

$f\text{CO}_2$ variability at the CARIACO tropical coastal upwelling time series station

Y.M. Astor^{a,1}, M.I. Scranton^b, F. Muller-Karger^{c,*}, R. Bohrer^d, J. García^{a,1}

^aFundacion La Salle de Ciencias Naturales, Estación de Investigaciones Marinas de Margarita, Apartado 144 Porlamar, Isla de Margarita, Venezuela

^bMarine Sciences Research Center, State University of New York, Stony Brook, NY 11794-5000, United States

^cUniversity of South Florida, College of Marine Science, St. Petersburg, FL 33701, United States

^dBeach Dr. Apt. 1601, St. Petersburg, FL 33701, United States

Received 10 May 2004; received in revised form 4 April 2005; accepted 19 April 2005

Available online 23 June 2005

Abstract

Monthly seawater pH and alkalinity measurements were collected between January 1996 and December 2000 at 10°30'N, 64°40'W as part of the CARIACO (CARbon Retention In A COlored Ocean) oceanographic time series. One key objective of CARIACO is to study temporal variability in Total CO₂ (TCO₂) concentrations and CO₂ fugacity ($f\text{CO}_2$) at this tropical coastal wind-driven upwelling site. Between 1996 and 2000, the difference between atmospheric and surface ocean CO₂ concentrations ranged from about −64.3 to +62.3 μatm. Physical and biochemical factors, specifically upwelling, temperature, primary production, and TCO₂ concentrations interacted to control temporal variations in $f\text{CO}_2$. Air–sea CO₂ fluxes were typically depressed (0 to +10 mmol C m^{−2} day^{−1}) in the first few months of the year during upwelling. Fluxes were higher during June–November (+10 to 20 mmol C m^{−2} day^{−1}). Fluxes were generally independent of the slight changes in salinity normally seen at the station, but low positive flux values were seen in the second half of 1999 during a period of anomalously heavy rains and land-derived runoff. During the 5 years of monthly data examined, only two episodes of negative air–sea CO₂ flux were observed. These occurred during short but intense upwelling events in March 1997 (−10 mmol C m^{−2} day^{−1}) and March 1998 (−50 mmol C m^{−2} day^{−1}). Therefore, the Cariaco Basin generally acted as a source of CO₂ to the atmosphere in spite of primary productivity in excess of between 300 and 600 g C m^{−2} year^{−1}.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Upwelling; $f\text{CO}_2$; Air–sea exchange; Oceanographic time series; Cariaco Basin

* Corresponding author. Tel.: +1 727 553 3335; fax: +1 727 553 1103.

E-mail addresses: yastor@edimar.org (Y.M. Astor), mscranton@notes.cc.sunysb.edu (M.I. Scranton), carib@marine.usf.edu (F. Muller-Karger), rbohrer@sea.edu (R. Bohrer).

¹ Fax: +58 295 2398051.

1. Introduction

Continental margins are sites of active physical and biogeochemical processes of direct relevance to the global carbon cycle (Liu et al., 2000; Koblenz-

Mishke et al., 1970). Indeed, the physical and biogeochemical modulation of the fugacity of CO_2 ($f\text{CO}_2$) in coastal and shelf waters leads to sharp changes in this parameter over short time scales (Borges and Frankignoulle, 2002; Gago et al., 2003; Sarma, 2003). In coastal systems, nutrient levels can be high, favoring growth of phytoplankton and thus removal of CO_2 from the water. The solubility of CO_2 near the surface can also be affected by changes in salinity due to riverine influence, respiration and remineralization of particulate and dissolved organic matter (DOM), photolysis of DOM, or upwelling of deep waters and mixing (Legendre and Gosselin, 1989; Sato et al., 1996; Temon et al., 2000; Gago et al., 2003). Carbon fixed by phytoplankton that is not remineralized is thought to either sink in place or be transported across the shelf to the slope or the open ocean, where burial in the sediments may represent a long-term sink of CO_2 (Berger, 1989; Walsh, 1988, 1991; Chen et al., 2001; Muller-Karger et al., 2005). However, the net effect of burial of coastal productivity on global or even local CO_2 fugacity ($f\text{CO}_2$) remains poorly understood (Roos and Gravenhorst, 1984; Andri  et al., 1986; Boehme et al., 1998).

The Cariaco Basin, located at 10.5° N, 64.67° W, on the continental shelf of northern South America in the Caribbean Sea, is part of a large regional system that experiences strong seasonal and interannual variations in wind-driven coastal upwelling (Richards and Vaccaro, 1956; Richards, 1960, 1975; Herrera and Febres-Ortega, 1975; Muller-Karger and Aparicio, 1994; Black et al., 1999; Astor et al., 1998, 2003). Each year, upward migration of isopycnals within the upper 150 m occurs between November and May, when the Trade Winds and the Caribbean Current are most intense. In addition, a secondary upwelling event is present every year between July and August (Astor et al., 2003). Upwelling relaxation is observed when winds and the Caribbean Current decrease in intensity (August–October).

The flux of nutrients from rivers into the Cariaco Basin is minimal (Werne et al., 2000); therefore, upwelling of water from below the euphotic zone is the main source of nutrients for primary production. However, nutrient concentrations are always low in the upper 35–55 m due to consumption by phytoplankton (Thunell et al., 2004). Integrated primary

production ranged from 371 to 649 $\text{g C m}^{-2} \text{ year}^{-1}$ between 1996 and 2000, with 1996 and 1998 showing the highest and lowest production, respectively. On average, the sinking particulate organic carbon flux to 1400 m is 9–10 $\text{g C m}^{-2} \text{ year}^{-1}$ (Thunell et al., 2000; Muller-Karger et al., 2000, 2001, 2004).

In the Cariaco Basin, the carbonate system is influenced by a variety of physical and chemical processes including upwelling, seasonal temperature changes, exchange of water with the Caribbean by advection, gas exchange with the atmosphere, periodic riverine freshwater input and variations in the balance between precipitation and evaporation. The water column within the Cariaco Basin consists of a surface oxic layer of up to ~375 m thickness overlying an anoxic zone that extends to the bottom of the basin at 1400 m. Photosynthesis, organic matter consumption, remineralization and respiration, CaCO_3 precipitation and dissolution, and sinking particulates are important biogeochemical processes in the oxic layer. In the anoxic layer, processes such as bacterial respiration (including sulfate reduction) and CaCO_3 dissolution affect TCO_2 concentrations. Eddies moving along the Venezuelan continental shelf may be important ventilation agents (Scranton et al., 2001; Astor et al., 2003). Catastrophic events that have affected the hydrography include an earthquake in July 1997 (Thunell et al., 1999) and torrential rains with associated massive runoff and sediment discharge in December 1999.

In this paper, we report measurements of the CO_2 system parameters conducted between 1996 and 2000 at the CARIACO time-series station. We show the seasonal and interannual variability of pH, TA, calculated TCO_2 and $f\text{CO}_2$ based on monthly samples. The study focused on the annual to interannual variability in the carbonate system of the upper water column in a tropical coastal upwelling system. In particular, we calculated the air–sea CO_2 flux at the time series station and examined whether this coastal upwelling area represents a source or a sink of CO_2 to the atmosphere.

2. Methods

This paper examines data collected between 1996 and 2000 as part of the CARbon Retention In A

Colored Ocean (CARIACO) time series. CARIACO collected monthly samples at 10°30' N, 64°40' W within the eastern Cariaco Basin using the R/V *Hermano Ginés* (Fundación La Salle de Ciencias Naturales de Venezuela). During each cruise, water was collected from up to 20 depths between the surface and 1310 m. Continuous hydrographic profiles were collected using a SeaBird SBE-19 (January to September 1996) or a SBE-25 (all subsequent cruises) CTD system equipped with oxygen, fluorescence and beam attenuation sensors (see Astor et al., 2003). All CARIACO data including the time series of pH (pH on the total hydrogen ion concentration scale often called pH_T), alkalinity, TCO₂, and fCO₂ are publicly available on the CARIACO web page (<http://www.imars.usf.edu>) and via the NOAA National Oceanographic Data Center (NOAA NODC).

Discrete samples for pH and alkalinity were collected during the upcast. A seawater sample was drawn directly from each Niskin bottle into a 10-cm path cell. pH was measured on board within 1 h of sample collection using a spectrophotometric method (Clayton and Byrne, 1993; DOE, 1994) as modified by DelValls and Dickson (1998). This method uses the absorbance measured at 434 nm and 578 nm before and after the addition of the indicator *m*-cresol purple. The cell was placed in a water bath at 25 °C for 15 min, and absorbances were then measured using an Ocean Optics SD-1000 spectrophotometer. We compared results from this spectrometer to results from a dual beam Hewlett Packard spectrophotometer in the laboratory and made small corrections to the absorbance readings at each wavelength based on measurements over the pH range of 6.7–8.3. pH was calculated using the equation presented in Clayton and Byrne with addition of a constant (0.0047). This addition results from a correction to the buffers used in the original paper (Byrne, personal communication). The analytical precision for pH is ± 0.003 .

Samples for alkalinity were collected in 250-ml borosilicate glass bottles and poisoned with 50 μ l of saturated HgCl₂ solution (giving a Hg level of about 50 μ M). Samples were stored at 4 °C and analyzed in the laboratory. Alkalinity analyses followed the method of Breland and Byrne (1993) as modified by recommendations of Dr. Robert Byrne (University of South Florida). Seawater was acidified by a titra-

tion to the inflexion point using bromocresol green as indicator. CO₂ was then purged from the sample by bubbling with nitrogen gas, and the acid excess was measured at 25 °C by spectrophotometer. Alkalinity was calculated from absorbance readings (444 nm and 616 nm), the known amount of hydrogen ion added, and the excess remaining. The precision of the method was $\pm 4 \mu\text{mol kg}^{-1}$. Small corrections to the absorbances were made based on a comparison to results from a dual beam Hewlett Packard spectrophotometer over a pH range of 3.2 to 4.4. Surface (~2 m) alkalinity data were normalized (nTA) to the mean surface salinity at CARIACO (36.8 on the practical salinity scale), to remove the effect of local precipitation and evaporation.

Accuracy in the alkalinity method is highly dependent on the amount and concentration of the acid added. Because of variability in the earlier acid determinations (from January 1996 to 1997, cruises 3–15), deep-water values were used as an internal standard to calculate the acid concentration. The deep-water alkalinity should be relatively constant over an 18+ month period. Zhang and Millero (1993) estimated an increase of approximately $2 \mu\text{mol kg}^{-1}$ per year in the alkalinity of deep Cariaco Basin waters. The mean values of total alkalinity for the deep samples (500, 750, 1000, and 1310 m) were calculated from CAR 6, 7, 8, 11, 15, 16, 17 and 18. The standard error of these means was approximately $2 \mu\text{mol kg}^{-1}$. The mean values were then treated as known concentrations for these depths and used to back-calculate the acid concentration. The average of the acid concentrations obtained from the four depths was used as the concentration for that cruise. This effectively normalized the data from each cruise to the average deep-water values. The acid concentration determined in this manner was used for cruises CAR3 to CAR15.

Following CAR 15, to improve the standardization of the acid, certified reference alkalinity solutions were obtained from A. G. Dickson (Scripps Institute of Oceanography) and used with each batch of samples from subsequent cruises. For each cruise, we took three measurements of the standard, and using the known alkalinity, calculated the acid concentration.

Another potential problem with the alkalinity method is related to the use of HgCl₂ as a preservative. Mercuric chloride could cause precipitation of hydro-

gen sulphide, which is present in deeper waters of the Cariaco Basin. We typically added 12 μmol of mercury to a 250-ml sample, and sulfide concentrations in bottom waters have ranged between 35 and 80 μM over the period covered by this paper. In one experiment, deep-water replicates were poisoned with different volumes of mercuric chloride solution in order to calculate the alkalinity change associated with the precipitation of HgS . However, no precipitation was observed and alkalinity values remained constant. Since no precipitation was observed, we speculate that Hg experiences strong complexes with chloride (Stumm and Morgan, 1981) or sulfide (Benoit et al., 1999), which may minimize the amount of HgS precipitation. We therefore subsequently assumed that no artifacts were introduced by storage or by poisoning.

Total dissolved inorganic carbon (TCO_2) was calculated from pH and total alkalinity using the K_1 and K_2 equilibrium constants of Mehrbach et al. (1973). Values for the other equilibrium constants were taken from Millero (1995). Results from the JGOFS Equatorial Pacific program suggested the use of other K_1 and K_2 constants for the best internal consistency of CO_2 system components (Millero et al., 1993). However, the correction mentioned above to the spectrophotometric pH determinations and recent corrections to the alkalinity measurements made on those cruises result in the greatest internal consistency with the Merzbach et al. constants (Robert Byrne, personal communication).

To validate our analyses, we compared our TCO_2 and alkalinity results with measurements conducted on CARIACO samples at the laboratory of Dr. Chris Sabine. Duplicate samples from each Niskin bottle collected at each depth for four separate monthly cruises were processed for TCO_2 by our group and by Dr. Sabine's group. We also processed duplicates for alkalinity from one cruise. Dr. Sabine's group used a closed-cell, potentiometric titration procedure for alkalinity and determined TCO_2 with an automated single-operator multiparameter metabolic analyzer (SOMMA) with coulometric detection of the CO_2 extracted from acidified samples (Johnson et al., 1993). Fig. 1 shows the TCO_2 estimated by both groups at all depths. We found excellent agreement between the two sets of measurements, although slight disagreement based on r^2 was observed between data collected between 0 and 1310 m, 2039–2360 $\mu\text{mol kg}^{-1}$ (Fig. 1a) and shallow-water data, 0–

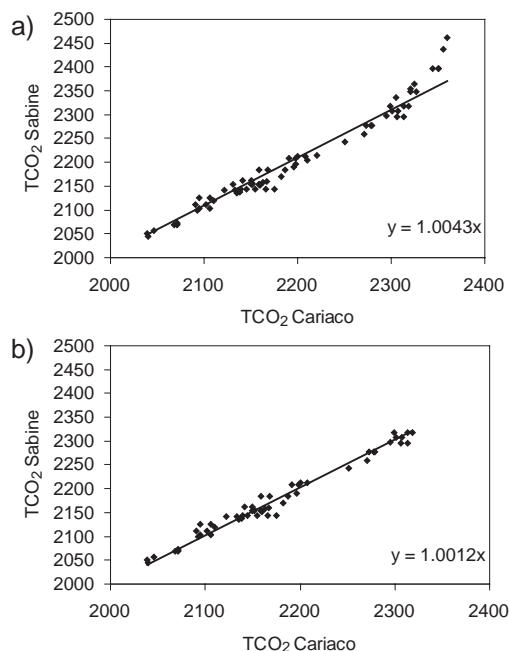


Fig. 1. Comparison of TCO_2 ($\mu\text{mol kg}^{-1}$) as determined by EDI-MAR and by C. Sabine for samples collected from five CARIACO cruises. (a) All observations ($n=70$); (b) Data between 0 and 350 m ($n=56$).

350 m, 2039–2319 $\mu\text{mol kg}^{-1}$ (Fig. 1b). The r^2 was 0.977 for only the data from 0 to 350 m, but 0.957 when all data pairs were included. For alkalinity, the correlation was $r^2=0.999$. The internal consistency with the Merzbach et al. constants was confirmed by comparisons with samples measured also by Dr. Christopher Sabine on three cruises. The pooled standard deviation from 42 samples was 5.6 $\mu\text{mol kg}^{-1}$ with no significant difference between the direct measurements and the calculated values (paired t -test=0.05). Given our precision of 0.003 for pH and 4 $\mu\text{mol kg}^{-1}$ for total alkalinity, this is the approximate TCO_2 precision we expected. Assuming the direct TCO_2 measurements are accurate, this standard deviation is also a measure of the accuracy of our TCO_2 estimates.

The fugacity of carbon dioxide in seawater was calculated from the pH and total alkalinity using the same choice of equilibrium constants as for TCO_2 . In this case, the calculated TCO_2 is combined with the measured TA and the ambient temperature to give the $f\text{CO}_2$ at the ambient temperature. No direct estimate of precision is possible, but based on the precision of our

pH and alkalinity measurements, we estimate our $f\text{CO}_2$ calculations to have an uncertainty of at least 5 μatm .

In order to assess air–sea CO_2 flux (see Discussion), it is necessary to have an estimate of the partial pressure of CO_2 in the atmosphere. We did not directly measure atmospheric CO_2 during our study. Instead, we used data from the flask site in Barbados operated by the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL; data accessible via <ftp.cmdl.noaa.gov/ccg/co2/flask/month/rpbmm.co2>). Over the course of our study, annual mean atmospheric $p\text{CO}_2$ at Barbados showed an increasing trend from ~ 360 μatm to ~ 370 μatm . A seasonal variability of ~ 9 μatm was superimposed on this trend, with maxima in May and minima in September, coinciding approximately with upwelling maxima and minima, respectively. Therefore, we derived an overall mean (366 μatm) to compare with the CARIACO flux data.

Samples for nitrate and nitrite-N measurements were filtered through a 0.7- μm GF/F filter within minutes of collection and frozen in plastic bottles until analysis at either the Universidad de Oriente (Cumaná, Venezuela) or the University of South Florida (USF). The analyses followed the standard techniques described by Strickland and Parsons (1972). USF follows the WOCE WHP recommendations of Gordon et al. (1993) for nutrient analysis.

3. Results

3.1. Seasonal variability in upwelling and primary production

Muller-Karger et al. (2000, 2001, 2004) and Astor et al. (2003) have described the seasonal variability of hydrographic properties and primary production within the Cariaco Basin over short periods. The present study expands on the earlier publications and helps better understand the controls of annual and interannual variability in productivity and carbon system parameters.

Fig. 2 shows the depth of the 21 °C isotherm and surface primary production between 1996 and 2000 at the CARIACO station. Low Sea Surface Temperature (SST) generally corresponds to an upward migration of the 21 °C isotherm. The correlation between the depth of the isotherm and SST was $r^2=0.66$ between January and May (upwelling season) for all years.

Upwelling and primary production were more intense toward the beginning of the time series relative to the second half. Integrated primary production (Table 1) changed substantially both annually and interannually, in part because the annual cycle was punctuated by strong events. Peak primary production events occurred toward the beginning of the year

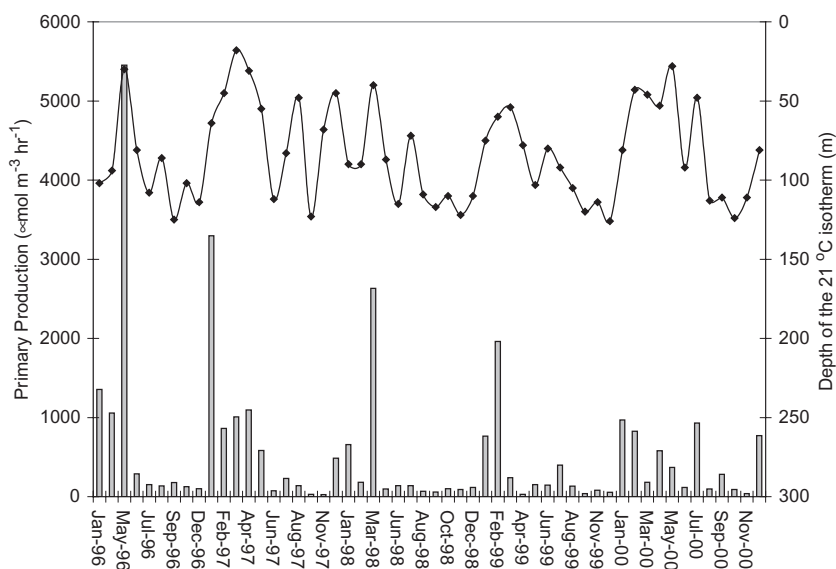


Fig. 2. Time series of observations of primary production ($\mu\text{mol C m}^{-3} \text{ h}^{-1}$; bars) and depth of the 21 °C isotherm (upwelling indicator; line and diamonds) at the CARIACO Station from January 1996 to December 2000.

Table 1

Primary production estimates, based on 12 monthly measurements per year and integrated to 100 m depth

Year	Diurnal average January–June ^a	Diurnal average July–December ^a	Integrated annual production ^b
1996	2.53	1.02	649
1997	2.37	0.84	574
1998	1.38	0.68	371
1999	1.85	0.78	483
2000	1.42	1.12	448

^a Diurnal average gC m⁻² day⁻¹.

^b Annual production gC m⁻² year⁻¹.

(January and February) and during periods of upwelling enhancement (May 1996 and March 1998). Extremely high production events are likely to be under-sampled since they are of short duration and our sampling frequency was once approximately every 30 days.

During the peak of the upwelling episodes of 1996 and 1997, the 21 °C isotherm was located as much as 70 m above the depth where it was found the previous January (about 100 m). Production levels were very high during this time ($>3000 \mu\text{mol C m}^{-3} \text{ h}^{-1}$). In mid-1997, coincident with the onset of an intense El Niño, productivity decreased ($<100 \mu\text{mol C m}^{-3} \text{ h}^{-1}$) and the depth of the 21 °C isotherm varied but remained deeper than was seen during the earlier upwelling events of 1996 and 1997. During 1998 and 1999, the upwelling was relatively weak with the 21 °C isotherm remaining below 40 m. An intense productivity event occurred in March 1998 ($2634 \mu\text{mol C m}^{-3} \text{ h}^{-1}$), but it was much shorter and intense than similar events in the previous years (May 1996, $5454 \mu\text{mol C m}^{-3} \text{ h}^{-1}$; January 1997, $3296 \mu\text{mol C m}^{-3} \text{ h}^{-1}$). The 21 °C isotherm only reached 54 m during 1999 (Fig. 2), and productivity in 1999 continued to decline in spite of a high production peak in February ($1662 \mu\text{mol C m}^{-3} \text{ h}^{-1}$). In 2000, the 21 °C was shallow ($<50 \text{ m}$) from January through May. While no large productivity peaks were observed, there were several consecutive months of elevated productivity. In 2000, primary production during the upwelling season was low ($438 \mu\text{mol C m}^{-3} \text{ h}^{-1}$) when compared to 1996 ($895 \mu\text{mol C m}^{-3} \text{ h}^{-1}$) and 1997 ($658 \mu\text{mol C m}^{-3} \text{ h}^{-1}$).

Close examination of Figs. 2 and 3 suggests that the upward movement of colder water by itself does

not control primary production. Scranton et al. (in press) examine in detail the relationship between mixed layer depth and primary productivity. Production peaks seem to take place when upwelling occurs simultaneously with a relatively deep ($>25 \text{ m}$) mixed layer. In Cariaco, mixed layer depths range from 8 to 45 m with seasonal variability around 22 m. In the absence of deep ($>25 \text{ m}$) mixing, the water column becomes stratified and nutrients in the mixed layer are depleted. For example, during 2000, winds were relatively normal during the upwelling season (order of $6\text{--}8 \text{ m s}^{-1}$) and led to upwelling as detected in the 21 °C isotherm (Fig. 2). The 21 °C isotherm reached depths $<50 \text{ m}$, but the mixed layer remained shallow during the 1999–2000 upwelling season ($<25 \text{ m}$; Scranton et al., in press). This was associated with below-normal phytoplankton primary production relative to that in other years (Fig. 2). Only a weak correlation was observed during this year between primary production and the depth of the 21 °C isotherm ($r^2=0.25$), and between production and sea surface temperature ($r^2=0.21$).

Other dynamic processes such as eddies that migrate westward in the southern Caribbean also can contribute to an increase or decrease in the intensity of upwelling as has been described by Astor et al. (2003), who noted that, on occasion intrusions can enhance upwelling and lead to high-productivity events (January 1997 and March 1998).

3.2. pH

Fig. 4a shows values of pH for the top 400 m in the Cariaco Basin over the 5-year study period (1996–2000). Maximum pH values were observed in the upper 35 m (pH range= $8.017\text{--}8.123$) with the highest pH during phytoplankton blooms due to biological uptake of CO₂. pH values decreased markedly with depth due to the oxidation of organic matter, reaching a value of 7.659 ± 0.012 at 225 m in the steepest part of the oxygen gradient, and decreasing further but slowly to values of 7.584 ± 0.005 at 1310 m (data not shown).

3.3. Total alkalinity

Fig. 4b shows the variation in TA to 400 m depth with time. Fig. 3g shows the anomaly in surface TA at

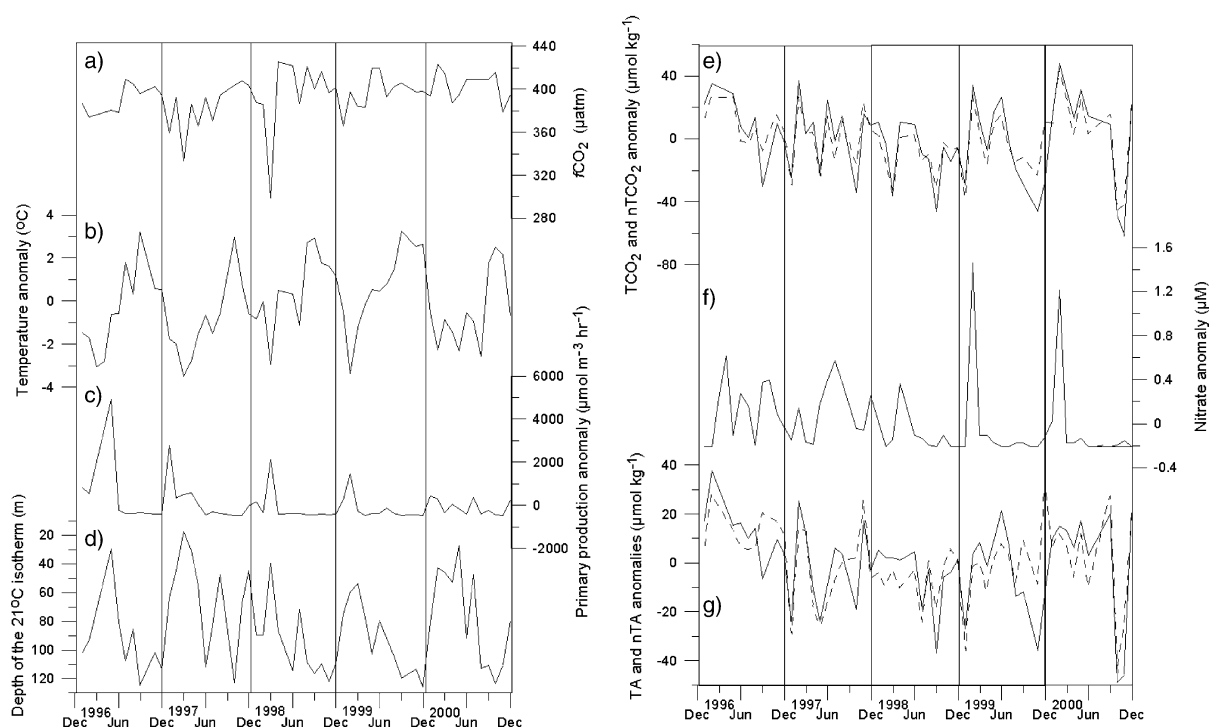


Fig. 3. Time series of factors affecting the surface $f\text{CO}_2$ in the Cariaco Basin. Anomalies were derived by subtracting the overall mean from the monthly observations (note: mean SST = 25.92°C ; mean primary production = $549 \mu\text{mol C m}^{-3} \text{h}^{-1}$; mean $\text{TCO}_2 = 2070 \mu\text{mol kg}^{-1}$; mean $\text{nTCO}_2 = 2072 \mu\text{mol kg}^{-1}$; mean nitrate = $0.19 \mu\text{M}$; mean TA = $2411 \mu\text{mol kg}^{-1}$; mean nTA = $2413 \mu\text{mol kg}^{-1}$). From top to bottom: (a) surface $f\text{CO}_2$; (b) SST anomaly; (c) primary production anomaly; (d) depth of the 21°C isotherm (an indicator of upwelling); (e) TCO_2 anomaly (solid line) and nTCO_2 anomaly (broken line); (f) nitrate-N anomaly; (g) TA anomaly (solid line); nTA anomaly (broken line).

the CARIACO station. Surface total alkalinity (TA) variability over time was relatively high, with an anomaly of about $\pm 40 \mu\text{mol kg}^{-1}$ around an overall mean TA of $2411 \mu\text{mol kg}^{-1}$. Surface TA was $2424 \pm 10 \mu\text{mol kg}^{-1}$ for a typical March, and lower ($2402 \pm 23 \mu\text{mol kg}^{-1}$) in September. The lower surface TA in September was likely related to lower salinity (36.4) compared to March (36.8). September is the peak of the rainy season, and this relatively low-salinity water at the surface has a riverine origin confirmed by the high dissolved silicate concentrations compared to surface waters at other times of the year (data not shown). While Orinoco River water has significant impact on the eastern Caribbean during early fall, its influence is felt primarily far to the north and east of the Cariaco Basin (Muller-Karger et al., 1989; Muller-Karger and Varela, 1990). Instead, the low-salinity water that reaches the CARIACO station in September seems to be derived from several smaller rivers that flow into the

Cariaco Basin along its southern margin (Laura Lorenzoni, University of South Florida, personal communication). During the second part of 1999, surface TA was unusually low (Fig. 3g), likely due to the heavy rain and catastrophic runoff that affected the region; in other years, alkalinity only showed a decrease in the month of September.

During upwelling (Fig. 4b), TA values were high at the surface and decreased sharply with depth reaching a minimum near 160 m ($\sim 2390 \pm 10 \mu\text{mol kg}^{-1}$). This corresponds with the sill depth of the Cariaco Basin and the depth of maximum nitrate concentration (Thunell et al., 2004). During the non-upwelling period (September), near-surface TA was relatively low and increased to a shallow maximum located between 35 and 110 m, with a minimum between 120 and 250 m.

Elevated TA values were found associated with the salinity maximum above 200 m, when it was present. The salinity and TA maxima identify the Subtropical Mode Water (also called Subtropical Underwater or

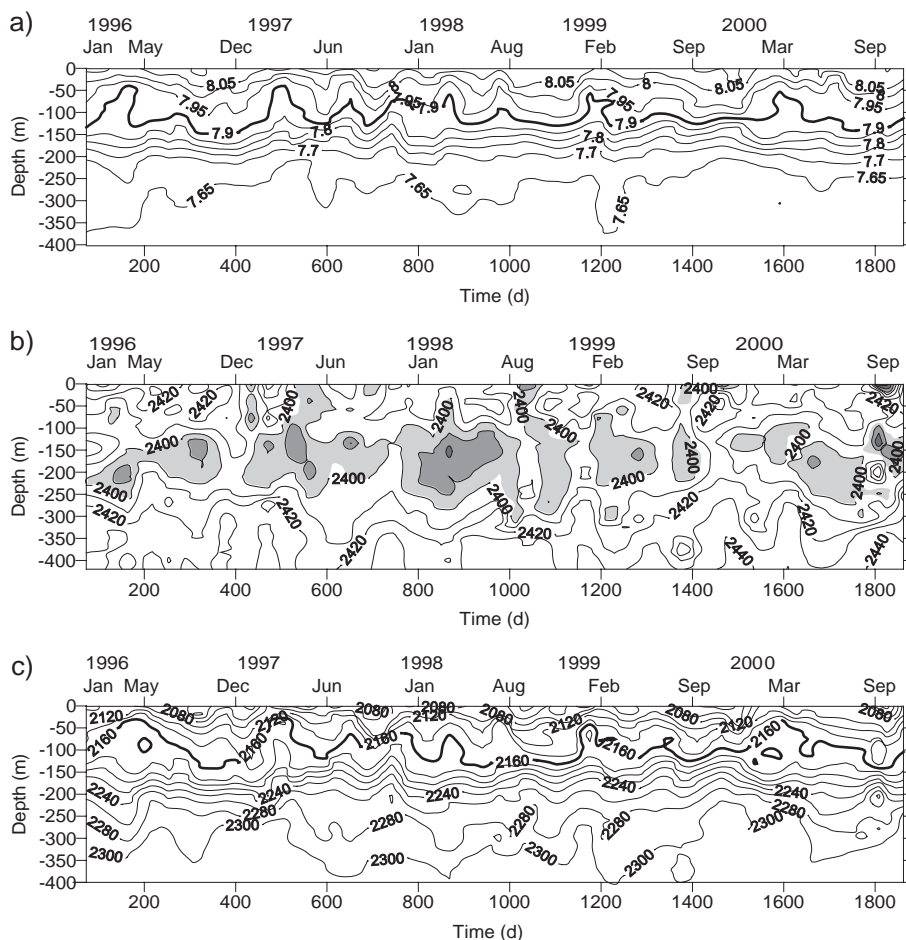
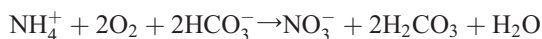


Fig. 4. (a) Variability in pH, (b) TA ($\mu\text{mol kg}^{-1}$), and (c) TCO₂ ($\mu\text{mol kg}^{-1}$) at the CARIACO station between January 1996 and December 2000 between the surface and 400 m. Contour intervals are 0.05 for pH, 10 $\mu\text{mol kg}^{-1}$ for TA and 20 $\mu\text{mol kg}^{-1}$ for TCO₂. Shaded areas in Fig. 4b identify alkalinities lower than 2400 $\mu\text{mol kg}^{-1}$.

SUW). Strong upwelling brings the SUW core to the surface. This leads to higher than otherwise, but still variable, surface TA values (above 2420 $\mu\text{mol kg}^{-1}$, particularly in 1996). In 1997 in particular, more month-to-month variability was observed than in other years. Surface values below 2420 $\mu\text{mol kg}^{-1}$ were only observed during the upwelling season of 1998.

Although the TA maximum is associated with SUW, the minimum TA layer located underneath the maximum was also observed both in TA and when alkalinity was normalized to salinity (nTA). This suggests that the minimum was not due to changes in water masses, but perhaps due to local

chemical processes. The minimum TA layer grew in size vertically during the first half of 1997 and 1998. This coincided with strong ventilation events registered in the Cariaco Basin (Astor et al., 2003). These events bring oxygenated water into the Cariaco Basin. We speculate that during ventilation, nitrification is enhanced and that this leads to alkalinity consumption by the reaction



Below 250 m, TA increased steadily toward the bottom, reaching values of $2480 \pm 15 \mu\text{mol kg}^{-1}$ at 1310 m (data not shown).

TA variability depends on changing month-to-month surface water mass characteristics, upwelling intensity, evaporation and precipitation, and precipitation of calcite in surface waters by calcareous organisms. For example, upwelling brought high TA waters found between 35 and 110 m to the surface in Cariaco during January 1997, February 1996, 1999, and 2000, August 1997 and May 2000, but lower surface values were observed during March 1997, March 1998 and June 1999 when upwelling also occurred (Figs. 2 and 4b). This decrease in alkalinity during the latter dates could be due to calcium carbonate precipitation as it may be inferred from the CaCO_3 particle flux data from the sediment trap at 275 m, which showed high fluxes for March 1998 and June 1999; no CaCO_3 trap flux data were available for March and April 1997.

3.4. TCO_2 concentrations

During non-upwelling months, shallow TCO_2 minima with surface values $<2010 \mu\text{mol kg}^{-1}$ were observed (Fig. 4c). During upwelling, surface TCO_2 values of about $2118 \mu\text{mol kg}^{-1}$ were observed. Between the surface and 100–200 m, the TCO_2 increased by $\sim 200 \mu\text{mol kg}^{-1}$ (Fig. 4c). This is due mainly to the oxic respiration of organic matter, as described by Goyet et al. (1991) for the Black Sea, as no similar change was seen for alkalinity. The TCO_2 difference between the surface and Cariaco Basin bottom waters at 1310 m was approximately $309 \mu\text{mol kg}^{-1}$ (data not shown).

We can compare our TCO_2 data with that collected in June (non-upwelling) in 1990 by Zhang and Millero (1993) at a nearby station in the eastern Cariaco Basin. These workers found surface values of 2056

$\mu\text{mol kg}^{-1}$ and bottom (1300 m) values of $2395 \mu\text{mol kg}^{-1}$, which are very similar to our results.

Surface TCO_2 showed a weak inverse correlation with sea surface temperature ($r^2=0.36$) probably as a result of upwelling of cold, CO_2 -rich water. In 1996, 1999 and 2000, the highest surface TCO_2 occurred at the same time as the minimum surface temperature. However, in 1997, the highest surface TCO_2 was reached in February, 1 month before the minimum temperature was observed. A strong surface TCO_2 minimum was observed in March 1998 when the seasonal SST was lowest and primary production was very high. In 1998, high surface TCO_2 values occurred 2 months prior to the minimum temperature. These results differ from open ocean observations at the Hawaii Ocean Time-series (ALOHA/HOT) and the Bermuda–Atlantic Time Series (BATS), where high surface TCO_2 typically lags the temperature minimum by 1 month (Winn et al., 1994; Bates et al., 1996).

$n\text{TCO}_2$ is the TCO_2 normalized to constant salinity (Fig. 3e). Both of these variables show the same pattern. This is further evidence that salinity is not an important factor in controlling TCO_2 , $f\text{CO}_2$ or alkalinity in the CARIACO station.

3.5. $f\text{CO}_2$

Waters in the upper 100 m in the Cariaco Basin showed marked fluctuations in CO_2 fugacity with time (Fig. 5). Surface $f\text{CO}_2$ values varied between 298 and $425 \mu\text{atm}$, with a mean of $393 \pm 22 \mu\text{atm}$ over the 5-year series (Fig. 6). These values are high relative to the oceanic values reported in Takahashi et al. (1997). $f\text{CO}_2$ was usually above average atmospheric CO_2

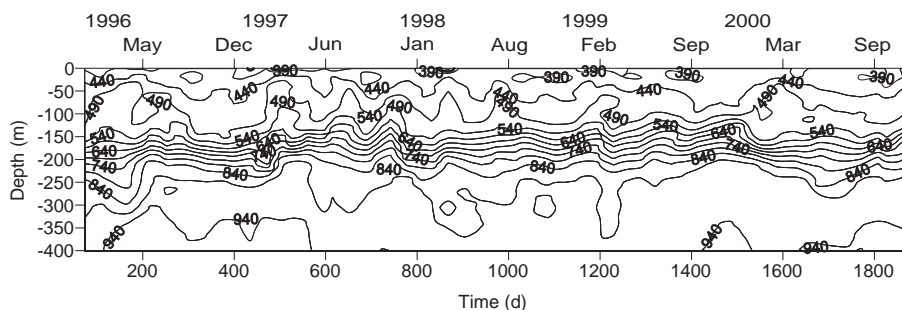


Fig. 5. Fugacity of CO_2 ($f\text{CO}_2$; μatm) in the upper 400 m at the CARIACO time-series station from January 1996 to December 2000. Contour interval is $50 \mu\text{atm}$.

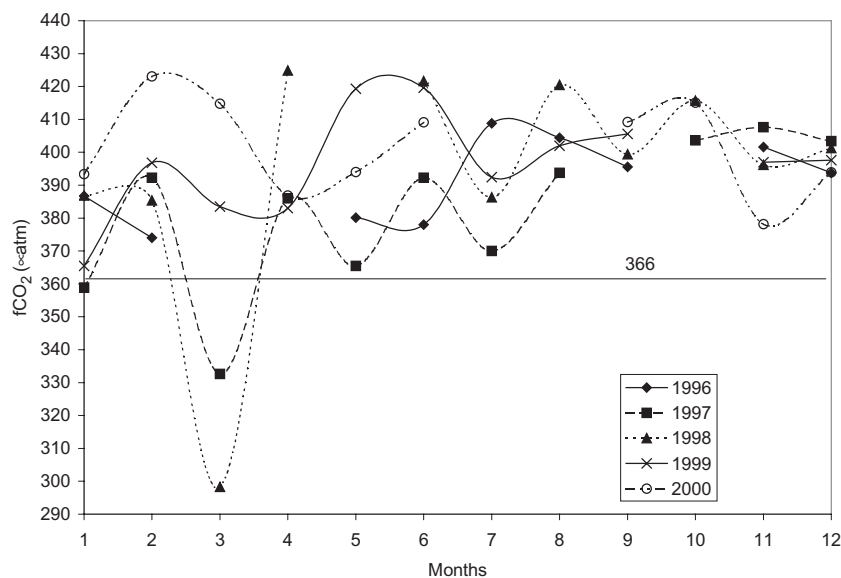


Fig. 6. Surface $f\text{CO}_2$ (μatm) from January 1996 to December 2000. 1996: solid line with filled diamond; 1997: broken line with filled squares; 1998: broken line with filled triangles; 1999: solid line with an \times ; and 2000: broken line with open circles.

partial pressure ($p\text{CO}_2=366 \mu\text{atm}$). High and stable surface $f\text{CO}_2$ values ($393\text{--}421 \mu\text{atm}$; $\text{mean}=401 \pm 9 \mu\text{atm}$) were observed between August and December every year, when upwelling and productivity were low, temperatures were high, and strong winds were less frequent. Between January and June (during upwelling, stronger winds, and high primary production), $f\text{CO}_2$ variability was greater. The largest range in surface values within 1 year was seen in 1998 ($298\text{--}425 \mu\text{atm}$), followed by 1997 ($333\text{--}408 \mu\text{atm}$). Both years showed unusually low $f\text{CO}_2$ during March. The intense upwelling event of March 1998 was particularly distinctive since upwelling that year was otherwise generally muted relative to other years.

Between 50 and 100 m depth, $f\text{CO}_2$ increased during periods of upwelling (Fig. 5), but maxima ($>490 \mu\text{atm}$) were seen in the 1–2 months following upwelling and primary productivity maxima (i.e., March–May). However, in 1998, the subsurface $f\text{CO}_2$ peak for March to May was muted, as was upwelling and productivity. In 1999, this peak was absent altogether. In early fall (September–October), $f\text{CO}_2$ between 5 and 100 m decreased to $405\text{--}450 \mu\text{atm}$, with the lowest values at and near the surface. This pattern was particularly clear in 1996, 1997 and in 2000.

4. Discussion

Boehme et al. (1998) have described how different processes that control $f\text{CO}_2$ can at times balance each other, to result in both large and small net changes in $f\text{CO}_2$ at the ocean's surface. In the tropical coastal upwelling system of the Cariaco Basin, the changes in $f\text{CO}_2$ near the surface show an irregular pattern superimposed on a seasonal cycle (Fig. 6). Our temporal resolution is coarser than the observations of Borges and Frankignoulle (2002), who examined high-frequency fluctuations in $f\text{CO}_2$ in a coastal upwelling region in a series of cruises off Spain. However, the CARIACO time series allows the study of seasonal and interannual variation of the air–sea exchange of CO_2 in a coastal upwelling system over a period spanning several years. In Cariaco, three periods of the year are evident: (a) December–May (primary upwelling period), (b) June, July or August (secondary upwelling period) and (c) September–November (non-upwelling).

Each year, the observed $f\text{CO}_2$ month-to-month variation in surface waters shows marked changes during the primary and secondary upwelling periods. High biological activity, temperature and the upward flow of TCO_2 induced by upwelling modulate this

variability. Similar patterns were observed in 1996, 1997 and 2000, but patterns of productivity and temperature were different in 1998 and 1999.

The irregularities observed in the upwelling characteristics of 1998 may have been caused by the large El Niño–Southern Oscillation (ENSO) event, which was observed between 1997 and 1998 (Nerem et al., 1999). The weak upwelling observed in 1999 occurred probably as a result of the abnormal climatological conditions that prevailed most of the year, with low winds ($\sim 4.6 \text{ m s}^{-1}$) and heavy rains. These differences in the upwelling pattern make the role of biological production in controlling the parameters in the CO_2 system quite variable and difficult to assess.

The complexity of the impact of the simultaneous supply of CO_2 by upwelling and its consumption by primary producers can be illustrated with specific observations at the CARIACO station. SST minima, high winds ($>9 \text{ m s}^{-1}$), and high primary productivity can independently lead to $f\text{CO}_2$ loss from surface waters. Phytoplankton blooms occurred in the Cariaco Basin at least 1 month out of every year throughout our study period (Fig. 3c). However, net negative fluxes of CO_2 (flux from the atmosphere into the water) were rare. The time series shows that the basin was a net sink for atmospheric CO_2 only when high winds, low SST and high productivity coincided. The short duration events of high production have a significant impact on seasonal $f\text{CO}_2$, but they may be undersampled and thus are perhaps not completely accurate in the data. Based on the sediment trap data (Thunell, personal communication), however, we think it is unlikely that we missed many large productivity events.

By looking at typical situations, we can get a sense of the relative importance of the variety of factors contributing to $f\text{CO}_2$. Periods of high production and low temperatures can contribute to a decrease in the $f\text{CO}_2$ signal while upwelling is in progress. During January–February 1996 and December–January 1999, high production (>1000 and $700 \mu\text{mol m}^{-3} \text{ h}^{-1}$, respectively) and low temperatures kept $f\text{CO}_2$ values relatively low ($<374 \mu\text{atm}$) in spite of the upwelling of high TCO_2 concentration waters ($>2110 \mu\text{mol kg}^{-1}$) (Fig. 3a–c). In contrast, in 1999, weaker upwelling led to low primary productivity and high surface $f\text{CO}_2$ values were seen throughout the year (Fig. 3a and c).

On other occasions, the dominant control on $f\text{CO}_2$ seems conclusively to have been the phytoplankton productivity. For example, in May 1996, an intense primary production event ($\sim 5454 \mu\text{mol C m}^{-3} \text{ h}^{-1}$) generated enough sinking organic detritus to clog all four CARIACO sediment traps moored at depths between 280 and 1200 m (Thunell et al., 2000). Waters with TCO_2 concentrations around $2140 \mu\text{mol kg}^{-1}$ at 25 m in April were raised to the surface in May (Fig. 4c). TCO_2 values at the surface remained below $2099 \mu\text{mol kg}^{-1}$, likely due to removal by phytoplankton, even as long as May. The compensation between upwelling and primary production was such that $f\text{CO}_2$ values were constant throughout this extremely intense productivity event (at least at our relatively coarse sampling resolution), at around $380 \mu\text{atm}$. When high production events were coupled with high winds and low SST ($\sim 22.5^\circ\text{C}$), a minimum in $f\text{CO}_2 < 335 \mu\text{atm}$ was observed (Fig. 3a–c).

There were situations when wind declined strongly from one month to the other, causing upwelling to subside. $f\text{CO}_2$ values increased considerably during these periods. For example, $f\text{CO}_2$ rose in April 1998 to $425 \mu\text{atm}$ as SST increased to 26.41°C while upwelling subsided. The 30% higher $f\text{CO}_2$ (Fig. 3a) observed at the surface in April relative to March 1998 was not the result of additional supply from below. It also was not due solely to warming of surface waters, which may increase $f\text{CO}_2$. In the present case, the change in temperature alone only contributed 1/3 to the increase. The remaining increase of $f\text{CO}_2$ of 20% was likely due to organic matter remineralization, combined with a decline in uptake by primary production. A significant increase in nitrate (from 0.06 to $0.57 \mu\text{M}$, Fig. 3f) and silicate (from 0.00 to $0.79 \mu\text{M}$) concentrations in surface waters was observed between March and April, consistent with lack of productivity by diatoms and perhaps rapid in situ remineralization including nitrification. It is not clear why the availability of these nutrients did not result in additional uptake by phytoplankton.

During the secondary upwelling period (June–July), variations in surface $f\text{CO}_2$ seemed to be largely due to temperature changes (Fig. 3b). From thermodynamic considerations, temperature changes may cause variations of 4.13 – 4.23% $f\text{CO}_2$ per 1°C (Gordon and Jones, 1973; Takahashi et al., 1993). Between

July and August 1996, upwelling brought waters with TCO_2 concentrations around $2120 \mu\text{mol kg}^{-1}$ and $f\text{CO}_2$ of $428 \mu\text{atm}$ to the surface. In August, surface waters again had lower TCO_2 concentrations ($2084 \mu\text{mol kg}^{-1}$) and $f\text{CO}_2$ ($404 \mu\text{atm}$). The shallow upwelling did not significantly increase production and, since salinity did not change, the decrease of $27 \mu\text{atm}$ is most likely due to the decrease in temperature of 1.5°C , as was observed between June–July 1997 and 1998. Then, the temperature decrease may account for 73% of the decrease in $f\text{CO}_2$.

The upwelling season is the dry season in the southern Caribbean, when surface salinity values reach 36.6 – 37.0 and sea surface temperatures reach 22 – 23°C . Periods without upwelling correspond to the rainy season and the months of highest sea surface temperatures ($>27^\circ\text{C}$). Lower surface salinities (36.4 – 36.5) were observed during September every year. Over the regular seasonal salinity range, the solubility coefficient of CO_2 changes by only 0.47% . TCO_2 and nTCO_2 were similar most of the time, except during the salinity minima of September. Particularly low salinities (36.08 – 36.45) occurred during a period of torrential rains over northern Venezuela in October–December 1999, when exceptionally low surface TCO_2 levels were seen (Fig. 3e). The decrease in TCO_2 due to low salinities is likely offset by the increase in $f\text{CO}_2$ that accompanies higher seasonal temperatures. We conclude that the amount of dissolved inorganic carbon transported by freshwater plumes into the Cariaco Basin is normally very small relative to that already in surface waters.

4.1. Air–sea CO_2 flux

Over the course of our study, the Cariaco Basin showed an average supersaturation of $31 \pm 22.3 \mu\text{atm}$ of CO_2 based on a comparison against an overall mean $p\text{CO}_2$ of $366 \mu\text{atm}$ over the 5-year study period. The difference ($\Delta f\text{CO}_2$) between oceanic CO_2 concentrations and the mean atmospheric $p\text{CO}_2$ at Barbados ranged between -64.3 and $+62.3 \mu\text{atm}$, with strong month-to-month variation. Since atmospheric $p\text{CO}_2$ varied over a seasonal range of $<9 \mu\text{atm}$, $\Delta f\text{CO}_2$ was driven primarily by oceanic concentrations and forcing other than changes in atmospheric $p\text{CO}_2$. Persistent positive and high $\Delta f\text{CO}_2$ values were mainly due to upwelling or high sea surface

temperatures. The variability observed in the Cariaco Basin is similar to or greater than that reported for the northwest African upwelling area (Mauritania, Lefèvre et al., 1998), the west Equatorial Atlantic (Keeling and Waterman, 1968), and the Caribbean Sea over the Beata Ridge (Roos and Gravenhorst, 1984), although data sets for those systems are less extensive.

The sustained high $\Delta f\text{CO}_2$ must result in a net transfer of CO_2 from the sea to the atmosphere in the Cariaco Basin. Air–sea fluxes at the CARIACO station were calculated using the following equation:

$$F = k\alpha\Delta f\text{CO}_2$$

where k is the CO_2 gas transfer velocity, α is the solubility of CO_2 (Weiss, 1974) and $\Delta f\text{CO}_2$ is the difference between the fugacity of CO_2 in surface ocean water and the partial pressure of CO_2 in the atmosphere ($f\text{CO}_{2\text{ocean}} - p\text{CO}_{2\text{atm}}$). A positive flux indicates evasion of CO_2 from the ocean to the atmosphere, and negative values indicates invasion of CO_2 into the water.

Several formulations exist to calculate k (Liss and Merlivat, 1986; Tans et al., 1990; Wanninkhof, 1992). Fluxes derived using the Liss and Merlivat (1986) relationship are suspected to be underestimates, while the Tans et al. (1990) relationship yields zero gas flux at wind speeds below 3 m s^{-1} . The algorithm by Wanninkhof (1992) tends to yield higher flux values. Here, we present flux calculations based on both the Liss and Merlivat (1986) and Wanninkhof (1992) algorithms in order to provide a range of estimates. We used daily average wind speeds derived from two meteorological stations located about 80 km to the northeast of the CARIACO station on Margarita Island, Venezuela (specifically one at $10^\circ56'\text{N}$, $64^\circ6'\text{W}$ in Punta de Piedras, and a nearby station at Porlamar International Airport). The quality of these data was assessed in Muller-Karger et al. (2001) and reviewed more critically again in Astor et al. (2003).

CO_2 fluxes are shown in Fig. 7. An overall mean $p\text{CO}_2$ of $366 \mu\text{atm}$ over the 5-year study period leads to a mean overall air–ocean flux of $2.8 \text{ mol m}^{-2} \text{ year}^{-1}$ using the Wanninkhof method (Table 2). The difference in flux computed using the seasonal extremes in atmospheric $p\text{CO}_2$ as opposed to using the overall mean $p\text{CO}_2$ value (as shown in Table 2) was only of $\pm 0.5 \text{ mol m}^{-2} \text{ year}^{-1}$. This is small relative to errors between different methods of esti-

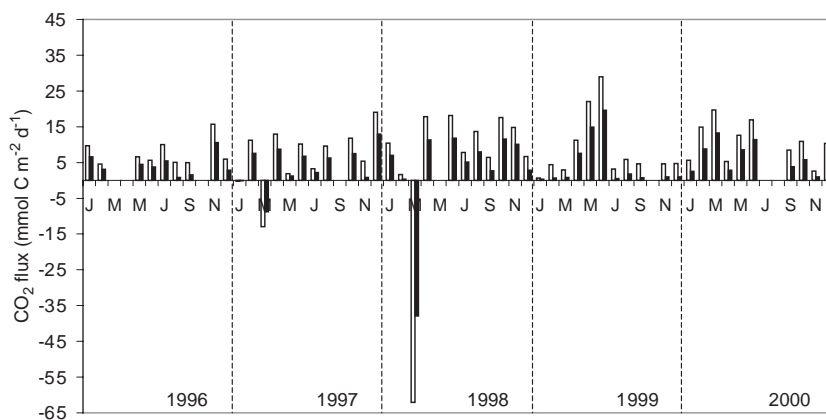


Fig. 7. Variability of CO_2 flux ($\text{mmol m}^{-2} \text{d}^{-1}$) from January 1996 to December 2000 at the CARIACO time-series station. Black bar denotes flux estimated based on the formulation for the gas exchange constant, k , of Liss and Merlivat (1986). White bar denotes k as calculated by Wanninkhof (1992).

imating the flux. The difference between the Wanninkhof (1992) and the Liss and Merlivat (1986) methods is on average $5.2 \pm 1.6 \text{ mmol m}^{-2} \text{day}^{-1}$, with the Liss and Merlivat (1986) relationship yielding lower fluxes by an average of 47%.

Overall, the flux from the sea to the atmosphere is greatly depressed or even negative during the brief and strong upwelling events accompanied with high production observed during the first half of each year. There was also substantial variability in the flux from one month to the next. The most dramatic month-to-month differences in flux were observed between February 1997 (about $+10 \text{ mmol m}^{-2} \text{day}^{-1}$) and March 1997 ($-10 \text{ mmol m}^{-2} \text{day}^{-1}$), March 1998 ($-40 \text{ mmol m}^{-2} \text{day}^{-1}$) and April 1998 ($+15 \text{ mmol m}^{-2} \text{day}^{-1}$), June 1999 ($+25 \text{ mmol m}^{-2} \text{day}^{-1}$) and July 1999 ($\sim 0 \text{ mmol m}^{-2} \text{day}^{-1}$), and March 2000 ($+20 \text{ mmol m}^{-2} \text{day}^{-1}$) and April 2000 ($+5 \text{ mmol m}^{-2} \text{day}^{-1}$). A simple correlation analysis between air-sea CO_2 flux and $\Delta f\text{CO}_2$ shows a strong correlation ($R^2=0.72$, p value <0.01). There was no significant correlation between air-sea CO_2 flux and wind speed ($R^2=0.02$, p value >0.1). Therefore, the air-sea CO_2 flux variability in the Cariaco Basin depends

more strongly on changes in physical and biological parameters in seawater, which control $\Delta f\text{CO}_2$, than on wind speed.

Table 2 provides an estimate of the approximate net annual air-sea CO_2 flux from the Cariaco system and an overall average flux over the study period. We may have missed some intense short-term influx or efflux events due to the monthly nature of our sampling, but we feel the length of the time series is such that we have a relatively good idea of the general patterns in air-sea CO_2 flux at the CARIACO site. CO_2 fluxes were computed assuming that each monthly CARIACO observation represented typical values for the respective month, and then integrating over time.

During the 5-year time series, only 2 months, namely, March 1997 and March 1998, showed invasion of CO_2 from the atmosphere to the water. Due to the uncertainty in the calculations, we consider the small negative flux in January 1997 as negligible. The greatest intra-year variability was observed in 1998, which was also the year of the lowest average positive flux ($\sim 1.45 \text{ mol m}^{-2} \text{year}^{-1}$ averaging results of the methods of Wanninkhof (1992) and

Table 2

Time series of average annual air-sea CO_2 flux ($\text{mol m}^{-2} \text{year}^{-1}$), based on two different algorithms

Method	1996	1997	1998	1999	2000	Net average (5 years)
Liss and Merlivat (1986)	1.6 ± 1.08	1.5 ± 2.13	1.1 ± 5.18	1.6 ± 2.46	2.4 ± 1.47	1.64 ± 2.46
Wanninkhof (1992)	2.8 ± 1.33	2.4 ± 3.12	1.8 ± 8.36	3.1 ± 3.27	3.9 ± 2.00	2.81 ± 3.62

Liss and Merlivat (1986)). The highest average flux was observed in 2000 ($\sim 3.15 \text{ mol m}^{-2} \text{ year}^{-1}$). The net average (5 years) CO_2 flux was $1.6 \pm 2.5 \text{ mol m}^{-2} \text{ year}^{-1}$ based on Liss and Merlivat (1986) and $2.8 \pm 3.6 \text{ mol m}^{-2} \text{ year}^{-1}$ based on Wanninkhof (1992). This last value was very similar to the maximum value ($2.7 \text{ mol m}^{-2} \text{ year}^{-1}$) reported by Smethie et al. (1985) at 8°S 28°W in the tropical Atlantic Ocean. That computation used gas transfer velocities derived from ^{222}Rn profiles.

4.2. Regional impact on the carbon cycle

The most recent assessments of the oceanic carbon cycle (e.g., Gruber et al., 2002) have concluded that the mid-North Atlantic ($15\text{--}40^\circ\text{N}$) constitutes the largest ocean sink for atmospheric CO_2 in the Northern Hemisphere, on average taking up about $0.7 \pm 0.1 \text{ Pg C year}^{-1}$ (1 Petagram = 10^{15} g). One important question is whether ventilation of the SUW (i.e., exposure to the atmosphere) in coastal upwelling areas, such as the Cariaco Basin located around the periphery of the ocean, plays a role in offsetting this CO_2 influx.

Our data suggest that if upwelling processes over the entire southern Caribbean act in a manner similar to that observed in Cariaco, then this entire region acts as a net source of CO_2 to the air. The coastal wind-driven upwelling associated with the Cariaco Basin extends along the southern Caribbean margin, from Trinidad to northeastern Colombia (Corredor, 1979; Muller-Karger and Aparicio, 1994; Castellanos et al., 2002; Andrade and Barton, 2005). Indeed, the Caribbean Sea and Gulf of Mexico host a number of major upwelling areas that are understudied, including the Cariaco Basin, the Paraguaná and Goajira Peninsulas, Serranilla Bank, and the area north of the Yucatan Peninsula.

To obtain a crude estimate of annual regional flux exerted by upwelling zones located along the southern Caribbean margin, from northern Trinidad to northeastern Colombia, we assumed that the annual net fluxes estimated for the Cariaco Basin are representative of rates in the upwelling zones that span this region. Assuming a conservative average annual air–sea CO_2 flux of $1.6 \text{ mol m}^{-2} \text{ year}^{-1}$ (Table 2, $19.2 \text{ g C m}^{-2} \text{ year}^{-1}$) over a surface area of about half of the maximum area covered by the upwelling plumes of

the southern Caribbean ($3 \times 10^4 \text{ km}^2$; Castellanos et al., 2002), the average flux of CO_2 from the ocean into the atmosphere for the combined southern Caribbean upwelling regions would be about $0.6 \times 10^{-3} \text{ Pg C year}^{-1}$.

The annual rates of particulate organic carbon delivery to the bottom are of the order of $10\text{--}11 \text{ g C m}^{-2} \text{ year}^{-1}$ (Muller-Karger et al., 2000, 2004; Thunell et al., 2000). When applied over the same plume surface area for upwelling regions of the southern Caribbean Sea margin, we estimate approximately $0.3 \times 10^{-3} \text{ Pg C year}^{-1}$ are delivered to sediments. (This value is not corrected for the shallower depths that may characterize shelf areas other than Cariaco). It therefore appears that the amount of carbon lost from the sea via air–sea flux is comparable to the amount of organic carbon falling to the bottom each year.

5. Conclusion

An oceanographic time series established at 10.5°N , 64.67°W in the Cariaco Basin permitted the study of changes in $f\text{CO}_2$ between 1996 and 2000 in a tropical coastal upwelling ecosystem. Subtropical Underwater (SUW) generated in mid-latitudes of the Atlantic Ocean enters the Cariaco Basin and is exposed to the atmosphere during coastal wind-driven upwelling. This process brings high TCO_2 to the surface, where increasing temperature due to insolation lead to an increase in $f\text{CO}_2$. High primary production acts to balance the $f\text{CO}_2$ supply by removal of TCO_2 . In spite of primary production values of the order of or exceeding $500 \text{ g C m}^{-2} \text{ year}^{-1}$, which decreases $f\text{CO}_2$, there was a net flux of CO_2 from the ocean to the atmosphere in the Cariaco Basin. Average net CO_2 flux to the atmosphere over 5 years was on the order of 1.6 ± 2.5 to $2.8 \pm 3.6 \text{ mol m}^{-2} \text{ year}^{-1}$ depending on methodology. Negative fluxes were only seen when there was a coincidence of factors, specifically extremely high winds, strong upwelling, and high primary production.

Future studies should attempt to understand the relationship between TCO_2 advected into a location like the Cariaco Basin, air–sea exchange, changes due to biological processes of productivity, respiration and remineralization, and the role that these processes play on continental margins relative to the open ocean.

Acknowledgements

We are indebted to the personnel of the Fundación La Salle de Ciencias Naturales, Estación de Investigaciones Marinas Isla Margarita (FLASA/EDIMAR) and the crew of the R/V *Hermano Ginés* for their enthusiasm and professional support: Federico Buitrago, Javier Gutierrez, Juan Capelo, Jesús Narvaez, Glenda Arias, Anadiuska Rondon (all at FLASA/EDIMAR), and John Akl and Ana Lucia Odriozola (at USF). In particular, we thank Dr. Pablo Mandazen (Hermano Gines, Honorary President, FLASA) for his confidence in our activities. Ramon Varela provided unwavering leadership in coordinating and carrying out field expeditions. Luis Troccoli, Wilfredo Patiño, Luis Sanchez, and William Senior, from the Universidad de Oriente, Cumaná, Venezuela, and Kent Fanning from the University of South Florida provided nutrient data. The authors are grateful to Dr. Chris Sabine for his help in the calibration comparisons, and we are also thankful to Andrew Dickson for the continued supply of certified references materials for TCO₂. The National Science Foundation (NSF Grants OCE-0326268, OCE-0118491, OCE-9729284 and OCE-9216626 to FMK and OCE-0326175, OCE-0118491; OCE-9711318, OCE-9730278 and OCE-9415790 to MIS), the Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT, Venezuela, Grant 96280221 to Ramon Varela) and the Fondo Nacional de Ciencia, Tecnología e Innovación (FONACIT, Grant 2000001702 to Ramon Varela) supported this work.

References

- Andrade, C.A., Barton E.D., 2005. The Guajira upwelling system. *Continental Shelf Research* 25 (9), 1003–1022.
- Andrié, C., Oudot, C., Genthon, C., Merlivat, L., 1986. CO₂ fluxes in the tropical Atlantic during FOCAL cruises. *Journal of Geophysical Research* 91 (C10), 11741–11755.
- Astor, Y., Meri, J., Muller-Karger, F., 1998. Variabilidad estacional hidrográfica en la Fosa de Cariaco. *Memorias Sociedad Ciencias Naturales La Salle* 53 (149), 61–72.
- Astor, Y., Muller-Karger, F., Scranton, M., 2003. Seasonal and interannual variation in the hydrography of the Cariaco Basin: implications for basin ventilation. *Continental Shelf Research* 23 (1), 125–144.
- Bates, N.R., Michaels, A.F., Knap, A.H., 1996. Seasonal and interannual variability of oceanic carbon dioxide species at the U.S., JGOFS Bermuda Atlantic Time-series Study (BATS) site. *Deep-Sea Research Part II* 43 (2–3), 347–383.
- Benoit, J.M., Gilmour, C.C., Mason, R.P., Heyes, A., 1999. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment porewater. *Environmental Science and Technology* 33 (6), 951–957.
- Berger, W.H., 1989. Appendix: global maps of ocean productivity. In: Berger, W.H., Smetacek, W.G. (Eds.), *Productivity of the Ocean, Present and Past*. John Wiley & Sons, New York, pp. 429–455.
- Black, D.E., Peterson, L.C., Overpeck, J.T., Kaplan, A., Evans, M.N., Kashgarian, M., 1999. Eight centuries of North Atlantic Ocean atmosphere variability. *Science* 286, 1709–1713.
- Boehme, S.E., Sabine, C.L., Reimers, C.E., 1998. CO₂ fluxes from a coastal transect: a time-series approach. *Marine Chemistry* 63, 49–67.
- Borges, A.V., Frankignoulle, M., 2002. Distribution of surface carbon dioxide and air–sea exchange in the upwelling system off the Galician coast. *Global Biogeochemical Cycles* 16 (2).
- Breland, J.A. II, Byrne, R.H., 1993. Spectrophotometric procedures for determination of seawater alkalinity using bromocresol green. *Deep-Sea Research I* 40 (3), 629–641.
- Castellanos, P., Varela, R., Muller-Karger, F., 2002. Descripción de las áreas de surgencia al sur del Mar Caribe examinadas con el sensor infrarrojo AVHRR. *Memorias de la Fundación La Salle de Ciencias Naturales* 154, 55–76.
- Chen, C.-T.A., Liu, K.K., MacDonald R., 2001. Continental margins and seas as carbon sink. Scientific Committee on Problems of the Environment-SCOPE, XI General Assembly and Scientific Symposia. September 24–28, 2001. Germany.
- Clayton, T.D., Byrne, R.H., 1993. Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of *m*-cresol purple and at-sea results. *Deep-Sea Research. Part 1. Oceanographic Research Papers* 40 (10), 2115–2129.
- Corredor, J.E., 1979. Phytoplankton response to low level nutrient enrichment through upwelling in the Colombian Caribbean Basin. *Deep-Sea Research* (26A), 731–741.
- DelValls, T.A., Dickson, A.G., 1998. The pH of buffers based on 2-amino-2-hydroxymethyl-1,3-propanediol ('tris') in synthetic sea water. *Deep-Sea Research I* 45, 1541–1554.
- DOE, 1994. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2, In: Dickson, A.G., Goyet, C., (Eds.), ORNL/CDIAC-74.
- Gago, J., Gilcoto, M., Pérez, F.F., Ríos, A.F., 2003. Short-term variability of *f*CO₂ in seawater and air–sea CO₂ fluxes in a coastal upwelling system (Ría de Vigo NW Spain). *Marine Chemistry* 80, 247–264.
- Gordon, L.I., Jones, L.B., 1973. The effect of temperature on carbon dioxide partial pressure in seawater. *Marine Chemistry* 1, 317–322.
- Gordon, L.I., Jennings Jr., J.C., Ross, A.A., Crest, J.M., 1993. A suggested protocol for continuous flow automated analysis of seawater nutrients. In: WOCE Operation Manual. WHP Office Report 90-1, WOCE Report 77 No. 68/91, pp. 1–52.
- Goyet, C., Bradshaw, A.L., Brewer, P.G., 1991. The carbonate system in the Black Sea. *Deep-Sea Research* 38 (Supplementary 2A), S1049–S1068.

- Gruber, N., Keeling, C.D., Bates, N.R., 2002. Interannual Variability in the North Atlantic Ocean Carbon Sink. *Science* 298, 2374–2378.
- Herrera, L., Febres-Ortega, G., 1975. Procesos de surgencia y renovación de aguas en la Fosa de Cariaco, Mar Caribe. *Boletín del Instituto Oceanográfico de la Universidad de Oriente* 14 (1), 31–44.
- Johnson, K.M., Wills, K.D., Butler, D.B., Johnson, W.K., Wong, C.S., 1993. Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated gas extraction system and coulometric detector. *Marine Chemistry* 44, 167–187.
- Keeling, C.D., Waterman, L.S., 1968. Carbon dioxide in surface ocean waters: 3. Measurements on Lusiad Expeditions 1962–1963. *Journal of Geophysical Research* 73 (14), 4529–4541.
- Koblentz-Mishke, O.J., Volkovinskym, V.V., Kabanovam, J.G., 1970. Plankton primary production of the world ocean. In: Wooster II, W.S. (Ed.), *Scientific Exploration of the Southern Pacific*. National Academy of Science, Washington, DC, pp. 183–193.
- Lefèvre, N., Moore, G., Aiken, J., Watson, A., Cooper, D., Ling, R., 1998. Variability of $p\text{CO}_2$ in the tropical Atlantic in 1995. *Journal of Geophysical Research* 103 (C3), 5623–5634.
- Legendre, L., Gosselin, M., 1989. New production and export of organic matter to the deep ocean: consequences of some recent discoveries. *Limnology and Oceanography* 34, 1374–1380.
- Liss, P., Merlivat, L., 1986. Air–sea gas exchange rates: introduction and synthesis. In: Buat-Ménard, P., et al., (Eds.), *The Role of Air–Sea Exchange in Geochemical Cycling*. Reidel, Hingham, MA, pp. 113–127.
- Liu, K.-K., Atkinson, L., Chen, C.T.A., Gao, S., Hall, T., Macdonald, R.W., McManus, L., Quinones, R., 2000. Exploring continental margin carbon fluxes in the global context. *EOS, Transactions, American Geophysical Union*, 81 (52) 641, 642, 644.
- Mehrbach, C., Culberson, C.H., Hawley, J.E., Pytkowicz, R.M., 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnology and Oceanography* 18, 897–907.
- Millero, F., 1995. Thermodynamics of the carbon dioxide system in the oceans. *Geochimica et Cosmochimica Acta* 59 (4), 661–677.
- Millero, F.J., Byrne, F.H., Wanninkhof, R., Feely, F., Clayton, T., Murphy, P., Lamb, M.F., 1993. The internal consistency of CO_2 measurements in the equatorial Pacific. *Marine Chemistry* 44, 269–280.
- Muller-Karger, F.E., Aparicio, R., 1994. Mesoscale processes affecting phytoplankton abundance in the southern Caribbean Sea. *Continental Shelf Research* 14, 199–221.
- Muller-Karger, F.E., Varela, R., 1990. Influjo del Río Orinoco en el Mar Caribe: observaciones con el CZCS desde el espacio. *Memoria. Sociedad de Ciencias Naturales La Salle* 49–50 (131–134), 361–390.
- Muller-Karger, F.E., McClain, C.R., Fisher, T.R., Esaias, W.E., Varela, R., 1989. Pigment distribution in the Caribbean Sea: observations from space. *Progress in Oceanography* 23, 23–69.
- Muller-Karger, F.E., Varela, R., Thunell, R., Scranton, M., Bohrer, R., Taylor, G., Capelo, J., Astor, Y., Tappa, E., Ho, T.-Y., Iabichella, M., Walsh, J.J., Diaz, J.R., 2000. Sediment record linked to surface processes in the Cariaco Basin. *EOS, Transactions, American Geophysical Union* 81 (45), 529, 534–535.
- Muller-Karger, F.E., Varela, R., Thunell, R., Scranton, M., Bohrer, R., Taylor, G., Capelo, J., Astor, Y., Tappa, E., Ho, T.-Y., Walsh, J.J., 2001. Annual cycle of primary production in the Cariaco Basin: response to upwelling and implications for vertical export. *Journal of Geophysical Research* 106 (C3), 4527–4542.
- Muller-Karger, F.E., Varela, R., Thunell, R., Astor, Y., Zhang, H., Hu, C., 2004. Processes of Coastal Upwelling and Carbon Flux in the Cariaco Basin. *Deep-Sea Research II, Special Issue: Views of Ocean Processes from the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) Mission: Volume 2*. In: Siegel, D.A., Thomas, A.C., Marra, J. (Eds.), vol. 51/10–11 pp. 927–943.
- Muller-Karger, F.E., Varela, R., Thunell, R., Luerssen, R., Hu, C., Walsh, J.J., 2005. The importance of continental margins in the global carbon cycle. *Geophysical Research Letters* 32, L0160210.1029/2004GL021346.
- Nerem, R.S., Chambers, D.P., Leuliette, E.W., Mitchum, G.T., Giese, B.S., 1999. Variations in global mean sea level associated with the 1997–1998 ENSO event: implications for measuring long-term sea level change. *Geophysical Research Letters* 26 (19), 3005–3008.
- Richards, F.A., 1960. Some chemical and hydrographic observations along the north coast of South America: I. Cabo Tres Puntas to Curacao, including the Cariaco Trench and the Gulf of Cariaco. *Deep-Sea Research* 7, 163–182.
- Richards, F.A., 1975. The Cariaco Basin (Trench). *Oceanography and Marine Biology Annual Review* 13, 11–67.
- Richards, F.A., Vaccaro, R.F., 1956. The Cariaco Trench, an anaerobic basin in the Caribbean Sea. *Deep-Sea Research* 3, 214–228.
- Roos, M., Gravenhorst, G., 1984. The increase in oceanic carbon dioxide and the net CO_2 flux into the North Atlantic. *Journal of Geophysical Research* 89 (C5), 8181–8193.
- Sarma, V.V.S.S., 2003. Monthly variability in surface $p\text{CO}_2$ and net air–sea CO_2 flux in the Arabian Sea. *Journal of Geophysical Research* 108 (C8).
- Sato, T., Watanabe, S., Tsunogai, S., 1996. Fugacity of carbon dioxide in surface water of the East China Sea. *Caribbean Journal of Science* 32 (3), 282–283 (abstract).
- Scranton, M.I., Astor, Y., Bohrer, R., Ho, T.-Y., Muller-Karger, F.E., 2001. Controls on temporal variability of the geochemistry of the deep Cariaco Basin. *Deep-Sea Research. Part 1. Oceanographic Research Papers* 48, 1605–1625.
- Scranton, M.I., McIntyre, M., Astor, Y., Taylor, G.T., Muller-Karger, F., Fanning, K., in press. Temporal Variability in the Nutrient Chemistry of the Cariaco Basin. Past and Present Marine Water Column Anoxia. In: Jørgensen, B.B., Murray, J.W., Neretin, L.N. (Eds.), *NATO Science Series: IV*, Kluwer Press.
- Smethie, W.M. Jr., Takahashi, T., Chipman, D.W., 1985. Gas exchange and CO_2 flux in the tropical Atlantic Ocean determined from ^{222}Rn and $p\text{CO}_2$ measurements. *Journal of Geophysical Research* 90 (C4), 7005–7022.
- Strickland, J.D.H., Parsons, T.R., 1972. A practical handbook of seawater analysis, 2nd edition. Fisheries Research Board of Canada, vol. 167. 310 pp.

- Stumm, W., Morgan, J.J., 1981. *Aquatic Chemistry: An Introduction emphasizing Chemical Equilibria in Natural Waters*. John Wiley and Sons, New York, pp. 434.
- Takahashi, T., Olafsson, J., Goddard, J., Chipman, D.W., Sutherland, S., 1993. Seasonal variation of CO₂ and nutrients in the high-latitude surface oceans: a comparative study. *Global Biogeochemical Cycles* 7, 843–878.
- Takahashi, T., Feely, R.A., Weiss, R.F., Wanninkhof, R.H., Chipman, D.W., Sutherland, S.C., Takahashi, T.T., 1997. Global air-sea flux of CO₂. An estimate based on measurements of sea–air *p*CO₂ difference. *Proceedings of the National Academic Science* 94, 8929.
- Tans, P.P., Fung, I.Y., Takahashi, T., 1990. Observational constraints on the global atmospheric CO₂ budget. *Science* 247, 1431–1438.
- Ternon, J.F., Oudot, C., Dessier, A., Diverres, D., 2000. A seasonal tropical sink for atmospheric CO₂ in the Atlantic Ocean: the role of the Amazon River discharge. *Marine Chemistry* 68, 183–201.
- Thunell, R., Tappa, E., Varela, R., Llano, M., Astor, Y., Muller-Karger, F., Bohrer, R., 1999. Increased marine sediment suspension and fluxes following an earthquake. *Nature* 398, 233–236.
- Thunell, R., Varela, R., Llano, M., Collister, J., Muller-Karger, F., Bohrer, R., 2000. Organic carbon fluxes, degradation, and accumulation in an anoxic basin: sediment trap results from the Cariaco Basin. *Limnology and Oceanography* 45 (2), 300–308.
- Thunell, R.C., Sigman, D.M., Muller-Karger, F., Astor, Y., Varela, R., 2004. Nitrogen isotope dynamics of the Cariaco Basin, Venezuela. *Global Biogeochemical Cycles* 18, GB3001.
- Walsh, J.J., 1988. *On the Nature of Continental Shelves*. Academic Press, San Diego, pp. 1–520.
- Walsh, J.J., 1991. Importance of continental margins in the marine biogeochemical cycling of carbon and nitrogen. *Nature* 350, 53–55.
- Wanninkhof, R.H., 1992. Relationship between wind speed and gas exchange over the ocean. *Journal of Geophysical Research* 97, 7373–7382.
- Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine Chemistry* 2, 203–215.
- Werne, J.P., Hollander, D.J., Lyons, T.W., Peterson, L.C., 2000. Climate-induced variations in productivity and planktonic ecosystem structure from the Younger Dryas to Holocene in the Cariaco Basin, Venezuela. *Paleoceanography* 15 (1), 19–29.
- Winn, C.D., Mackenzie, F.T., Carillo, C.J., Sabine, C.L., Karl, D.M., 1994. Air–sea carbon dioxide exchange in the North Pacific Subtropical Gyre: implications for the global carbon budget. *Global Biogeochemical Cycles* 8 (2), 157–163.
- Zhang, J., Millero, F.J., 1993. The chemistry of the anoxic waters in the Cariaco Trench. *Deep-Sea Research. Part 1. Oceanographic Research Papers* 40 (5), 1023–1041.