

# CARIACO (CARbon Retention In A Colored Ocean) Project

University of South Florida, College of Marine Science

NSF Annual Report for Award # 0326268

Period Covered:

October 2004 – October 2005

**(Cruises CAR 105 – Car115)**

**Report updated 16 June, 2005**

## ACTIVITIES AND FINDINGS

CARIACO (CARbon Retention In A Colored Ocean) began in 1995 as a time-series program with its station located at 10 deg 30' N, 64 deg 40' W, off the coast of Eastern Venezuela. Monthly cruises are conducted to the station to collect core observations of this 1,400-m deep depression. The basin is openly connected to the Caribbean Sea by two shallow (~140 m) sills (Figure 1), and is anoxic below ~250m. The core cruises are supported by the University of South Florida (USF), but this program also includes seasonal cruises that focus on microbial processes (supported by the SUNY group), deployment and recovery of a sediment trap mooring (U. South Carolina), and a current meter mooring hosting two Acoustic Doppler Current Profiler (ADCP – USF). Additional cruises are conducted periodically to the station, at a frequency varying between bi-monthly and seasonally, to collect zooplankton samples in the upper 300 m for biomass and taxonomy estimates.

### *Methods*

During each monthly core cruise (Table 1), a set of key parameters is collected. Table 2 lists these parameters and general methods used. Because the methods have been described in detail by Muller-Karger et. al. (2001), and changes to those procedures were revised in the last NSF progress report, only new modifications and additions will be discussed here.

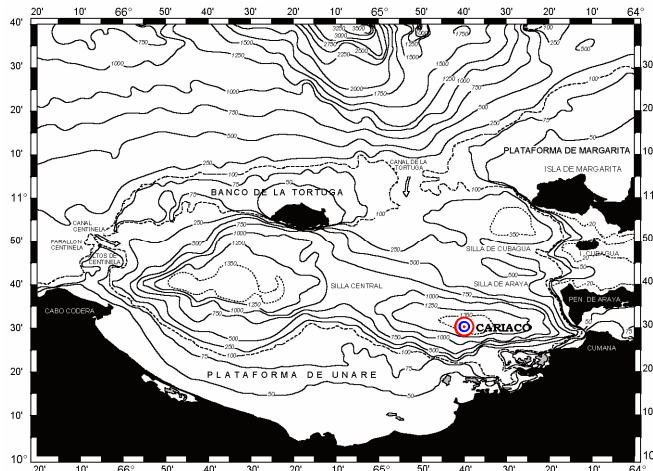


Figure 1: The Cariaco Basin. Location of the CARIACO time-series station is indicated (from Muller-Karger et al., 2001)

Table 1. Cruise number and dates carried out from 2001 up to date

Cruise number	Date	Cruise number	Date
62	Jan/11/2001	87	Mar/11/2003
63	Feb/16/2001	88	Apr/08/2003
64	Mar/14/2001	89	May/13/2003
65	Apr/04/2001	90	Jun/10/2003
66	May/05/2001	91	Jul/08/2003
67	May/11/2001	92	Aug/04/2003
68	Jul/09/2001	93	Sep/09/2003
69	Aug/06/2001	94	Nov/11/2003
70	Sep/11/2001	95	Dec/09/2003
71	Oct/08/2001	96	Jan/13/2004
72	Nov/05/2001	97	Feb/08/2004
73	Dec/11/2001	98	Mar/08/2004
74	Jan/11/2002	99	Apr/06/2004
75	Feb/16/2002	100	May/13/2004
76	Mar/14/2002	101	Jun/08/2004
77	Apr/04/2002	102	Jul/06/2004
78	May/05/2002	103	Aug/10/2004
79	Jun/12/2002	104	Sep/10/2004
80	Jul/09/2002	105	Oct/05/2004
81	Aug/06/2002	106	Nov/09/2004
82	Oct/03/2002	107	Dec/07/2004
83	Nov/07/2002	108	Jan/11/2005
84	Dec/05/2002	109	Feb/10/2005
85	Jan/14/2003	110	Mar/08/2005
86	Feb/11/2003	111	Apr/05/2005

Table 2. List of parameters collected during each CARIACO cruise, the depth range, instrument, and processed data available online.

Parameter	Depth Range	Instrument/Method	Processed Data (Cruise number range or year)
<b>1. Continuous Parameters</b>			
Pressure (Depth)	0-1310 m	SBE-25 (SeaBird)	1-111
Temperature	0-1310 m	SBE-25 (SeaBird)	1-111
Conductivity (Salinity)	0-1310 m	SBE-25 (SeaBird)	1-111
Dissolved Oxygen	0-1310 m	SBE-43 (SeaBird)	1-111
Fluorescence (Chl)	0-1310	Fluorometer	1-111
Beam attenuation (c660)	0-1310	C-Star (WetLabs)	1-111
<b>2. Water Column Chemical Measurements</b>			
Dissolved Oxygen	0-1310 m	Titration	1-107
DOC & TOC	0-1310 m	High Temp Comb	1-63; 110-111
Total Alkalinity	0-1310 m	Gran Titration	1-109
pH	0-1310 m	Spectrophotometer	1-106
Salinity	0-1310 m	Guildline Portasal 8410	1-109
Nitrate	0-1310 m	Autoanalyzer	1-103
Nitrite	0-1310 m	Autoanalyzer	1-103
Amonia	0-1310 m	Autoanalyzer	1-103
Phosphorus	0-1310 m	Autoanalyzer	1-103
Silicate	0-1310 m	Autoanalyzer	1-103
Diss. Org. Nitrogen	0-1310 m	Persulfate oxidation	102-107
Diss. Org. Phosphorous	0-1310 m	Persulfate oxidation	102-107
Partic. Organic Carbon	0-1310 m	High Temp Comb	1-105
Partic. Organic Nitrogen	0-1310 m	High Temp Comb	1-105
<b>3. Biomass Measurements</b>			
Chl. <i>a</i> and Phaeopig.	0-100 m	Flourometry	1-111
Bacteria	0-1310 m	(Various/SUNY)	(see SUNY report)
<b>4. Carbon Assimilation and Particle Flux</b>			
Primary Production	0-100 m	<sup>14</sup> C	1-110
Bacterial Production and Respiration	0-1310 m	(Various/SUNY)	(see SUNY report)
Protozoan grazing	0-1310 m	(Various/SUNY)	(see SUNY report)
<b>5. Optical Measurements</b>			
Incident Irradiance	Surface	Spectrascan	1-111
Upwelling Radiance and Downwelling Irradiance	0-150 m	PRR-600	1-99
<b>6. Moored Instruments</b>			
Sediment Traps	150, 275, 450, 900, 1200	(U. South Carolina)	(see USC report)
Acoustic Doppler Current Profiler (ADCP)	<200 m	ADCP (RDI)	1996-1998; 2002-2005
Lowered ADCP	1-1300 m	Sentinel 300 (RDI)	2005

### *Dissolved organic carbon (DOC)*

As indicated in Table 2, DOC sampling has been resumed, starting in March 2005. Our confidence in resampling this parameter came after we successfully sampled DOC throughout the entire Eastern Basin, as part of the extended cruise carried out in March 2004. DOC values and surface distribution in Cariaco during March 2004 were comparable to those measured by Alvarez Salgado et al. (1999) in similar upwelling conditions off the coast of the Iberian Peninsula.

DOC samples will be collected along with TOC samples, which will serve as a backup in case contamination of DOC occurs. They will be extracted directly from the Niskin bottle by gravity filtering through GF/F precombusted filters, and using silicone tubing. Samples and tubing will be handled using polyethylene gloves. The samples will be stored in Nalgene wide-mouthed translucent 60 ml acid-cleaned HDPE polyethylene bottles and frozen to -20 °C until analysis. The analysis will be carried out by Dr. Dennis A. Hansell at the Rosenstiel School of Marine and Atmospheric Science (RSMAS), University of Miami.

### *Chromophoric dissolved organic matter (CDOM)*

CDOM measurements have been regularly collected at the CARIACO time-series station since 1998 in the upper 100 m of the water column, but the resulting slopes and absorptions were not satisfactory. Starting in January 2005 a new protocol was applied, where the main change was the beginning of on-board filtration. Before January 2005, water was filtered through a 0.7 µm precombusted filter pad, and the filtrate was refrigerated in clear glass vials until analysis, when it was re-filtered through a 0.2 µm pore-size *anotop* filter. Because we now know that through the 0.7 µm filter small cells can still escape and potentially alter the original concentration of CDOM, filtration now is done on board, directly through a 0.2 µm pore-size *anotop* filter, using a glass syringe. Filtrate samples are now stored frozen (-20 °C) in acid cleaned amber-colored bottles until analysis, when they are re-filtered through a new 0.2 µm pore-size *anotop* filter in order to remove any salts that may have precipitated during the freezing process.

Samples measured using the new protocol have so far showed consistency and reasonable values (0.03 – 0.05 m<sup>-1</sup> at 400nm).

### *Particulate organic carbon (POC) sampling modifications*

Throughout the years the POC measurements of CARIACO have shown high variability, especially at depth. This was not likely to be real, due to the fact that POC decreases exponentially and below the interface should not show any abrupt increases. After several attempts at pinpointing the source of this variability, it was determined that it must lay somewhere in the handling of both the blank and the sample filter pads. Tin disks are now being used to place and cover the sample filter pad, and in doing so we reduce the amount of handling the filters get. Blanks are treated in the same way. This new methodology seems to have reduced the variability of POC measurements in the deep part of the Basin.

The CARIACO data are publicly available through the CARIACO web page (<http://www.imars.usf.edu/CAR/index.html>) upon passing quality control, within periods ranging from weeks to about 6 months, depending on the difficulty of processing an observation.

### **The Cariaco project: Ten years of sampling**

The year 2005 marks the tenth anniversary of the CARIACO Project. One of the strengths of this project is that, by sampling consistently the same location, it has allowed the observation of temporal variability of different parameters. By understanding the processes that occur today in the basin we have been able to accurately start to interpret the sedimentary record that is kept at the bottom of the Cariaco Basin. Being located in the tropics, the study of the Cariaco Basin has begun to answer some of the most important questions in paleoceanography and climate change, such as what role do the tropics play in climate regulation and is what we see at higher latitudes also visible in the tropics?

Below are some of the most significant findings of the CARIACO project:

- Upwelling in the Cariaco Basin is wind driven, lagging 1-2 weeks with respect to the changes in the wind intensity (Astor et al., 2003)
- Upwelling intensity varies from year to year, each strongly affecting the hydrography of the upper 150 m (Muller-Karger et al., 2001).
- A secondary upwelling has been noted to occur intermittently during the months of July-August; it is unclear whether this event is related to changes in the Trade Winds (Astor et al., 1997; Astor et al., 2003)
- Oxidic-anoxic interface location varies seasonally, being shallower during the upwelling season (Astor et al., 1998).
- Waters at the base of the mixed layer are the likely supply of nutrients to the phytoplankton populations (Scranton et al., 2005)
- Primary productivity in the Cariaco Basin is high ( $>500$  g C/m<sup>2</sup>/year) and varies seasonally and yearly (Muller-Karger et al., 2001)
- Most of the organic carbon that sinks through the water column is derived from surface productivity, with only a minor contribution from terrestrial origin (Thunell et al., 2000)
- Carbon fluxes vary seasonally and are proportional to surface productivity (Thunell et al., 2000)
- Anaerobic degradation of organic carbon in the anoxic portion of the Basin is as efficient as aerobic respiration (Thunell et al., 2000)
- Carbon remineralization throughout the water column is comparable to that seen in well oxygenated open ocean regions (Muller-Karger et al., 2001).
- Sinking nitrogen in the Basin has an isotopic signature which is controlled by the isotopic composition of nitrate in the thermocline (complete consumption of nitrate in the surface) (Thunell et al., 2004)
- The Cariaco Basin is seasonally influenced by the small, local rivers, rather than the larger, South American rivers (Lorenzoni, 2005)

- Phosphate distribution in the Basin differs from the patterns reported for the Black Sea. (Scranton et al., 2005)
- Conditions at the bottom of the Basin (depths greater than 1200 m) are not in steady-state (Scranton et al., 2005)
- Intrusions of oxygenated water below the oxic-anoxic interface occur intermittently. They may be caused in part by anticyclonic eddies traveling near the Venezuelan continental margin (Astor et al., 2003).
- Abnormal seasonal cycles observed in Cariaco during 1997-1998 could have been related to the strong ENSO event of that year (Astor et al., 2003).
- The Cariaco Basin acts as a source of CO<sub>2</sub> to the atmosphere (Astor et al., 2005)

Still, very little is known about the exchange processes between the Cariaco Basin and the open Caribbean, Eastern and Western Basin exchange and the basin's internal circulation.

## **ACTIVITIES AND FINDINGS IN 2004-2005**

### *Upwelling cycle of 2004-2005*

The CARIACO time-series station accurately records changes in the discharge of local rivers and precipitation patterns, rather than the larger, more distant South American rivers, like the Orinoco and Amazon (Lorenzoni, 2005). Yearly, the lowest salinity at the time-series station has been recorded in September (Astor et al. 1998), which corresponds to the month of highest discharge of local rivers. 2004 was somewhat different from the previous years. During October, November and December, higher than average precipitation was recorded in Margarita Island (Figure 2) and in the Eastern coast of the Venezuelan mainland, which resulted in a drop in surface salinity at the CARIACO time-series station (Figure 3). The alkalinity was also lower during the end of 2004, mirroring the salinity. In the second half of 1999, surface alkalinity was also low (Figure 4), likely caused by the heavy rains that affected the region during that period.

Seasonally, towards the end of the year, winds start increasing in strength and are the main factor that promotes upwelling in the Cariaco Basin (Astor et al., 2003). However, in December 2004, weaker than average winds were recorded at Punta de Piedras (Margarita Island) (3.1 m/s; average: 5 m/s). The lack of strong winds during the end of 2004 and beginning of 2005 was reflected in the low values of both chlorophyll and primary productivity. Usually, at the CARIACO station primary productivity at the surface during March averages 13.12 mgC/m<sup>3</sup>/hr; in March 2005 the production measured was 1.65 gC/m<sup>3</sup>/hr, the lowest that has ever been recorded for the month of March during the project. Low values (2.17 gC/m<sup>3</sup>/hr) were also observed in March 2000, following the heavy rains of 1999-2000.

### *Relationship between POC and particulate beam attenuation ( $c_p$ )*

Bishop (1999) suggested that transmissometer measurements could be used as means of estimating POC quantitatively, over diverse oceanographic environments. The CARIACO time-series project has been collecting transmissometer measurements since

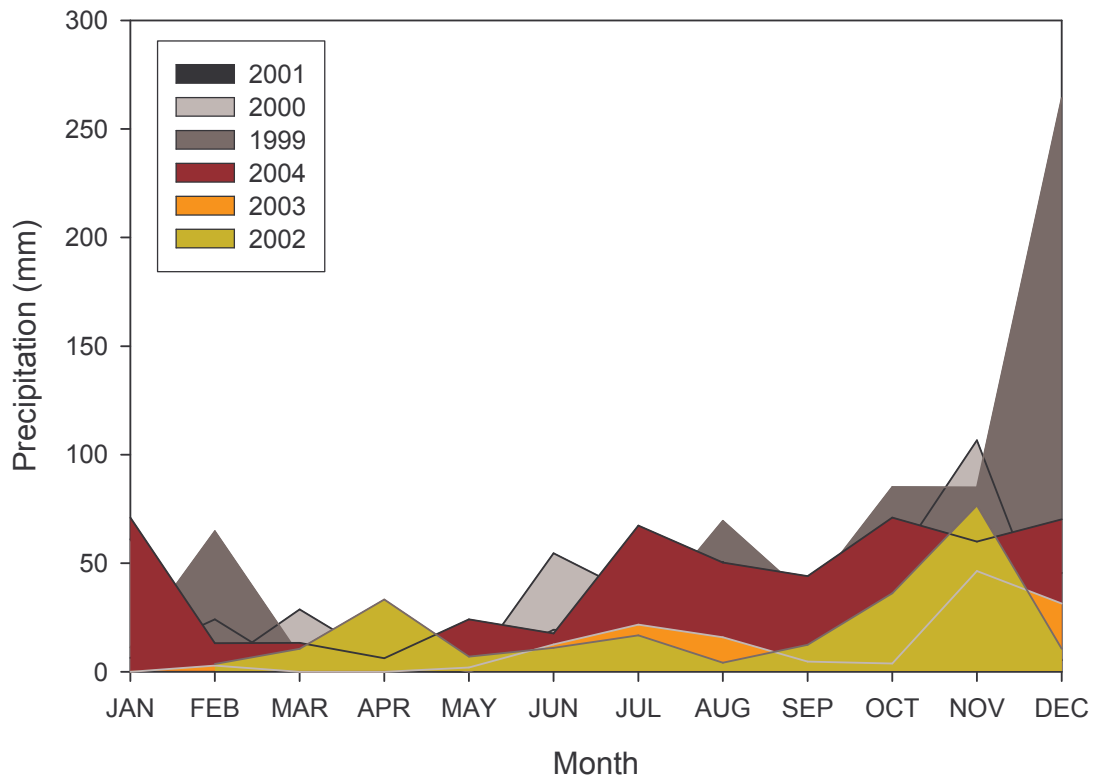


Figure 2: Precipitation recorded at Punta de Piedras, Margarita Island, for the years 1999 – 2004. Note the higher precipitation during October-December 2004.

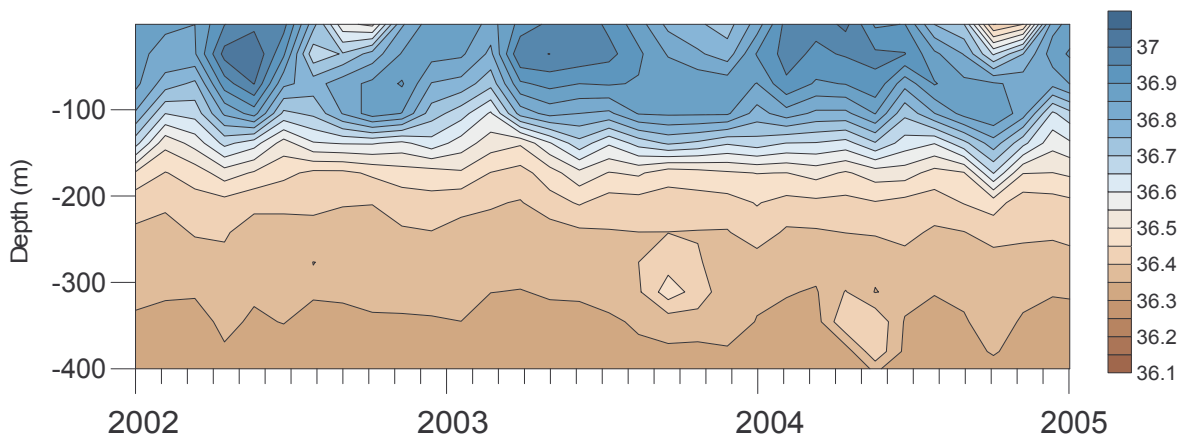


Figure 3: Time-series plot of salinity in the upper 400m at the CARIACO station

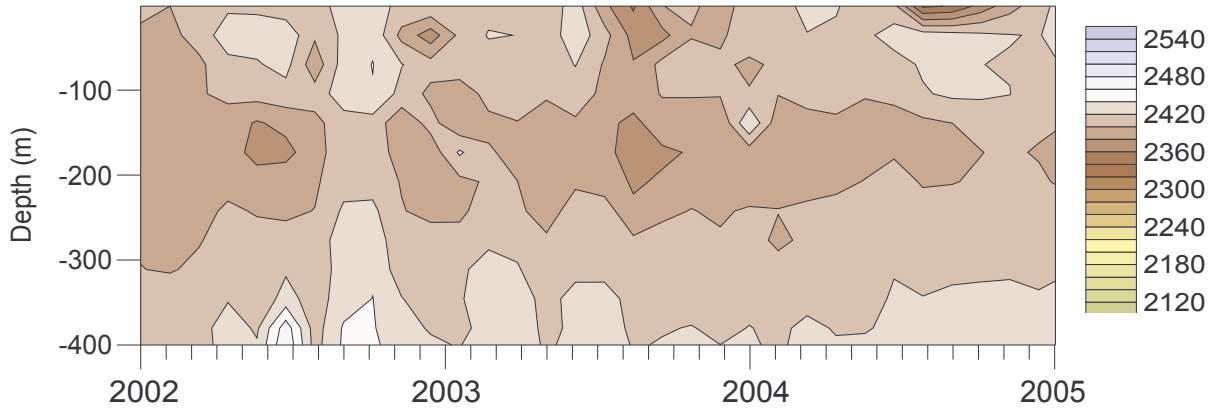


Figure 4: Time-series plot of alkalinity in the upper 400m at the CARIACO station

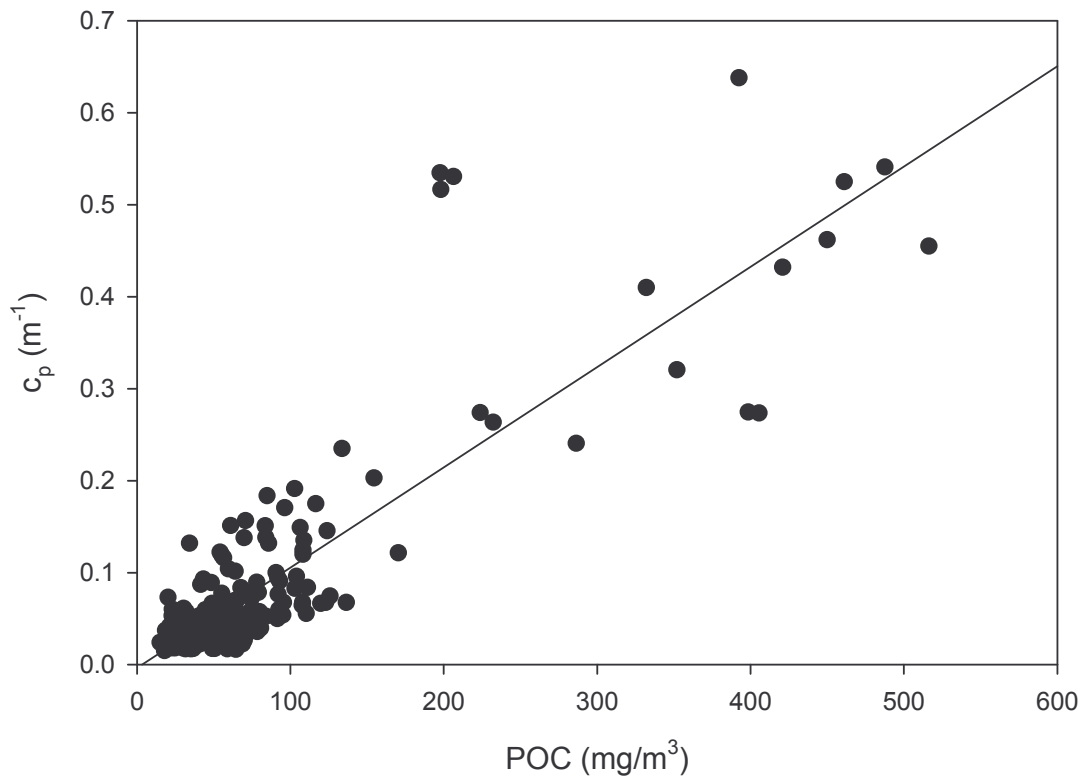


Figure 5: POC vs. particulate beam attenuation ( $c_p$ ) at the CARIACO station for the period between September 2003 and October 2004 ( $r^2 = 0.75$ ).



its beginning, but no apparent relationship had emerged between POC and attenuation due to particles ( $c_p$ ) in the basin. In September 2003 the old SeaTech transmissometer was replaced with a new C-Star transmissometer (WetLabs) and calibrated using an AC-9 during the first extended cruise to the Basin that same month. October 2004 marked one year of measurements with the new instrument and the relationship between POC and  $c_p$  was revisited. Changes to the sampling of POC were also applied in order to reduce the variability of these measurements (see *methods*). Figure 5 shows the relationship between POC and  $c_p$  ( $r^2 = 0.75$ ). There seems to be no significant difference in this relationship between upper ocean waters and the deep, anoxic ones, as well as between seasons (upwelling vs. non-upwelling). The scatter observed in the high POC, high  $c_p$  values, is most likely caused by the shipboard filtration measurements. However, this relationship will have to be studied further, as more data is collected, before  $c_p$  measurements can be used with confidence to estimate POC throughout the water column in the Cariaco Basin.

### *DOC, DON and DOP*

In March 2005, sampling of DOC started again, following the method suggested by Dr. Dennis Hansell (RSMAS, see *methods*). We also obtained the first results of the dissolved organic nitrogen (DON) and dissolved organic phosphorous (DOP) sampling, which included the months of July-December 2004; these results are plotted in Figure 6. The concentration of DON declines slightly with depth (from 6-10  $\mu\text{M}$  to 1-3  $\mu\text{M}$  at 1000 m), and the values measured are comparable with the ones obtained by Okuda et al. (1969). DON in the surface waters of the Cariaco Basin is also comparable to DON measured in the BATS and HOT time series stations. DOP in Cariaco seems to be higher than elsewhere and not to decrease significantly with depth. However, there is considerable scatter in both our DON and DOP samples throughout the water column. The scatter is likely not due to analytical errors, but can be caused by the sampling procedure.

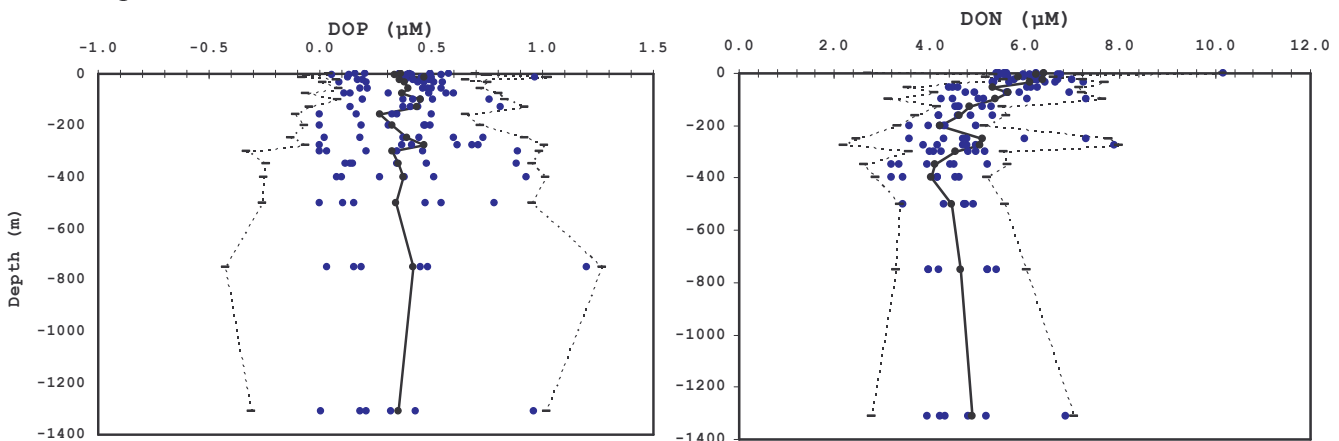


Figure 6: Dissolved organic Nitrogen (DON) and Phosphorous (DOP) sampled at the CARIACO station between July and December 2004. Solid black lines represent averaged measurements. Dotted black lines are  $\pm 2 \sigma$ . Scatter for DOP is 0.5-1.2  $\mu\text{M}$  and for DON 2-4  $\mu\text{M}$  (Dr. K. Fanning).

Currently, sampling of DON/DOP is done using a vacuum pump, and the pressure of the vacuum can be rupturing cells, which in turn release concentrated amounts of DON and DOP. We plan to test whether the scatter we are observing is caused by our sampling methodology by filtering the DON and DOP much in the same fashion as the DOC – using only gravity and directly from the Niskin bottle.

#### *ADCP measurements*

In January 2005, the lowered acoustic current Doppler profiler (LADCP) was deployed and the data sent to Dr. Martin Visbeck and Dr. Gerd Krahnmann (Lamont-Doherty Earth Observatory, Columbia University) for processing (as courtesy). Unfortunately, the cage used for deployment proved to be too light for the currents in the Basin, and the data was of low quality. A new deployment was done in May 2005, with an improved cage and new profiling parameters, as suggested by Dr. Visbeck and Dr. Krahnmann. May 2005 also marked the successful retrieval of the first data from the downward-looking ADCP, moored near the time-series station (10° 30.22' N, 64° 38.93' W). The data will be processed in the subsequent months and compared to the LADCP profile.

#### *All-Hands meeting*

In May 2005, a second All-Hands meeting was carried out at the Estación de Investigaciones Marinas (EDIMAR), in Margarita Island, Venezuela. This year, the meeting focused on the scientific achievements of the project and included only the PI's related to the project, both of the U.S. and Venezuela. Last year's action items were revised, and the accomplishments were evaluated. Each party presented their current and future work, and an open discussion followed each presentation. Because of the two past successful meetings (2004 and 2005), it was agreed that one all-hands PI meeting should be held each year, where the participants will present their work and updates on manuscripts.

## **OUTREACH**

The CARIACO project at present supports one graduate student at USF, MSc. Digna Rueda, who has recently completed her first year of the PhD Program. CARIACO has trained two young technicians, one in the US (Mr. John Akl) and one in Venezuela (Ms. Glenda Arias). Glenda Arias visited the Remote Sensing Lab. at the University of South Florida for a 4-week training period during Oct. 2001. MSc. Laura Lorenzoni, who recently graduated from USF with the support of the CARIACO Project, is currently working as the CARIACO technician.

The project continues a very positive and productive collaboration with Mr. Ramon Varela and MSc. Yrene Astor, of the Fundación La Salle in Venezuela, who assist in carrying out the logistics of monthly cruises, data processing and sample analyses.

## **FUTURE PLANS**

During 2005-2006 we plan to continue the monthly CARIACO field program as described in our original proposal. We will continue to collect and evaluate the regular measurements taken during each core cruise, as well as closely monitor the DOC, CDOM and POC data. We will also be evaluating the DON/DOP sampling protocol. We will re-deploy the lowered ADCP and progressively integrate it to the regular core measurements, once the data has been adequately evaluated.

Originally we had planned for a third spatially extensive cruise that would correspond to the cruise made during March 2004. However, we re-evaluated the objectives of the cruise and determined it would be more beneficial to the project to carry out a more spatially extensive cruise, for which we require more days of ship time. This cruise would attempt to answer some of the pressing questions we have, such as the interaction of the Basin with the open Caribbean, both through the Northern Channel and the Eastern Channel, and the potential exchange that exists between the Eastern and Western Cariaco Basin. Future plans still include a closer look at the Basin's southern coast, to better understand the transport of sediments into the basin by local rivers, and the connection between paleoceanographic data and local processes.

During May 2006 we will carry out another CARIACO meeting, much in the fashion as the one carried out in 2005. The objective of the meeting will be to discuss the yearly achievements, status of publications and possible new scientific directions for the project.

## **PAPERS, ABSTRACTS, and PRESENTATIONS**

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Low phylogenetic diversity of prokaryotes at the O<sub>2</sub>/H<sub>2</sub>S interface of the Cariaco Basin. FEMS Microbiology Letters.

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Smoak, J. W. Moore and R. Thunnell. 234 Th, 228 Th, and 210 Pb fluxes in the contrasting chemical environment of the Cariaco Basin. Deep-Sea Research.

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