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Distribution and variability of the dissolved inorganic carbon system in the Cariaco Basin, Venezuela

Y.M. Astor[a,*], L. Lorenzoni[b], L. Guzman[a], G. Fuentes[a,1], F. Muller-Karger[b], R. Varela[a], M. Scranton[c], G.T. Taylor[c], R. Thunell[d]

[a] Fundación La Salle de Ciencias Naturales, Estación de Investigaciones Marinas de Margarita, Punta de Piedras, Isla de Margarita 6318, Venezuela
[b] University of South Florida, College of Marine Science, St. Petersburg, FL 33701, USA
[c] School of Marine and Atmospheric Science, Stony Brook University, Stony Brook, New York 11794, USA
[d] Department of Earth and Ocean Sciences, University of South Carolina, Columbia, SC 29208, USA

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ABSTRACT

A study was conducted to characterize the variability of dissolved inorganic carbon concentration and speciation in surface waters (upper 100 m) of the southern Caribbean Sea in the Cariaco Basin, located off Venezuela. The spatial distribution of total CO_2 (TCO_2), partial pressure of CO_2 (pCO_2), and the saturation state with respect to aragonite (Ω_{arg}) was evaluated by measuring pH and total alkalinity (TA) in transects across the Basin during upwelling (dry season in March 2004 and 2009) and during the rainy season (September 2006 and 2008). Alkalinity was more strongly related to salinity in the western half of the Cariaco Basin ($R^2 = 0.87$ and $R^2 = 0.80$ for September 2008 and March 2009, $p < 0.001$) than in the eastern sub-basin ($R^2 = 0.20$, $p > 0.01$ for March 2004, and $R^2 = 0.37$ and $R^2 = 0.31$ for September 2008 and March 2009, $p > 0.001$). In the western sub-basin, high pH (> 8.1) and low pCO_2 (< 380 μatm) were observed near the estuaries of the Tuy and Neveri Rivers. In the eastern sub-basin, pH was low (< 8.0) and pCO_2 was high (> 400 μatm) in surface waters during upwelling. The TA-salinity relationship followed a two end-member mixing model (upwelled waters and river input). pCO_2 in surface waters ranged from 366 to 525 μatm during upwelling (March), and 385 to 452 μatm during the rainy period (September). Waters were supersaturated with respect to aragonite saturation state throughout the Cariaco Basin. The Basin was typically over-saturated with CO_2 with respect to the atmosphere. Under-saturation was only observed near the coast, such as near the mouth of the Tuy River. The flux of CO_2 over most of the Cariaco Basin was generally from the ocean to the atmosphere in both seasons. Fluxes tend to remain between 0 and 10 mmol CO_2 m^{-2} day^{-1}, with average values for the whole basin of 11.39 ± 17.17 mmol CO_2 m^{-2} day^{-1} in March 2004, 7.19 ± 2.17 mmol CO_2 m^{-2} day^{-1} in September 2006, 6.32 ± 2.42 mmol CO_2 m^{-2} day^{-1} in September 2008 and 4.35 ± 3.97 mmol CO_2 m^{-2} day^{-1} in March 2009.

1. Introduction

Atmospheric CO_2 has increased approximately 280 ppmv since 1750–1800 (Houghton et al., 1990) and is expected to continue to rise. The oceans are a major sink of this anthropogenic CO_2. The flux of CO_2 from the atmosphere to the ocean has increased from 1.1 GtC $year^{-1}$ in the 1960's to 2.6 GtC $year^{-1}$ in the period of 2005–2014 (Quéré et al., 2015). Dissolution of this CO_2 in seawater alters the carbon and biogeochemical cycles of the ocean, with a measurable, progressive alteration in seawater pH, carbonate ion concentration, and saturation state (Ω) with respect of calcium carbonate ($CaCO_3$) minerals (Bates et al., 2012; Sutton et al., 2016). These changes are driving significant research efforts to characterize the oceanic carbonate system, the air-sea exchange of CO_2, and the potential impact on life in the oceans.

Coastal margins can absorb atmospheric CO_2 and transport it to the interior of the ocean in the form of organic and inorganic carbon (Walsh, 1991). Continental margins comprise only ~7% of the world's ocean surface area, but they play a significant role in the global oceanic carbon cycle (Cao et al., 2011; Liu et al., 2010). Over 0.62 Pg C $year^{-1}$ settles to the seafloor, and at least 0.06 Pg C $year^{-1}$ may be buried in

* Corresponding author.
E-mail addresses: ireneastorsa@mail.usf.edu (Y.M. Astor), ramon.varela@fundacionlasalle.org.ve (R. Varela), mary.scranton@stonybrook.edu (M. Scranton), gordon.taylor@stonybrook.edu (G.T. Taylor), thunell@geol.sc.edu (R. Thunell).
[1] Present address: Calle Arismendi. Edif. Sol Arena sur. APT 5A. Lecherias, Municipio Urbaneja, Edo. Anzoategui. Venezuela.

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sediments on coastal margins (Muller-Karger et al., 2005). Inorganic carbon system variables in ocean margin ecosystems can be highly complex because large CO_2 flux variations occur over short time and small spatial scales (Liu et al., 2000; Borges and Frankignoulle, 2003; Chavez et al., 2007). Coastal upwelling, riverine/estuarine inputs, air-sea gas exchange, biological fixation and respiration, precipitation and dissolution of $CaCO_3$, sea level fluctuations, strong currents, sediment burial, and tectonic movements with material inputs are among the processes that contribute to this variability. Coastal upwelling and river discharge plumes also affect the carbonate system over large areas, contributing to the heterogeneity in carbon fluxes on continental shelves. Therefore, these regions are greatly undersampled, especially in low latitude areas (Borges and Frankignoulle, 2003; Borges et al., 2005; Cai et al., 2006).

Coastal upwelling often brings water to the surface that is enriched in CO_2 and nutrients compared to surrounding surface waters. This can lead to CO_2 oversaturation of surface ocean water relative to the atmosphere. Simultaneously, the elevated nutrient concentrations brought in upwelling waters may stimulate carbon fixation by phytoplankton. Fresh water discharge from land delivers inorganic and organic carbon, nutrients, and sediments to coastal and shelf areas. These also stimulate phytoplankton blooms in coastal waters (Cao et al., 2011). Rivers that drain calcareous bedrock may supply alkalinity to coastal waters (Hjalmarsson et al., 2008). Although the influence of small rivers on continental margins is spatially limited, their importance can increase when they are part of closely-spaced estuaries or during flood events (Devlin et al., 2001; Soto et al., 2009). All of these processes affect biological communities and lead to a patchy distribution in dissolved inorganic carbon.

A time series of dissolved inorganic carbon observations spanning > 20 years was collected in the Southern Caribbean by the CARIACO Ocean Time-Series Program (Astor et al., 2005; Astor et al., 2013). This time series provided information on temporal variations in pH, total alkalinity (TA), dissolved inorganic carbon (TCO_2), and the partial pressure of CO_2 (pCO_2) in the Cariaco Basin, Venezuela. Here, we discuss the spatial variability of pH and total alkalinity around the CARIACO station using samples collected between 2004 and 2009 during four separate cruises. One of the goals was to assess the spatial distribution of the CO_2 system in response to coastal upwelling and river plume dynamics. Sampling was conducted on board the *R/V Hermano Ginés* in the Cariaco Basin. Two of the cruises were limited to the eastern margin whereas the other two extended over the whole basin (Fig. 1).

1.1. The Cariaco Basin

The Cariaco Basin is a tectonic slip-fault formation, 1400 m deep, located on the continental shelf off Venezuela. It is an anoxic basin of oceanic character, connected to the Caribbean Sea by two channels no deeper than 150 m each. The basin is divided in two sub-basins (eastern and western) separated by a 900 m deep sill. The Unare Platform defines the southern-central margin of the southern Cariaco Basin. It is generally ~50 km in width but becomes very narrow in the south-eastern margin of the basin, in an area called Mochima. Strong seasonal wind-driven coastal upwelling occurs along the eastern and southern margin of the basin and particularly in Mochima (Muller-Karger et al., 2010). The dry period typically begins in January, when northeasterly Trade Winds gain strength over this region (Astor et al., 2003). These winds induce Ekman-driven upwelling, bringing pulses of nutrient and CO_2-rich waters from 50 to 100 m depth onto the continental shelf. Duration of the upwelling period (typically January–May) as well as its intensity varies interannually (Astor et al., 2013). A secondary upwelling period occurs regularly between July and August (Rueda-Roa and Muller-Karger, 2013). This is followed by a rainy period when the winds and upwelling relax, between September and December (Lorenzoni et al., 2012).

Several small rivers drain from the mountains across a narrow coastal plain and into the Cariaco Basin, between the city of Cumana and Cape Codera (Fig. 1). These rivers are the Tuy, Unare, and Neverí. The Tuy River drains into the western sub-basin (mean discharge = 62 $m^3 s^{-1}$). The other two drain into the eastern sub-basin (mean discharges = 56 $m^3 s^{-1}$ for the Unare and 32 $m^3 s^{-1}$ for the Neveri Rivers; McConnell et al., 2009). The Tuy River has a number of tributaries that collect wastewater from a drainage basin area of 6600 km^2 that includes the city of Caracas and its main satellite cities, agricultural, and industrial areas (Jaffe et al., 1995). The highest flows of these rivers occur between July and December (Peterson and Haug, 2006).

2. Methods

The upper 100 m of the water column were sampled on four cruises of the *R/V* Hermano Ginés (Fundación La Salle de Ciencias Naturales, Venezuela). Two cruises sampled the dry, upwelling season (15–19 March 2004: 11 stations; and 9–13 March 2009: 36 stations). Two cruises sampled the rainy, non-upwelling season (26–30 September 2006: 19 surface samples; and 1–5 September 2008: 36 stations). Samples were taken in the eastern sub-basin only in March 2004 and September 2006. The eastern and western sub-basins were sampled

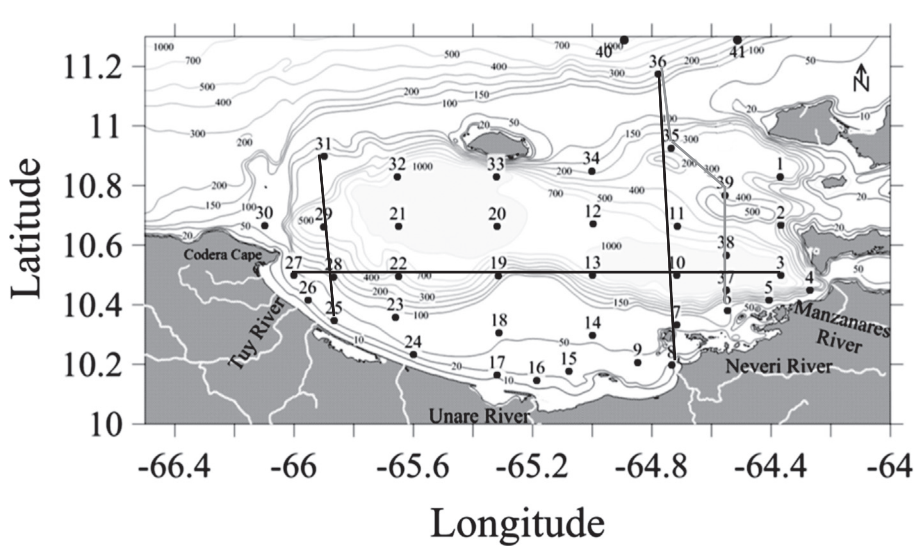

Fig. 1. The Cariaco Basin. The black lines indicate the location of the transects for September 2008 and March 2009: N-S western sub-basin, N-S eastern sub-basin, E-W across the basin. The grey line indicates the N-S transect for March 2004. In March 2004, stations 40 and 41 were included during sampling.