Ocean Carbon and Biogeochemistry: CARIACO Data System

CARIACO cruises
Niskin bottle sample methodology

PI: CARIACO Project Investigators

02 March 2006: Prepared for OCB data system by Cyndy Chandler (OCB DMO) from documentation contributed by Laura Lorenzoni (IMaRS, USF).

OCB DMO processing notes

The OCB DMO makes very few modifications to the data as contributed by the CARIACO team. The following is an itemized list of all changes:

093,1,09,09,2003,160 ... missing values for: TCO2 and fCO2

Date parameter added by OCB-DMO:
date=YYYYMMDD (YYYY+MM+DD)
and all missing values (-9999*) replaced with nd (for consistency with OCB database convention)

Although the published methodology (duplicated below) reports "Total_alkalinity (m mol/kg)", in April 2007 the OCB DMO confirmed that CARIACO Alkalinity is in fact reported in units of moles/kg_of_seawater.

Methods

The CARIACO (CArbon Retention In A Colored Ocean) time series observations started on November 1995. Monthly cruises are conducted to the CARIACO station (10.5° N, 64.67° W) onboard the R/V *Hermano Ginés* of the Fundación La Salle de Ciencias Naturales de Venezuela. The data are presented as composite profiles assembled from multiple casts. Chlorophyll and primary productivity data are taken out of the first cast, done around 4 AM, local time. The rest of the parameters are split between the morning cast (deep) and the noon cast (shallow), so anything below 200m was sampled in the morning (~9 AM) and observations from surface to 160 meters are from the noon cast. The following sections describe the methods used in collecting the core observations at the CARIACO station.

Hydrocasts : CTD and Rosette Sample

During each cruise, a minimum of four hydrocasts are performed to collect a suite of core monthly observations. Additional hydrocasts may be performed for specific process studies. We conduct separate shallow and deep casts to obtain better vertical resolution for chemical observations, and for productivity and pigment observations. Water is collected with a SeaBird rosette equipped with 12 (8 liter) teflon-coated Niskin bottles (bottle springs are also teflon-coated) at 20 depths between the surface and 1310 m. The rosette houses the CTD, which collects

continuous profiles of temperature and salinity. The CTD also has an SBE43 oxygen probe and a Wetlabs ECO fluorometer outfitted for chlorophyll- a estimates. A C-Star transmissometer (660 nm, Wetlabs) is also part of the instrument suite. Beam attenuation measurements were added to the time series on its 11 th month, originally using a SeaTech transmissometer. The rosette is controlled with a SeaBird deck unit via conducting cable, but alternatively has been actuated automatically based on pressure recordings via an Autofire Module (SBE AFM) when breaks in cable conductivity have occurred.

Between November 1995 and September 1996, three separate SBE-19 CTDs were used in repeated casts until a reliable salinity profile was obtained below the oxycline. The SBE-19 model CTDs frequently failed to provide reliable conductivity values below the oxycline in the Cariaco Basin. Starting in September 1996, the SBE-19 CTDs were replaced by an SBE-25 CTD, which provided extremely accurate and reliable data in anoxic waters.

All CTDs were calibrated at the Sea-Bird factory once per year. The accuracy of the pressure sensor is 3.5 m and has a resolution of 0.7 m. The temperatures accuracy is 0.002°C with a resolution of 0.0003°C. The conductivity accuracy is 0.003 mmho/cm with a resolution of 0.0004 mmho/cm.

Salinity

Continuous salinity profiles are calculated from the CTD measurements. Discrete salinity samples are analyzed using a Guildline Portasal 8410 salinometer standardized with IAPSO Standard Seawater, with a precision of better than ± 0.003 and a resolution of 0.0003 mS/cm at 15° C and 35 psu, the accuracy is ±0.003 at the same set point temperature as standardization and within -2° and +4°C of ambient. These salinity values are used to check, and when necessary calibrate, the CTD salinity profiles.

Discrete Oxygen

Continuous dissolved oxygen (O 2) profiles are obtained with a YSI 23-Y sensor coupled to the SBE-25 CTD. Discrete oxygen samples are collected in duplicate using glass-stoppered bottles and analyzed by Winkler titration (**Strickland and Parsons, 1972** , as modified by **Aminot , 1983)**. The analytical precision for discrete oxygen analysis is ±3 m M, based on analysis of duplicate samples, with a detection limit of 5 m M.

Nutrients

Since CAR72 (06 Nov. 2001) all samples have been filtered through a 0.8 µm Nucleopore filter within minutes of collection, as recommended by the JGOFS protocol, and frozen in plastic bottles until analysis at the University of South Florida (USF). Previous to November 2001, nutrients were filtered through a 0.7 µm GF/F filter before freezing. This data is still considered reliable, as tests using glass fiber filters show no significant contamination. The analyses follow the standard techniques described by **Strickland and Parsons (1972)** . USF follows the recommendations of **Gordon et al. (1993)** for the WOCE WHP project for nutrient analysis.

Since CAR69 (07 Aug. 2001) all silica samples are kept unfrozen; they are refrigerated and kept in the dark. Prior to CAR69, silicates were frozen and those exhibiting high concentration of silica (> 40µM, below 300m in CARIACO) were affected by polimerization. All deep samples that were frozen showed low values due to polimerization loss, except CAR63 and CAR68 which showed high values. CAR69 was analyzed by Yrene Astor at EDIMAR from the separate unfrozen bottles and at USF from other, frozen, bottles. Unfrozen CAR69 resulted higher with deep values close to what is expected (e.g. ~ 92µM at 1310m).

Detection limits for CARIACO nutrient analysis

The limits below were determined by calculating the concentrations in triplicate standards, averaging the results within each triplicate group, calculating the standard deviation for each group, averaging the standard deviations, and finally doubling the averages to get the detection limits. These samples were analyzed on an ALPKEM RFA II. Subsequent Cariaco analyses were performed on a Technicon Analyzer II

	ALPKEM RFA II	**Technicon Analyzer II**	
Nutrient Type	**Detection limits**	**Errors of analysis**	**Detection limits**
PO 4 Phosphate	0.03 µmol	<0.01 µM	0.02 µM
Si(OH) 4 Silica	0.14 µmol	0.2 µM	0.4 µM
NO 3 Nitrate	0.06µmol	0.02 µM	0.04 µM
NO 2 Nitrite	0.02µmol	<0.01 µM	0.01 µM
NH 4 Ammonia	0.07µmol	0.05 µM	0.1 µM

Primary Production

Primary productivity measurements are made using a modified **Steeman Nielsen (1952)** NaH 14 CO 3 uptake assay. The productivity measurements consist of *in situ* incubations of water collected at 8 depths and inoculated with 14 C-labeled bicarbonate. One hour before sunrise, a shallow cast is performed to obtain water from 1, 7, 15, 25, 35, 55, 75, and 100 meters. As the productivity cast is taken, a Licor Photosynthetically-Active Radiation (PAR) integrator, placed high above the ship's bridge, is activated. Water is poured directly from the Niskin bottle under low light conditions into 250 ml clear polycarbonate bottles. These bottles have been previously acid-washed, rinsed, and soaked in de-ionized water for over 48 hours. Bottles are rinsed three times before filling, a near total fill (the volume within the bottles is actually 290 ml of sea water). Four clear polycarbonate bottles are filled from each depth. We wrap one inoculated bottle from each depth in aluminum foil

to obtain the dark 14-C uptake rates. An extra bottle for 1, 15, 35, and 75 m is filled, but not inoculated, to provide time-zero (t 0) filter and seawater blanks. The t 0 samples are kept in the dark in the laboratory and are filtered after deploying the floating incubation buoy.

We inoculate each sample under low light conditions with 1,000 ml (4 mCi) of the 14 C sodium bicarbonate working solution. A 200 ml aliquot for counting total added 14 C activity is removed from one of the 3 bottles from each depth and placed in a 20 ml glass scintillation vial containing 250 ml ethanolamine. The mixture is held at 5°C until subsequent liquid scintillation analysis on shore. We also place 50 ml of the 14 C working solution in a vial with ethanolamine (250 ml) for reference counting.

The dark bottle and 3 light bottles are hooked together with a combination of plastic tie wraps and nylon cord, and kept in the dark while preparations are made for deployment of the productivity incubation float. At approximately 07:00 hours, the productivity array is deployed. The entire productivity ensemble is attached to a buoy equipped with a flag and radar reflector.

Productivity observations were initiated in December 1995. Between December 1995 and November 1996, we incubated samples from 06:00 to 10:00 hours. Starting December 1996, we changed our protocol to incubate between 07:00 and 11:00 hours. This more accurately represents 1/3 of the daily photoperiod and 1/3 of the total energy received in one day on a year-round basis at 10°30'N, as verified with the PAR light sensor.

Approximately 4 hours after deployment, the productivity array is recovered. We decided to use 4-hour incubation periods due to the potentially high productivity (>1,000 mg /(m^2d)) of this continental margin. Sample bottles are detached from the line and placed in labeled, dark plastic bags until filtration. Time and position of recovery are recorded. Maintaining low light conditions, a 50 ml aliquot is withdrawn from each productivity bottle using a 50 ml plastic syringe. This aliquot is filtered onto a 25 mm Whatman GF/F glass fiber filter, maintaining vacuum levels of ~ 1/3 atm. The filter is rinsed with 0.25 ml 0.5 N HCl, and placed in a 20 ml glass scintillation vial, covered, and held at 5°C until subsequent processing on shore. At the shore laboratory, immediately upon return and within 15 hours of sample collection, 10 ml of liquid scintillation cocktail are added to the vials with the filters. These vials are refrigerated until they are ready for analysis on a BetaScout (PerkinElmer)scintillation counter.

Carbon uptake calculations follow the standard formulation outlined in the JGOFS manual (UNESCO, 1994), taking into consideration a (very low) quenching curve. Specifically, we subtract the blank from all bottles, and then subtract the dark bottle uptake from the average uptake in the light bottles to correct for non-photoautotrophic carbon fixation or absorption. Dark uptake values have always been very low. A scaling factor (~ 3) is applied to convert the hourly production value to a "daily mean hourly average". This factor varies slightly, as it is based on the fraction of the energy received during the incubation period relative to the total energy received in a day. Daily rates are derived by multiplying the hourly rate by 12. **Gieskes and Van Bennekom (1973) , Peterson (1980) ,** and **Carpenter and Lively (1980)** review the historical background, problems, and assumptions

involved in the application of the radiocarbon technique to aquatic productivity. **Muller-Karger (1984)** also summarizes the technique and corrections involved.

pH and Alkakinity

pH samples are collected directly in 10-cm cells and analyzed on board. We perform pH and total Alkalinity estimates using the precise spectrophotometric dye methods developed by **Robert-Baldo et al. (1985)** , **Byrne and Breland (1989)** , and which we have now modified from Clayton and Byrne (1993) and **Breland and Byrne (1993)** . These methods circumvent the problem that arises when potentiometric electrodes are transferred from dilute buffers to sea water samples due to the sample's high ionic strength. pHT at 25°C (total_hydrogen_ion_scale), analytical precision= ±0.003. Total_alkalinity (m mol/kg), precision= 5 m mol/kg.

Chlorophyll

Chlorophyll sample collection and storage: water samples are collected from Niskin bottles into 1 L dark polyethylene bottles. These samples are immediately filtered through 25 mm Whatman GF/F filters using a vacuum of less than 100 mm Hg. During the upwelling season (approx. January-May) we filter 250 ml seawater, and during the rest of the year we filter 500 ml. Three replicates are taken per depth during the upwelling season, but only two are collected when biomass is obviously at its minimum, during the non-upwelling season. Filters are folded in half twice and placed in glass centrifuge tubes, labeled and frozen. Storage time is kept as short as possible (less than a week) before measurement.

Chlorophyll procedure: after removal from the freezer, the filters are extracted in 10 ml of methanol. The samples are allowed to extract for 24 hours in the refrigerator. Following extraction, samples are centrifuged for 20 minutes to remove debris. The fluorometer (Turner fluorometer model 10-AU-005) is allowed to warm up and stabilize for 30 minutes prior to use. Pure methanol is measured to confirm the zero position. Samples are transferred to 1-cm cells and they are measured directly into the fluorometer (Fo). 100 µl of 0.48N HCl is added to each cell. A second reading is taken from the fluorometer for each cell (Fa). Standardization: The fluorometer is calibrated every year with a commercially available chlorophyll *a* standard (Σ). The concentration of chlorophyll a and phaeopigments in the sample are calculated using Yentsh and Menzel (1963) equation, with a specific absorption coefficient of 74.5 (chlorophyll in methanol).

POC and PON

POC and PON sample collection and storage: water samples are collected from Niskin bottles into 2 L dark polyethylene bottles. These samples are immediately filtered through 25 mm Whatman GF/F filters (precombusted for 5 hours at 450°C) using a vacuum of less than 100 mm Hg. Filters are placed on expendable tin disks and then into aluminum foil envelops (also precombusted for 5 hours at 450°C) labeled and frozen. In the laboratory, filters are dried at 65°C for 12-15 hours then stored with silica gel.

Measurement: The filters are folded inside a tin disk and analyzed on a Perkin Elmer 2400 Elemental Analyzer. The samples are combusted at 1200-1300°C and

then passed through a reduction tube to removes the oxygen added to raise the combustion temperature. The C and N are then separated in a chromatographic column and are measured on a Thermal Conductivity Detector. Carbon and nitrogen standards, and blank filters are used to calibrate the data. The accuracy of the instrument is <0.3% and the precision of the instrument is <0.2%. . These are published values and we find that we are always within these limits (usually ±0.15% for carbon and ±0.1% for nitrogen). We run cystine as our standard (29.99% Carbon, 11.66% Nitrogen). The analytical range of the instrument is: Carbon= .001 to 3.6 mg and Nitrogen= 0.001 to 6.0 mg.

Dissolved organic Carbon, Nitrogen and Phosphorous (DOC, DON and DOP)

Measurements of DOC were taken since the beginning of the project in November 1995 but suspended in February 2001 due to irregularity of results. DOC was reinitiated in March 2005 using a new protocol. DOC samples are collected monthly and analyzed at the Organic Biogeochemistry Lab in the Rosenstiel School of Marine & Atmospheric Science at the University of Miami. Samples are gravity-filtered directly from the Niskin bottles through 45 mm GF/F precombusted filters using acid cleaned polycarbonate in-line filter holder. Immediately after filtration the polyethylene bottles are frozen at -20°C until analysis.

DON and DOP measurements were added to the regular CARIACO cruises in July 2004. Samples are filtered through GF/F filters using a specially built vacuum filter rack. The DON method is based on Solorzano and Sharp (1980) "Determination of total dissolved nitrogen in natural waters" Limnol. Oceanogr . 25:753-756. This procedure produces a filtered seawater sample for analysis of total dissolved fixed nitrogen (=nitrate + nitrite + ammonium + DON). DON concentration is obtained by difference from nitrate, nitrite, and ammonium measured in the standard nutrient protocol. DOP is analyzed in the same persulfate-oxidized filtrate solution as DON. That solution yields total inorganic phosphate concentration, which is composed of the inorganic phosphate concentration originally in the seawater, plus an additional phosphate concentration due to the conversion of DOP to phosphate. DOP concentration is then obtained by difference from the inorganic phosphate in the unoxidized sample measured through the standard nutrient protocol.

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