ARTICLE IN PRESS

Marine Chemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Seasonal variability of carbonate chemistry and decadal changes in waters of a marine sanctuary in the Northwestern Gulf of Mexico

Xinping Hu[a,*], Marissa F. Nuttall[b,c], Hongjie Wang[a], Hongming Yao[a], Cory J. Staryk[a], Melissa R. McCutcheon[a], Ryan J. Eckert[b,1], John A. Embesi[b,c], Michelle A. Johnston[b], Emma L. Hickerson[b], George P. Schmahl[b], Derek Manzello[d], Ian C. Enochs[d,e], Steven DiMarco[f], Leticia Barbero[d]

[a] Department of Physical and Environmental Sciences, Texas A&M University–Corpus Christi, Corpus Christi, TX 78412, United States
[b] NOAA Office of National Marine Sanctuaries, Flower Garden Banks National Marine Sanctuary, Galveston, TX 77551, United States
[c] CPC, San Diego, CA 92108, United States
[d] Atlantic Oceanographic and Meteorological Laboratory, NOAA, Miami, FL 33149, United States
[e] Cooperative Institute for Marine and Atmospheric Studies, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149, United States
[f] Department of Oceanography, Texas A&M University, College Station, TX 77843, United States

ARTICLE INFO

Keywords:
Coral reef
Ocean acidification
Gulf of Mexico
Flower Garden Banks National Marine Sanctuary
Anthropogenic CO_2

ABSTRACT

We report seasonal water column carbonate chemistry data collected over a three-year period (late 2013 to 2016) at Flower Garden Banks National Marine Sanctuary (FGBNMS) located on the subtropical shelf edge of the northwestern Gulf of Mexico. The FGBNMS hosts the northernmost tropical coral species in the contiguous United States, with over 50% living coral cover. Presented here are results from samples of the upper 25 m of the water column collected from September 2013 to November 2016. Additionally, following a localized mortality event likely associated with major continental flooding in summer 2016, water samples from up to ~250 m depth were collected in the broader FGBNMS area on a rapid response cruise to examine the seawater carbonate system. Both surface (< 5 m) total alkalinity (TA) and total dissolved inorganic carbon (DIC) vary over small ranges ($2391 \pm 19\,\mu mol\,kg^{-1}$ and $2060 \pm 19\,\mu mol\,kg^{-1}$, respectively) for all times-series samples. Temperature and salinity both played an important role in controlling the surface water carbonate system dynamics, although temperature was the sole significant factor when there was no flooding. The FGBNMS area acted as a sink for atmospheric CO_2 in winter and a CO_2 source in summer, while the time-integrated CO_2 flux is close to zero (-0.14 ± 1.96 mmol-C $m^{-2}\,yr^{-1}$). Results from three cruises, i.e., the Gulf of Mexico and East Coast Carbon Project (GOMECC-1) in 2007, the rapid response study, and the Gulf of Mexico Ecosystems and Carbon Cruise (GOMECC-3), revealed decreases in both pH and saturation state with respect to aragonite (Ω_{arag}) in subsurface waters (~100–250 m) over time. These decreases are larger than those observed in other tropical and subtropical waters. Based on reaction stoichiometry, calculated anthropogenic CO_2 contributed 30–41% of the overall DIC increase, while elevated respiration accounted for the rest.

1. Introduction

Coral reefs in low latitude environments have attracted considerable attention from the scientific community as these environments provide significant ecosystem services. However, current climatic and ocean chemistry changes threaten important reef organisms and the skeletal structures they provide, including decreasing coral grow rates under warmer conditions (Cantin et al., 2010), decreasing coral calcification rates (Erez et al., 2011; Hoegh-Guldberg et al., 2007; Kleypas and Yates, 2009), decreasing coral skeletal density (Mollica et al., 2018), and even enhanced dissolution of coral sand (Eyre et al., 2018) under current ocean acidification conditions. There are, however, coral reefs and coral communities in higher latitude environments, such as in the northwestern Gulf of Mexico, with distributions constrained by temperature and light availability, which are also ecologically and economically important (DeBose et al., 2013; Kleypas et al., 2001; Johnston et al.,

* Corresponding author.
E-mail address: xinping.hu@tamucc.edu (X. Hu).
[1] Current address: Harbor Branch Oceanographic Institute, Florida Atlantic University, 5600 US 1 North, Fort Pierce, FL 34946.

https://doi.org/10.1016/j.marchem.2018.07.006
Received 6 November 2017; Received in revised form 26 June 2018; Accepted 14 July 2018

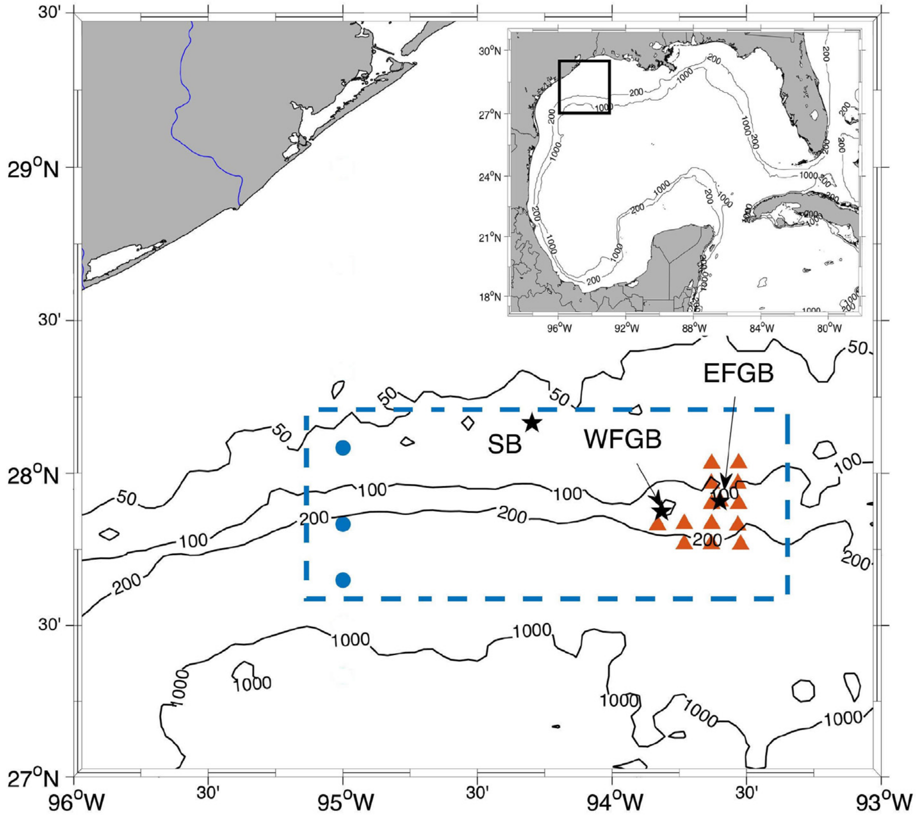

Fig. 1. Sampling stations (filled circles) of the 2007 GOMECC-1 and the 2017 GOMECC-3 cruises both on board *R/V* Ron Brown (Galveston transect) and the 2016 rapid response cruise on board *R/V* Manta (filled triangles). Data from the three stations from the GOMECC cruises within the rectangle were chosen to compare with those from 2016. Stetson Bank (SB), West Flower Garden Bank (WFGB), and East Flower Garden Bank (EFGB) are marked with filled stars. Note that both EFGB and WFGB are sitting on the 100 m isobath. The square in the map insert shows the general sampling area in this study.

2016). Coral communities of the Flower Garden Banks National Marine Sanctuary in the northwestern Gulf of Mexico (FGBNMS, Fig. 1), part of the federally managed National Marine Sanctuary System protecting submerged sites of national significance under *The National Marine Sanctuaries Act*, represent the northernmost tropical species around the contiguous United States (Bright, 1977; DeBose et al., 2013; Johnston et al., 2017a; Lang et al., 2001). FGBNMS consists of three separate banks (Fig. 1) - East Flower Garden Bank (EFGB), West Flower Garden Bank (WFGB), and Stetson Bank (SB) - located along the outer continental shelf (Johnston et al., 2017a). Whereas annual monitoring to document the benthic and fish communities has been conducted at these sites since 1989 (EFGB and WFGB) and 1993 (SB), the biogeochemical characteristics of this area are not fully understood.

Corals in the FGBNMS region, living in marginal environmental conditions for their development and growth (DeBose et al., 2013), are subject to greater temperature fluctuations than their counterparts in the tropical Atlantic, especially for the SB location that is closest to land. Additionally, occasional continental flooding introduces freshwater that depresses seawater salinity and hurricanes cause physical disturbance to the benthic environment in these outer shelf regions (Robbart et al., 2008). Therefore, understanding both spatial and temporal variability of the physicochemical conditions of these coral habitats and their long-term changes is important.

Monitoring of water quality parameters (temperature, salinity, chlorophyll, nitrate, nitrite, phosphorus, and ammonia) at the EFGB and WFGB sites started in 1989 as part of a long-term program (Johnston et al., 2017a), shortly before the establishment of the marine sanctuary in 1992. Seawater carbonate system characterization was not included in this monitoring program until late 2013 with the initiation of biennial sampling as part of NOAA's National Coral Reef Monitoring Program (NCRMP) (NOAA Coral Program, 2014). In November 2013, the Carbon Cycle Laboratory (CCL) at Texas A&M University–Corpus Christi partnered with FGBNMS to start seawater sample collection for carbonate system analysis on a roughly quarterly basis at all three FGBNMS sites, as a complement to the sanctuary's long-term monitoring program (Johnston et al., 2017a; Nuttall et al., 2017).

In this study, we examined seasonal variability of both measured and derived carbonate system parameters (total alkalinity or TA, total dissolved inorganic carbon or DIC, pH, saturation state with respect to aragonite or Ω_{arag}, and partial pressure of CO_2 or pCO_2) in the water column of FGBNMS and identified the controlling factors of these parameters. We also compared decadal changes in water column carbonate system parameters using data from a rapid response cruise following a localized mortality event at the EFGB in the summer of 2016 (Johnston et al., 2017b) and two cross-shelf cruises that sampled an area close to the FGBNMS in the summers of 2007 and 2017, i.e., the first Gulf of Mexico and East Coast Carbon Project (GOMECC-1) and the Gulf of Mexico Ecosystems and Carbon Cruise (GOMECC-3) (Table 1). The three stations chosen from the GOMECC cruises are about 150 km and 80 km to the west of EFGB and SB, respectively (Fig. 1).

2. Materials and methods

2.1. Study sites

Underlying all three FGBNMS banks within the sanctuary boundaries are salt dome formations with salt deposits from the Jurassic, a common occurrence in the northern Gulf of Mexico. EFGB and WFGB, approximately 190 km south of the Texas-Louisiana border, range in depth from 16 to 150 m and are capped with coral reef communities with > 50% living coral cover (Fig. 1). SB, considered a mid-shelf bank, is located approximately 56 km northwest of WFGB and approximately 100 km offshore (Fig. 1). SB is an uplifted claystone feature ranging in depth from 17 to 53 m and capped with coral and sponge communities (Nuttall et al., 2017). All these banks provide three-dimensional hard bottom habitats and support diverse communities of hermatypic corals, black corals, and octocorals, in addition to abundant fish and invertebrate communities. Due to the closer proximity of SB to shore,