

DIC, TA, calculated pH and carbonate saturation state in the summer bottom water in North Gulf of Mexico from 2006 to 2017

Website: <https://www.bco-dmo.org/dataset/818773>

Data Type: Cruise Results

Version: 1

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Project

» [Collaborative Research: pH Dynamics and Interactive Effects of Multiple Processes in a River-Dominated Eutrophic Coastal Ocean](#) (nGOMx acidification)

Contributors	Affiliation	Role
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Abstract

DIC, TA, calculated pH and carbonate saturation state in the summer bottom water in North Gulf of Mexico from 2006 to 2017

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Coverage

Spatial Extent: N:30 E:-88 S:27.5 W:-94

Temporal Extent: 2006-06 - 2017-07

Acquisition Description

DIC and TA

Measure of DIC using NDIR method and of TA using Gran titration. DIC and TA were measured using the instruments from Apollo Scitech Inc. Briefly, for DIC analysis, samples were analyzed at room temperatures. Each seawater sample (0.5 mL) was acidified using phosphoric acid and the evolved CO₂

gas was extracted and carried by pure N₂ gas to an infrared CO₂ detector (Li-Cor 6262) for quantification. TA was determined on 25 mL seawater sample by potentiometric titration, using 0.1 M hydrochloric acid and an open-cell titration system. All TA samples were analyzed in pre-thermostated (25 °C) glass cells. For each DIC or TA sample, sub-samples were sequentially analyzed 2 or 3 times until we obtained two replicates with a precision within 0.1%. The average of the two values is reported. The precision of both the TA and DIC measurements was +/- 2 umol/kg. The accuracies of the TA and DIC measurements were determined by routine analysis of certified reference material (CRM) provided by A. G. Dickson, Scripps Institution of Oceanography.

pH_elec

pH samples were drawn in 60 ml glass bottles and temperature equilibrated at 25 oC. An Orion Combination electrode connected to a pH meter (Orion Star A211) was used to measure the potential (EMF, mV) generated by the H⁺ ions. EMF was calibrated using three NBS buffer solutions at pH 4.01, 7.0, and 10.01 purchased from Fisher Scientific. Probe was kept immersed in the sample until the EMF stabilized. Two EMF readings at a difference of 1 minute were obtained for each sample and average value used with calibration to calculate the pH. Precision on pH is estimated from the standard deviation of the mean of two EMF readings. Samples where such deviation exceeded 0.16% of the mean EMF are flagged.

pH_spec

Discrete sample pH_spec was measured spectrophotometrically at 25 degrees Celsius on the total pH scale using purified M-Cresol Purple purchased from R. Byrne at the University of South Florida [Clayton and Byrne, 1993; Liu et al., 2011]. The spectrophotometric pH (25 oC, total scale) was calculated from the ratio of the measured absorbances of mCP at wavelengths I₂ = 578 nm and I₁ = 434 nm following the dissociation constants proposed by Liu et al 2011].

pHcal[at25C] and Omegacal[at25C]

pHcal[at25C] and Omegacal[at25C] was calculated using the CO₂SYs program and the measured DIC and TA as the input pair (van Heuven, 2011). Silicate and phosphate concentrations were assigned as 0 in CO₂SYs. The coefficients for pH and Ω calculation were selected as: K₁ and K₂ value from Lueker et al. (2000); KHF⁻ was from Dickson & Riley (1979); KHSO₄ was from Dickson (1990) and BT (total boron) was from Uppström (1974).

Processing Description

The software to do data processing is Microsoft Excel. CTD data was downloaded from CTD directly without any further data processing. Both TA and DIC was converted to units of μmol/kg from μmol/L with density equation. The difference between pH_spec and pHcal@25C was 0.00±0.02.

BCO-DMO Data Manager Processing Notes:

- * added a conventional header with dataset name, PI name, version date
- * modified parameter names to conform with BCO-DMO naming conventions
- * blank values in this dataset are displayed as "nd" for "no data." nd is the default missing data identifier in the BCO-DMO system.

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Related Publications

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 I: Oceanographic Research Papers, 40(10), 2115–2129. doi:10.1016/0967-0637(93)90048-8
[https://doi.org/https://doi.org/10.1016/0967-0637\(93\)90048-8](https://doi.org/https://doi.org/10.1016/0967-0637(93)90048-8)

Methods

Dickson, A. ., & Riley, J. . (1979). The estimation of acid dissociation constants in sea-water media from potentiometric titrations with strong base. II. The dissociation of phosphoric acid. Marine Chemistry, 7(2), 101–109. doi:10.1016/0304-4203(79)90002-1 [https://doi.org/https://doi.org/10.1016/0304-4203\(79\)90002-1](https://doi.org/https://doi.org/10.1016/0304-4203(79)90002-1)

Methods

Dickson, A. G. (1990). Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. Deep Sea Research Part A. Oceanographic Research Papers, 37(5), 755–766. doi:10.1016/0198-0149(90)90004-f [https://doi.org/https://doi.org/10.1016/0198-0149\(90\)90004-F](https://doi.org/https://doi.org/10.1016/0198-0149(90)90004-F)

Methods

Douglas, N. K., & Byrne, R. H. (2017). Achieving accurate spectrophotometric pH measurements using unpurified meta-cresol purple. Marine Chemistry, 190, 66–72. doi:10.1016/j.marchem.2017.02.004 <https://doi.org/https://doi.org/10.1016/j.marchem.2017.02.004>

Methods

Liu, X., Patsavas, M. C., & Byrne, R. H. (2011). Purification and Characterization of meta-Cresol Purple for Spectrophotometric Seawater pH Measurements. Environmental Science & Technology, 45(11), 4862–4868. doi:[10.1021/es200665d](https://doi.org/10.1021/es200665d)

Methods

Müller, J. D., & Rehder, G. (2018). Metrology of pH Measurements in Brackish Waters—Part 2: Experimental Characterization of Purified meta-Cresol Purple for Spectrophotometric pH Measurements. Frontiers in Marine Science, 5. doi:[10.3389/fmars.2018.00177](https://doi.org/10.3389/fmars.2018.00177)

Methods

Uppström, L. R. (1974). The boron/chlorinity ratio of deep-sea water from the Pacific Ocean. Deep Sea Research and Oceanographic Abstracts, 21(2), 161–162. doi:[10.1016/0011-7471\(74\)90074-6](https://doi.org/10.1016/0011-7471(74)90074-6)

Methods

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Parameters

Parameter	Description	Units
Year	Sampling year	unitless
Month	Sampling month	unitless
Longitude	Longitude, west is negative	Decimal degrees
Latitude	Latitude, south is negative	Decimal degrees
Depth	sampling depth	meter (m)
Temperature	temperature in sampling depth	Degrees Celsius (°C)
Salinity	salinity in sampling depth	PSU
OxygenSBE	CTD Dissolved oxygen concentration	Milligram per liter (mg/L)
TA_final	Total Alkalinity	Micromole per kilogram (umol/kg)
flag_TA	TA_final_flag flag_1 means missing value; flag_2 means precision 0.1%	unitless
DIC_final	Total dissolved inorganic carbon	Micromole per kilogram (umol/kg)
flag_DIC	DIC_final_flag flag_1 means missing value; flag_2 means precision 0.1%	unitless
pHelec_NBS_at25	NBS pH measured by electrode	unitless
flag_pHelec	pHelec_flag flag_1 means missing value; flag_2 means precision ±0.02	unitless
pHspec_at25C	total scale pH measured by spectrometer	unitless
flag_pHspec	pHspec_flag flag_1 means missing value; flag_2 means precision ±0.005	unitless
pHcal	Calculated pH from DIC and TA	unitless
Omegacal	Calculated carbonate saturation states from DIC and TA	unitless

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Instruments

Dataset-specific Instrument Name	24-bottle rosette equipped with a SeaBird CTD 911
Generic Instrument Name	CTD Sea-Bird 911
Generic Instrument Description	The Sea-Bird SBE 911 is a type of CTD instrument package. The SBE 911 includes the SBE 9 Underwater Unit and the SBE 11 Deck Unit (for real-time readout using conductive wire) for deployment from a vessel. The combination of the SBE 9 and SBE 11 is called a SBE 911. The SBE 9 uses Sea-Bird's standard modular temperature and conductivity sensors (SBE 3 and SBE 4). The SBE 9 CTD can be configured with auxiliary sensors to measure other parameters including dissolved oxygen, pH, turbidity, fluorescence, light (PAR), light transmission, etc.). More information from Sea-Bird Electronics.

Dataset-specific Instrument Name	Semi-automated titrator (AS-ALK2 Apollo Scitech)
Generic Instrument Name	Automatic titrator
Dataset-specific Description	AS-ALK2 is designed for both laboratory and shipboard use with small sample volume (10 – 25 mL) and high precision (0.1% or better). The titrator is fully automated with standardization and sample analysis. AS-ALK2 provides Gran titration for alkalinity determination of both seawater and brackish waters. Full temperature control is provided on all liquids. Water jackets are used to surround the digital syringes for temperature control. For best data quality, a water bath must be used to supply water with a constant temperature to control the titration temperature.
Generic Instrument Description	Instruments that incrementally add quantified aliquots of a reagent to a sample until the end-point of a chemical reaction is reached.

Dataset-specific Instrument Name	
Generic Instrument Name	Apollo SciTech AS-C3 Dissolved Inorganic Carbon (DIC) analyzer
Generic Instrument Description	A Dissolved Inorganic Carbon (DIC) analyzer, for use in aquatic carbon dioxide parameter analysis of coastal waters, sediment pore-waters, and time-series incubation samples. The analyzer consists of a solid state infrared CO ₂ detector, a mass-flow controller, and a digital pump for transferring accurate amounts of reagent and sample. The analyzer uses an electronic cooling system to keep the reactor temperature below 3 degrees Celsius, and a Nacion dry tube to reduce the water vapour and keep the analyzer drift-free and maintenance-free for longer. The analyzer can handle sample volumes from 0.1 - 1.5 milliliters, however the best results are obtained from sample volumes between 0.5 - 1 milliliters. It takes approximately 3 minutes per analysis, and measurement precision is plus or minus 2 micromoles per kilogram or higher for surface seawater. It is designed for both land based and shipboard laboratory use.

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Deployments

PE08-52

Website	https://www.bco-dmo.org/deployment/823774
Platform	R/V Pelican
Start Date	2008-05-01
End Date	2008-05-09

PE09-43

Website	https://www.bco-dmo.org/deployment/823776
Platform	R/V Pelican
Start Date	2009-06-28
End Date	2009-07-05

PE11-02

Website	https://www.bco-dmo.org/deployment/823778
Platform	R/V Pelican
Start Date	2010-07-25
End Date	2010-08-01

PE12-03

Website	https://www.bco-dmo.org/deployment/823780
Platform	R/V Pelican
Start Date	2011-07-24
End Date	2011-07-31

PE13-03

Website	https://www.bco-dmo.org/deployment/823782
Platform	R/V Pelican
Start Date	2012-07-22
End Date	2012-07-28

PE14-04

Website	https://www.bco-dmo.org/deployment/823784
Platform	R/V Pelican
Start Date	2013-07-21
End Date	2013-07-28

PE15-03

Website	https://www.bco-dmo.org/deployment/823786
Platform	R/V Pelican
Start Date	2014-07-26
End Date	2014-08-02

PE16-03

Website	https://www.bco-dmo.org/deployment/823788
Platform	R/V Pelican
Start Date	2015-07-28
End Date	2015-08-03

PE17-03

Website	https://www.bco-dmo.org/deployment/823790
Platform	R/V Pelican
Start Date	2016-08-22
End Date	2016-08-23

PE18-02

Website	https://www.bco-dmo.org/deployment/784911
Platform	R/V Pelican
Start Date	2017-07-07
End Date	2017-07-21

GM0606

Website	https://www.bco-dmo.org/deployment/824356
Platform	OSV Bold
Start Date	2006-06-06
End Date	2006-06-11

GM0609

Website	https://www.bco-dmo.org/deployment/824358
Platform	OSV Bold
Start Date	2006-09-06
End Date	2006-09-11

GM0705

Website	https://www.bco-dmo.org/deployment/824359
Platform	OSV Bold
Start Date	2007-05-02
End Date	2007-05-08

Project Information

Collaborative Research: pH Dynamics and Interactive Effects of Multiple Processes in a River-Dominated Eutrophic Coastal Ocean (nGOMx acidification)

Coverage: northern Gulf of Mexico, 27.5 N, 30 N, 88 W, 94 W

NSF Award Abstract: Ocean acidification (OA) refers to the lowering of ocean pH (or increasing acidity) due to uptake of atmospheric carbon dioxide (CO₂). A great deal of research has been done to understand how the open ocean is influenced by OA, but coastal systems have received little attention. In the northern Gulf of Mexico (nGOM) shelf region, pH in bottom waters can measure up to 0.45 units less than the pH of the pre-industrial surface ocean, in comparison to the 0.1 overall pH decrease across the entire ocean. Carbonate chemistry in the ocean is greatly influenced by even small changes in pH, so these seemingly minor changes lead to much greater impacts on the biology and chemistry of the ocean. The researchers plan to study coastal OA in the nGOM, a region subject to high inputs of nutrients from the Mississippi River. These inputs of anthropogenic nitrogen mostly derived from fertilizers leads to increased respiration rates which decreases oxygen concentrations in the water column to the point of hypoxia in the summer. This study will inform us how OA in coastal waters subject to eutrophication and hypoxia will impact the chemistry and biology of the region. The researchers are dedicated to outreach programs in the Gulf and east coast regions, interacting with K-12 students and teachers, undergraduate/graduate student training, and various outreach efforts (family workshops on OA, lectures for the public and federal, state, and local representatives). Also, a project website will be created to disseminate the research results to a wider audience. Increased uptakes of atmospheric carbon dioxide (CO₂) by the ocean has led to a 0.1 unit decrease in seawater pH and carbonate mineral saturation state, a process known as Ocean Acidification (OA), which threatens the health of marine organisms, alters marine ecosystems, and biogeochemical processes. Considerable attention has been focused on understanding the impact of OA on the open ocean but less attention has been given to coastal regions. Recent studies indicate that pH in bottom waters of the northern Gulf of Mexico (nGOM) shelf can be as much as 0.45 units lower relative to pre-industrial values. This occurs because the acidification resulting from increased CO₂ inputs (both atmospheric inputs and in-situ respiration) decreases the buffering capacity of seawater. This interactive effect will increase with time, decreasing summertime nGOM bottom-water pH by an estimated 0.85 units and driving carbonate minerals to undersaturation by the end of this century. Researchers from the University of Delaware and the Louisiana Universities Marine Consortium will carry out a combined field, laboratory, and modeling program to address the following questions. (1) What are the physical, chemical, and biological controls on acidification in coastal waters impacted by the large, nutrient-laden Mississippi River?; (2) What is the link between coastal-water acidification, eutrophication, and hypoxia; (3) How do low pH and high CO₂ concentrations in bottom waters affect CO₂ out-gassing during fall and winter and storm periods when the water column is mixed?; and (4) What are the influences of changing river inputs under anthropogenic forcing on coastal water acidification? Results from this research aim to further our understanding of the processes influencing ocean acidification in coastal waters subject to eutrophication and hypoxia both in the GOM and river-dominated shelf ecosystems globally.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1559279

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