Houston Galveston Bay Carbonate

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Project

» <u>RAPID: Capturing the Signature of Hurricane Harvey on Texas Coastal Lagoons</u> (Hurricane Harvey Texas Lagoons)

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Abstract

Quantifying the direction and magnitude of CO2 flux in estuaries is necessary to constrain the global carbon cycle, yet carbonate systems and CO2 flux in subtropical and urbanized estuaries are not yet fully determined. To estimate the CO2 flux for Galveston Bay, a subtropical estuary located in the northwestern Gulf of Mexico proximal to the Houston-Galveston metroplex, monthly cruises were conducted along a transect extending from the Houston ship channel to the mouth of Galveston Bay and Gulf of Mexico from October 2017 to September 2018. On these cruises, discrete water samples were collected for laboratory analyses of total alkalinity (TA), total dissolved inorganic carbon (DIC), and pH, and aragonite saturation state (Ω Ar) was calculated. Mean Bay water TA was 2062.0 \pm 213.2 μ mol kg-1, DIC was 1863.7 \pm 160.9 μ mol kg-1, pH was 8.09 \pm 0.17, and Ω Ar was 2.43 \pm 0.96. When compared to theoretical river-ocean mixing scenarios, TA values fell above the mixing line in winter and summer, indicating production, while DIC values displayed more spatial variability that included both production and consumption in different seasons. A large freshwater inflow event in spring was followed by a period of dilution (low salinity, TA, and DIC) and enhanced primary production (low pCO2, water, CO2 uptake, and high chlorophyll-a levels). Carbonate chemistry in Galveston Bay was regulated by an interaction between hydrology and biogeochemistry. The carbonate chemistry and CO2 uptake patterns of Galveston Bay differ from those that are common in temperate estuaries, which reiterates the need for further research in subtropical estuaries.

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Coverage

Location: Galveston Bay, an estuary situated adjacent to the Northwestern Gulf of Mexico Spatial Extent: N:30 E:95.5 S:29 W:94.5 Temporal Extent: 2017-10-21 - 2018-09-16

Field sampling

Galveston Bay is a semi-enclosed microtidal estuary located in the nwGOM [42]. With an average water depth of 3 m and surface area covering 1554 km², Galveston Bay is the seventh largest estuary in the U.S. and the second largest estuary on the Texas coast [35, 43, 44]. Galveston Bay receives freshwater from the Trinity River, San Jacinto River, Clear Creek, and smaller bayous and creeks, with the Trinity River providing 70% of the freshwater entering the Bay [35, 45, 43, 44]. The Bolivar Peninsula and Galveston Island separate Galveston Bay from the GOM, with exchange of water between the Bay and the GOM occurring through Bolivar Roads, i.e., the mouth of the Bay [46, 43].

Monthly cruises were conducted between October 2017 and September 2018 on board the *R/V* Trident. Timing of the study allowed for examination of the factors regulating CO_2 flux over the course of a year following Hurricane Harvey in late August of 2017. Although the study began more than 45 days (the residence time of the Bay) after Harvey, salinity recovery of the Bay was likely still ongoing in the inner and middle sections of the Bay [47, 48].

During each monthly survey, a transect was run between five water sampling stations, extending northwest from the Bay mouth (Station 1) opening to the Five Mile Marker on the Houston Ship Channel (Station 5). One offshore cruise in the nwGOM outside Galveston Bay was conducted in October of 2018. At each station, surface (~0.5 m below water surface) and bottom water (~0.5 m above the sediment) samples for carbonate analyses were collected. A van Dorn sampler was used to collect unfiltered surface and bottom water into 250 mL borosilicate glass bottles for total alkalinity (TA), dissolved inorganic carbon (DIC), and pH analyses. 100 μ L saturated HgCl₂ was added to each water sample to cease biological activity and bottle stoppers were replaced following the application of Apiezon® grease and secured with rubber bands and hose clamps. The samples were stored at 4 °C in the dark until analyses, usually within 2–3 weeks of sample collection. Surface and bottom unpreserved water samples were collected in 125 mL polypropylene bottles for Ca²⁺ analysis.

Discrete sample analyses

Water samples collected at the surface and bottom at each station were analyzed for DIC, TA, pH, and salinity as in [53, 34]. DIC was analyzed by acidifying 0.5 mL water samples with 0.5 mL 10% H_3PO_4 using a 2.5 mL syringe pump on an AS-C3 DIC analyzer (Apollo SciTech Inc.) with a precision of ±0.1%. TA was analyzed at 22.0±0.1°C using gran titration of a 25 mL water sample with 0.1 M HCl solution (in 0.5 M NaCl) on an AS-Alk2 alkalinity titrator (Apollo SciTech Inc.), with a precision of ±0.1%. Precisions were estimated based on randomly collected duplicate samples. Reference Material (RM) produced in the lab of Andrew Dickson at Scripps was used in both TA and DIC analysis to ensure data quality [54].

A spectrophotometric method with a precision of ± 0.0004 , and purified m-cresol purple (mCP) obtained from Dr. Robert Byrne's lab (University of South Florida) [55] was used for pH (on the total scale) analysis [56]. Prior to each sample analysis, a calibrated OrionTM RossTM glass electrode was used to adjust the indicator to pH 7.92 \pm 0.01. A 10 cm water-jacketed absorbance cell for pH measurements [56] was kept at 25 \pm 0.01 °C. Consecutive runs were done for each sample whereby two volumes (30 µL and 60 µL) of mCP were added to correct the dye effect [57]. Equations from Liu et al. [55] were used when salinity was greater than 20 for the entirety of a sampling trip, and equations from Douglas and Byrne [58], which allows for a wider salinity range (0-40 vs. 20-40) [15] were used when salinity was less than 20 for an entire sampling trip, for calculations of pH. Calculated pH values (on total scale) were converted to in situ temperature using the program CO2SYS with DIC as the other input parameter.

Salinity was measured with a benchtop salinometer (Orion StarTM A12, Thermo Scientific), which was calibrated using MilliQ water and known salinity CRM seawater before each sample analysis. Calcium ([Ca²⁺]) concentration was measured using automatic potentiometric titration with ethylene glycol tetraacetic acid (EGTA), with a precision of $\pm 0.2\%$ [59]. A Metrohm® Titrando calcium-selective electrode on a titration system (Metrohm Titrando 888) was used to detect the endpoint.

Meteorological data

United States Geological Survey [62] streamgages for the Trinity River (gage #08066500) and San Jacinto River, east fork (SJE; gage #08070200) and west fork (SJW; gage #08068000) were used to obtain freshwater discharge. These stations were identified as the closest gages to the mouths of the rivers having complete discharge data for the period of study. Discharges of less than or equal to 45 days (residence time of the Bay) prior to flux estimates were utilized [43, 44]. The Texas Commission on Environmental Quality (TCEQ) performs routine water quality monitoring, and TCEQ water sampling stations were used for river endmember values from the San Jacinto (average of west fork station #11243 and east fork station #11238) and Trinity (station # 10896) rivers [63]. River endmember DIC was calculated from TA and pH measurements using K_1 and K_2 constants from Millero [64], and pH value on the NBS scale. Seasonally weighted averages were calculated by summing the TA or DIC concentration multiplied by daily discharge values for all river measurements of that season and dividing by the sum of all discharge values for all river measurements of that season (using meteorological seasons).

Data Processing Description

Carbonate speciation was calculated under field conditions (temperature and pressure) using the Excel® version of program CO2SYS [69] based on DIC and lab measured pH (at 25 °C) from discrete samples. Carbonic acid dissociation constants (K_1 , K_2) from Millero [64], bisulfate dissociation constant from Dickson [70], dissociation constant of HF (K_F) from Dickson and Riley [71] and total boron concentration from Uppström [72] were used.

The CO2SYS output for carbonate saturation state with respect to aragonite ($\Omega_{Ar, CO2SYS}$) was corrected using measured Ca²⁺ concentration, which exhibited a near linear relationship with salinity ($R^2 = 0.96$). This corrections was necessary for the estuary due to non-zero [Ca²⁺] of the riverine end member (Eq. 1),

 $\Omega_{Ar} = \Omega_{Ar, CO2SYS} \times [Ca^{2+}]m/[Ca^{2+}]th (1)$

where $[Ca^{2+}]_m$ is the measured $[Ca^{2+}]$ and $[Ca^{2+}]_{th}$ is the theoretical $[Ca^{2+}]$ based on salinity conducted in the CO2SYS program.

Problem Description

Missing values for some samples were omitted from the final analyses.

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Related Publications

Bass, B., Torres, J. M., Irza, J. N., Proft, J., Sebastian, A., Dawson, C., & Bedient, P. (2018). Surge dynamics across a complex bay coastline, Galveston Bay, TX. Coastal Engineering, 138, 165–183. https://doi.org/<u>10.1016/j.coastaleng.2018.04.019</u> *Methods*

Carter, B. R., Radich, J. A., Doyle, H. L., & Dickson, A. G. (2013). An automated system for spectrophotometric seawater pH measurements. Limnology and Oceanography: Methods, 11(1), 16–27. doi:<u>10.4319/lom.2013.11.16</u> *Methods*

Chen, N., Bianchi, T. S., & McKee, B. A. (2005). Early diagenesis of chloropigment biomarkers in the lower Mississippi River and Louisiana shelf: implications for carbon cycling in a river-dominated margin. Marine Chemistry, 93(2–4), 159–177. https://doi.org/<u>10.1016/j.marchem.2004.08.005</u> *Methods*

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:<u>10.1016/0967-0637(93)90048-8</u> *Methods*

Dellapenna, T. M., Hoelscher, C., Hill, L., Al Mukaimi, M. E., & Knap, A. (2020). How tropical cyclone flooding caused erosion and dispersal of mercury-contaminated sediment in an urban estuary: The impact of Hurricane Harvey on Buffalo Bayou and the San Jacinto Estuary, Galveston Bay, USA. Science of The Total Environment, 748, 141226. https://doi.org/<u>10.1016/j.scitotenv.2020.141226</u> *Methods*

Dickson, A. G., Afghan, J. D., & Anderson, G. C. (2003). Reference materials for oceanic CO2 analysis: a

method for the certification of total alkalinity. Marine Chemistry, 80(2), 185–197. https://doi.org/<u>10.1016/S0304-4203(02)00133-0</u> *Methods*

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

Du, J., & Park, K. (2019). Estuarine salinity recovery from an extreme precipitation event: Hurricane Harvey in Galveston Bay. Science of The Total Environment, 670, 1049–1059. https://doi.org/<u>10.1016/j.scitotenv.2019.03.265</u> *Methods*

Du, J., Park, K., Dellapenna, T. M., & Clay, J. M. (2019). Dramatic hydrodynamic and sedimentary responses in Galveston Bay and adjacent inner shelf to Hurricane Harvey. Science of The Total Environment, 653, 554–564. https://doi.org/<u>10.1016/j.scitotenv.2018.10.403</u> *Methods*

Glass, L. A., Rooker, J. R., Kraus, R. T., & Holt, G. J. (2008). Distribution, condition, and growth of newly settled southern flounder (Paralichthys lethostigma) in the Galveston Bay Estuary, TX. Journal of Sea Research, 59(4), 259–268. https://doi.org/<u>10.1016/j.seares.2008.02.006</u> *Methods*

Kanamori, S., & Ikegami, H. (1980). Computer-processed potentiometric titration for the determination of calcium and magnesium in sea water. Journal of the Oceanographical Society of Japan, 36(4), 177–184. https://doi.org/10.1007/bf02070330 <u>https://doi.org/10.1007/BF02070330</u> *Methods*

Lewis, E. R., & Wallace, D. W. R. (1998). Program Developed for CO2 System Calculations. Environmental System Science Data Infrastructure for a Virtual Ecosystem. https://doi.org/<u>10.15485/1464255</u> *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:<u>10.1021/es200665d</u>

Methods

Liu, Z., & Xue, J. (2020). The Lability and Source of Particulate Organic Matter in the Northern Gulf of Mexico Hypoxic Zone. Journal of Geophysical Research: Biogeosciences, 125(9). Portico. https://doi.org/10.1029/2020jg005653 <u>https://doi.org/10.1029/2020JG005653</u> *Methods*

Liu, Z., Lee, C., & Wakeham, S. G. (2006). Effects of mercuric chloride and protease inhibitors on degradation of particulate organic matter from the diatom Thalassiosira pseudonana. Organic Geochemistry, 37(9), 1003–1018. https://doi.org/<u>10.1016/j.orggeochem.2006.05.013</u> *Methods*

Montagna, P. A., Palmer, T. A., & Beseres Pollack, J. (2013). Hydrological Changes and Estuarine Dynamics. In SpringerBriefs in Environmental Science. Springer New York. https://doi.org/<u>10.1007/978-1-4614-5833-3</u> *Methods*

Morse, J. W., Presley, B. J., Taylor, R. J., Benoit, G., & Santschi, P. (1993). Trace metal chemistry of Galveston Bay: water, sediments and biota. Marine Environmental Research, 36(1), 1–37. https://doi.org/10.1016/0141-1136(93)90087-g https://doi.org/10.1016/0141-1136(93)90087-G Methods

Solis, R. S., & Powell, G. L. (1999). Hydrography, mixing characteristics, and residence times of Gulf of Mexico estuaries. In T. S. Bianchi, J. R. Pennock, & R. R. Twilley (Eds.), Biogeochemistry of Gulf of Mexico estuaries (pp. 29–62). New York, NY: John Wiley & Sons. *Methods*

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Parameters

Parameters for this dataset have not yet been identified

Instruments

Dataset- specific Instrument Name	AS-Alk2 alkalinity titrator (Apollo SciTech Inc.)
Generic Instrument Name	Apollo SciTech AS-ALK2 total alkalinity titrator
Dataset- specific Description	Total Alkalinity measurements were made with an AS-Alk2 alkalinity titrator (Apollo SciTech Inc.) and analyzed at 22.0+/-0.1 deg.C using gran titration of a 25 mL water sample with 0.1 M Hal solution (in 0.5 M NaCl), with a precision of +/-0.1%.
Generic Instrument Description	An automated acid-base titrator for use in aquatic carbon dioxide parameter analysis. The titrator provides standardisation and sample analysis, using the Gran titration procedure for alkalinity determination of seawater and brackish waters. It is designed for both shipboard and land based laboratory use. The precision of the instrument is 0.1 percent or higher, and sample volumes may range from 10-25 ml. Titration takes approximately 8 minutes per sample, and the repeatability is within plus or minus 1-2 micromoles per kg.

Dataset- specific Instrument Name	AS-C3 DIC analyzer (Apollo SciTech Inc.)
Generic Instrument Name	Apollo SciTech AS-C3 Dissolved Inorganic Carbon (DIC) analyzer
Dataset- specific Description	Dissolved Inorganic Carbon (DIC) measurements were performed with an AS-C3 DIC analyzer (Apollo SciTech Inc.) and analyzed by acidifying 0.5 mL water samples with 0.5 mL 10% H3PO4 using a 2.5 mL syringe pump, with a precision of +/-0.1%.
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 CO2 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 Nafion 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.

Dataset- specific Instrument Name	Titration System (Metrohm Titrando 888)
Generic Instrument Name	Automatic titrator
Dataset- specific Description	Calcium [Ca2+] concentration measurements were made with a Metrohm Titrando calcium- selective electrode on a titration system (Metrohm Titrando 888) and measured using automatic potentiometric titration with ethylene glycol tetra acetic acid (EGTA), with a precision of +/-0.2%
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	Benchtop Salinometer (OrionStar A12, Thermo Scientific)
Generic Instrument Name	Salinometer
Dataset- specific Description	Salinity was measured with a benchtop salinometer (Orion StarTM A12, Thermo Scientific), which was calibrated using MilliQ water and known salinity CRM seawater before each sample analysis. Calcium ([Ca2+]) concentration was measured using automatic potentiometric titration with ethylene glycol tetraacetic acid (EGTA), with a precision of ±0.2% [59]. A Metrohm® Titrando calcium-selective electrode on a titration system (Metrohm Titrando 888) was used to detect the endpoint.
Generic Instrument Description	A salinometer is a device designed to measure the salinity, or dissolved salt content, of a solution.

Dataset- specific Instrument Name	Spectrophotometric Method
Generic Instrument Name	Spectrophotometer
Dataset- specific Description	pH was analyzed using the spectrophotometric method and purified m-cresol purple (mCP) obtained from Dr. Robert Byrne's lab (University of South Florida), and was analyzed on the total scale with a precision of +/-0.0004. Prior to analyses, a calibrated OrionRoss glass electrode was used to adjust the indicator to pH 7.92+/-0.01, and a 10 cm water-jacketed absorbance cell of pH was kept at 25+/-0.01 deg.C.
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.

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Project Information

RAPID: Capturing the Signature of Hurricane Harvey on Texas Coastal Lagoons (Hurricane Harvey Texas Lagoons)

Coverage: Northwest Gulf of Mexico estuaries on Texas Coast

NSF Award Abstract:

Hurricane Harvey made landfall Friday 25 August 2017 about 30 miles northeast of Corpus Christi, Texas as a Category 4 hurricane with winds up to 130 mph. This is the strongest hurricane to hit the middle Texas coast since Carla in 1961. After the wind storm and storm surge, coastal flooding occurred due to the storm lingering over Texas for four more days, dumping as much as 50 inches of rain near Houston. This will produce one of the largest floods ever to hit the Texas coast, and it is estimated that the flood will be a one in a thousand year event. The Texas coast is characterized by lagoons behind barrier islands, and their ecology and biogeochemistry are strongly influenced by coastal hydrology. Because this coastline is dominated by open water systems and productivity is driven by the amount of freshwater inflow, Hurricane Harvey represents a massive inflow event that will likely cause tremendous changes to the coastal environments. Therefore, questions arise regarding how biogeochemical cycles of carbon, nutrients, and oxygen will be altered, whether massive phytoplankton blooms will occur, whether estuarine species will die when these systems turn into lakes, and how long recovery will take? The investigators are uniquely situated to mount this study not only

because of their location, just south of the path of the storm, but most importantly because the lead investigator has conducted sampling of these bays regularly for the past thirty years, providing a tremendous context in which to interpret the new data gathered. The knowledge gained from this study will provide a broader understanding of the effects of similar high intensity rainfall events, which are expected to increase in frequency and/or intensity in the future.

The primary research hypothesis is that: Increased inflows to estuaries will cause increased loads of inorganic and organic matter, which will in turn drive primary production and biological responses, and at the same time significantly enhance respiration of coastal blue carbon. A secondary hypothesis is that: The large change in salinity and dissolved oxygen deficits will kill or stress many estuarine and marine organisms. To test these hypotheses it is necessary to measure the temporal change in key indicators of biogeochemical processes, and biodiversity shifts. Thus, changes to the carbon, nitrogen and oxygen cycles, and the diversity of benthic organisms will be measured and compared to existing baselines. The PIs propose to sample the Lavaca-Colorado, Guadalupe, Nueces, and Laguna Madre estuaries as follows: 1) continuous sampling (via autonomous instruments) of salinity, temperature, pH, dissolved oxygen, and depth (i.e. tidal elevation); 2) biweekly to monthly sampling for dissolved and total organic carbon and organic nitrogen, carbonate system parameters, nutrients, and phytoplankton community composition; 3) quarterly measurements of sediment characteristics and benthic infauna. The project will support two graduate students. The PIs will communicate results to the public and to state agencies through existing collaborations.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1760006

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