Acidification in the Gulf: Insights from measurements of pH and $[CO_3^{2-}]$ on GOMECC-3

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1. Introduction

The 2017 Gulf of Mexico Ecosystems and Carbon Cruise (GOMECC-3) was carried out between July 18th and August 21st. The expedition surveyed transects in the northern Gulf of Mexico that have been studied on previous GOMECC cruises (in 2007 and 2012). It also surveyed Mexican waters in the western and southern Gulf, the Yucatán Channel between the Yucatán Peninsula and Cuba, and the Straits of Florida between Cuba and the Florida Keys (Figure A). This novel compilation of areas allows for (1) a basin-wide assessment of carbonate chemistry in the Gulf, (2) temporal comparison over a decade in the northern Gulf and East of Florida, and (3) introduction of baseline data for areas in the western and southern Gulf not studied on previous GOMECC cruises or by any other comprehensive effort.

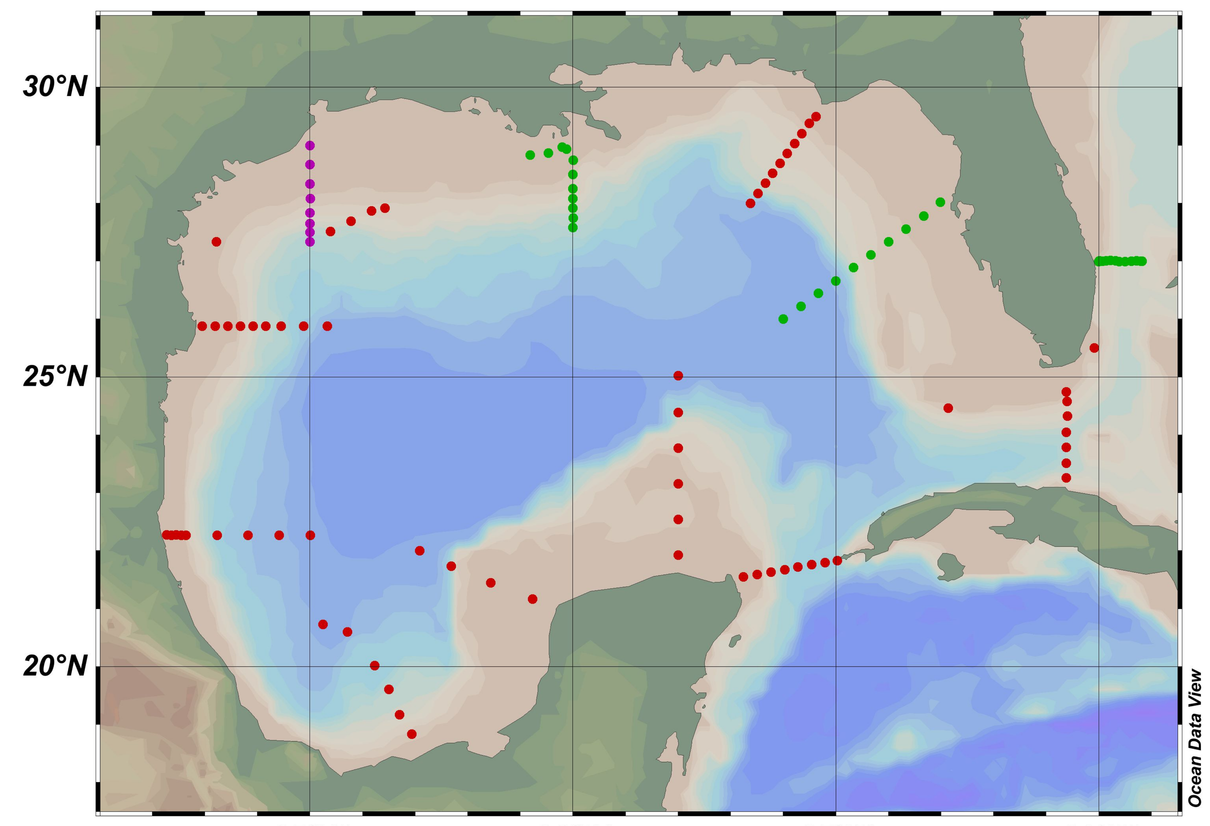

Figure A. Station locations for GOMECC-3. Green dots represent transects that were repeated on all three GOMECC cruises. Purple dots represent the transect that was surveyed in 2007 and 2017 only.

2. Measurements of pH_T and $[CO_3^{2-}]_T$

Our group measured seawater pH on the total scale (pH_T) and total carbonate ion concentrations ($[CO_3^{2-}]_T$). Each chemical parameter was measured spectrophotometrically at 25°C. The procedures of Liu et al. (2011)[1] were used for pH_T and the procedures of Sharp et al. (2017)[2] were used for $[CO_3^{2-}]_T$. Over 1,500 samples were analyzed for each parameter. Duplicate samples demonstrated a precision of ±0.001 for pH_T (n = 170) and ±1.4 µmol/kg for $[CO_3^{2-}]_T$ (n = 159).

3. Summary of pH_T and $[CO_3^{2-}]_T$ in the Gulf

To outline carbonate chemistry within the Gulf, three noteworthy zones were specified based on depth and underlying bathymetry: (1) surface waters overlying the continental shelf, (2) surface waters in offshore areas, and (3) offshore deep pH and $[CO_3^{2-}]_T$ minimum zones. Samples with salinity less than 30 were excluded to eliminate anomalous values influenced by river input. At offshore deep stations, minimum values of pH_T occur at an average depth of 656 m, while minimum values of $[CO_3^{2-}]_T$ occur at approximately 678 m. Table 1 summarizes these data.

Table 1. Average values of pH_T and $[CO_3^{2-}]_T$ in different zones within the Gulf in 2017 (excluding the transect east of FL).

Zone	Avg. pH_T	Avg. $[CO_3^{2-}]_T$ (µmol/kg)
Surface Overlying the Continental Shelf (station depth < 140 m)	8.090 ± 0.03 (n = 39)	240.3 ± 12 (n = 39)
Surface Overlying Offshore Areas (station depth > 140 m)	8.102 ± 0.01 (n = 53)	251.5 ± 7 (n = 51)
Offshore Subsurface Minimum Zones (station depth > 600 m)	7.6004 ± 0.006 (n = 39)	91.03 ± 1.5 (n = 39)

4. Notable Depth Sections

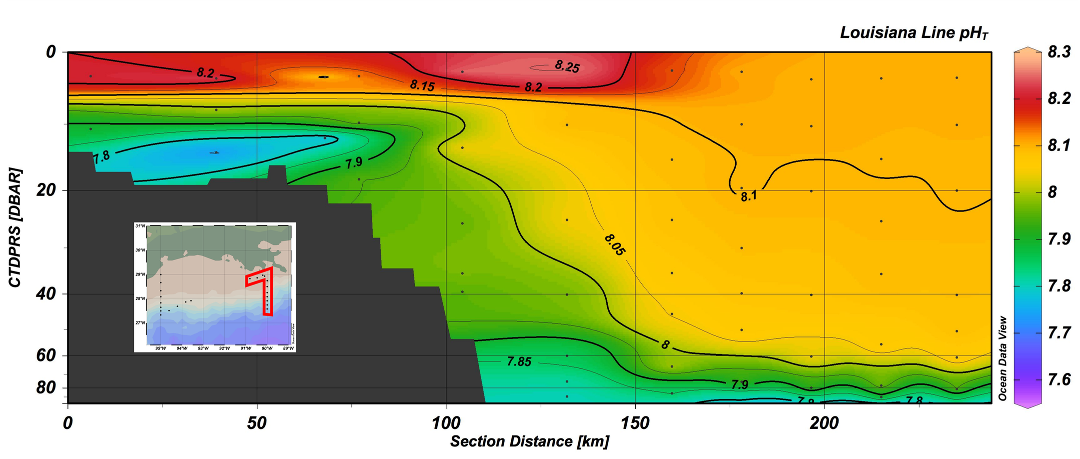

Figure B. Depth section of pH_T off the coast of Louisiana near the Mississippi and Atchafalaya River Deltas. The left side of the section plot represents the left side of the red outline on the map.

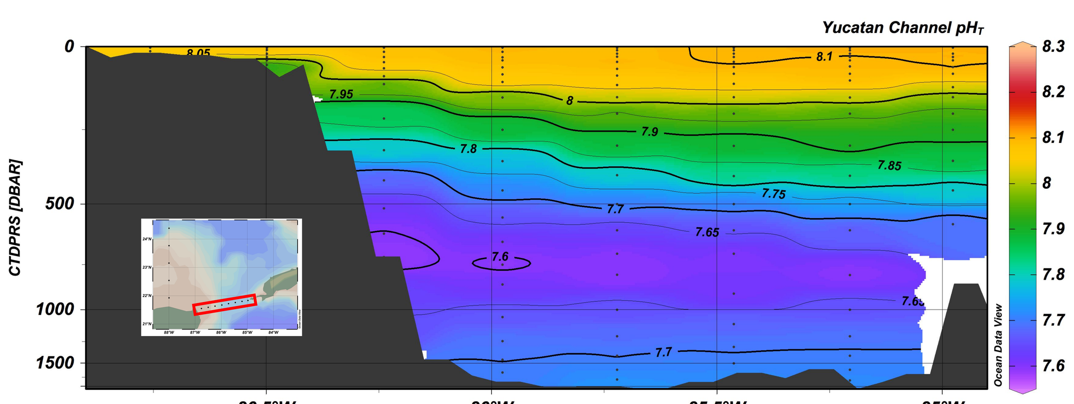

Figure C. Depth section of pH_T across the Yucatán Channel between Cuba in the east and the Yucatán Peninsula in the west.

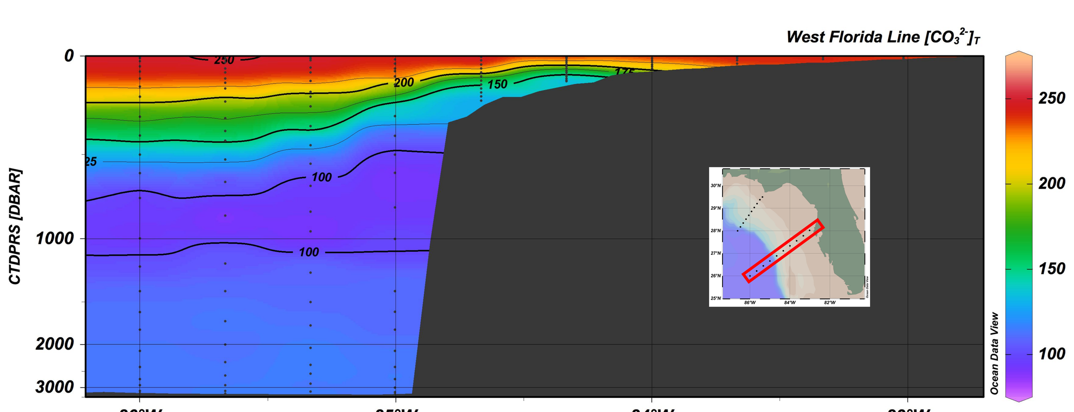

Figure D. Carbonate ion concentrations for the transect off the coast of Clearwater, FL. Note the bathymetry of the broad West Florida Shelf.

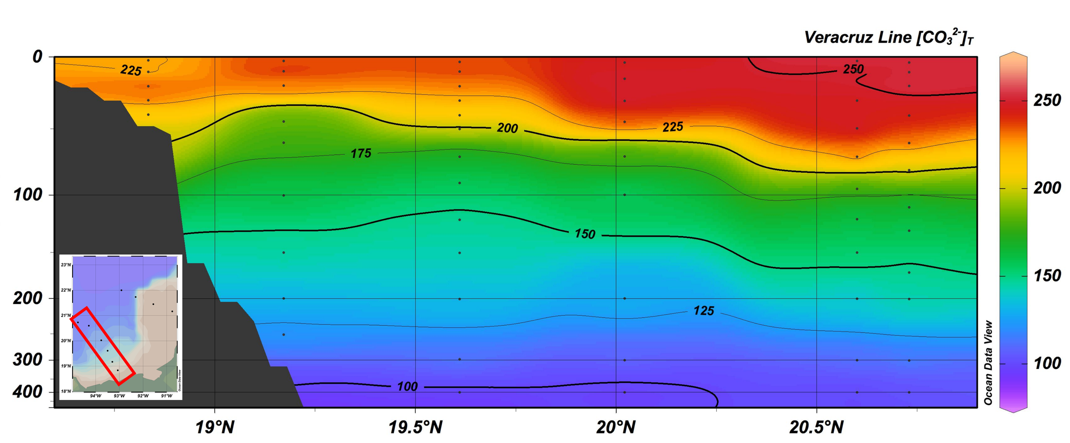

Figure E. Depth section of carbonate ion concentrations for the southern Gulf transect near Veracruz, MX.

5. Surface Chemistry

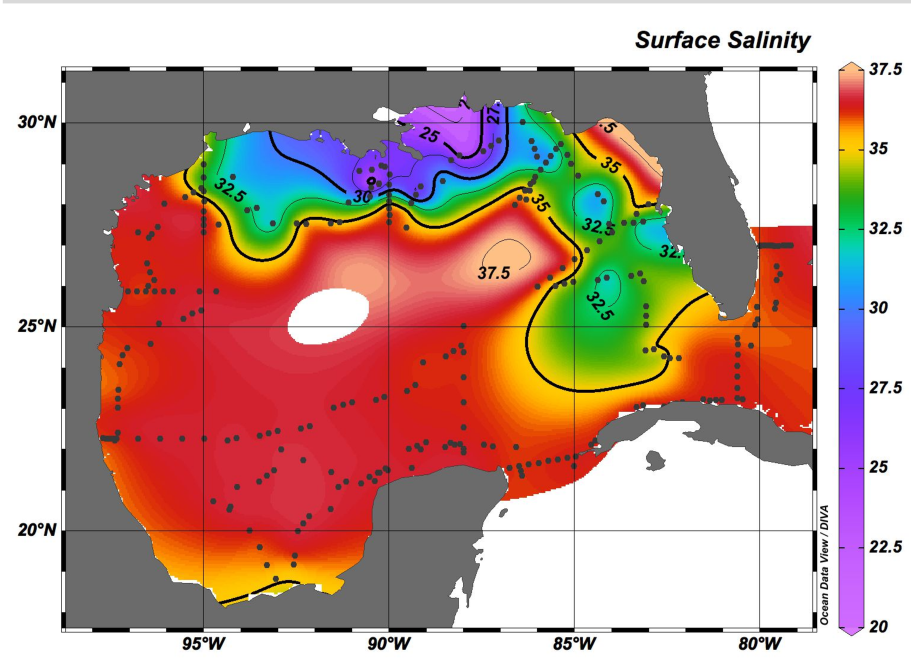

Figure F. Map of surface salinity from GOMECC-3, derived from both discrete bottle samples and discrete underway samples.

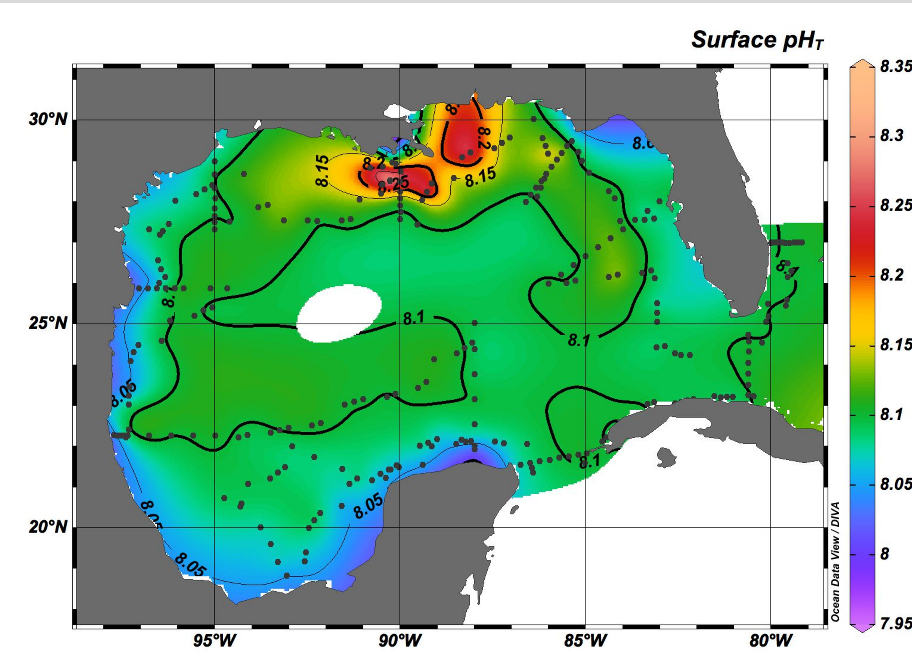

Figure G. Map of surface pH_T from GOMECC-3, also derived from both discrete bottle samples and discrete underway samples.

6. Changes in pH_T and $[CO_3^{2-}]_T$ over a decade of GOMECC cruises

Four of the transects covered on GOMECC-3 have been repeated on multiple GOMECC cruises.[3,4] Within each transect, six density layers were defined according to potential density anomaly (σ_θ) and compared across three years of GOMECC sampling (2007, 2012, and 2017). Values of pH_T for GOMECC-1 were calculated using DIC and TA and corrected for the known discrepancy[5] between $pH_{T(DIC,TA)}$ and $pH_{T(spec)}$ using a linear relationship determined from GOMECC-2 data. Carbonate ion concentrations for GOMECC-1 were calculated using DIC and f_{CO2}, and all carbonate concentrations were normalized to a salinity of 35, because salinity variations significantly affect $[CO_3^{2-}]_T$.

In each transect, the σ_θ layer closest to the surface ($0 < \sigma_\theta < 23$; avg. = 12.6 dbars; max. = 60 dbars) shows a statistically significant temporal decline in both pH_T and $[CO_3^{2-}]_T$. Only 63% of non-surface density layers display statistically significant negative temporal trends. Some of the surface layer trends are displayed in Figure H (values more than two standard deviations from the mean of each group are excluded). Most surface density layers also show negative trends between 2012 and 2017 only, but just a few are statistically significant.

These results suggest that acidification and carbonate ion decline are indeed detectable in surface waters in the Gulf of Mexico and off the east coast of Florida over the course of the last decade. The magnitudes of the trends vary, but the East FL and West FL transects show yearly pH_T declines (–0.0018 and –0.0012) that compare well with trends observed in the open ocean.[6] Furthermore, negative trends in $[CO_3^{2-}]_T$ are consistent with those calculated from measured pH_T, providing further evidence that the temporal trends are authentic and robust.

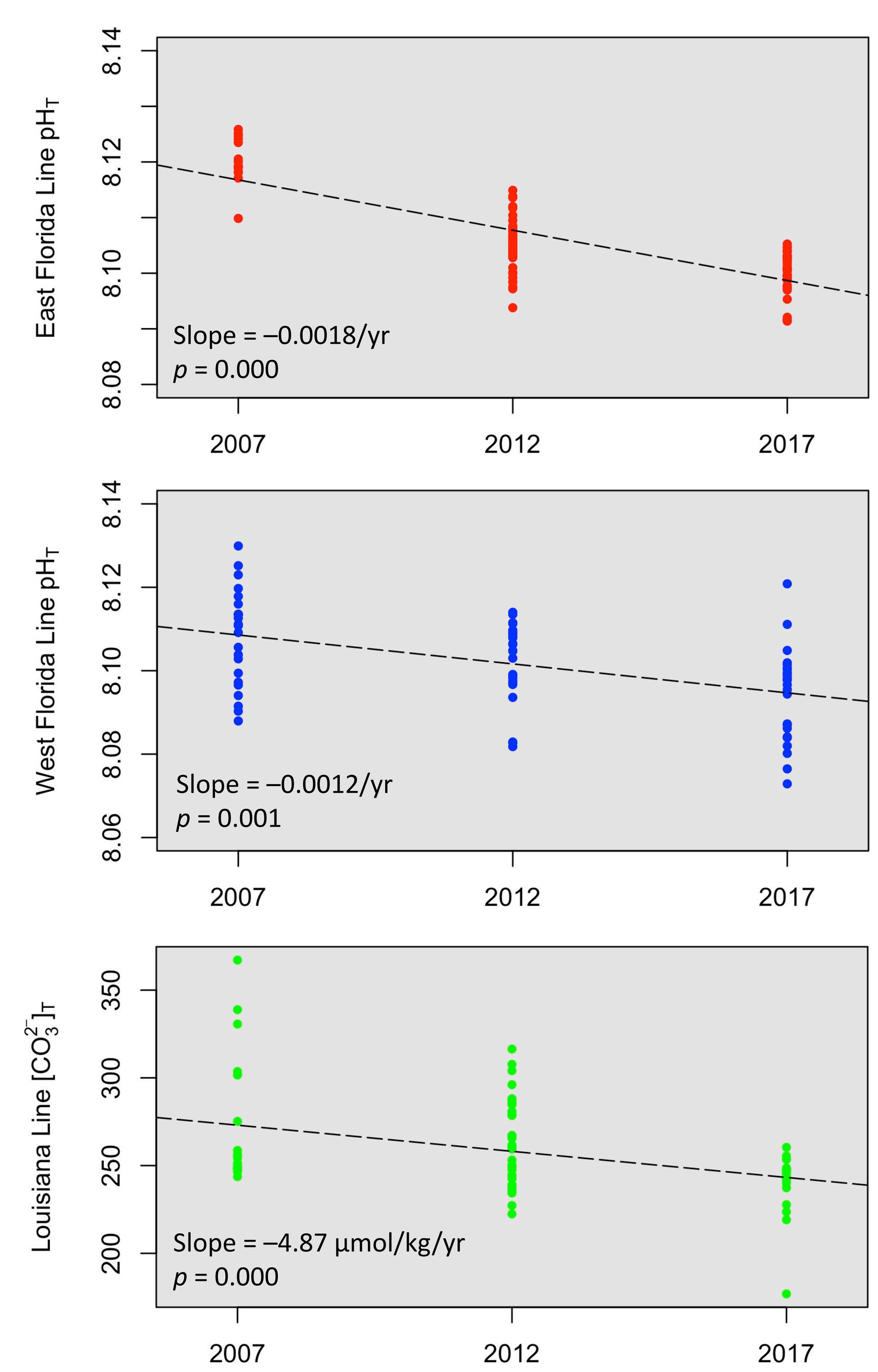

Figure H. Plots of pH_T and $[CO_3^{2-}]_T$ in the uppermost density layer of three transects over a decade of GOMECC cruises.

7. Acknowledgements

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8. References

(1) Liu, X., et al., 2011. Environ. Sci. Technol. 45, 4862–4868.
(2) Sharp, J.D., et al., 2017. Environ. Sci. Technol. 51, 9127–9136.
(3) Langdon, C., and RSMAS, 2011. National Oceanographic Data Center, NOAA.
(4) Wanninkhof, R., et al., 2016. National Centers for Environmental Information, NOAA.
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(6) Woosley, R.J., et al., 2016. Global Biogeochem. Cycles 30, 70–90.