DIC, TA, pH from R/V Pelican cruise conducted in the northern Gulf of Mexico in April and July 2017

Website: https://www.bco-dmo.org/dataset/772513
Data Type: Cruise Results
Version: 2
Version Date: 2019-12-20

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

Contributors	Affiliation	Role
Cai, Wei-Jun	University of Delaware	Principal Investigator, Contact
Fennel, Katja	Dalhousie University	Co-Principal Investigator
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Abstract
Dissolved inorganic carbon, total alkalinity and pH from R/V Pelican cruises conducted in the northern Gulf of Mexico (27.5 N, 30 N, 88 W, 94 W) from April 5 to 16 and July 7 to 21 in 2017

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Coverage

Spatial Extent: **N**:29.6415 **E**:-88.5901 **S**:27.4999 **W**:-93.4167
Temporal Extent: 2017-04-06 - 2017-07-21

Dataset Description

Dissolved inorganic carbon, total alkalinity and pH from R/V Pelican cruises conducted in the northern Gulf of Mexico (27.5 N, 30 N, 88 W, 94 W) from April 5 to 16 and July 7 to 21 in 2017.

Methods & Sampling

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 CO_2 gas was extracted and carried by pure N_2 gas to an infrared CO_2 detector (Li-Cor 6262) for quantification. TS 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.

DO_spec

Winkler titration was used for DO analysis. Samples were drawn from Niskin bottles directly into 60 ml BOD bottles and pickled using manganese chloride and sodium iodide/sodium hydroxide. Iodine liberated by acidifying pickled sample was then measured spectrophotometrically using Genesis 30 (Thomas Scientific) spectrophotometer at 466 nm. Blank absorbance from sample turbidity was obtained by adding a few drops of sodium thiosulfate to the sample solution and subtracted from sample absorbance. Calibration was performed by spiking known amounts of potassium iodate. Error on DO was from the uncertainty of measuring absorbance (0.001), which is equivalent of 0.7 uM. Samples which had blank absorbance exceeding 5% of sample absorbance were flagged.

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 l2 = 578 nm and l1 = 434 nm following the dissociation constants proposed by Liu et al 2011].

Sampling and analytical procedures:

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. TS 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.

Winkler titration was used for DO analysis. Samples were drawn from Niskin bottles directly into 60 ml BOD bottles and pickled using manganese chloride and sodium iodide/sodium hydroxide. Iodine liberated by acidifying pickled sample was then measured spectrophotometrically using Genesis 30 (Thomas Scientific) spectrophotometer at 466 nm. Blank absorbance from sample turbidity was obtained by adding a few drops of sodium thiosulfate to the sample solution and subtracted from sample absorbance. Calibration was performed by spiking known amounts of potassium iodate. Error on DO was from the uncertainty of measuring absorbance (0.001), which is equivalent of 0.7 uM. Samples which had blank absorbance exceeding 5% of sample absorbance were flagged.

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. 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).

Instruments:

1. 24-bottle rosette equipped with a SeaBird CTD 911.
2. DIC and TA were measured using the instruments from Apollo Scitech Inc.
3. Certified reference material (CRM) provided by A. G. Dickson, Scripps Institution of Oceanography was used to check the accuracies of the TA and DIC measurements.
4. Winkler titration was used for DO_spec analysis. DO_spec samples were measured spectrophotometrically using Genesis 30 (Thomas Scientific) spectrophotometer at 466 nm.
5. M-Cresol Purple purchased from R. Byrne at the University of South Florida was used for pH_spec measurement.

Data Processing Description

Dataset processing notes:

- 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.
- DO_spec was converted to unit of µmol L-1 at 25°C.
- pH_spec was calibrated based on Douglas and Byrne [2017] or Müller and Rehder [2018]. The difference between Douglas and Byrne (2017) and Müller and Rehder (2018) was 0.002±0.001 for 2017 April cruise.

Data manager processing notes:

- Added ISO_DateTime_UTC column
- Negative sign added to longitudinal values (locations at western part of prime meridian) to data acquired during April 2017
- 4 digits after the decimal for latitude and longitude values
- Version History:
  - Version 1: Original data received 2019-06-07, discrete data acquired during April 2017
  - Version 2: Data received 2019-10-22, added discrete data acquired during July 2017

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Data Files

File
discrete_samples_concat.csv (Comma Separated Values (.csv), 189.90 KB) MD5:ef241dd798bc37a7dd73853331b82590 Primary data file for dataset ID 772513

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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
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

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
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 pHT Measurements. Frontiers in Marine Science, 5. doi:10.3389/fmars.2018.00177
Methods

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Parameters

Parameter	Description	Units
Cruise	Cruise name	unitless
Date	Date in format YYYY-MM-DD	unitless
Time	Time in format HH:MM:SS	unitless
Station	Station name	unitless
Longitude	Longitude, west is negative	decimal degrees
Latitude	Latitude, south is negative	decimal degrees
Bottom_Depth	Bottom depth	meter (m)
Sample_Depth	Sampling depth	meter (m)
Temperature	Temperature in sampling depth	degrees Celsius (°C)
Salinity	Salinity in sampling depth	PSU
OxygenSBE1	CTD Dissolved oxygen concentration	micromole per kilogram (umol/kg)
OxygenSBE2	CTD Dissolved oxygen concentration	milligram per liter (mg/L)
FluorescenceChl	CTD Fluorescence Chl	microgram per liter (ug/L)

wetCDOM	CTD wetCDOM	milligram per cubic meters (mg/m^3)
SPAR	CTD Surficial Photosynthetically Available	microEinsteins per square meter per second (uEinsteins/m^2/second)
PAR	CTD Photosynthetically Available [Active] Radiation	microEinsteins per square meter per second (uEinsteins/m^2/second)
Turbidity	CTD Turbidity	FTU
Attenuation	CTD Attenuation	1 per meter (1/m)
Transmission	CTD Transmission	%
TA	Total Alkalinity	micromole per kilogram (umol/kg)
flag_TA	Total Alkalinity final flag - flag_2 means precision <0.1%; Flag_3 means precision>0.1%	unitless
DIC	Total dissolved inorganic carbon	micromole per kilogram (umol/kg)
flag_DIC	Total dissolved inorganic carbon final flag - flag_2 means precision <0.1%; Flag_3 means precision>0.1%	unitless
pH_Electrode	pH measured by electrode (NBS scale)	unitless
flag_pHelec	pH measured by electrode final flag - flag_2 means precision <+-0.02; Flag_3 means precision>+-0.02	unitless
pH_Spec	Total scale pH measured by spectrometer	unitless
flag_pHspec	pH measure by spectrometer final flag - flag_2 means precision <+-0.005; Flag_3 means precision>+-0.005	unitless
DO_Spec	Dissolved oxygen measured by spectrometer at 25 degrees celcius	umol/L
flag_DOspec	Dissolved oxygen final flag - flag_2 means precision <+-0.7 umol L-1; Flag_3 means precision>0.7umol L-1	unitless

ISO_DateTime_UTC	Date/Time UTC in ISO format (YYYY-MM-DDTHH:MM:SSZ)	YYYY-MM-DDTHH:MM:SSZ

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Instruments

Dataset-specific Instrument Name	
Generic Instrument Name	CTD Sea-Bird 911
Dataset-specific Description	24-bottle rosette equipped with a SeaBird CTD 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	
Generic Instrument Name	Niskin bottle
Dataset-specific Description	24-bottle rosette
Generic Instrument Description	A Niskin bottle (a next generation water sampler based on the Nansen bottle) is a cylindrical, non-metallic water collection device with stoppers at both ends. The bottles can be attached individually on a hydrowire or deployed in 12, 24, or 36 bottle Rosette systems mounted on a frame and combined with a CTD. Niskin bottles are used to collect discrete water samples for a range of measurements including pigments, nutrients, plankton, etc.

Dataset-specific Instrument Name	
Generic Instrument Name	Spectrophotometer
Dataset-specific Description	Genesis 30 (Thomas Scientific) spectrophotometer at 466 nm
Generic Instrument Description	An instrument used to measure the relative absorption of electromagnetic radiation of different wavelengths in the near infra-red, visible and ultraviolet wavebands by samples.

Dataset-specific Instrument Name	
Generic Instrument Name	Winkler Oxygen Titrator
Dataset-specific Description	Used for DO_spec analysis
Generic Instrument Description	A Winkler Oxygen Titration system is used for determining concentration of dissolved oxygen in seawater.

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Deployments

PE17-18

Website	https://www.bco-dmo.org/deployment/772116
Platform	R/V Pelican
Start Date	2017-04-05
End Date	2017-04-16

PE18-02

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

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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 heath 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.

Related Project note:

There are overlapping cruises with the project "Sed Control on OA" https://www.bco-dmo.org/project/815333. Thus, while some water column data can be found under this project "nGOMx acidification", all benthic data can be found under the "Sed Control on OA" project.

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Funding

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

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