map of Chl fluorescence is presented in Figure 5, showing the higher concentrations closed to the rivers.

Profiles of bio-optical data are another evidence of the effect of river discharge (Figure 6). Lenses of low salinity and high optical properties (absorption, attenuation, and backscattering) are clearly identified on the top of the water column.





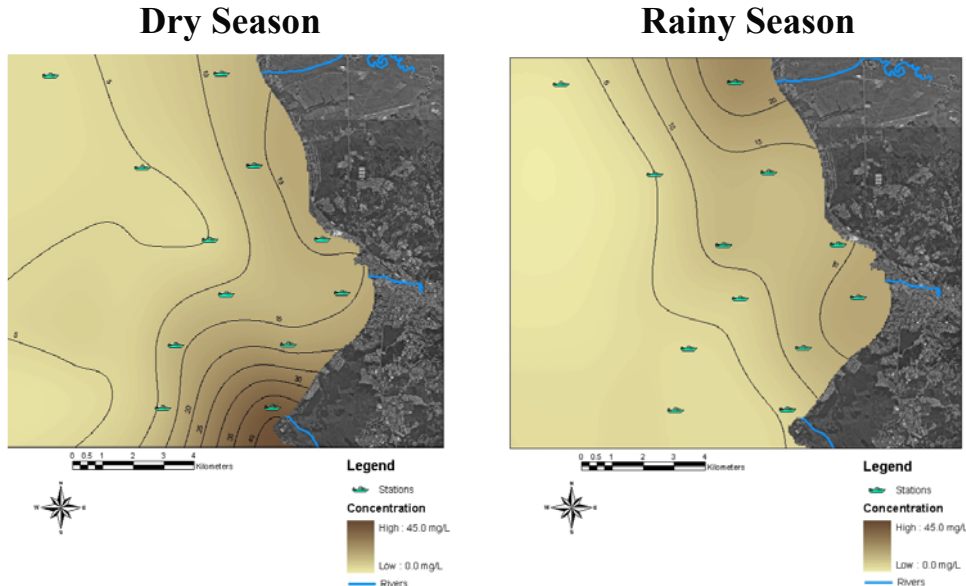
**Figure 5: Chlorophyll fluorescence as measured with the bio-optical rosette.**



**Figure 6: Profiles of water optical properties as measure in one station with the rosette.**

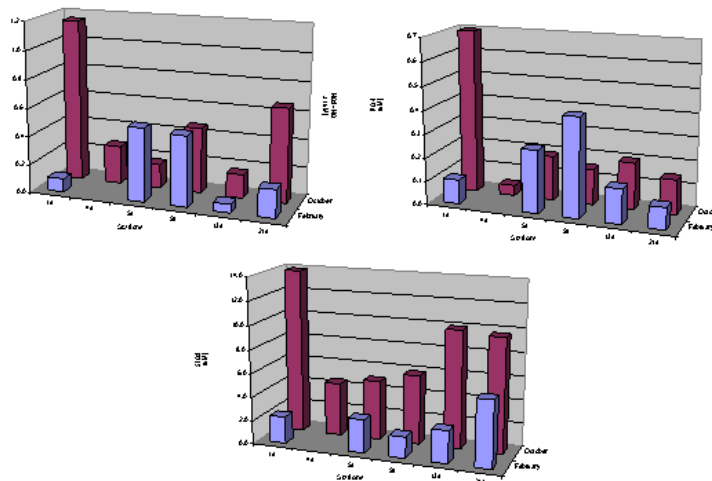


Changes in bio-optical properties are highly correlated with the riverine input of suspended sediments. The distribution of suspended sediments follows the seasonality and magnitude of river discharge (Figure 7). During the wet season (October) the northern stations of the bay show the higher concentrations and during the dry season (February) the southern stations have the higher concentrations. Perhaps this is another evidence for the possible effect of wind-driven and anthropogenic effects.



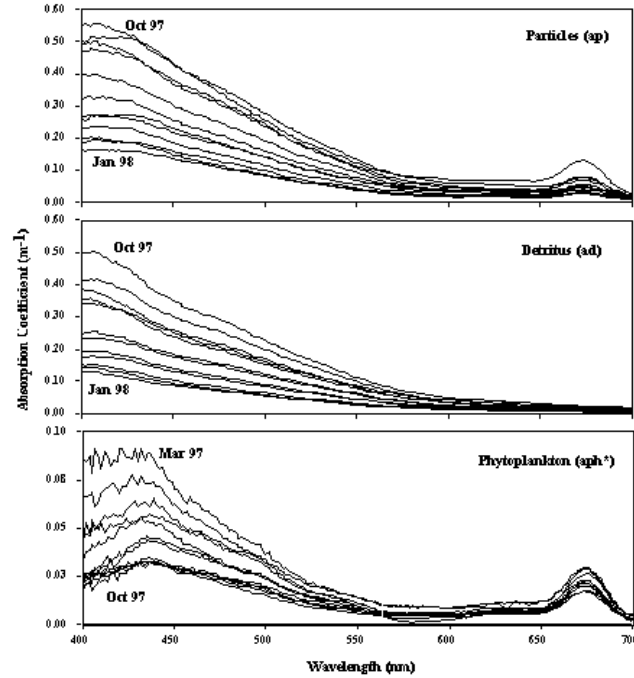
**Figure 7: Suspended sediments at surface waters of Mayagüez Bay.**

Nutrients concentration is another piece of evidence for the important effect of rivers discharge. Figure 8 shows how the nutrients clearly increase during the wet season, especially at those stations closed to the river mouths.



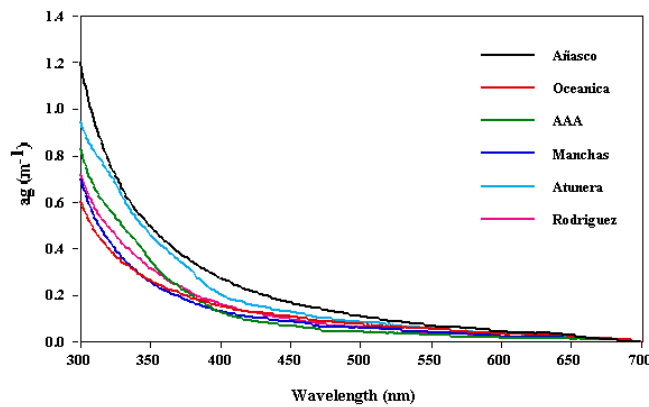
**Figure 8: Nutrients concentration at surface waters of Mayagüez Bay. Top left panel shows  $\text{NO}_2+\text{NO}_3$ , top right panel shows  $\text{PO}_4$ , and bottom panel shows  $\text{SiO}_4$ .**

Land-sea interactions are also shown with the absorption coefficients of particles, detritus, and phytoplankton (Figure 9). The collected data demonstrate that these optical properties are also affected by the rainy season, where October is the peak of river discharge.



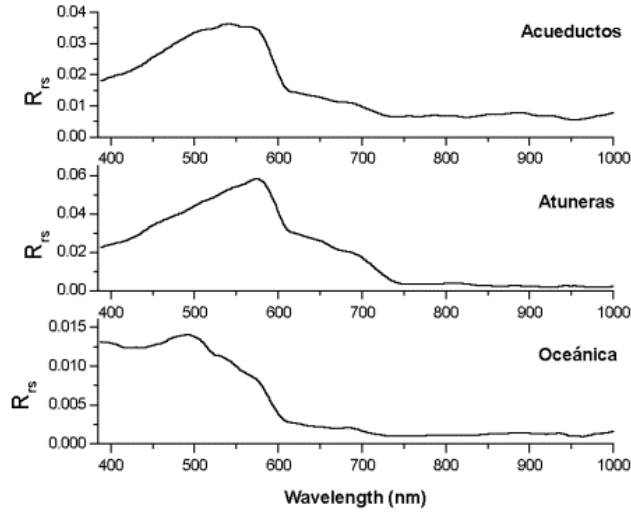
**Figure 9:** *Absorption coefficients of particles, detritus, and phytoplankton at surface waters in an inshore station of Mayagüez Bay.*

The absorption of colored dissolved organic matter ( $a_g$ ) is also affected by all the processes described above. Those stations closed to the rivers, like the Añasco Station in Figure 10, show the higher absorption of CDOM.



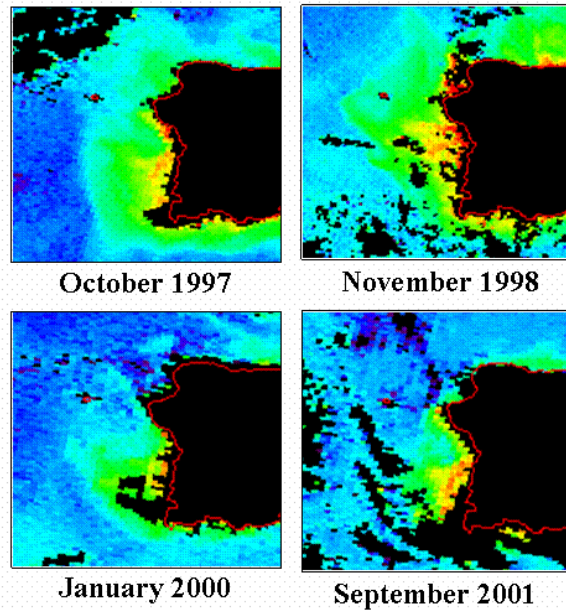
**Figure 10:** *Absorption coefficient of colored dissolved organic matter at surface waters of selected stations in Mayagüez Bay.*

As demonstrated, our preliminary analyses of Mayagüez Bay indicate that the bio-optical variability is very large, even though this is a relative small geographic area. Therefore, it must be considered in order to apply ocean color remote sensing. Measurements of remote sensing reflectance clearly show such differences, and at least three different curves have been identified in shape and magnitude (Figure 11).



**Figure 11: Examples of remote sensing reflectance ( $R_{rs}$ ) curves found in the Mayagüez Bay.**

The large variability in bio-optical properties at such small geographic region makes the use of current ocean color sensors very difficult. This is the case of SeaWiFS, where the pixels size (1 km) is too large for studying the Mayagüez Bay. However, even under such conditions the land effect on sea conditions are appreciated on large scale (Figure 12).



**Figure 12: SeaWiFS images showing the Mayagüez Bay.**

## Validation of Bio-Optical Algorithms

A large bio-optical data set ( $n = 92$ ) was collected in several cruises to Mayagüez Bay. The cruises were performed from February 1997 to February 2002. Water leaving radiance, remote sensing reflectance and chlorophyll-a concentration were among the parameters measured. Those values were used to evaluate SeaWiFS OC-2 and OC-4 and CZCS Case-1 and Case-2 bio-optical algorithms in the region. Remote sensed chlorophyll-a concentrations were compared against *in situ* chlorophyll-a concentrations obtained by fluorometric analysis. Regression coefficients were low for the algorithms considered ( $R^2 < 0.4$ ). Percent errors fluctuated from  $-99.9$  to  $7433.8$  for the complete data set. Low regression coefficients and high percent errors are attributed to high concentrations of total suspended sediments and high CDOM absorption.

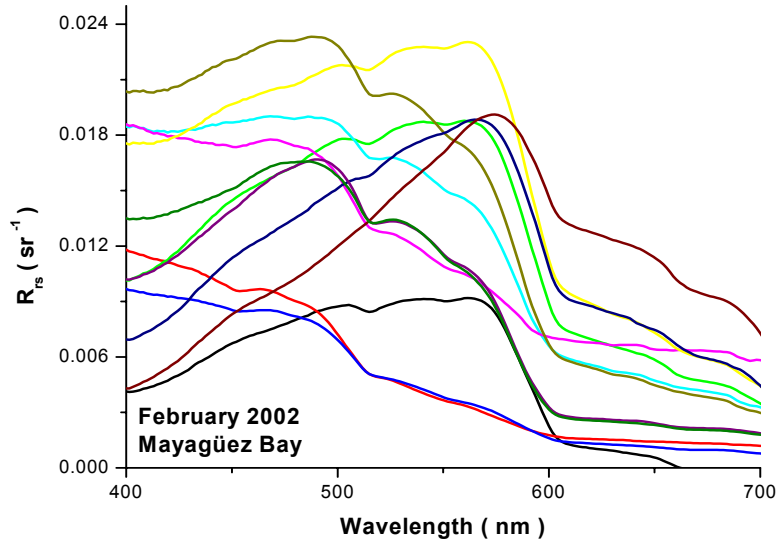
Although coastal waters comprise a relatively small percentage of the global ocean surface (about 8%), they account for 40% of the oceanic primary production (Longhurst and Pauly, 1987, Levinton, 1982). Accurate values of chlorophyll-a (Chl-a) concentration in these areas are a must if a better understanding of the global carbon cycle is the goal. Until now, the only cost-effective tool for large-scale chlorophyll-measurements is ocean color remote sensing (Banse and English, 1994). Unfortunately, the methods for measuring pigment concentrations using remote sensing are not completely developed for coastal waters. Several factors make a challenge out of measuring Chl-a remotely in coastal environments. Due to the optical complexity of coastal (case 2) waters, the traditional algorithms do not produce satisfactory results as in oceanic (case 1) waters (Kirk, 1994). These algorithms assume that phytoplankton pigments are responsible for most part of the ocean color (Gordon et al., 1983). River runoff, anthropogenic influence and bottom sediments resuspension are a few examples of possible sources of error in remote assessment of Chl-a.

Water for Chl-a analysis was sampled on amber 1 liter plastic bottles and a known volume filtered using Whatman GF/F filters ( $0.7 \mu\text{m}$  nominal pore size). The filters were inserted in 15 ml centrifuge tubes, 10 ml of HPLC grade methanol added and refrigerated for 24 hours. After the extraction period, the samples were centrifuged and the supernatant was collected in a 13 mm cuvette. The concentration of Chl-a was measured with a 10-AU Turner Designs fluorometer using the method proposed by Welschmeyer (1994). The fluorometric Chl-a concentration was then converted to seawater Chl-a concentration ( $\mu\text{g/ml}$ ). Remote sensing reflectance ( $R_{rs}$ ) was calculated as the ratio of water leaving radiance,  $L_w(\lambda)$  and the above surface downwelling irradiance,  $E_d(0^+, \lambda)$  as measured with a GER 1500 spectroradiometer (Figure 13). Chl-a was calculated from ( $R_{rs}$ ) to using the SeaWiFS OC-2, SeaWiFS OC-4 and from  $L_w(\lambda)$  using CZCS Case 1 and Case 2 algorithms. The Chl-a concentration estimated from the algorithms was plotted against *in situ* Chl-a and regression analysis performed. The percent error ( $((\text{observed} - \text{expected}) / \text{expected}) * 100$ ) between measured and remote sensed Chl-a was calculated for the algorithms considered.

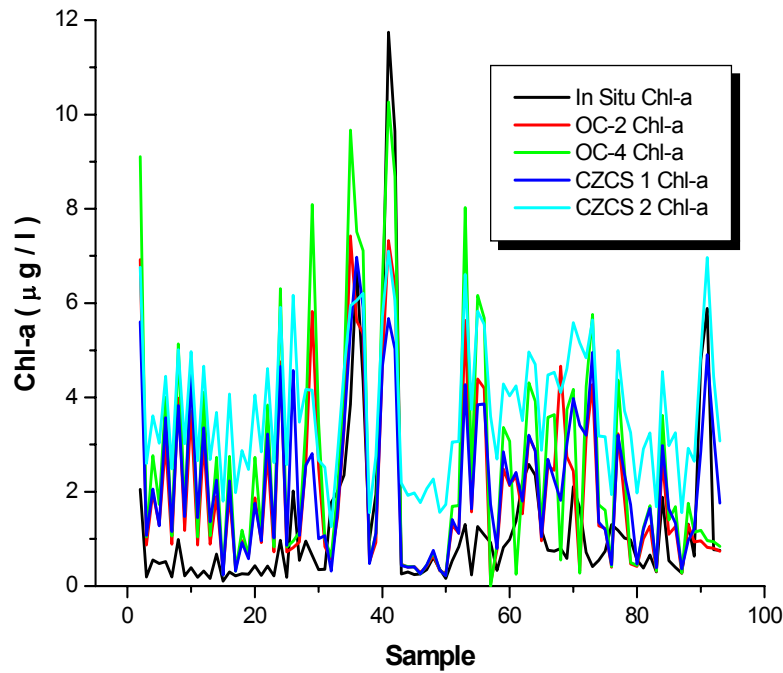
The comparison between measured and estimated Chl-a is shown in Figure 14. The regression analysis yielded similar  $R^2$  coefficients for the bio-optical algorithms considered (Figure 15). The algorithms tended to overestimate *in situ* Chl-a concentrations most of the time. Percent error fluctuated from  $-99.9$  to  $1651.8 \%$  for the complete data set (Figure 16). The number of samples between  $\pm 35 \%$  error was 22 for SeaWiFS OC-2, 18 for SeaWiFS OC-4, 19 for CZCS case-1 and 5 for CZCS case-2 algorithms.

Such a high discrepancy between measured and remote sensed Chl-a concentrations was attributed mostly to absorption in the blue region of the spectra by high CDOM concentrations and

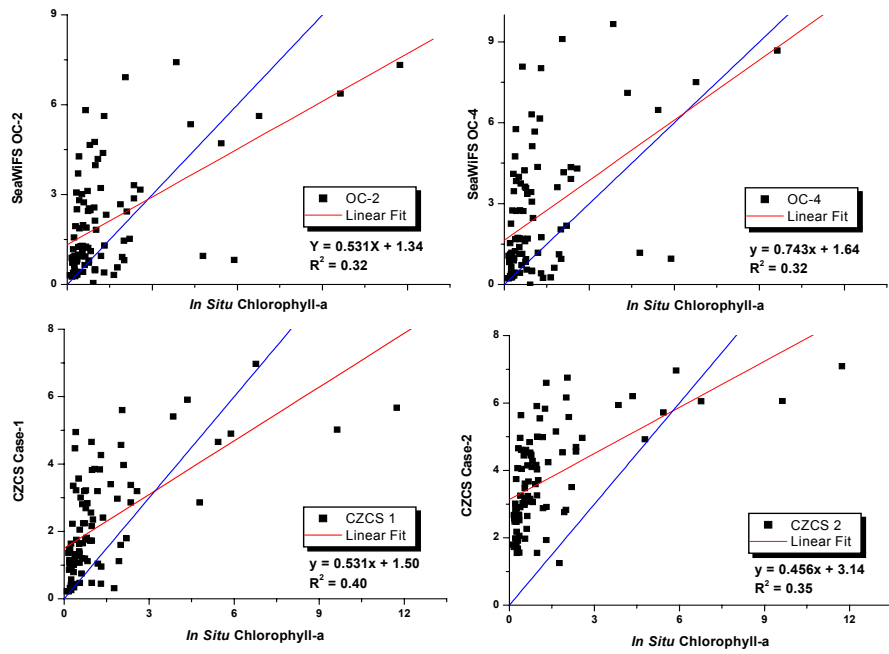
increased reflection by suspended sediments (Rosado, 2000). New algorithms that take into account the complexity of case-2 waters are needed in order to improve Chl-a remote sensing.



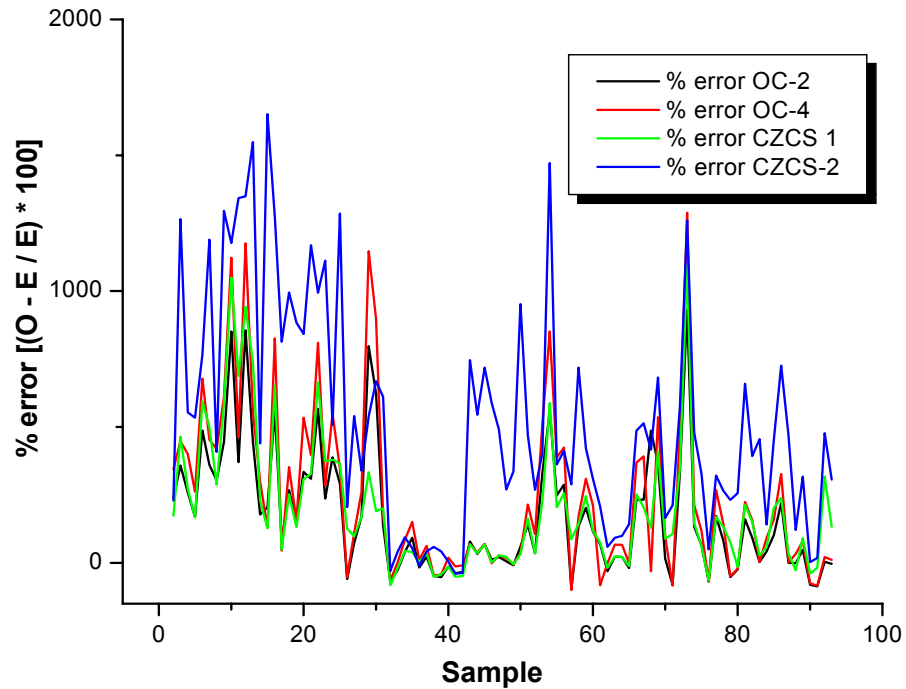
**Figure 13:** Remote sensing reflectance ( $R_{rs}$ ) curves from February 2002.



**Figure 14:** Chlorophyll-a measured in situ and estimated with several bio-optical algorithms.



**Figure 15:** Comparisons between in situ Chl-a concentration and remote sensed Chl-a. The blue line represents the function  $y = x$ . The number of samples for all data sets is  $n = 92$ .



**Figure 16:** Percent error between in situ Chl-a and remote sensed Chl-a.

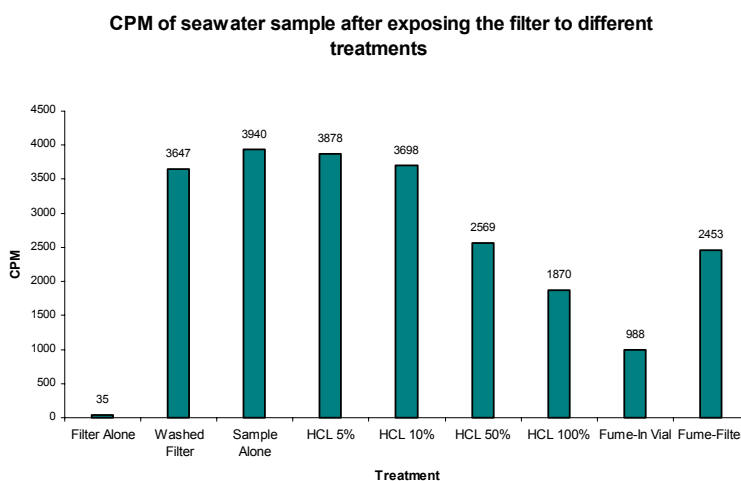
## Primary Production Experiments

In addition to propose work, preliminary experiments of primary production were made. In experiments using the Carbon 14 method, it has been observed that retention of C14 in the filter pore can cause overestimation of primary production (Peterson, 1980). Filters can be decontaminated with the use of HCL, which releases the inorganic carbon in the form of carbonic acid. In this experiment, Whatmann 934-AH filters with water sample were exposed to different treatments with HCL. The results were compared to observe which treatment was more effective in achieving less C14 retention.

Water samples were taken from Mayagüez Bay near the mouth of the Guanajibo River. Two bottles of 438ml were filled with sample and inoculated with 350 $\mu$ l of carbon-14. The inoculated water was divided into 30, 25ml bottles. The samples were not incubated, and each bottle was directly filtered through Whatmann 934-AH filters. The filters were exposed to the following treatment and were placed in scintillation vials:

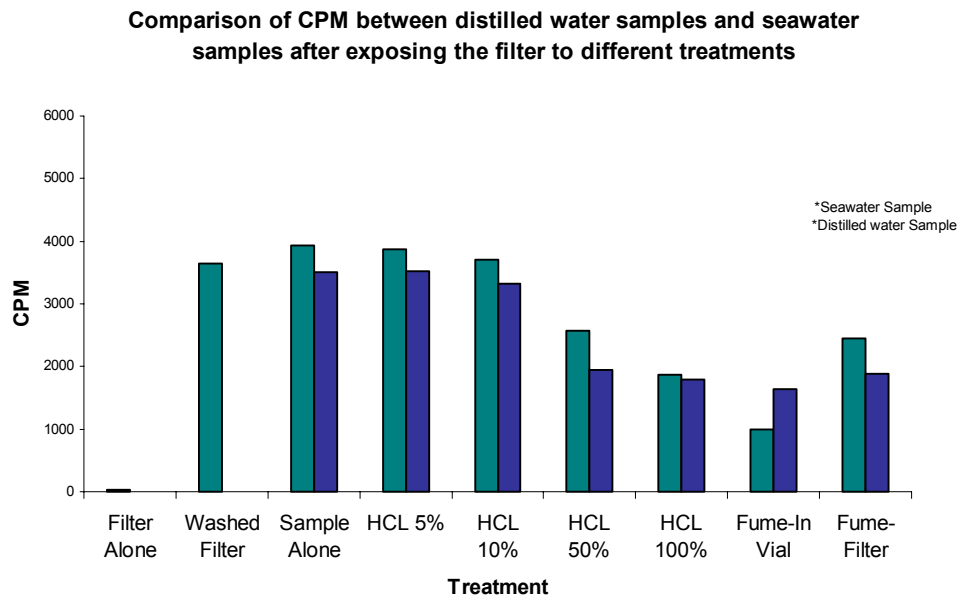
- 3 new filters with no treatment
- 3 filters with water sample
- 3 filters with water sample, washed with 25ml of filtered seawater.
- 3 filters with water samples and 250  $\mu$ l of HCL –5%\*.
- 3 filters with water samples and 250  $\mu$ l of HCL –10%\*.
- 3 filters with water samples and 250  $\mu$ l of HCL –50%\*.
- 3 filters with water samples and 250  $\mu$ l of HCL –100%\*.
- 3 filters with water sample were placed in vials and left fuming with HCL.
- 3 filters with water sample were placed in trays and left fuming with HCL.

After 24 hrs, 10 ml of scintillation liquid was added to each vial and they were taken to a scintillation counter to obtain the counts per minute (CPM). The same process was repeated for distilled water to correct for any primary production that could have taken place during the duration of the experiment.



**Figure 17: Comparison of the counts per minutes of seawater samples after exposure of the filter to different treatments with HCL.**





***Figure 18: Comparison of the counts per minutes between distilled water samples and seawater samples after exposure of the filter to different treatments.***

In this experiment it was observed that retention of inorganic carbon (C14) in the filter pore could have significant effects on the results obtained. Figure 1 shows the counts per minute of seawater samples filtered through Whatmann 934-AH filters that were exposed to different treatments of HCL. It was found that when using HCL at 5%\* or 10%\*, Whatmann 934-AH filters, retains plenty of C14, and no significant difference is observed from one another. The difference in retention occurs with HCL at concentrations higher than 50%\* and when exposed to fuming, which presents the best results of them all. The distilled water samples (figure 2) were used as a standard to compare with the seawater samples, since some primary production could have taken place during the duration of the experiment. The retention was very similar for both samples, being slightly smaller for the distilled water samples except when fuming on vial, which showed greater retention for distilled water. This result is not expected, and it could be due some technical error during the duration of experiment.

From these results it can be inferred that HCL of concentrations less than 50%\* should not be used for the extraction of inorganic carbon in primary production experiments. The best method was found to be exposure of filter in vials to HCL fumes.

## GENERAL CONCLUSIONS

The rainy versus the dry seasons, and therefore the river discharge, appear to be the principal factor regulating the bio-optical properties in Mayagüez Bay, including the phytoplankton populations. Anthropogenic activities in the river basins affect the composition of the rivers input in the bay and the characteristics of the water masses entering the bay. The western basin of Puerto Rico is highly developed and deforested, which favors erosion and transference of soil particles

into the river waters. These suspended particles increase scattering and absorption, effectively attenuating light, but also increase nutrient concentrations. During the dry season, resuspension of sediments and organic matter by wind and waves seems to be especially important (Alfonso, 1995, Gilbes *et al.*, 1996). Another possibility is the intrusion of internal waves into Mayagüez Bay, suspending sediments and organic matter deposited earlier within the coastal zone (Edwin Alfonso, personal communication; Bogucki and Redekopp, 1999). At smaller spatial scales, the anthropogenic effects of the tuna industry and sewage processing plants may be important. Nutrients in the vicinity of the Atuneras and Acueductos stations were high, especially organic nitrogen (Mónica Alfaro, unpublished data). Phytoplankton populations will respond to increased nutrient supply at these stations. Increased predation of zooplankton by gelatinous plankton (medusae and ctenophores) may be another mechanism accounting for larger phytoplankton biomass in these stations. Large populations of these organisms have been reported in Acueductos and Atuneras stations (Mónica Alfaro, unpublished data). This predation regulates abundance of zooplankton populations, resulting in lower grazing pressure over phytoplankton. This preliminary, but comprehensive, study of the bio-optical properties of Mayagüez Bay is establishing the basis for our next step toward a better understanding of land-sea interactions. It is clear that new and improved techniques of remote sensing are necessary for this region. But we are already working on that.

## METRICS

### Students Participation

Marcos Rosado, a master student of the Department of Marine Sciences, was involved in the collection and analyses of the bio-optical data. He was supported through this project and finished his master degree in November 2000. He is now working in a paper titled "Bio-Optical Variability of Mayagüez Bay, Puerto Rico" that will be submitted to the Caribbean Journal of Science. In January 2001, he started doctoral studies at UPRM and received a NASA fellowship through Stennis Space Center. Marcos' dissertation represents the continuation of his master research work. He has already traveled to SSC and worked with Dr. Carlos Del Castillo.

Another master student from Marine Sciences, Aurora Justiniano, was selected for the assistantship of the project when Marcos finished. Her thesis topic is the estimation of primary production in Mayagüez Bay using optical properties, especially by using the data collected with the optical package. Aurora's research will complement the current Marcos' research. She just finished the experiments of primary production and is now analyzing the data and writing her tesis.

In the three years project Patrick Reyes, a student of Marine Sciences was helping in the project with the samples of Colored Dissolved Organic Matter. Through this experience he got very interested in the topic that decided to continue doctoral studies on that. He is now in the second year and getting ready the proposal for his dissertation.

The possibility of incorporating other students into the Mayagüez Bay project is now in progress. My incorporation to the Department of Geology as assistant professor is bringing new students and ideas to the project. Other research areas will be expand the current scope and will allow a better understanding of the bay the application of remote sensing of coastal waters.

## **Publications and Meeting Presentations**

- Gilbes, F.**, Armstrong, R., Miller, R.L., Del Castillo, C.E., Rosado, M., and Ramirez, N. (2002) Bio-Optical Evidence of Land-Sea Interactions in the Western Coast of Puerto Rico. (Oral and Poster Presentation) Ocean Optics XVI Meeting, Santa Fe, Nuevo Mexico.
- Lee-Borges, J., R. A. Armstrong, and **F. Gilbes**. (In Preparation) Contribution of picoplankton to community structure in the Eastern Caribbean Sea.
- Rosado, M. A., **F. Gilbes**, R. A. Armstrong, J. R. Garcia, and R. L. Miller. (In Preparation) Spatial and Temporal Variability of Bio-Optical Properties in the Western Coast of Puerto Rico.
- Rosado, M., **Gilbes, F.**, Armstrong, R. and Lee-Borges, J. (2002) Validation of Bio-Optical Algorithms in the Western Coast of Puerto Rico. (Poster Presentation) Ocean Optics XVI Meeting, Santa Fe, Nuevo Mexico.

## **New Collaborations and Proposals**

In order to expand the scope of the project, Dr. Carlos Del Castillo from University of South Florida (now at NASA Stennis Space Center) and myself submitted the proposal entitled "Effect of CDOM upon the performance of three bio-optical algorithms" to the NASA SIMBIOS program. The main objective of the project was to evaluate the role of colored dissolved organic matter in the development of algorithms for Mayagüez Bay and the Gulf of Mexico. It was also intended to incorporate in the current partnership project a new level of collaboration with Dr. Richard Miller. Unfortunately, the proposal was denied. Another proposal was submitted to the Water Resources Institute of the UPRM in collaboration with Dr. Nazario Ramirez, professor of the Department of Industrial Engineering. The title of this proposal is "Water Quality Parameters of Mayagüez Bay." It was granted for three years with \$50,000 per year. This has allowed continuing the sampling that started with this NASA project. Most recently, a new proposal entitled "Bio-Optical Properties and Remote Sensing of Mayagüez Bay" was submitted to NOAA and it was approved as part of the regional project called CREST(NOAA Cooperative Center for Remote Sensing Science and Technology). \$50,000 was granted per year for three years.

## **CITED LITERATURE**

- Alfonso E., 1995. The coastal current regime in Añasco Bay during a one year period. Master of Science Thesis. UPRM. Department of Marine Sciences.
- Banse, K., and English D.C. 1994. Seasonality of coastal zone color scanner phytoplankton pigment in the offshore oceans. *J. of Geophysical Research*, 99(C4), 7323 -7345.
- Bogucki, D. J., and. Redekopp L. A 1999. A mechanism for sediment resuspension by internal solitary waves. *Geophysical Research Letters* 26(9): 1317-1320.
- Bricaud, A., Morel A., and Prieur L. 1981. Absorption by dissolved organic matter of the sea (yellow substance) in UV and visible domains. *Limnology and Oceanography*, 26:43-53.
- Bricaud, A., and Stramski D. 1990. Spectral absorption coefficients of living phytoplankton and nonalgal biogenous matter: A comparison between the Peru upwelling area and the Sargasso Sea. *Limnology and Oceanography*, 35(3):562-582.
- Carder, K. L., Steward, R. G., Harvey, G. R., & Ortner, P. B. 1989. Marine humic and fulvic acids: Their effects on remote sensing of ocean chlorophyll. *Limnol. Oceanogr.*, 34: 68-81.

- Gilbes, F., López J.M., and Yoshioka P.M. 1996. Spatial and temporal variations of phytoplankton chlorophyll-*a* and suspended particulate matter in Mayagüez Bay, Puerto Rico. *Journal of Plankton Research*, 18(1):29-43.
- Gordon, H.R., Clark D.K., Brown J.W., Brown O.B., Evans R.H., and Broenkow W.W. 1983. Phytoplankton pigment concentrations in the Middle Atlantic Bight: comparisons of ship determinations and CZCS estimates. *Applied Optics*, 22(1), 20-36.
- Levinton, J.S. 1982. *Marine Ecology*. Prentice-Hall, New York.
- Longhurst, A.R., and Pauly D. 1987 *Ecology of the tropical oceans*. Academic Press Inc. San Diego. 407 pp.
- Mitchell, B.G., and Kiefer D.A. 1984. Determination of absorption and fluorescence excitation spectra for phytoplankton. In: *Marine phytoplankton and productivity*. Holm-Hansen, O., Bolis L., and Giles R. (Ed.). Springer-Verlag, Berlin. 157-169 pp.
- Roesler, C.S., Perry M.J., and Carder K.L. 1989. Modeling in situ phytoplankton absorption from total absorption spectra in productive inland marine waters. *Limnology and Oceanography*, 34(8):1510-1523.
- Rosado, M. 2000. Bio-optical variability of Mayagüez Bay, Puerto Rico. Master Thesis, University of Puerto Rico at Mayagüez, Mayagüez, Puerto Rico.
- Kirk, J. T. O. (1994) *Light and Photosynthesis in Aquatic Ecosystems*. Cambridge University Press, Cambridge.
- Welschmeyer, N.A. 1994. Fluorometric analysis of chlorophyll *a* in the presence of chlorophyll *b* and pheopigments. *Limnol. Oceanogr.* 39(8) 1985-1992.

**APPENDIX ONE:**  
**BIO-OPTICAL ROSETTE DEVELOPED THROUGH THIS PROJECT**



**APPENDIX TWO:**

**Spatial And Temporal Variability Of Bio-Optical Properties**

**In The Western Coast Of Puerto Rico**

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and Richard L. Miller<sup>3</sup>

Bio-optical variability in Puerto Rico

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## **ACKNOWLEDGEMENTS**

This work was supported by NASA Grant NAG 13-54 and NASA Grant NAG 13-99029. We thank the captain of the R/V Sultana, Dennis Corales, and all graduate students that made possible the field and laboratory work. We also appreciate the valuable suggestions and comments to the manuscript of Carlos Del Castillo.

## **ABSTRACT**

Particulate absorption coefficient, colored dissolved organic matter absorption coefficient, backscattering coefficient, remote sensing reflectance, chlorophyll-a concentration and salinity were measured during several cruises in Mayagüez Bay, Puerto Rico, from February 1997 to October 1999. The objective of this study was to quantify temporal and spatial variability in both apparent and inherent optical properties and to examine the sources of such variability. High temporal and spatial variability was found for all the bio-optical properties. Several optical provinces were identified. The dominance of colored dissolved organic matter and detritus absorption over phytoplankton absorption suggests that ocean color is highly influenced by river input in the bay. High chlorophyll concentration was associated with strong light-attenuating waters.



## INTRODUCTION

Coastal waters are known for their large variability in bio-optical properties (Kirk, 1994). This is the result of a complex and dynamic array of processes that operate in these systems. The interaction of these processes, both in temporal and spatial scale, causes variation in the abiotic and biotic components of the water column, which affects its optical characteristics. Assessing the range and sources of this variability is important for the development of remote sensing algorithms capable of accurately measuring chlorophyll-a (Chl-a). Establishing regional algorithms for calculating Chl-a concentration from satellite data is required to obtain proper estimates of phytoplankton biomass and primary production (García et. al., 1998).

Puerto Rico offers a good opportunity to study optical properties in tropical coastal waters. In the tropics, the seasonal rainfall patterns produce clear changes in river discharge. Changes in both the amount and the biogeochemical nature of river discharge occur through the year due to large variations in climatic and topographic conditions combined with anthropogenic factors (Gilbes *et al.*, 1996). These sources of variation, affect important oceanic parameters such as salinity, nutrient concentration, light attenuation, and suspended sediments, thus affecting bio-optical properties.

Mayagüez Bay is an excellent natural laboratory to study optical properties. Located in the west coast of Puerto Rico, it is subjected to the influence of three major rivers. The Añasco, Yagüez and Guanajibo rivers supply a considerable load of terrigenous sediments, especially during the rainy season, extending from September through November. According to Gilbes *et al.* (1996), the Añasco- Mayagüez basin receives an average precipitation range of 200 - 250 cm per year. The mean discharge of these rivers during 1997-1998 varied from  $2.21 \text{ m}^3\text{s}^{-1}$  to  $13.55 \text{ m}^3\text{s}^{-1}$  for Añasco River and  $0.71 \text{ m}^3\text{s}^{-1}$  to  $13.85 \text{ m}^3\text{s}^{-1}$  for the Guanajibo River (US Geological Survey,

1998). The Añasco River is the largest river of the west coast, and although its basin was used for agriculture in the past, nowadays is much more developed. The Yagüez basin is highly developed and highly influenced by anthropogenic activities. The Guanajibo basin was traditionally dedicated to agriculture, especially to the sugar cane industry, but it is not being cultivated actively in the present. Beside these rivers, a number of smaller streams discharge to the bay.

The location of tuna processing facilities close to the Yagüez River mouth is another source of nutrients and particulate matter to the bay. These industries dump wastewaters into the bay ( $18^{\circ}13.171'N$   $67^{\circ}10.237'W$ ) on a regular basis. Mayagüez Bay is also subjected to sewage waters input. The Puerto Rico Waters Authority also discharges primary treated water from the city sewer systems through a diffuser tube located between the Añasco River mouth and the tuna factories ( $18^{\circ}14.022'N$   $67^{\circ}11.467'W$ ). Both the riverine and the anthropogenic inputs to the bay supply nutrients and suspended particles to the system. All these interactions may suggest the existence of several bio-optical provinces in a relatively small area.

The main objective of this work is to characterize the spatial and temporal variability of inherent and apparent optical properties in Mayagüez Bay. A secondary objective is to study how this variability is regulated by the abiotic and biotic factors in the system. The analysis of how these variables are related may provide a better understanding of the behavior of phytoplankton assemblages in Mayagüez Bay. The hypotheses considered in this work were:

1. Bio-optical properties in Mayagüez Bay are highly variable and influenced mostly by rainy and dry seasonal patterns.
2. Correlation exists between river discharge and absorption, backscattering and reflectance measurements in the bay.
3. Light is the limiting factor for phytoplankton populations during the rainy season.

## METHODS

### Field Work

Six stations were routinely sampled at Mayagüez Bay (Figure 1) to evaluate the influence of the seasonal river discharge and industrial effluents on the bio-optical properties. Monthly samples were collected from February 1997 to January 1998. At each station, water samples were taken from the surface for Chl-a concentration and absorption measurements. Salinity profiles were obtained at each station using a SBE-19 CTD from Sea- Bird Electronics. Profiles of the backscattering coefficient ( $b_b$ ) at six wavelengths were obtained using the Hydrosat-6 (from Hobi Labs). Water radiance,  $L_0(\lambda)$ , sky radiance,  $L_s(\lambda)$ , and the above surface downwelling irradiance,  $E_d(0^+, \lambda)$  were measured using a GER 1500 portable spectroradiometer.  $L_0(\lambda)$  was measured aiming the spectroradiometer  $45^\circ$  to the vertical into the water surface, maintaining an azimuth of  $90^\circ$  from the solar plane to minimize sun glint.  $L_s(\lambda)$ , was measured pointing the spectroradiometer  $45^\circ$  to the vertical to the sky, maintaining an azimuth of  $90^\circ$  from the solar plane.  $E_d(0^+, \lambda)$  was measured pointing directly upward using a cosine collector attached to the spectroradiometer. The remote sensing reflectance,  $R_{rs}(\lambda)$ , was calculated using the following equation:

$$R_{rs}(\lambda) = \frac{L_0(\lambda) - f(L_s(\lambda))}{E_d(0^+, \lambda)}$$

Where  $f$  is the Fresnel's number ( $=0.28$  at  $45^\circ$  angle), the percent of sky radiance reflected back to the atmosphere.

An additional cruise took place in July 1998. All of the above measurements were taken. In addition, samples for measuring the absorption of Colored Dissolved Organic Matter (CDOM) were collected. Two more cruises were carried out in October 1999. During the October 19

cruise six stations were sampled at different distances from the Guanajibo River mouth (Figure 1). Samples were also taken for determination of total suspended particulate matter concentrations. On October 24, five stations were sampled approaching the Yagüez River mouth (Figure 1). In this cruise an optical package containing an AC-9 (Wet Labs), a SBE-19 CTD, a WetStar fluorometer (Wet Labs), and a OCR- 200 Profiling radiometer (Satlantic) was deployed.

### **Laboratory work**

Water samples were filtered *in situ* using the filter pad technique proposed by Mitchell and Kieffer (1984). The samples were collected on 25 mm Whatman GF/F filters. These filters were kept at 0°C until absorption measurements were done. The absorption spectra between 375 and 800 nm was measured using a GER 1500 portable spectroradiometer attached to a Licor integrating sphere through a fiber optic cable. A blank filter was made passing a volume of 200 milliliters of distilled water. The difference in absorption between the sample and the blank spectra was the particulate absorption spectrum ( $a_p$ ) as defined by standard NASA protocols (Fargion and Mueller, 2000). Following this measure, hot methanol was passed through the filter (Kishino *et al.*, 1985), and the measurement procedure repeated. These spectra were taken as absorption by non-methanol extractable detrital material ( $a_d$ ). The difference between  $a_p$  and  $a_d$  represents the phytoplankton absorption ( $a_{ph}$ ). This value, divided by the Chl-a concentration corresponds to the specific absorption coefficient of phytoplankton ( $a_{ph}^*$ ). All spectra were shifted to zero absorbance at 750 nm and corrected for pathlength amplification using the  $\beta$  factor from Bricaud and Stramsky (1990). Chl-a concentration extracted in methanol was measured with a Turner Designs Model 10-AU fluorometer using the method developed by Welschmeyer (1994). This set-up provides the

capacity of measuring the Chl-a concentration directly, without acidification of the sample. The fluorometer was calibrated using Chl-a from the alga *Anacystis nidulans*.

CDOM samples were obtained using only materials made of crystal and Teflon® to avoid contamination. All materials were thoroughly cleaned with 1M HCl and 1M NaOH solutions, and rinsed with distilled water. Crystalware and filters were combusted for at least 6 hours at 300°C to remove any trace of organic matter. Absorption spectra of CDOM ( $a_g$ ) were obtained filtering seawater through a pre-combusted GF/F filter and collecting the filtrate in amber glass bottles. The absorbances of the samples were measured from 250 to 750 nm in a Pelkin Elmer Lambda 18 dual beam spectrophotometer following the suggestions of Bricaud *et al.* (1981).

The concentration of total suspended particulate matter (SPM) was measured using Millipore HA 0.45  $\mu\text{m}$  cellulose acetate filters. The filters were desiccated in an oven for 24 hours at 70-80°C. The weight of each filter was recorded using a Mettler analytical balance. Filters were stored in a glass dessicator with silica gel until use. A known volume of seawater was filtered and the filters were desiccated in the oven again to remove the water content before weighing for second time. The difference between the filter weight before and after filtration was taken as the SPM ( $\text{mg l}^{-1}$ ).

## Data analysis

Two-way analyses of variance (ANOVA) were used to evaluate the temporal and spatial variability of  $a_p$ ,  $a_d$ ,  $a_{ph}$  and  $a_{ph}^*$ . The analyzed wavelengths correspond to those found in the Sea-viewing Wide Field-of-view Sensor (SeaWiFS), namely 412, 443, 490, 510, 555 and 670 nm. The data were analyzed using the  $\log_{10}$  transformation to normalize them. Similar calculations were done with  $b_b$ ,  $a_g$ , and  $R_{rs}$ , trying to establish the sources of variation from both the ANOVA results

and graphic examination of the data. Correlation analysis were performed between several optical variables, Chl-a and river discharge. The CDOM spectral slopes were calculated from linear-least-square regressions of the plot of  $\ln a_g(\lambda)$  vs. wavelength for the interval between 412 and 443 nm. This interval was chosen because CDOM absorption is greater there and those wavelengths have been suggested to discriminate between Chl-a and CDOM in future bio-optical algorithms.

## RESULTS

### Inherent Optical Properties

The variability of the absorption coefficients obtained in selected stations of Mayagüez Bay from February 1997 to January 1998 is shown in Figure 2. The spatial variability of  $a_p$ , was highly significant ( $p < 0.001$ ) at the six analyzed wavelengths. Significant temporal differences at those wavelengths except for 555 nm were also shown by  $a_p$ . The highest particulate absorption values were found during October 1997 in Añasco station, and the lowest values were found during March 1997 in Manchas station. This pattern is shown in the six analyzed wavelengths. The Añasco station also showed the greatest range in  $a_p$  values during this study. Correlations made between  $a_p$  at 443, 555, 670 nm and Chl-a did not reveal any strong relationship. In general,  $a_p$  was highest in Añasco station and lowest in Oceánica station through time. April, August, and October were the months with the highest  $a_p$  values.

The  $a_d$  followed a similar trend to  $a_p$ . It was highly significant in space ( $p < 0.001$ ) but it did not show temporal differences except for 412 and 443 nm ( $P < 0.01$  and  $P < 0.05$ , respectively). The highest  $a_d$  value was found at Añasco station during October 1997 and the lowest  $a_d$  value was found in Oceánica station during June 1997.

The  $a_{ph}^*$  was significantly different in space only at 412 and 443 nm ( $P < 0.05$ ), but it was significantly different in time at all wavelengths except for 670 nm. The maximum value was at Añasco station during February 1997 and the minimum value was at Añasco station during April 1997. A summary of the results for all the absorption analyses is presented in Table 1.

Figure 3 shows  $a_g$  curves measured in Mayagüez Bay during July 1998. The highest  $a_g$  was found in Añasco station with  $0.43 \text{ m}^{-1}$  at 412 nm. Other stations had values ranging from 0.10 to  $0.17 \text{ m}^{-1}$  (at 412 nm). In October 1999, the  $a_g$  showed the highest values in stations closer to the river mouth, namely station 4 and Station 10 (Figure 3). In station 4, the maximum value was  $2.38 \text{ m}^{-1}$  at 412 nm. A maximum value of  $1.06 \text{ m}^{-1}$  at 412 nm was observed at station 10. The spectral slopes of all  $a_g$  curves are shown in Table 2.

From November 1997 to July 1998,  $b_b$  showed significant spatial differences ( $P < 0.001$  to  $P < 0.01$ ) in the six channels of the Hydrosat-6, (442, 470, 510, 589, 620 and 671 nm). Significant temporal differences ( $P < 0.01$  to  $P < 0.05$ ) were also found at most wavelengths except at 589 nm. Maximum values were found in December 1997 at the Atuneras station, and minimum values were found at the Oceánica station in January 1998 (Figure 4). Atuneras station had the highest  $b_b$  values through the year, followed by Añasco and Acueductos the smallest values were recorded at the Oceánica station. The profiles showed a tendency of decreasing  $b_b$  with increasing wavelength. This pattern is not observed in the red wavelengths (620 and 671 nm). For July 98, the data show the highest backscattering values for Añasco station, followed by Atuneras and Acueductos stations, and the lowest values for Oceánica, Manchas and Rodriguez stations. Backscattering profiles for Oceánica, Atuneras and Añasco stations are shown in Figure 4.

A correlation analysis of  $b_b$  and  $a_p$  revealed a strong positive relationship at the three pairs of wavelengths considered (442 x 443, 589 x 555 and 671 x 670 nm). The correlation coefficient



between  $b_b$  (671) and  $a_p$  (670) was especially strong ( $r=0.93$ ,  $n=17$ ). A linear regression curve fitted to the data yielded a regression coefficient of 0.86 (Figure 5).

Profiles from the October 1999 cruise are shown in Figures 6 (Station 7) and 7 (Station 9). In Station 7, an attenuation maximum was apparent at the halocline, (2 m) while absorption ( $a$ ) and beam attenuation coefficients ( $c$ ) maximum were apparent at a depth of 4 meters. Raw fluorescence and  $b_b$  profiles were fairly uniform. In Station 9, all parameters appeared to be affected by the freshwater interface. Station 9 was closer to the Yagüez River mouth than Station 7 (see Figure 1) and showed higher values. In general, freshwater appear to be associated with more absorption and scattering than saltwater, probably due to higher concentration of suspended sediments (Grove, 1977).

### **Apparent Optical Properties**

Remote sensing reflectance ( $R_{rs}$ ) from June 1997 to July 1998, showed large spatial and temporal differences in most bands (Figure 8). Correlation analyses showed a moderate relationship between  $R_{rs}$  490 and Chl- $a$  ( $r=0.54$ ). Although the shape of the spectral curve varied among stations and months, some trends were identified. The Oceánica station tended to maintain the shape of the  $R_{rs}$  thru the year, with a broad peak around 490 nm, and very little  $R_{rs}$  on wavelengths above 600 nm. The other stations usually had a peak of  $R_{rs}$  around 550 nm, with shoulders around 700 nm. A third type of spectral shape was found in inshore stations consisting of a very broad flattened peak extending from 400 nm to 590 nm, lower in magnitude than the previous type of curve. Examples of the typical reflectance curves in Mayagüez Bay are shown in Figure 9.

## Ancillary Data

Chl-a showed high significant differences in both space and time ( $P < 0.01$ ). The highest value was measured in Atuneras during April 1997 ( $= 6.39 \mu\text{g l}^{-1}$ ). The lowest value ( $= 0.097 \mu\text{g l}^{-1}$ ) was recorded at the Oceánica station during April 1997. The peaks in Chl-a were found in April and October (Figure 11). During July 1998, Chl-a was highest in Añasco station ( $5.88 \mu\text{g l}^{-1}$ ), followed by Atuneras station ( $4.79 \mu\text{g l}^{-1}$ ). The lowest values were found in Manchas station ( $0.63 \mu\text{g l}^{-1}$ ). Rodriguez and Acueductos had relatively low Chl-a concentration during July 1998 ( $0.75$  and  $0.77 \mu\text{g l}^{-1}$ , respectively). A high correlation ( $r = 0.868$ ,  $n = 77$ ) between  $a_{\text{ph}}$  at 670 nm and Chl-a was found. The correlation analysis between  $bb$  at 671 nm and Chl-a also showed a high correlation coefficient ( $r = 0.891$ ,  $n = 22$ ). Two very high Chl-a values suspected to be outliers were removed from both correlation analyses (Atuneras and Acueductos of April, 1998). These results are shown in Figure 10.

Salinity profiles in the bay ranged from 34.46 to 36.24 from February 1997 to January 1998 (Figure 10). Most of the variability occurs in the first few meters. In general, June 1997 and January 1998 were the months with the highest salinity values while August 1997, September 1997 and November 1997 were the months with the lowest salinities at Mayagüez Bay.

Figure 11 shows the discharge of Añasco and Guanajibo rivers during the study period. Añasco River had a major discharge peak in October 1997 ( $13.55 \text{ m}^3 \text{ s}^{-1}$ ) and a smaller peak in August 1997 ( $9.85 \text{ m}^3 \text{ s}^{-1}$ ). The smallest discharge at Añasco River was measured in April ( $2.21 \text{ m}^3 \text{ s}^{-1}$ ). During that same period, Guanajibo River had its greater discharge in October 1997 ( $13.85 \text{ m}^3 \text{ s}^{-1}$ ), with a second peak occurring in August 1997 ( $3.90 \text{ m}^3 \text{ s}^{-1}$ ). The lowest discharge recorded in Guanajibo River during this study was  $0.71 \text{ m}^3 \text{ s}^{-1}$  in May 1997. In July 1998, Añasco River had a

mean discharge of  $3.07 \text{ m}^3 \text{ s}^{-1}$  and Guanajibo River had a mean discharge of  $1.36 \text{ m}^3 \text{ s}^{-1}$ . These river discharge values are the average of the daily discharge for three days before the sampling.

## DISCUSSION

Mayagüez Bay is a complex bio-optical system. The synergistic effect of rivers, industrial effluents, and coastal geomorphology creates a variety of optical provinces in a relatively small geographical area.

Two components, detritus and CDOM, dominate absorption in the inner part of the bay. Detritus is responsible for about half of the particulate absorption in Añasco and Atuneras stations (Figure 2). This suggests that these two stations receive high freshwater inputs throughout the year. In Rodríguez and Oceánica stations, absorption is dominated by phytoplankton in the dry season and by detritus in the rainy season. These findings suggest that during the rainy season freshwater mixes throughout Mayagüez Bay, affecting the optical properties even in the stations farthest from the coast. In July 98, CDOM dominated absorption, being higher than particulate absorption in all stations. July 98 was an average month in terms of river discharge, with the Añasco River discharging  $3.07 \text{ m}^3 \text{ s}^{-1}$  and the Guanajibo River discharging  $1.36 \text{ m}^3 \text{ s}^{-1}$ , respectively. Since this was a dry month with average discharge, it is expected that CDOM values are considerably higher during the rainy season. These high absorptions of CDOM and detritus suggest that light is been absorbed very effectively in the blue end of the spectrum. As consequence, less blue light in the water column may stimulate phytoplankton to alter their pigment compositions in order to capture light at other wavelengths and possibly increase their Chl-a content (Kirk, 1994). This can be observed in the  $a_{ph}$  peaks around 550 and 650 nm (Figure 2). Another possible effect is the

occurrence of seasonal successions of phytoplankton species in response to the varying light quality. In October of 1999 it was evident that total absorption increased toward the rivers mouth, where CDOM and detritus absorption dominated. During October there is a peak of river discharge in Mayagüez Bay. Therefore, in these highly light attenuating conditions, phytoplankton may be limited by light instead of nutrients. Notice that absorption by phytoplankton is about one order of magnitude less than particulate absorption and two orders magnitude less than CDOM absorption.

Profiles of  $b_b$  show a highly stratified distribution of particles (Figure 4). These features may be associated to sediment resuspension caused by wind or by internal waves reflected into Mayagüez Bay. This is especially feasible during the dry season, when there is not a significant input of sediment from rivers into the bay, but still the  $a_p$  and  $b_b$  are high. Backscattering was very high in Atuneras, Añasco and Acueductos stations. These stations also showed the highest particulate absorption values during this study. The fact that  $a_p$  and  $b_b$  are well correlated in Mayagüez Bay, suggests that a common factor regulates these parameters in the bay. Inanimate particles concentration could be a possibility. This is supported if we consider the nature of the optical components. Inanimate matter dominates  $a_p$  at the bay (as we discussed earlier) and  $a_{ph}$  is usually low. Inanimate matter at typical concentrations does not absorb light strongly but scatters quite intensely (Kirk, 1994). At the high concentrations encountered in Mayagüez Bay, inanimate particulate matter may be very important in the absorption and scattering processes.

The remote sensing reflectance signal provides additional evidence on the optical properties of Mayagüez Bay. Water absorbs light strongly at 750 nm, yet reflectance was far from zero at this wavelength in all stations except Oceánica (Figure 8). This was more pronounced during rainy months such as August, October and November. This high reflectance in the red ( $\lambda > 670$  nm) is consistent with the red clay minerals washed down by local rivers. From the reflectance data we

can also infer that the two stations with the higher concentration of blue absorbing components (CDOM and detritus) are Atuneras and Añasco (Figure 8). The other stations only showed low reflectance in the blue during the peak of the rainy season, except Oceánica that was offshore and received the lowest impact from river run-off. It is also evident in some stations the Rrs peaks at 550 nm. These peaks are associated with high concentrations of Chl-a and are characteristic in Atuneras and Añasco stations, although in the peak of the rainy season all inshore stations showed a similar low blue-high green reflectance curve. Although these stations had higher values of absorption and backscattering (hence attenuation), they also had the highest values of Chl-a. In the October 1999 cruise, it was clearly shown that the magnitude of Rrs curve increased and the spectral shape changed to a low reflectance in the blue and a very high peak in 550 nm as the salinity (distance to the river mouth) decreased. This may be explained by an increase in CDOM and detritus, increasing absorption in the blue region, and an increase in nutrients, fertilizing the phytoplankton. These results are in agreement with the findings of Gilbes *et al.* (1996).

Chl-a concentrations measured at Mayagüez Bay are within those measured in other bays. Webb and Gómez (1998) reported Chl-a concentrations averaging  $2 \mu\text{g l}^{-1}$  in San Juan Bay. Gilbes *et al.* (1996) measured Chl-a concentrations up to  $2.4 \mu\text{g l}^{-1}$  in the Añasco River mouth. Chl-a peaks in October could be explained as the result of a peak in the river discharge during the rainy season (Figure 10). This explanation is supported by the findings of Gilbes *et al.* (1996). The Chl-a peak of April 1997 is more difficult to explain. The weak correlation between Chl-a and river discharge suggest that other factors besides river discharge may play a role in the phytoplankton dynamics of Mayagüez Bay. These factors may include anthropogenic activities, wind driven organic matter resuspension and internal waves.

In Mayagüez Bay, seasonal river discharge appears to be the principal factor regulating the bio-optical properties, and hence the phytoplankton populations. Anthropogenic activities in the river basins affect the composition of the rivers input in the bay and therefore the characteristics of the water masses entering the bay (Kirk, 1994). The western basin of Puerto Rico is highly developed and deforested, which favors erosion and transference of soil particles into the river waters. These suspended particles increase scattering and absorption, effectively attenuating light, but also increase nutrient concentrations (Gilbes *et al.* 1996). Resuspension of sediments by wind and waves seems to be especially important in the dry season, from February to April (Alfonso, 1995, Gilbes *et al.*, 1996). Another possibility is the intrusion of internal waves into Mayagüez Bay, suspending sediments and organic matter deposited earlier within the coastal zone (Edwin Alfonso, personal communication; Bogucki and Redekopp, 1999). At smaller spatial scales, the anthropogenic effects of the tuna industry and sewage processing plants may be important. Nutrients in the vicinity of the Atuneras and Acueductos stations were high, especially organic nitrogen (Mónica Alfaro, unpublished data). Phytoplankton populations will respond to increased nutrient supply at these stations. Increased predation of zooplankton by gelatinous plankton (medusae and ctenophores) may be another mechanism accounting for larger phytoplankton biomass in these stations. Large populations of these organisms have been reported in Acueductos and Atuneras station (Mónica Alfaro, unpublished data). This predation regulates abundance of zooplankton populations, resulting in lower grazing pressure over phytoplankton.

The high range of variability found in bio-optical properties in Mayagüez Bay points out the necessity of developing algorithms capable of discerning Chl-a signature from other components of the coastal aquatic environment. The complex processes occurring in the bay need to be studied in more detail in order to formulate functional relationships between Rrs and Chl-a.

## **CONCLUSION**

Mayagüez Bay is a highly dynamic environment from a bio-optical perspective. Spatial and temporal variability is very high in the bay. Bio-optics appears to be largely determined by river input, but anthropogenic factors may play a role at a smaller spatial scale. There is probably a synergistic effect in those stations closer to the anthropogenic influence. Other oceanographic processes may be important defining the bio-optical characteristics of the bay but river input is probably the single most important factor. Specific conclusions drawn from this work are:

1. Bio-optical properties are highly variable in Mayagüez Bay and are related to river discharge.
2. There are high correlations between absorption and backscattering in the bay, but no clear pattern of correlations was found. This is probably the result of the bio-optical complexity of the bay.
3. Although some data may suggest the possibility of light limitation of phytoplankton communities in the bay, there is no clear evidence in this study. Therefore more research is needed.

Future studies should take into account vertical variability in optical properties and its effect on the values observed at surface. It is also recommended to study taxonomical composition of phytoplankton assemblages in the bay and perform photosynthetic efficiency and primary production studies. Other studies that may provide essential data and should be considered in the future are photosynthetic pigment analysis using the HPLC method and nutrients analysis.

## **REFERENCES**

Ackleson S. G., 1998. Variability in the inherent optical properties of ocean waters around Lee Stocking Island, Bahamas. Ocean Optics XIV, Kailua-Kona, Hawaii.

Alfonso E., 1995. The coastal current regime in Añasco Bay during a one year period. Master of Science Thesis. UPRM. Department of Marine Sciences.

Banase, K., and English D. C. 1994. Seasonality of coastal zone color scanner phytoplankton pigment in the offshore oceans. *J. of Geophysical Research*, **99(C4)**: 7323-7345.

Bogucki, D. J., and. Redekopp L. A 1999. A mechanism for sediment resuspension by internal solitary waves. *Geophysical Research Letters* **26(9)**: 1317-1320.

Bricaud, A., Morel A. and Prieur L. 1981. Absorption by dissolved organic matter of the sea (yellow substance) in UV and visible domains. *Limnol. Oceanogr.* **26**: 43-53.

Bricaud, A. and Stramski, D. 1990. Spectral absorption coefficients of living phytoplankton and nonalgal biogenous matter: A comparison between the Peru upwelling and the Sargasso Sea. *Limnol. Oceanogr.*, **35(3)**: 562-582.

Carder, K. L., Steward, R. G., Harvey, G. R., & Ortner, P. B. (1989). Marine humic and fulvic acids: Their effects on remote sensing of ocean chlorophyll. *Limnol. Oceanogr.*, **34**: 68-81.

Del Castillo C. E., Coble P. G., Morell J. M., López J. M. and J. E. Corredor. 1999. Análisis of the optical properties of the Orinoco River Plume by absorption and fluorescence spectroscopy. *Marine Chemistry*, **66**: 35-51.

Denny M. W. 1993. *Air and Water, The biology and physics of life's media*, Princeton University Press, Princeton, New Jersey 341 pp.

D'Sa E. J., Steward R. G., Vodacek A., Blough, N. V. and Phinney D. 1999. Determining optical absorption of colored dissolved organic matter in seawater with a liquid capillary waveguide. *Limnol. Oceanogr.*, **44(4)**: 1142-1148.

Eppley, R. W. 1977. The growth and culture of diatoms, in the biology of diatoms, Werner, D., Ed., Blackwell Scientific, Oxford.

Fargion G. S. and Mueller, J.S. 2000. Ocean optics protocols for satellite ocean color sensors validation, revision 2. SeaWiFS postlaunch technical report series, NASA tech. Memo 200-209966, NASA Goddard Space Flight Center, Greenbelt, Md.

Figueiras, F. G., and Arbones B. 1999. Implications of bio-optical modeling of phytoplankton photosynthesis in Antarctic waters: Further evidence of no light limitation in the Bransfield Strait. *Limnol. Oceanogr.*, **44(7)**: 1599-1608.

García, C. A., V. M. García, A. S. González and Omachi C. Y. 1998. Bio-optical characteristics of southern Brazilian waters. *Ocean Optics XIV*, Kailua-Kona, Hawaii.

Garrison, D. L. 1984. Planktonic Diatoms, in *Marine Plankton Life Cycle Strategies*, Steidinger, K. A. and Walker L. M., Eds., CRC Press, Boca Raton, Florida.



Gilbes, F., López, J. M. and Yoshioka P. 1996. Spatial and temporal variations of phytoplankton chlorophyll a and suspended particulate matter in Mayagüez Bay, Puerto Rico. *J. of Plankton Res.* **18**: 29-43.

Gordon, H. R., Clark D. K., Brown J. W., Brown O. B., Evans R. H., and Broenkow W. W. 1983. Phytoplankton pigment concentrations in the Middle Atlantic Bight: comparisons of ship determinations and CZCS estimates. *Applied Optics*, **22(1)**: 20-36.

Gordon, H. R. and Morel, A. Y. 1983. Remote assessment of ocean colour for interpretation of satellite imagery. A review. Springer, New York.

Grove, K., 1977. Sedimentation in Añasco Bay and river estuary: Western Puerto Rico. Master of Science Thesis. UPRM. Department of Marine Sciences.

Kirk, J. T. O. 1994. Light and Photosynthesis in Aquatic Ecosystems. Cambridge University Press, Cambridge.

Levinton, J. S. 1982. Marine Ecology. Prentice-Hall, New York.

Li, Y. and T. J. Smayda. 1998. Temporal variability of chlorophyll in Narrangansett Bay, 1973-1990. *ICES Journal of Marine Science*, **55**: 562-573

Longhurst, A.R., and Pauly D. 1987. Ecology of the tropical oceans. Academic Press Inc. San Diego. 407 pp.

Kishino, M., Okami N. and Ichimura S. 1985 Estimation of the spectral absorption coefficients of phytoplankton in the sea. *Bull. Mar Sci.* **37**: 634-642.

Mitchell, B. G. and Kiefer, D. A. 1984. Determination of absorption and fluorescence excitation spectra of phytoplankton. In: Marine phytoplankton and productivity. Holm-Halsen, O., Bolis L., Giles R. (Ed.) Springer-Verlag, Berlin. 157-169 pp.

Morel, A. 1987. Chlorophyll-specific scattering coefficient of phytoplankton. A simplified theoretical approach. *Deep-Sea Res.* **34**: 1093-1105.

Morelock, J., Grove, K., and Hernández, M. L. 1983. Oceanography and patterns of shelf sediments in Mayagüez, Puerto Rico. *J. Sed. Petrol.* **53**: 371-381

Nybakken, J. W. 1993. Marine Biology An ecological approach. Harper Collins, New York. 462 pp.

Platt, T. [ED.] 1981. Physiological bases of phytoplankton ecology. *Can. Bull. Aquat. Sci.* **210**: 346

R. M. Pope and Fry, E. S.. 1997. Absorption spectrum (380-700 nm) of pure water. II. Integrating cavity measurements. *Appl. Opt.*, **36**: 8710-8723

- Raymont, J. E. G. 1980. Plankton and productivity in the oceans, 2ed. Vol. 1 Pergamon Press, Oxford.
- Smayda, T.J. 1970. The suspension and sinking of phytoplankton in the sea, *Oceanogr. Mar. Biol. Ann. Rev.*, **8**: 853.
- Steidinger, K.A. and Walker, L.M. 1984. Introduction, in *Marine plankton life cycle strategies*, Steidinger, K.A. and Walker, L.M., Eds., CRC Press, Boca Raton, Florida
- Sumich, J.L. 1984. *Biology of Marine Life* Wm. C. Brown Publishers, Dubuque, Iowa 386 PP.
- Thurman, H.V. and Webber, H.H. 1984. *Marine Biology*, Charles E. Merrill, Columbus, Ohio
- Walker, L. M. 1984. Life histories, dispersal and survival in marine, planktonic dinoflagellates, in *Marine plankton life cycle strategies*, Steidinger, K.A. and Walker, L.M., Eds., CRC Press, Boca Raton, Florida
- Webb, R. M. T. and Gómez F. 1998. Synoptic survey of water quality and bottom sediments, San Juan Bay Estuary System, Puerto Rico, December 1994-July 1995. U.S. Geological Survey, Water-Resources Investigations Report 97-4144
- Weidemann, A. D. and Bannister, T. T. 1986. Absorption and scattering coefficients in Irondequoit Bay. *Limnol. Oceanogr.*, **31(3)**: 567-583.
- Welschmeyer, N. A. 1994. Fluorometric analysis of chlorophyll *a* in the presence of chlorophyll *b* and pheopigments. *Limnol. Oceanogr.* **39(8)**: 1985-1992.

Table 1. Analysis of Variance (two-way, without replicates) between stations and months for the absorption coefficients (S. = Significant, N.S = Non significant). P equals probability of no statistically significant differences.

Parameter	Significance in Space	P	Significance in Time	P
a <sub>p</sub> 412	S.	<0.001	S.	<0.01
a <sub>p</sub> 443	S.	<0.001	S.	<0.05
a <sub>p</sub> 490	S.	<0.001	S.	<0.05
a <sub>p</sub> 510	S.	<0.001	S.	<0.05
a <sub>p</sub> 555	S.	<0.001	N.S.	N.S.
a <sub>p</sub> 670	S.	<0.001	S.	<0.01
a <sub>d</sub> 412	S.	<0.001	S.	<0.01
a <sub>d</sub> 443	S.	<0.001	S.	<0.05
a <sub>d</sub> 490	S.	<0.001	N.S.	N.S.
a <sub>d</sub> 510	S.	<0.001	N.S.	N.S.
a <sub>d</sub> 555	S.	<0.001	N.S.	N.S.
a <sub>d</sub> 670	S.	<0.001	N.S.	N.S.
a <sub>ph</sub> 412	S.	<0.001	S.	<0.01
a <sub>ph</sub> 443	S.	<0.001	N.S.	N.S.
a <sub>ph</sub> 490	S.	<0.001	S.	<0.001
a <sub>ph</sub> 510	S.	<0.001	S.	<0.01
a <sub>ph</sub> 555	S.	<0.001	S.	<0.001
a <sub>ph</sub> 670	S.	<0.001	S.	<0.001
a <sub>ph</sub> * 412	S.	<0.05	S.	<0.001
a <sub>ph</sub> * 443	S.	<0.05	S.	<0.001
a <sub>ph</sub> * 490	N.S.	N.S.	S.	<0.05
a <sub>ph</sub> * 510	N.S.	N.S.	S.	<0.01
a <sub>ph</sub> * 555	N.S.	N.S.	S.	<0.001
a <sub>ph</sub> * 670	N.S.	N.S.	N.S.	N.S.

Table 2. Absorption coefficients of CDOM ( $a_g$ ) at 412 and 443 nm and spectral slopes during July 98 and October 99.

<b>Sample</b>	<b><i>Date</i></b>	<b><math>a_g</math> 412 nm</b>	<b><math>a_g</math> 443 nm</b>	<b>Spectral Slopes</b>
Oceánica	July 98	0.2308	0.1823	0.00732
Manchas	July 98	0.1159	0.0900	0.00781
Atuneras	July 98	0.1772	0.1338	0.00915
Añasco	July 98	0.4286	0.3445	0.00695
Acueductos	July 98	0.1910	0.1397	0.00989
Rodríguez	July 98	0.1416	0.1031	0.00958
station 1	October 99	0.1249	0.0908	0.0103
station 2	October 99	0.1727	0.1160	0.0129
station 3	October 99	0.4498	0.3083	0.0122
station 4	October 99	2.3819	1.4989	0.0149
station 5	October 99	0.3281	0.2229	0.0124
station 6	October 99	0.5656	0.3746	0.0132
station 7	October 99	0.1209	0.0880	0.0103
station 8	October 99	0.1810	0.1330	0.0099
station 9	October 99	0.6277	0.4632	0.0098
station 10	October 99	1.0550	0.6471	0.0158
station 11	October 99	0.8853	0.5774	0.0138
<b>Mean</b>		0.4811	0.3243	0.0110
<b>Std. Dev.</b>		0.5641	0.3505	0.0026
<b>Min.</b>		0.1159	0.0880	0.0070
<b>Max.</b>		2.3819	1.4989	0.0158

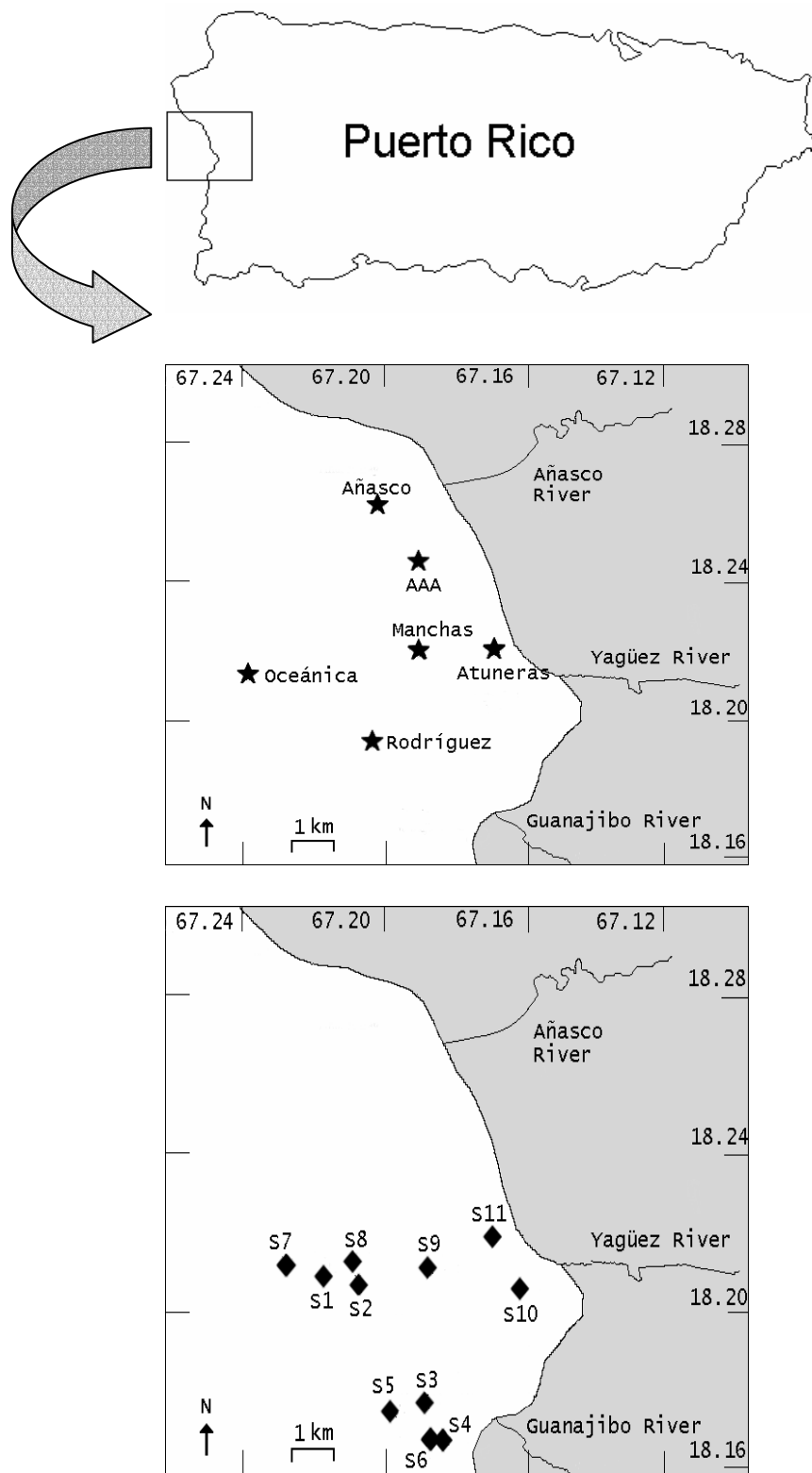


Figure 1. Map of western Puerto Rico showing the stations sampled on Feb 97 – July 98 time series and stations sampled on October 1999.

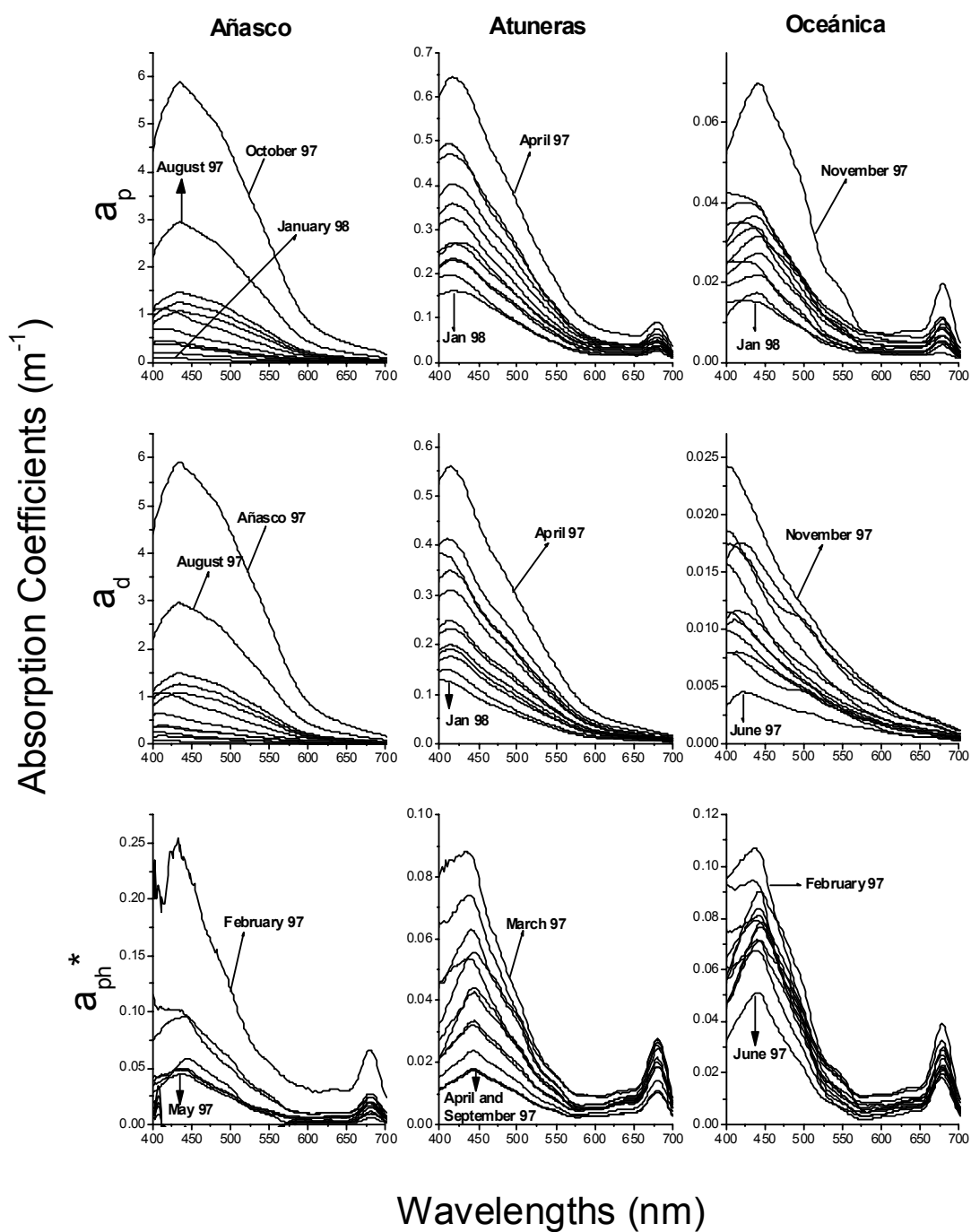


Figure 2. Absorption coefficients for selected stations collected on the Feb 97 – July 98 time series in Mayagüez Bay. Note the variability in particles absorption coefficient ( $a_p$ ), detritus absorption coefficient ( $a_d$ ) and specific phytoplankton absorption coefficient ( $a_{ph}^*$ ).

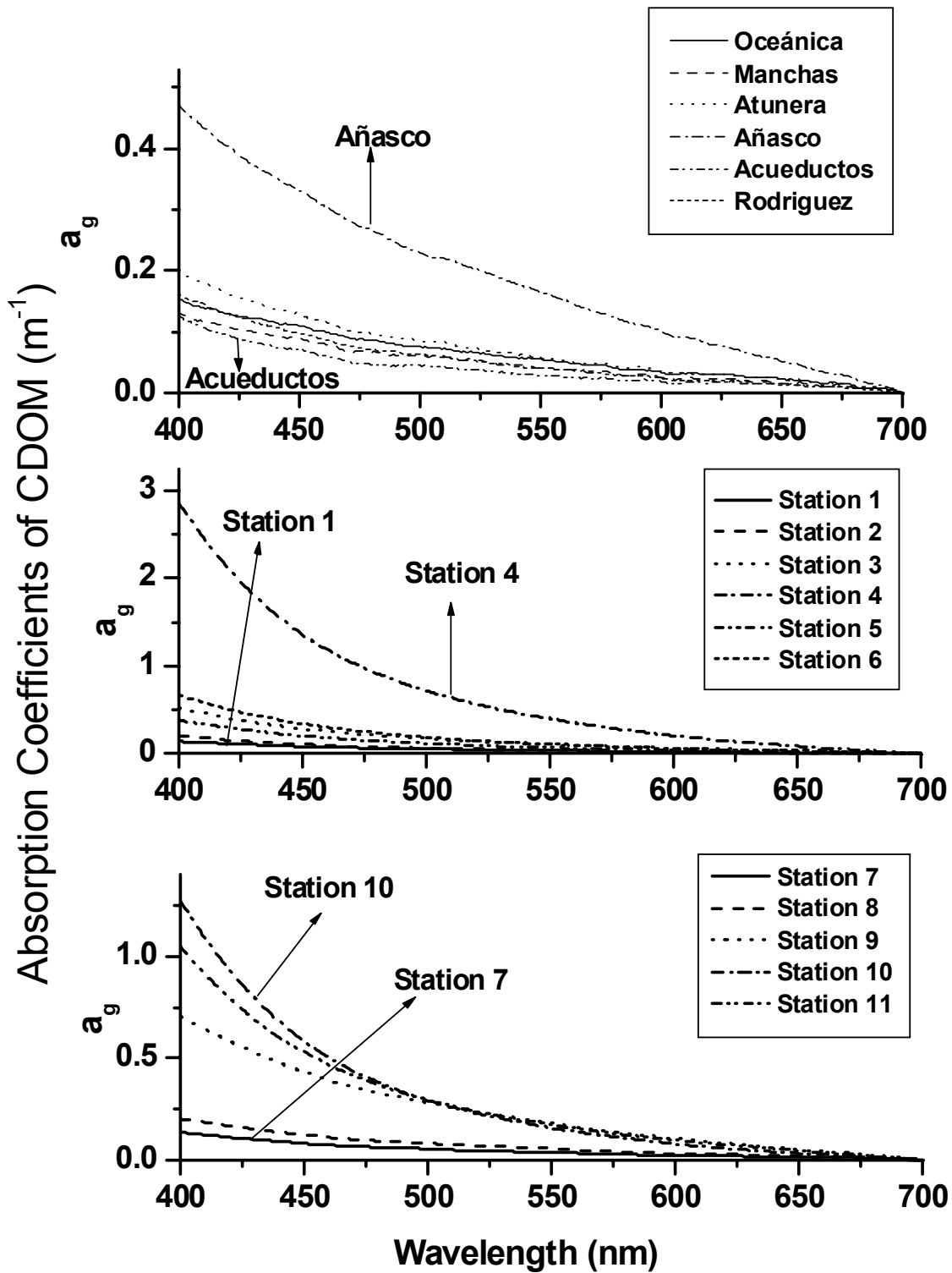


Figure 3. Colored dissolved organic matter absorption coefficient ( $a_g$ ) spectra obtained on Feb 97 – July 98 time series and on the October 1999 cruise in Mayagüez Bay.

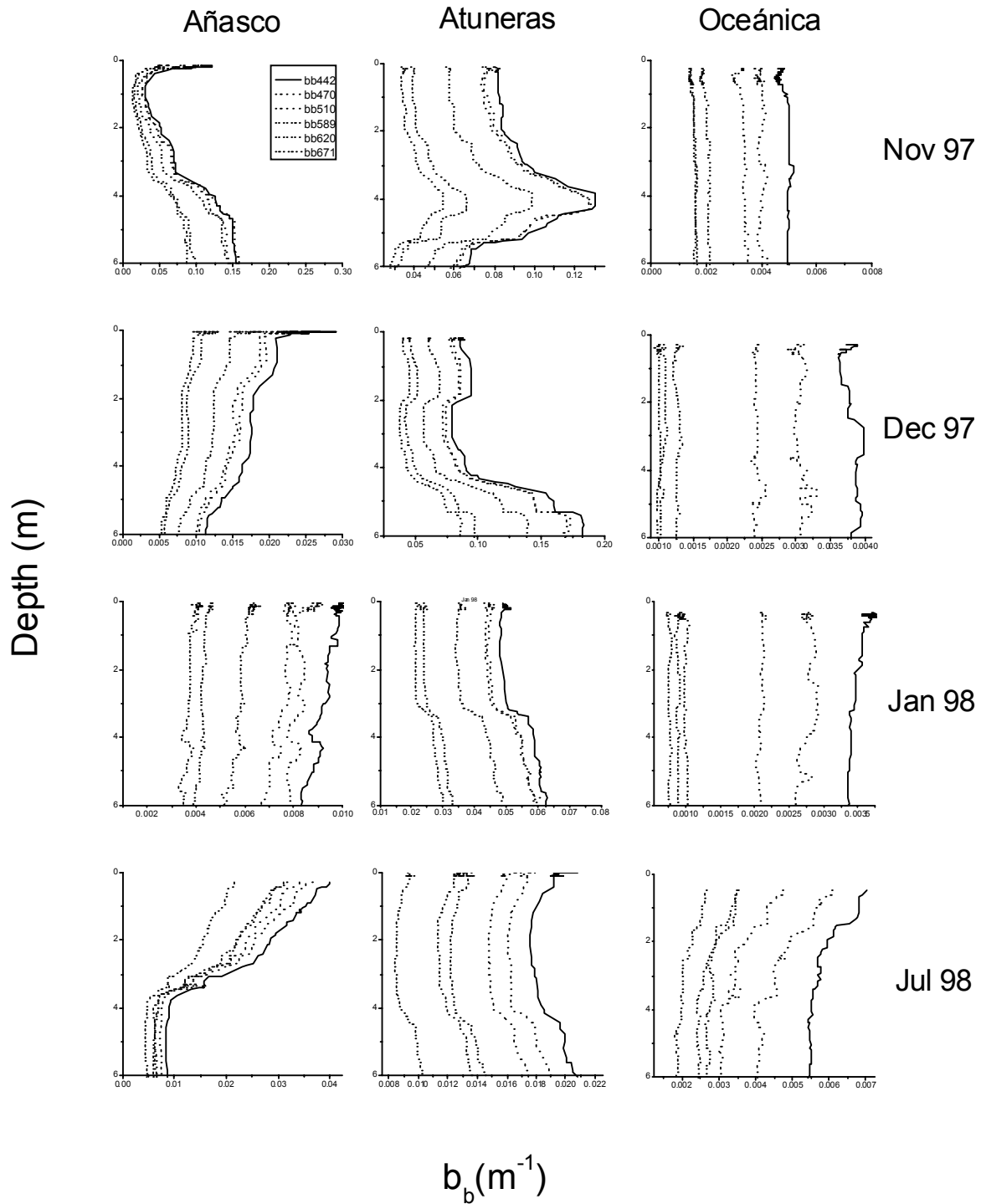


Figure 4. Profiles of the backscattering coefficient ( $b_b$ ) for Añasco, Atuneras and Oceánica stations. Profiles shown were sampled on November 97, December 98, January 98 and July 98. The legend at the top left corner applies to all graphs.



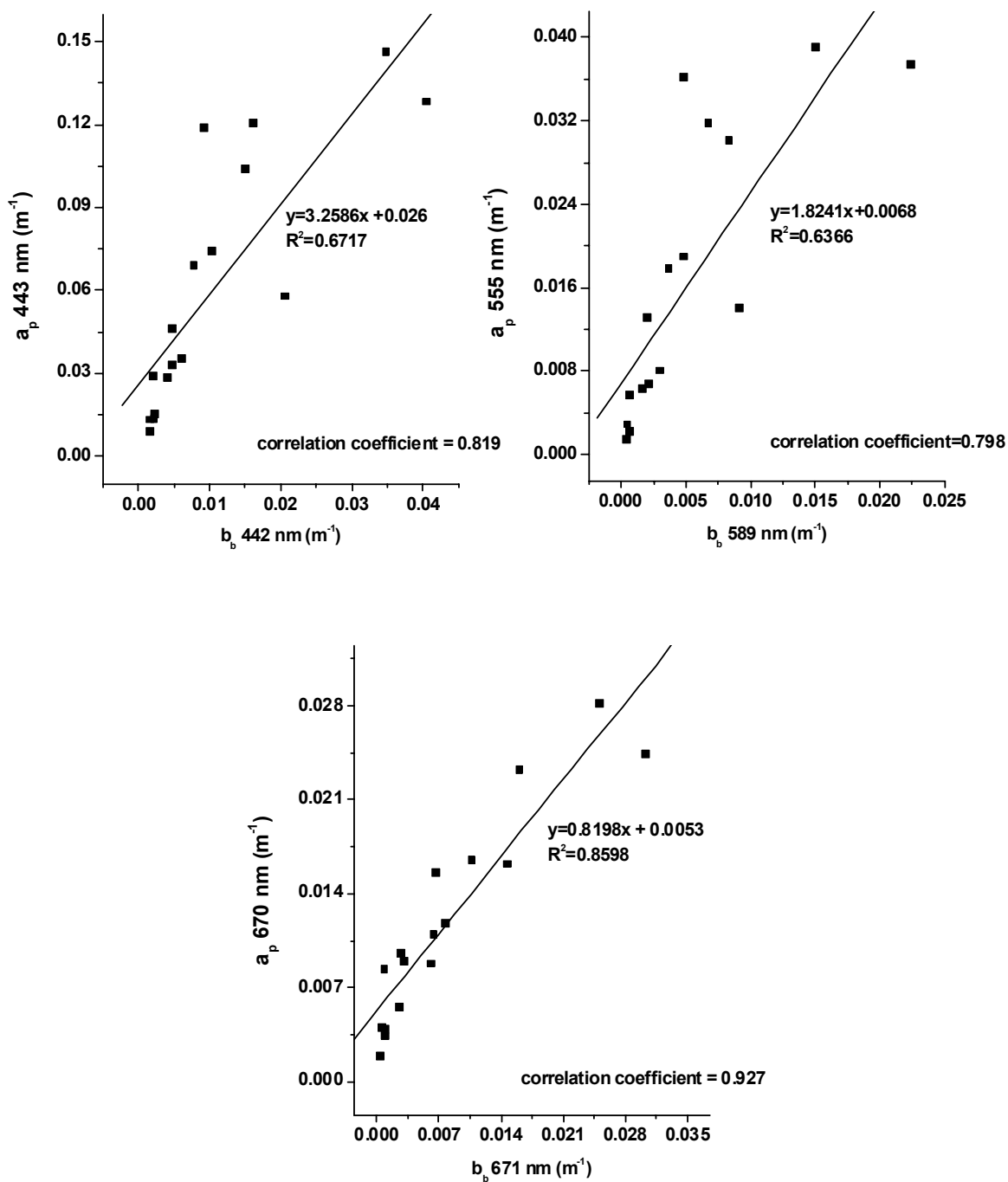


Figure 5. Linear fits and correlation coefficients of  $b_b$  vs.  $a_p$  at the selected wavelengths.

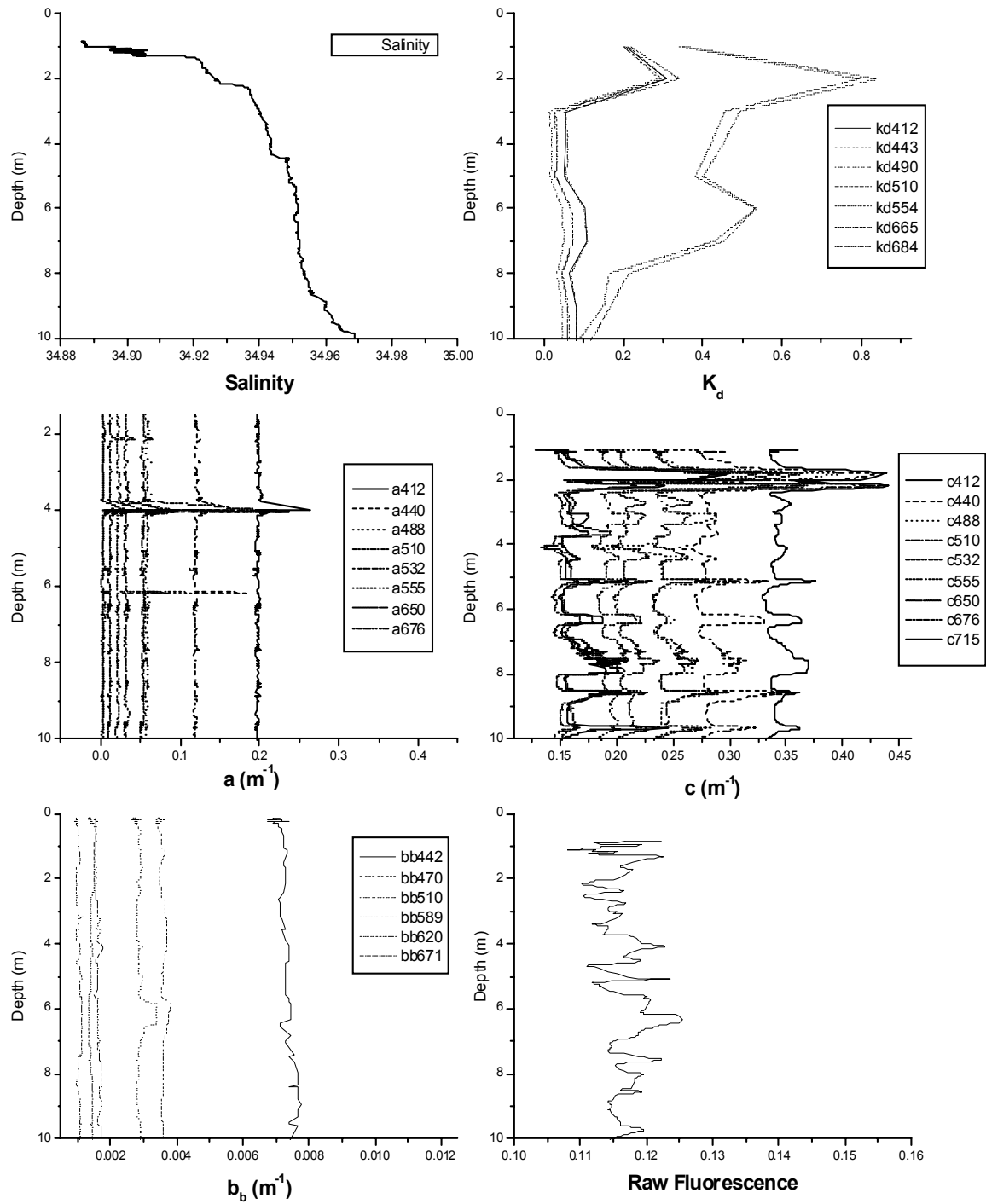


Figure 6. Salinity, diffuse attenuation coefficient ( $k_d$ ), absorption ( $a$ ), beam attenuation coefficient ( $c$ ), backscattering ( $b_b$ ) and fluorescence profiles measured on Station 7 during October 99.

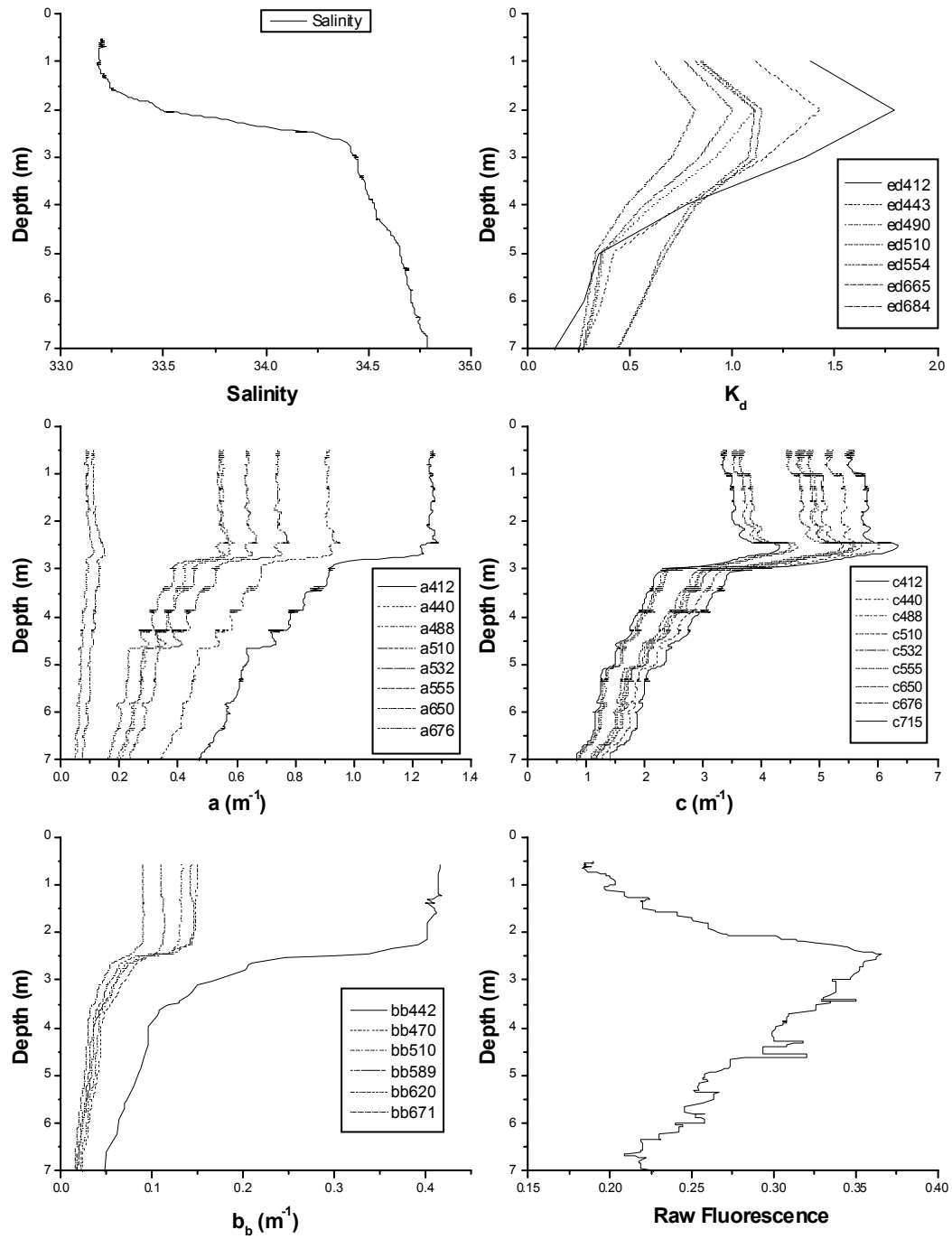


Figure 7. Salinity, diffuse attenuation coefficient ( $k_d$ ), absorption ( $a$ ), beam attenuation coefficient ( $c$ ), backscattering ( $b_b$ ) and fluorescence profiles measured on Station 9 during October 99.

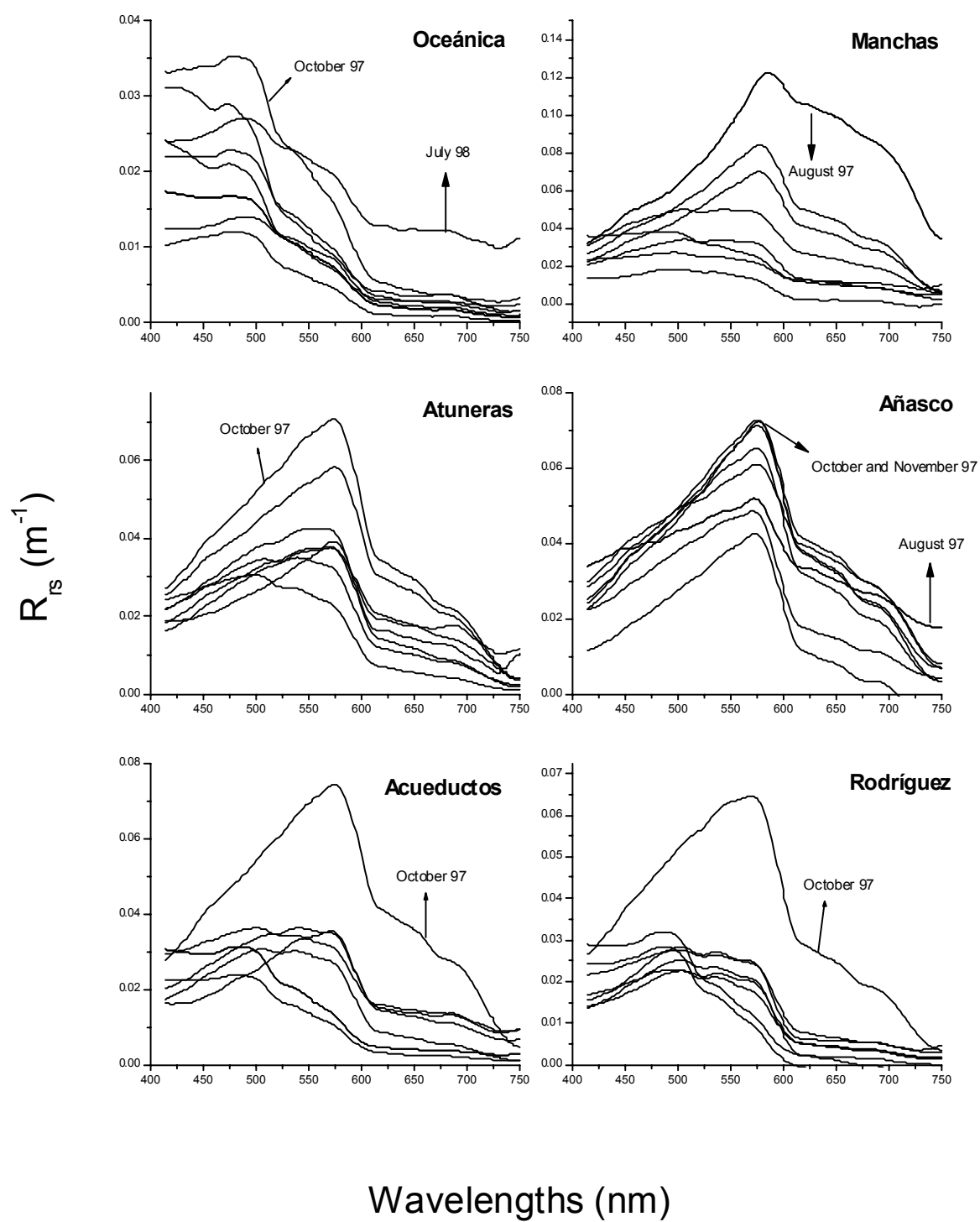


Figure 8. Remote sensing reflectance ( $R_{rs}$ ) curves measured on Mayagüez Bay from June 97 to July 98.

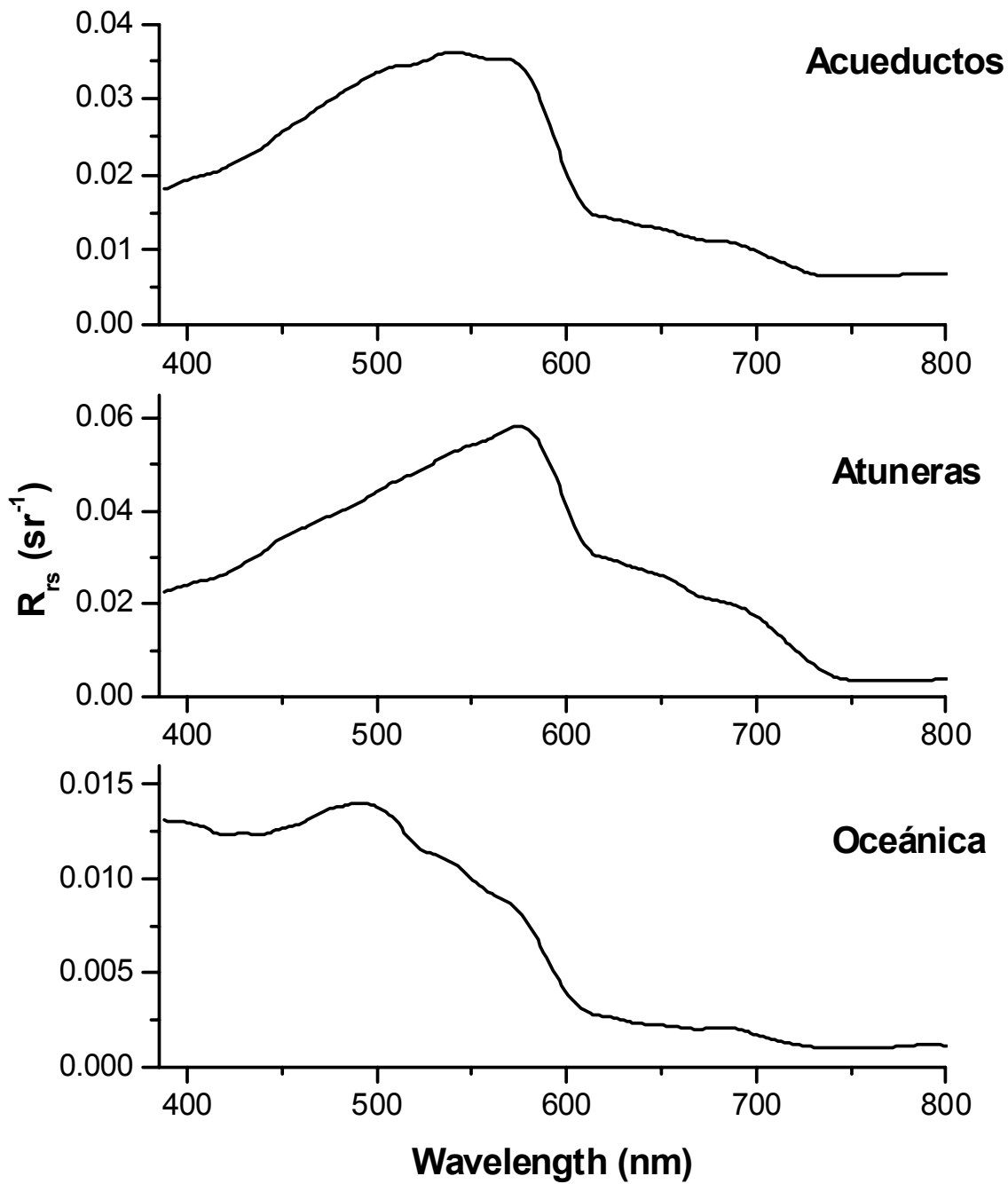


Figure 9. The three typical spectral shapes of remote sensing reflectance ( $R_{rs}$ ) curves obtained in Mayagüez Bay. These examples are from November 1997. Notice the difference in magnitudes of the y axis.

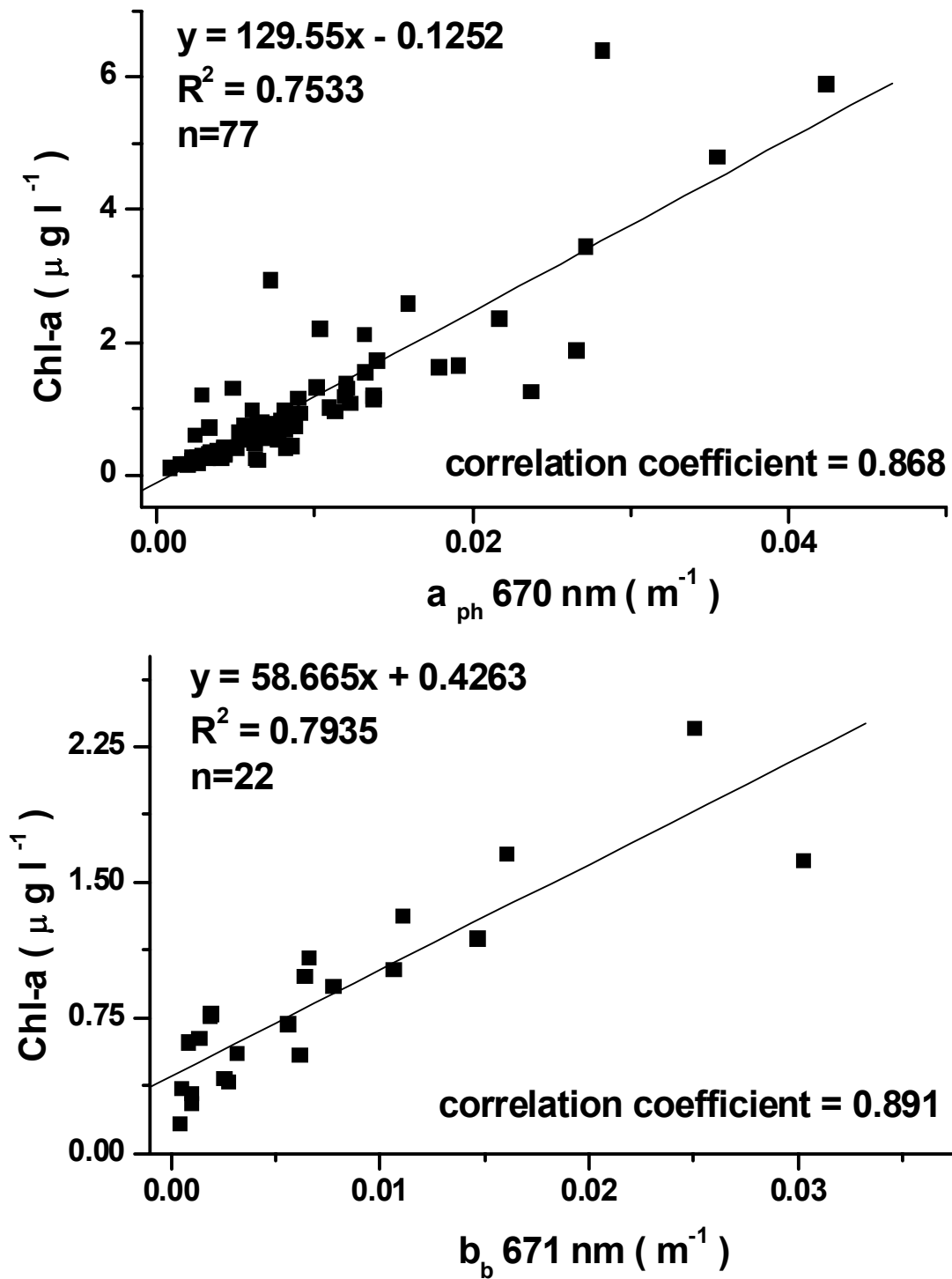


Figure 10. Linear fits and correlation coefficients of Chlorophyll-a vs.  $a_{\text{ph}}$  (670 nm), and Chlorophyll-a vs.  $b_b$  (671 nm).

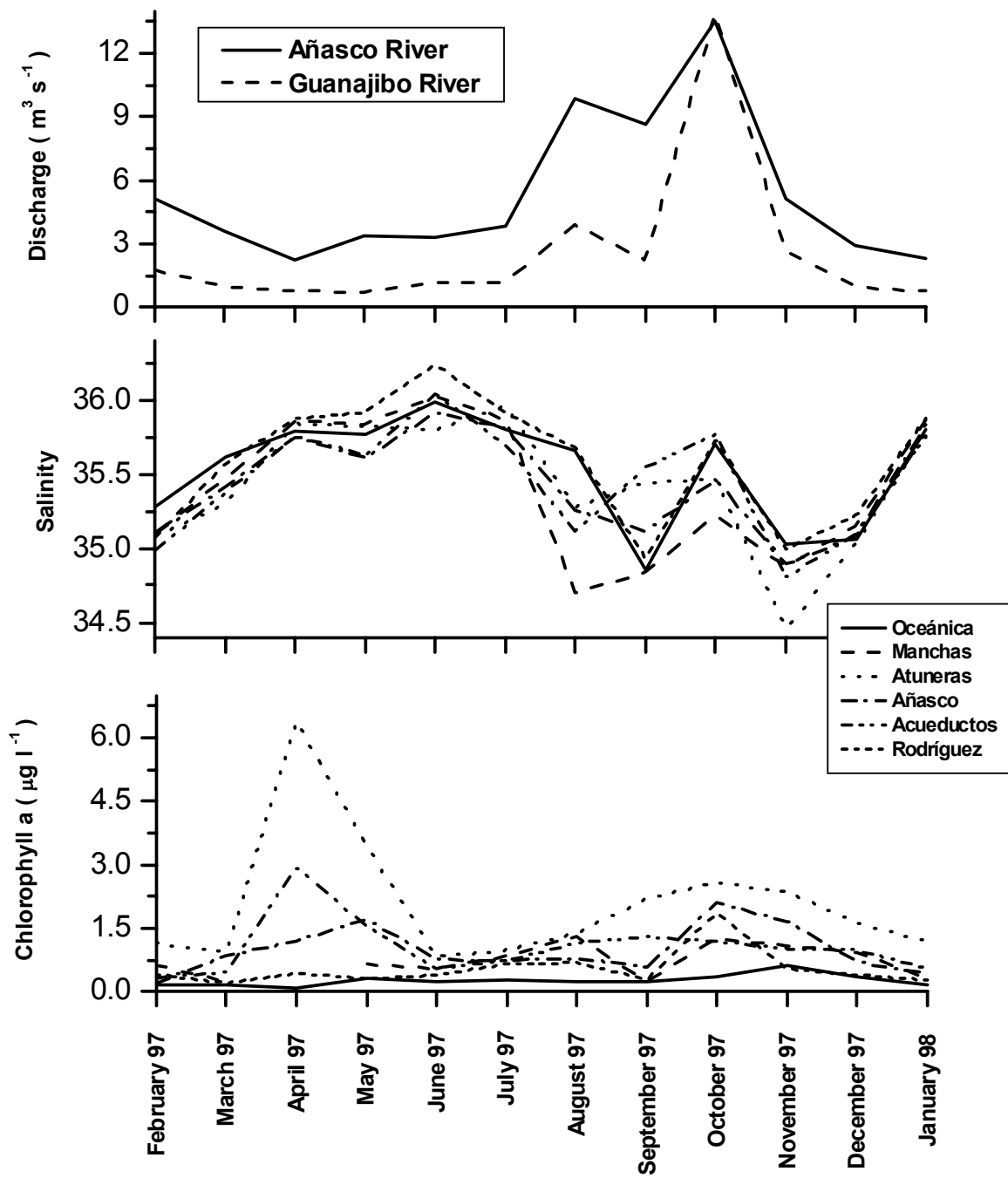


Figure 11. River discharge, salinity and Chl-a measured in Mayagüez Bay from February 1997 to January 1998.