Interannual variability in sea surface temperature and \( f_{\text{CO}_2} \) changes in the Cariaco Basin

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**ABSTRACT**

We examined the variability of sea surface carbon dioxide fugacity (\( f_{\text{CO}_2} \)) and its relation to temperature at the Cariaco Basin ocean time-series location (10º30’N, 64 40’W) for the period from 1996 through 2008. Periods of warm (positive) and cold (negative) anomalies at the station were related to variability in coastal upwelling intensity. A positive temporal trend in monthly-deseasonalized sea surface temperatures (SST) was observed, leading to an overall increase of 1.13 \( ^\circ \)C over 13 years. Surface \( f_{\text{CO}_2} \) displayed significant short-term variation (month to month) with a range of 330–445 \( \mu \text{atm} \). In addition to a large seasonal range (58 ± 17 \( \mu \text{atm} \)), deseasonalized \( f_{\text{CO}_2} \) data showed an interannual positive trend of 1.77 ± 0.43 \( \mu \text{atm} \text{yr}^{-1} \). In the Cariaco Basin, positive and negative anomalies of temperature and \( f_{\text{CO}_2} \) are in phase. An increase/decrease of 1 \( ^\circ \)C coincides with an increase/decrease of 16–20 \( \mu \text{atm} \) of \( f_{\text{CO}_2} \). Deseasonalized \( f_{\text{CO}_2} \) normalized to 26.05 \( ^\circ \)C, the mean Cariaco SST, shows a lower rate of increase (0.51 ± 0.49 \( \mu \text{atm yr}^{-1} \)). Based on these observations, 72% of the increase in \( f_{\text{CO}_2} \) in Cariaco Basin between 1996 and 2008 can be attributed to an increasing temperature trend of surface waters, making this the primary factor controlling fugacity at this location. During this period, a decrease in upwelling intensity was also observed. The phytoplankton community changed from large diatom-dominated blooms during upwelling in the late 1990’s to blooms dominated by smaller cells in the first decade of the 21st century. The average net sea-air CO2 flux over the study period is 2.0 ± 2.6 mol C m\(^{-2}\) yr\(^{-1}\) employing the Wanninkhof parameterization, and 2.1 ± 2.5 mol C m\(^{-2}\) yr\(^{-1}\) based on Nightingale’s model. To further understand the connection between the changes observed in the Cariaco Basin, the relationships between interannual variability in the temperature anomaly with three modes of climate variability (AMO, NAO and ENSO) were examined. The correlations between SST and two of these climate modes (AMO and ENSO) only show very weak relationships, although they were significant.

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1. Introduction

Although continental margins represent only about 0.5% of the ocean volume and occupy less than 8% of the seafloor, they play an important role in regulating the exchange of carbon dioxide (CO\(_2\)) and the storage of carbon within the global ocean (Donn et al., 2009; Liu et al., 2000; Muller-Karger et al., 2005). Due to high primary production and carbon storage rates in sediments, many continental margin areas are considered CO\(_2\) sinks (Chen and Borges, 2009). However, the balance between biogeochemical processes (CO\(_2\) uptake/prodduction, CaCO\(_3\) fixation/dissolution), transport (advection/turbulent diffusion), convective mixing, airsea gas exchange, and riverine input determine whether a particular region functions as a net source or sink of CO\(_2\).

Long-term and frequent observations of fugacity of seawater CO\(_2\) (\( f_{\text{CO}_2} \)) are required to help reduce the large uncertainties in the global estimates of CO\(_2\) flux (Nemoto et al., 2009). Indeed, both seasonal and spatial variability of CO\(_2\) concentrations in the ocean may mask any long-term changes if careful observations are not conducted within a time series framework (Bates, 2001).
Long time-series are a powerful tool for investigating biogeochemical cycles and marine ecosystems and their role in and response to climate variability. This important concept has led to the initiation of a number of biogeochemical ocean time-series stations, both in open ocean and continental margin sites. For example, in the deep North Pacific Ocean at ocean time-series station ALOHA (A Long-term Oligotrophic Habitat Assessment; 22°45′N, 158°00′W), observations have revealed an increase of 2.84 ± 0.28 μmol kg⁻¹ yr⁻¹ in surface total carbon dioxide (TCO₂) between 1989 and 2001 (Dore et al., 2003). In the deep subtropical North Atlantic, at the Bermuda Atlantic Time-series Study (BATS; 31°45′N, 64°10′W), surface TCO₂ increased by 1.37 ± 0.16 μmol kg⁻¹ yr⁻¹ between 1983 and 2005 (Bates, 2007), with surface and atmospheric pCO₂ increasing at 1.67 ± 0.28 μatm yr⁻¹ and 1.78 ± 0.02 μatm yr⁻¹ respectively over this 22 year period (Bates, 2007).

However, whether surface water CO₂ varies over similar timescales in continental margin settings within the tropics are yet unknown. Since November 1995, the Cariaco Basin ocean time-series program (CARIACO) has conducted biogeochemical and ecological observations at a location on the northern Venezuelan margin (10°30′N, 64°40′W, Fig. 1) to examine the linkages between water column processes and the flux of particles settling to the seafloor. The Cariaco Basin is an ideal location to examine this question because past changes in surface ocean processes are well preserved in the sediment record accumulating in the basin. The Cariaco Basin has a unique set of oceanographic characteristics. The open exchange of water and materials with the Caribbean Sea only occurs above a 140 m deep sill. Consequently, there is a restriction (or limitation) of deep water circulation and mixing, which allows the formation of anoxic waters below 320 m. The restricted circulation within the basin isolates it from the open ocean and makes it a trap for sinking materials. The seasonally alternating coastal wind-driven upwelling controls the high seasonal biological productivity and particulate sediment flux.

While the Cariaco Basin has a long history of oceanographic studies, very few have focused on the carbon dioxide system. Avila-Melean (1976) analyzed the relationship between TCO₂ and dissolved oxygen in the nearby Gulf of Santa Fe. Hastings and Emerson (1988) measured TCO₂ and total alkalinity (TA) in a study of sulfate reduction above the O₂–H₂S interface. Zhang and Millero (1993) measured TCO₂, pH, and TA in the eastern and western basins of the Cariaco Basin. Astor et al. (2005a,b) observed the interactions between physical and biochemical parameters that lead to temporal variations in fCO₂sea, finding that even during periods of high production, the CO₂ flux between the ocean and the atmosphere decreased but remained positive, i.e. CO₂ escaped from the ocean to the atmosphere.

In this paper, we report the results of CO₂ observations at the CARIACO time-series station. We look at changes observed during periods of upwelling (dry season) and non-upwelling (rainy season). We evaluate the rates of change of several hydrographic parameters over the period 1996–2008, and examine possible connections with different modes of climate variability.

### 1.1. Study area

The Cariaco Basin, located on the continental margin of Venezuela, is a tectonic depression (~1400 m deep) subject to seasonal changes in atmospheric forcing that affect the water column’s upper layers. Intermittent easterly trade winds (≥ 6 m s⁻¹) are responsible for offshore surface Ekman transport and wind-driven coastal upwelling during winter and early spring (January–April). Rainy conditions and weak winds are typical between September and December, the months of non-upwelling. A transition period occurs between June and August when a short and relatively weak secondary upwelling event occurs with characteristics and timing that vary from year to year (Astor et al., 2003). The causes of this secondary upwelling event are linked to variations in the wind curl (Rueda-Roa, 2012). During the primary upwelling event, high

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**Fig. 1.** Map depicting the Cariaco Basin and indicating the location of the CARIACO time series station.
salinity (S > 36.8) Subtropical Underwater (SUW) reaches the surface (Morrison and Smith, 1990). This nutrient- and carbon-rich water stimulates primary production (> 1.5 g C m⁻² d⁻¹, Muller-Karger et al., 2001) during the period of upwelling. The remineralization of the sinking particulate organic matter and limited circulation maintain a suboxic zone (dissolved oxygen and sulfide <5 μM) between 200 and 320 m, with anoxic conditions fully developed deeper than about 320 m.

2. Methods

Observations of the inorganic carbon system were made between January 1996 and December 2000, and from March 2002 to December 2008 on board the R/V Hermano Ginés (Fundación La Salle de Ciencias Naturales de Venezuela). All data, including the time series of pH (pH on the total hydrogen ion concentration, pHₜ), total alkalinity (TA), TCO₂, and fCO₂sea are publicly available on the CARAICO web page (http://www.imars.usf.edu/CAR/index.html) and through the Ocean Carbon and Biogeochemistry (OCB) Data Management Office (http://mapservice.bco-dmo.org/mapsbin/global/map). Continuous hydrographic profiles and water samples were collected using a CTD system (SeaBird SBE-19 from January to September 1996; SBE-25 for all subsequent cruises). Sampling details were described in Astor et al. (2003, 2005a).

The parameters measured to characterize the various components of the carbonate system are pH and TA. TA samples were collected in 250-mL glass amber bottles and poisoned with 50 μL of saturated HgCl₂ solution (final Hg concentration of about 50 μM). Samples were stored at 4 °C and analyzed in the laboratory. For pH, seawater samples were drawn directly from each Niskin bottle into a 10 cm spectrophotometer cell. Colorimetric analyses were made on board ship within 1 h of sample collection. Samples for pH were measured using the spectrophotometric method of Clayton and Byrne (1993) as modified by DelValls and Dickson (1998) and Dickson et al. (2007). TA analyses followed the method of Breland and Byrne (1993), and Yao and Byrne (1998), with modifications suggested by Dr. Wensheng Yao (personal communication). Further details on the alkalinity and pH methods can be found in Astor et al. (2005a).

The precision of the alkalinity and pH measurements are 4 μmol kg⁻¹ and 0.003 units of pH, respectively. Certified alkalinity reference materials (CRM’s) supplied by A.G. Dickson (Scripps Institute of Oceanography) were analyzed for TA with each batch of samples for each cruise. The standard deviation between the mean value of alkalinity measurements of the standards and the certified value was 2 μmol kg⁻¹.

TCO₂ and fCO₂sea were calculated using CO2SYS (Lewis and Wallace, 1998), applying the carbonic acid dissociation constants of Mehrbach et al. (1973) as modified by Dickson and Millero (1987), and equilibrium constants from Millero (1995). The precision of TCO₂ and fCO₂sea measurements were estimated through 1000 Monte Carlo simulations using the average and standard deviation for each data parameter. The uncertainty associated with TCO₂ was about 2 μmol kg⁻¹ and for fCO₂sea about 4 μatm. Surface TA and TCO₂ data were normalized (nTA and nTCO₂) to the mean surface salinity (36.8) at the Cariaco time-series site (nTA = 36.8TA/S; nTCO₂ = 36.8TCO₂/S) to remove the effects of local precipitation and evaporation. To normalize associated with TCO₂ was about 2/3 the period of 1996 and 2008. An average value of atmospheric CO₂ changes in the Cariaco Basin.

The coastal upwelling

where M is the meridional Ekman transport resulting from the zonal wind stress (τₓ), and f is the Coriolis parameter. Because the zonal wind at the CARIACO site is negative by convention, the sign of the offshore component of the Ekman transport estimated along the Venezuelan shoreline was modified to reflect that negative (offshore) Ekman transport leads to positive (upwelling) vertical transport. Thus, transport values reported here are shown as positive.

Wind data were derived from two meteorological stations located to the northeast of the CARIACO time-series station on Margarita Island, Venezuela (one at 10°56′N 64°06′W in Punta de Pedras, and the other at a nearby station at 10°54′N 63°58′W in Porlamar International Airport). Zonal wind stress was estimated from the monthly mean wind speed since wind speeds are relatively stable over periods of weeks to months in this tropical setting.

Phytoplankton biomass was estimated as chlorophyll a (Chla) extracted in methanol and measured on a Turner Designs fluorometer using standard methods (Falkowski and Kiefer, 1985; Holm-Hansen et al., 1965). Primary productivity observations were made at the same depths as Chla using a modified Steeneman Nielsen (1952) NaHCO₃ uptake assay. Further details on the primary production method can be found in Muller-Karger et al. (2001). Primary productivity and Chla values were integrated from 1 to 7 m for consistency with all other parameters. Phytoplankton samples for taxonomy were fixed with neutralized formalin and were analyzed in the laboratory with the Utermöhl technique (Hasle, 1978).

A single mooring containing five automated sediment traps is used to measure the vertical flux of particles at various depths in the Cariaco Basin water column. Further details on the characteristics of this mooring can be found in Thunell et al. (2008). The ratio of organic to inorganic carbon (Cₒ/Cᵢ) in the total carbon flux derived from sediment trap samples collected at 225 m at the study site was calculated.

The sea-air CO₂ flux, F, was calculated according to:

where k is the transfer velocity for sea-air CO₂ exchange, z is the solubility of CO₂ and ΔCO₂ is the sea-air fCO₂ difference (fCO₂sea – fCO₂atm). ΔfCO₂ was calculated from the difference between the average value of fCO₂sea and the fugacity of CO₂ in the atmosphere (fCO₂atm). Data for atmospheric CO₂ was taken from Conway et al. (2009) for Ragged Point in Barbados (13°10′N 59°26′W) within the period of 1996 and 2008. An average value of atmospheric CO₂ at this site for each month was used for calculations.

The solubility of CO₂ is a function of temperature and salinity and was calculated according to Weiss (1974). The CO₂ gas transfer velocity is the exchange parameter between the ocean and the atmosphere, and different parameterizations yield roughly a factor of two differences in gas transfer values over the oceans (Wanninkhof et al., 2004); therefore, to assess the
uncertainty in the estimates of sea-air CO$_2$ fluxes, two parameter-
izations were considered, namely Nightingale et al. (2000) and
Wanninkhof (1992)

$$k = 0.31u^2(Sc/660)^{-0.5} \quad \text{Wanninkhof (1992)}$$

$$k = (0.222u^2 + 0.333u)(Sc/600)^{-0.5} \quad \text{Nightingale et al. (2000)}$$

where $Sc$ is the Schmidt number and $u$ is the monthly mean wind
speed measured at 10 m above the ground. The Schmidt
number is the ratio of the kinematic viscosity of seawater to the
a aqueous diffusion coefficient of CO$_2$ in water, and it was calcu-

Three indices designed to assess climate variability (the North
Atlantic Oscillation (NAO), the Southern Oscillation Index (SOI),
and the Atlantic Multidecadal Oscillation (AMO) index) were
obtained from NOAA’s Climate Prediction Center (http://www.
cpc.ncep.noaa.gov/) and compared to the time series of CARIACO sea
surface temperature anomalies (SSTA). The NAO describes a large-
scale meridional oscillation in atmospheric mass between the
Azores High and the Iceland Low. The Southern Oscillation Index
(SOI), an indicator of large-scale variability in the Pacific Ocean
associated with the El Niño phenomenon, is calculated from
monthly fluctuations of atmospheric sea level pressure between
Darwin, Australia and Tahiti. The AMO is an index that tracks
variability in temperatures of the North Atlantic Ocean.

2.1. Statistical analyses

The annual cycle was statistically removed (deseasonalized)
from SST, salinity, pH, TA, TCO$_2$, and fCO$_2$ by subtracting monthly
observations from 13-yr means (for SST and salinity) and 11-yr
means (for CO$_2$ parameters) and adding the overall mean (e.g.,
Bates, 2007). The years 2001 and 2002 were excluded from CO$_2$
statistics in this analysis because all CO$_2$ data from 2001 and six
months from 2002 were missing due to equipment failure. The
observed and deseasonalized monthly values were regressed
linearly against time (year) to obtain the rate of change. Anoma-
lies were derived by subtracting the climatological mean from
monthly observations. The relationship among 10 environmental
variables (TCO$_2$, temperature, salinity, MLD, chlorophyll $a$, fCO$_2$sea,
primary production, upwelling index, ratio of organic to inorganic
carbon (C$_o$/C$_i$), and diatom/coccolithophore (D/C) ratio) were
analyzed by Principal Coordinate Analysis (PCO or PCoA). PCO is
an ordination method similar to Principal Component Analysis
(PCA). The PCO is an eigenanalysis routine where the analysis
places the samples onto Euclidean axes using only a matrix of
inter-point dissimilarities, rather than from a correlation or
covariance matrix. The values for each variable were normalized
by having their mean subtracted and were divided by their
standard deviation. Euclidean distances among centroids in the
space were calculated to normalized data to produce a resem-
blance matrix that formed the basis of the analyses. This matrix
was used as an ordination method to visually compare group
differences and patterns through a projection of the data onto
axes (Anderson et al., 2008). The analysis was performed using
Permanova+ add-on package for Primer software.

3. Results and discussion

3.1. Hydrography

Several authors have documented the seasonal hydrographic,
biological, and chemical characteristics of the water column at
the CARIACO station (Astor et al., 1998, 2003, 2005a,b, 2006; Muller-
Karger et al., 2001, 2010; Scranton et al., 2001, 2006a,b; Taylor et al.,
2012; Virmani and Weisberg, 2009). Fig. 2 shows time-series of sea
surface temperature (SST), sea surface salinity (SSS), wind speed and
upwelling index. The highest SST typically occurred in association
with the lowest SSS in September and October (Fig. 2a and b).
Conversely, the lowest SST and highest SSS were observed from
January through April, when stronger winds resulted in greater
vertical mixing and upwelling. In addition to this pronounced
seasonal cycle, there was significant interannual variability in SST
and SSS, particularly in the seasonal minima for both parameters.
An average seasonal SST range of 6 ± 0.6 °C, and a seasonal range of
SSS of 0.63 ± 0.22 were observed between 1996 and 2008. The MLD

![Fig. 2. Time-series of monthly observations of (a) SST (°C), (b) SSS, and (c) upwelling index (m$^3$ s$^{-1}$ per 100 m of coastline, black line-closed diamonds) and wind speed (m s$^{-1}$, dashed line-open triangles) at the CARIACO time-series station from January 1996 to December 2008. In (a) and (b), the thin black line and dashed line-open squares indicate monthly individual and deseasonalized measurements, respectively. Linear trends are indicated in a and b for individual values (black solid line) and deseasonalized data (dashed line). Trends are given in Table 1. In (c), linear trend for upwelling index is indicated by the black line and for wind speed by the dashed line.](http://dx.doi.org/10.1016/j.dsr2.2013.01.002)
was typically shallow with an average seasonal range of 21 ± 7.6 m. Occasionally, eddies drifting near the shelf break injected oxygenated nutrient rich water into the basin enhancing biological activity that resulted in a drawdown of CO₂ (Astor et al., 2003, 2005a). Unfortunately, our data on the influence of eddies on the biogeochemistry of the basin is limited and precludes us from drawing further conclusions on the importance of these sporadic events.

The wind speed also showed strong seasonal and interannual fluctuations, leading to variations in the strength of the upwelling (Fig. 2c). Periods with stronger upwelling (1996–1998, 2001–2003) were followed by years of weak upwelling (1999–2000, 2004–2008). A linear fit model between SST and the upwelling index shows a correlation coefficient equals to −0.60 ($R^2=0.37$) indicating a moderately strong relationship between the two variables.

Fig. 3 illustrates the SSTA from 1996 to 2008. A 12-month running mean was applied to the monthly values. The SSTA data revealed two cold periods (January 1996–March 1998, June 2000–December 2003) and two warm periods (April 1998–May 2000, January 2004–December 2008). Between 1996 and 2008, SSTA values oscillated ±1 °C around the mean. When compared to the upwelling index, the periods of cold and warm anomalies coincided with periods of strong and weak upwelling intensities, respectively (Fig. 2c). A PCO analysis shows similar patterns in the distribution. The years with similar characteristics occupy the same location in multivariate space separating the years into cold and warm periods. The first axis (PCO1) is strongly associated to the cold periods and years of weak upwelling. The second axis (PCO2) is associated to the warm periods and years of strong upwelling. Both axes combined explain 77.9% of the total variation.

The high standard deviation at CARIACO reflects the higher environmental variability of coastal waters, where controlling factors such as upwelling of a water mass and changing productivity are important. At the CARIACO station, TA changes may also occur due to biogenic precipitation of calcium carbonate and the dissolution of calcareous shells or skeletons. Biogenic precipitation was evident on January 1997, January 1999, March 2007, and February 2008, when nTA values dropped by more than 20 µmol kg⁻¹ and the number of coccolithophore cells in surface waters increased significantly (Luis Troccoli, pers. comm., Universidad de Oriente). Elevated TA values were usually associated to salinities greater than 36.8 which identifies Subtropical Underwater (Astor et al., 2003). This water mass may reach the surface during the peak of upwelling (February–March) with high TA values.

Surface TCO₂ and nTCO₂ (Fig. 5c, nTCO₂ not shown) varied between 1988 and 2137 (mean value 2072 ± 26 µmol kg⁻¹), and 1978 and 2132 µmol kg⁻¹ (mean value 2074 ± 21 µmol kg⁻¹), respectively, over the 13-year study period. Higher surface values (> 2100 µmol kg⁻¹) were typical during periods of high upwelling and low precipitation. The relationship between TCO₂ and salinity was significant ($R^2=0.38$, $p<0.01$). In 2004, surface values throughout the year were closer to the overall mean (2070 µmol kg⁻¹). Seasonal variation of TCO₂ over the entire study period had an average range of 83 ± 18 µmol kg⁻¹. Since differences between surface TA and nTA, and TCO₂ and nTCO₂ are minimal, we can say that changes in salinity due to mixing, evaporation, and precipitation had minimal effects on the CO₂ parameters at the CARIACO station.

3.2. CO₂ parameters: Surface values

Over the 13-year study period, surface pH fluctuated from 8.014 to 8.113 (Fig. 5a). This range is similar to what we had observed previously over the shorter period of 1996–2000 (Astor et al., 2005a). Surface TA and nTA (Fig. 5b, nTA not shown) had mean values of 2413 ± 19 and 2416 ± 15 µmol kg⁻¹, respectively.

3.3. Interannual trends from 1996 to 2008 at the CARIACO Time-series station

3.3.1. Observed hydrographic and CO₂ parameters.

Salinity, pH, TCO₂, nTCO₂, TA and nTA did not show significant changes through time. For all these parameters, seasonality
determines variability, thus increasing the uncertainty in calculating interannual trends. In contrast, the observed SST, the upwelling index, and \( f_{\text{CO}_2}\text{sea} \) at the CARIACO time-series station all display linear interannual trends for the period 1996–2008 (Figs. 2 and 6, and Table 1).

A statistically significant change was observed for SST. The rate of change of measured SST at CARIACO was 0.17 ± 0.04 °C yr\(^{-1}\) (\( R^2 = 0.04, p < 0.01 \); Fig. 2a, Table 1). This is similar to the surface warming (0.11 ± 0.03 °C yr\(^{-1}\)) reported by Padin et al. (2010) for the equatorial upwelling system of the Atlantic Ocean. During this time, upwelling intensity (measured through the Bakun upwelling index) and the observed SST, the upwelling index, and \( f_{\text{CO}_2}\text{sea} \) at the CARIACO time-series station all display linear interannual trends for the period 1996–2008 (Figs. 2 and 6, and Table 1).

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Fig. 5. Time-series of monthly observations (individual and deseasonalized) of (a) pH; (b) total alkalinity (\( \mu\text{mol kg}^{-1} \)) and (b) total CO\(_2\) (\( \mu\text{mol kg}^{-1} \)) at the CARIACO time-series station from January 1996 to December 2008. The thin line and dashed line-open squares indicate monthly individual and deseasonalized measurements, respectively. Linear trends are indicated for individual and deseasonalized data (black and dashed lines). Trends are given in Table 1.

Fig. 6. Time-series of monthly individual and deseasonalized of: (a) surface CO\(_2\) fugacity, \( f_{\text{CO}_2}\text{sea}, \mu\text{atm} \) and (b) normalized CO\(_2\) fugacity (\( n_{f_{\text{CO}_2}\text{sea}}\)), \( \mu\text{atm} \) at the CARIACO time-series station from January 1996 to December 2008. The thin line and dashed line-open squares indicate monthly individual and deseasonalized measurements, respectively. Linear trends are indicated for individual values (black line) and deseasonalized data (dashed black line). Trends are given in Table 1.

Table 1

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<td>&lt;0.01</td>
</tr>
<tr>
<td>n( f_{\text{CO}_2}\text{sea} )</td>
<td>0.40</td>
<td>-406</td>
<td>0.61</td>
<td>112</td>
<td>&lt;0.01</td>
<td>0.51</td>
</tr>
<tr>
<td>Upwelling index</td>
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<td>60050</td>
<td>12.3</td>
<td>151</td>
<td>0.04</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Wind speed</td>
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<td>111.9</td>
<td>0.02</td>
<td>151</td>
<td>0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td><strong>Deseasonalized</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>T</td>
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<td>-148.2</td>
<td>0.02</td>
<td>150</td>
<td>0.09</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>S</td>
<td>0.11</td>
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<td>150</td>
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<td>0.0004</td>
<td>118</td>
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</tr>
<tr>
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<td>0.41</td>
</tr>
<tr>
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<td>0.31</td>
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<td>nTCO(_2)</td>
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<td>0.44</td>
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<tr>
<td>( f_{\text{CO}_2}\text{sea} )</td>
<td>1.77</td>
<td>-3142</td>
<td>0.43</td>
<td>112</td>
<td>&lt;0.13</td>
<td>&lt;0.01</td>
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<td>n( f_{\text{CO}_2}\text{sea} )</td>
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<td>-631</td>
<td>0.49</td>
<td>112</td>
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<td>0.29</td>
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and wind speed at CARIACO have been decreasing (Fig. 2c). These parameters showed a rate of change of $-29.3 \pm 12.3 \text{ m}^3 \text{s}^{-1}$ per 100 m of coastline yr$^{-1}$ ($R^2 = 0.04$, $p < 0.02$) and $-0.05 \pm 0.02 \text{ m}^3 \text{s}^{-1} \text{yr}^{-1}$ ($R^2 = 0.03$, $p < 0.03$), respectively. Upwelling intensity and wind speed are closely related and have a great influence on SST at the station.

The $f_{\text{CO}_2}$ data also showed a statistical significant positive trend of $1.95 \pm 0.48 \text{ ppm} \text{ yr}^{-1}$ ($R^2 = 0.13$, $p < 0.01$: Fig. 6a, Table 1). The total observed variation in $f_{\text{CO}_2}$ at the CARIACO station from 1996 to 2008 was $-24 \text{ ppm}$, representing a change of 6% during the study period. If the effect of temperature is removed, the $n_{\text{CO}_2}$ shows a lower rate of increase of $0.40 \pm 0.61 \text{ ppm} \text{ yr}^{-1}$, which yields a statistically insignificant trend ($R^2 = <0.01$, $p > 0.5$, Fig. 6b and Table 1). Therefore, the effect of SST on $f_{\text{CO}_2}$ at CARIACO is very significant.

### 3.3.2. Deseasonalized hydrographic and $\text{CO}_2$ parameters

The amplitude of the seasonal variability in the measured parameters is large and easily mask low-amplitude, low-frequency interannual changes. Therefore, the annual cycle was removed (deseasonalized) to evaluate long-term trends (e.g., Bates, 2007). Deseasonalized SST and $f_{\text{CO}_2}$ trends were statistically significant (Table 1, Figs. 2 and 6a). SST increased $0.09 \pm 0.02 \text{ C} \text{ yr}^{-1}$ ($R^2 = 0.09$, $p < 0.01$), and $f_{\text{CO}_2}$ increased at $1.77 \pm 0.43 \text{ ppm} \text{ yr}^{-1}$ ($R^2 = 0.13$, $p < 0.01$). Deseasonalized $n_{\text{CO}_2}$ data showed an increase of $0.51 \pm 0.49 \text{ ppm} \text{ yr}^{-1}$ ($R^2 = <0.01$, $p > 0.3$), but this change was not statistically significant.

### 3.4. Factors controlling $f_{\text{CO}_2}$ variability

From thermodynamics 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., 1992). Therefore, surface warming of 1 °C would drive a ~16 ppm increase in $f_{\text{CO}_2}$ at CARIACO. Fig. 3 shows that SST and $f_{\text{CO}_2}$ anomalies are mostly in phase with each other. An increase/decrease of 1 °C is usually followed by an increase/decrease of 16–20 ppm of $f_{\text{CO}_2}$. Thus, the SST increase of 1.3 °C between 1996 and 2008 accounted for 16 ppm increase in $f_{\text{CO}_2}$, explaining around 72% of the $f_{\text{CO}_2}$ observed variation. This suggests that the changes measured in $f_{\text{CO}_2}$ were primarily the result of surface-ocean warming in Cariaco Basin.

Upwelling of subsurface water plays an important role in bringing high concentrations of $\text{TCO}_2$ to the surface, favoring an increase of $f_{\text{CO}_2}$. However, upwelling also brings low-temperature, high-nutrient waters to the surface, which can counter the effect of high $\text{TCO}_2$ concentrations by lowering $f_{\text{CO}_2}$ through an increase in $\text{CO}_2$ solubility and changes in $\text{H}_2\text{CO}_3$ dissociation constants, together with an increase in carbon fixation that enhances the removal of $\text{CO}_2$ from surface waters. There is a strong inverse relationship between chlorophyll $a$ concentration and SST ($R^2 = 0.45$, $p < 0.01$). The highest chlorophyll $a$ levels were observed at the surface in 1996 and 2001 in conjunction with temperatures below 22 °C. After 2004, surface water temperatures were consistently above the annual mean, while chlorophyll $a$ levels were low and $\text{TCO}_2$ concentrations were high.

The decrease in intensity of upwelling events since 2004, associated with a weakening in wind stress during boreal winter, resulted in the upwelling of waters from shallower depths. However, higher concentrations of $\text{TCO}_2$ likely from subsurface waters, still reach the surface during this period, as noted in a sharp increase in TCO$_2$ below 15 m during the upwelling season. Changes in SST, nutrients and $\text{TCO}_2$ concentrations observed in surface waters depend not only on upwelling intensity, but also on the vertical gradients of these parameters beneath the mixed layer (Mahadevan et al., 2004). Surface waters at CARIACO normally show consistently low nutrients levels in the upper 35–55 m and only occasionally during strong upwelling events, when upwelled waters come from 60–80 m, do they have nitrate concentrations above 1 μM (Scranton et al., 2006b). The weak upwelling that prevailed between 2004 and 2008 at the CARIACO station only brought shallow subsurface water (20–30 m) to the surface. Hence, the low nutrient concentration effectively reduced carbon fixation, which led to an accumulation of $\text{CO}_2$ in surface waters. Additionally, weaker winds decreased vertical mixing, exposing the recently upwelled water to heating for a longer period. The warming of this upwelled subsurface water with high $\text{TCO}_2$ concentration strengthened the thermally driven evasion of $\text{CO}_2$ from the sea to the atmosphere.

Another source of $\text{CO}_2$ to surface waters is the respiration of dissolved organic carbon (DOC) by bacteria (Jiao et al., 2010). DOC concentrations at the CARIACO site are controlled by biological and physical processes, mainly extracellular release of DOC by phytoplankton, grazing by zooplankton, and decomposition by bacteria, and upwelling/stratification of the water column (Lorenzoni et al., submitted for publication). The CARIACO site does not receive significant input of DOC from land (Lorenzoni et al., 2009). Variations in the concentration of DOC between the upwelling and rainy season is ~6%, with higher DOC concentrations during the rainy season due to the strong thermal stratification the basin experiences. During upwelling, the Subtropical Underwater that is injected into the surface is DOC-poor (average of ~57 mM, Del Castillo, 1998; CLIVAR-Repeat Hydrography, transect 22). It is possible that a fraction of the surface DOC is eventually degraded by bacteria upwelled with the underlying water. Carlson et al. (2004) showed that bacteria in the upper mesopelagic can consume surface accumulated DOM. Unfortunately, we currently have no estimate of what fraction of surface DOC can be degraded by microbial respiration, but it is our belief that this process is not one of the most significant controls of surface $f_{\text{CO}_2}$ in the Cariaco Basin.

Diatoms historically dominated the phytoplankton population at the CARIACO station during the upwelling season (Goñi et al., 2003; Thunell et al., 2000). Carbon fixation by these organisms reduces $\text{TCO}_2$ and $f_{\text{CO}_2}$. When upwelling decreases and surface waters warm smaller phytoplankton, such as coccolithophores, become more abundant. These organisms can affect surface water $f_{\text{CO}_2}$ through calcification, leading to depletion of dissolved carbonate ion ($\text{CO}_3^{2-}$) and an increase in $\text{CO}_2$ ( Archer, 2003) according to the reactions:

$$\text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow 2\text{HCO}_3^- + \text{Ca}^{2+} \leftrightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$$

In order to evaluate the influence of this biological process on $f_{\text{CO}_2}$ fugacity, we examined the ratio of organic to inorganic carbon ($\text{C}_o/\text{C}_i$) in the total carbon flux derived from sediment trap samples collected at 225 m at the study site. This ratio was then compared to the ratio of diatom to coccolithophore (D/C) cell numbers in surface water samples collected monthly at the study site. Previous work has shown that a decrease in surface $f_{\text{CO}_2}$ occurs when the $\text{C}_o/\text{C}_i$ ratio is larger than about 0.7 due to $\text{CO}_2$ uptake during net photosynthesis ( Honda et al., 1997). Conversely, a $\text{C}_o/\text{C}_i$ ratio below 0.7 is associated with the prevalence of calcification processes in surface waters that increases $f_{\text{CO}_2}$. Before 2005, $\text{C}_o/\text{C}_i$ values were above 0.7 in 48% of the sediment trap samples, while after 2005 only 13% of the samples had $\text{C}_o/\text{C}_i$ ratios above 0.7. This is consistent with a shift in the phytoplankton community from diatoms to CaCO$_3$-fixing organisms in the area. Before 2005, the D/C ratio was > 1 in 68% of the water samples, suggesting that diatoms were dominant in most of the samples. This number decreased to 52% after 2005. In addition to a shift in the composition of the phytoplankton community at the
station, there was also a significant decrease in overall phytoplankton biomass. The increase in calcifying organisms likely contributed to the observed increase in surface water CO$_2$; additionally, the decrease in upwelling observed after 2005 also affected the efficiency of the biological pump’s ability to remove CO$_2$. The coupling of these processes (i.e., the lack of removal of the upwelled TCO$_2$ due to a decrease in carbon fixation and the shift in phytoplankton population) may explain the remaining 28% increase observed in fCO$_2$sea, and these two processes, together with temperature, potentially contributed to the high fCO$_2$sea values observed during 2005–2008.

3.5. Sea-air CO$_2$ fluxes

At the CARIACO station, the monthly ΔfCO$_2$sea (ΔfCO$_2$sea = fCO$_2$sea – fCO$_2$atm) values (Fig. 7a) for 1996–2008 did not show significant differences relative to what was found for 1996–2000 (Astor et al., 2005a). The average value for the entire period was 23 ± 21.5 µatm. High positive values were present most of the year except during months of maximum upwelling (February and/or March). These observations confirm that this area is a consistent source of CO$_2$ to the atmosphere. Smaller variability was observed during months of relaxation, when temperatures were high (>28 °C) and primary production was low (<1 gC m$^{-2}$ d$^{-1}$). Strong negative ΔfCO$_2$sea were associated with the drawdown of CO$_2$ during strong upwelling events and an increase in net primary production above 3 gC m$^{-2}$ d$^{-1}$. During these events, the area becomes a sink of CO$_2$.

Fig. 7b illustrates the sea-air CO$_2$ fluxes at the CARIACO station. Negative CO$_2$ flux values denote net air to sea CO$_2$ flux, whereas positive values denote net evasion from the sea. Over the entire time series, values ranged between −16.2 mmol C m$^{-2}$ d$^{-1}$ in February 2003 and 16.9 mmol C m$^{-2}$ d$^{-1}$ in March 2007. Only 16% of the observations (n = 112) have negative values. The low wind speeds (5.2 ± 1.1 m s$^{-1}$) and the large positive ΔCO$_2$ values (0 < ΔCO$_2$sea µatm < 60) led to moderate supersaturation with respect to atmospheric CO$_2$ most of the time. Only during times of very high primary production was the system undersaturated. Due to the large difference in ΔCO$_2$sea, the average net sea-air CO$_2$ flux over the study period was 2.0 ± 2.6 mol C m$^{-2}$ yr$^{-1}$ employing the Wanninkhof (1992) parameterization, and 2.1 ± 2.5 mol C m$^{-2}$ yr$^{-1}$ based on Nightingale et al. (2000). These values were large compared to fluxes calculated in other upwelling systems (0.56 mol C m$^{-2}$ yr$^{-1}$ in the north of the Benguela system; Santana-Casiano et al., 2009; 0.9 mol C m$^{-2}$ yr$^{-1}$ in the Gulf of Oman; Goyet et al., 1998). However, they were lower than the rate calculated by Astor et al. (2005a), 2.8 ± 3.6 mol C m$^{-2}$ yr$^{-1}$ with the Wanninkhof (1992) parameterization for a shorter period of CARIACO observations. In the Cariaco Basin, the primary factors regulating sea-air CO$_2$ flux are the high seasonal variability of upwelling and its direct effect on both oceanographic conditions and biological production.

3.6. Effects of modes of climate variability on SST

Major changes have been observed from year to year in meteorological and oceanographic conditions in the Cariaco Basin. In order to establish whether the interannual variability observed in the SST at the CARIACO station is associated with modes of low-frequency climate variability, the SST time series was compared with several indices of climatic variability, including the North Atlantic Oscillation (NAO), the Atlantic Meridional Oscillation (AMO) and the El Niño/Southern Oscillation (ENSO).

Although the dominant mode of atmospheric variability in the North Atlantic region appears to be the NAO (Bates, 2001), we found very weak correlation between NAO and the SST at the CARIACO station. Crosscorrelation analysis between SST and the NAO index shows no significant relationship at a number of different lags. However, a visual examination of a 12-month running mean for SST and the NAO index (Fig. 8) does suggest that NAO and SST show a similar behavior between 2000 and 2004, and between 2007 and 2008.

The AMO (Enfield et al., 2001) is a global signal that is most intense in the North Atlantic, affecting the entire basin. The AMO index shows a cool phase when negative and a warm phase when positive. For our entire study period, AMO was in a cool phase. However, a well-defined periodicity in this index still needs to be established (Poore et al., 2009). The index has been linked to multi-year precipitation anomalies over North America, and appears to modulate ENSO teleconnections (Enfield et al., 2001; McCabe et al., 2004). When compared to the SST of the CARIACO station, a weak but significant relationship ($R^2 = 0.06, p < 0.01$) was observed.

Changes in the tropical Atlantic Ocean lag the ENSO variability in the tropical Pacific Ocean by 3–9 months (Enfield and Mayer, 1997; Giannini et al., 2000; Klein et al., 1999; Saravanan and Chan, 2000). More specifically, modes of climate variability originating in the Atlantic and Pacific affect the Intra-Americas Sea (IAS, Gulf of Mexico–Caribbean Sea; Giannini and Cane, 2001a). ENSO teleconnections affect multiple processes in the Caribbean Sea, including geostrophic transport (Alvera-Azzärête et al., 2009), precipitation (Jury et al., 2007), and the phytoplankton community structure within the Cariaco Basin (Romero et al., 2009). When the Southern Oscillation index (SOI) was compared to SST at CARIACO, no statistically significant relationship was observed. However, when a 9-month running mean was applied to both the SST and SOI, a pattern was observed where periods...
of warm SSTA followed a negative SOI with a 3–6 months lag, while cold SSTA lagged a positive SOI (Fig. 8b). A very strong negative SOI event occurred in 1997 and part of 1998, and warm temperatures were recorded at the CARIACO station between 1996 and 2008 at the CARIACO time-series station. The time-series of SSTA and SOI were smoothed by a 12-month running mean. The time-series of SSTA and SOI were smoothed by a 9-month running mean.

The interaction among several modes of climate variability and forcing mechanisms seem to modulate interannual SST variability in the Caribbean region (Muñoz et al., 2010); however, the correlations between SSTA and these climate signals in CARIACO only show very weak relationships. Nevertheless, the CARIACO time-series seems to be recording the signals generated from these interactions, and may prove invaluable in time for understanding the impacts of large-scale processes on regional biogeochemical and ecological changes.

4. Conclusions

The observations collected between 1996 and 2008 at the CARIACO time-series station provide new insight into seasonal and interannual controls of the inorganic carbon system in this upwelling-dominated tropical continental margin. The main process controlling the long-term changes in surface $f$CO$_2$ at CARIACO was temperature, with net community production playing a secondary role. Over the study period, deseasonalized SST increased by $0.09 \pm 0.02$ °C yr$^{-1}$, representing an overall increase of 1.13 °C in 13 years. Despite large seasonal variability, the deseasonalized $f$CO$_2$ data for the CARIACO time-series station also showed a statistically significant interannual increase of $1.77 \pm 0.43$ μatm yr$^{-1}$. Thermodynamic effects explained 72% of the $f$CO$_2$ variability in surface waters. A decrease in upwelling intensity between 2004 and 2008 also contributed to this change. Warmer waters with low primary production and high TCO$_2$ and $f$CO$_2$ prevailed for much of the period of observation. At the CARIACO site, the ocean is primarily a source of CO$_2$ to the atmosphere, except during strong upwelling events.

The relationship between SST and wind speed anomalies and modes of climate variability, such as NAO, AMO and SOI were also assessed. Weak but significant relationships between SST and the AMO (R$^2$=0.06, p < 0.01) and wind speed anomaly and SOI at one month lag (R$^2$=0.12, p < 0.01) were found. A weakening of the winds measured around the Cariaco Basin lagged a negative SOI by 1–3 months. Future studies should attempt to further understand the relationship among these modes of climate and their connection with the changes in hydrography in the Cariaco Basin, an important archive of past tropical climate change.

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