Discrete bottle sample measurements for carbonate chemistry, organic alkalinity and organic carbon from samples collected in Waquoit Bay and Vineyard Sound, MA in 2016

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Project
» Collaborative Research: The Paradox of Salt Marshes as a Source of Alkalinity and Low pH, High Carbon Dioxide Water to the Ocean: A First In-depth Study of A Diminishing Source (Salt Marsh Paradox)

Contributors	Affiliation	Role
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Abstract
Discrete bottle sample measurements for carbonate chemistry, organic alkalinity and organic carbon from samples collected in Waquoit Bay and Vineyard Sound, MA in 2016.

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Coverage

Spatial Extent: **N**:41.5546 **E**:-70.4 **S**:41.5 **W**:-70.5071
Temporal Extent: 2016-05-09 - 2018-07-09

Methods & Sampling

Time-series bottle samples were collected from the Sage Lot Pond salt marsh tidal creek at approx. 41.5546N, 70.5071W. Samples were collected at ~0.2 m below the surface of tidal creek water every 1-2 h at the sampling site using a peristaltic or diaphragm pump for periods of a full tidal cycle (~12–14 h).Two coastal water samples were collected from the Woods Hole Oceanographic Institution Environmental Systems Laboratory intake, located about 1.6 km offshore in Vineyard Sound. Three goundwater samples were collected at the edge of Sage Lot Pond salt marsh at the elevation of 0.42 m, 0.75 m, and 1.66 m (NAVD88), corresponding to 0.56 m, 0.89 m, and 1.8 m below the land surface, respectively.

The DIC, TA, and pH collection followed standard best practice procedures outlined by Dickson et al. (2007).

OrgAlk sample collection followed the TA sampling protocol. Samples were collected through purgeable capsule filters with 0.45 um pore size (Farrwest Environmental Supply, Texas, USA) into 250 mL borosilicate bottles, poisoned with 100 uL saturated mercuric chloride, sealed with a HDPE screw top or a glass stopper coated with APIEZON® – L grease, and se- cured with a rubber band. Samples for DOC analysis were filtered through 0.45 um pore size polyethersulfone cartridge filters into combusted borosilicate glass vials with Teflon-lined silicone septa caps, acidified to pH < 2 with hydrochloric acid and refrigerated until analysis.

DIC was analyzed using an Apollo SciTech DIC auto-analyzer (Model AS-C3), which uses a nondispersive infrared (NDIR) method. The sample is acidified with a 10% phosphoric acid in 10% sodium chloride solution, and CO_2 is purged with high purity nitrogen gas and measured by a LI-COR 7000 infrared analyzer (LI-COR Environmental, Nebraska, USA). Certified Reference Material (CRM) from Dr. A. Dickson at Scripps Institution of Oceanography was used to calibrate the DIC auto-analyzer at least once daily. In addition, CRM was measured as a sample every few hours to gauge and correct any potential drift. The precision and accuracy of the instrument was ~ ± 2.0 μmol kg^{-1}.

TA was measured with a Ross combination pH electrode and a pH meter (ORION 3 Star) to perform a modified Gran titration (Wang and Cai, 2004). The electrode and concentration of hydrochloric acid was calibrated every day. The CRMs were also measured as samples every few hours to correct any potential small drift. The accuracy and precision of the measurement was about 2.5±1.9 μmol kg^{-1}.

The pH samples were measured with a UV-visible spectrophotometer (Agilent 8454, Agilent Technologies, USA) at 25 ± 0.1°C using purified meta-cresol purple (mcp) as an indicator. The pH values are reported on the total proton concentration scale and converted from 25 ± 0.1°C to in-situ temperature using measured DIC and the CO2SYS program (van Heuven et al., 2011). The mean uncertainty of the pH measurement was ± 0.006 (range 0.0003 – 0.017), calculated as the mean difference between duplicate samples.

OrgAlk concentration was determined with a digital syringe pump, a Ross combination pH electrode and a pH meter (ORION 3 Star), based on the procedure reported in Cai et al. (1998). OrgAlk sample was titrated with a calibrated HCl solution (~ 0.1 M) until the sample pH was below 3.0 (first titration). CO_2 in the sample was then removed by bubbling with high purity N_2 gas (99.999%) for ~ 10 minutes. The acidified sample was then titrated with 0.1 M NaOH solution back to its initial pH (back titration). The NaOH solution was prepared in DI water bubbled with high purity N_2 gas to prevent CO_2 dissolution into the solution. Finally, the sample was titrated with HCl again until its pH was below 3.0 (second titration). OrgAlk was calculated as the TA from the second titration minus the borate alkalinity. The mean difference of OrgAlk concentrations between duplicate samples was 2.8 ± 2.1 μmol kg^{-1}. Due to the existence of a small amount of CO_2 in the NaOH solution, the OrgAlk results were corrected by subtracting introduced carbonate alkalinity based on the volume of NaOH solution added during the back titration.

DOC samples were analyzed on an O. I. Analytical Aurora 1030C Autoanalyzer by high-temperature catalytic oxidation followed by nondispersive infrared detection (HTCO-NDIR). Concentrations are reported relative to a potassium hydrogen phthalate (KHP) standard. Hansell deep seawater (University of Miami Hansell Laboratory, Lot# 01-14), and Suwannee River NOM (IHSS, Lot# 2R101N) reference materials were analyzed daily as additional checks on precision and accuracy of the analyses. Standards and reference materials typically vary by < 5%.

Tidal water samples for practical salinity were analyzed with a Guideline AutoSal instrument at Woods Hole Oceanographic Institution. A YSI EXO2 Sonde (YSI Inc., Ohio, USA) was submerged in the tidal creek to measure temperature and water depth. Groundwater salinity and temperature were measured with a YSI Pro30 (YSI Inc., Ohio, USA) during collection. The YSI EXO2 recorded at intervals ranging from 2 min to 8 min. Reported YSI EXO2 sensor accuracy specifications are: 1% of the reading for salinity and 0.05 °C for temperature.

Data Processing Description

All EXO2 sensors were cleaned and calibrated regularly according to manufacturer recommended methods to maintain performance, and antifouling measures were deployed including copper and automated wiping. After a deployment period of 2–4 weeks, YSI EXO2 data were evaluated for fouling and calibration drift. The YSI EXO2 was recalibrated and a correction factor based on calibration standards was applied linearly across the deployment as needed. A maximum correction up to ± 30% of the calibration value was allowed or otherwise discarded (Wagner et al., 2006). Salinity and temperature values were interpolated to match the same time as the bottle sample collection.

BCO-DMO Processing:
- added columns for sample_descrip, lat, and lon from header rows in original Excel file;
- converted date to ISO 8601 format;
- filled empty cells with "nd" (no data).

Data Files

File
carb_chem_2016.csv (Comma Separated Values (.csv), 5.30 KB) MD5:57aede3ea6994915c56a0db81946ae6f
Primary data file for dataset ID 794163

Related Publications

Cai, W.-J., Wang, Y., & Hodson, R. E. (1998). Acid-Base Properties of Dissolved Organic Matter in the Estuarine Waters of Georgia, USA. Geochimica et Cosmochimica Acta, 62(3), 473–483. doi:10.1016/s0016-7037(97)00363-3 https://doi.org/10.1016/S0016-7037(97)00363-3
Methods

Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to best practices for ocean CO2 measurements. PICES Special Publication 3, 191 pp. ISBN: 1-897176-07-4. URL: https://www.nodc.noaa.gov/ocads/oceans/Handbook_2007.html https://hdl.handle.net/11329/249
Methods

Song, S., Wang, Z. A., Gonneea, M. E., Kroeger, K. D., Chu, S. N., Li, D., & Liang, H. (2020). An Important Biogeochemical Link between Organic and Inorganic Carbon Cycling: Effects of Organic Alkalinity on Carbonate Chemistry in Coastal Waters Influenced by Intertidal Salt Marshes. Geochimica et Cosmochimica Acta. doi:10.1016/j.gca.2020.02.013
Results

Van Heuven, S., Pierrot, D., Rae, J. W. B., Lewis, E., & Wallace, D. W. R. (2011). MATLAB Program Developed for CO2 System Calculations. ORNL/CDIAC-105b. Carbon Dioxide Information Analysis Center (CDIAC). https://doi.org/10.3334/CDIAC/OTG.CO2SYS_MATLAB_V1.1 https://doi.org/10.3334/CDIAC/otg.CO2SYS_MATLAB_v1.1
Software

Wagner, R. J., Boulger, R. W., Oblinger, C. J., & Smith, B. A. (2006). Guidelines and standard procedures for continuous water-quality monitors: Station operation, record computation, and data reporting. Techniques and Methods. doi:10.3133/tm1d3 https://doi.org/10.3133/tm1D3
Methods

Wang, Z. A., & Cai, W.-J. (2004). Carbon dioxide degassing and inorganic carbon export from a marsh-dominated estuary (the Duplin River): A marsh CO2pump. Limnology and Oceanography, 49(2), 341–354. doi:10.4319/lo.2004.49.2.0341
Methods

Parameters

Parameter	Description	Units
sample_descrip	Sample description	unitless
lat	Latitude of sample collection	decimal degrees
lon	Longitude of sample collection	decimal degrees
DIC	Dissolved inorganic carbon	micromoles per kilogram (umol kg-1)
TA	Total alkalinity	micromoles per kilogram (umol kg-1)
OrgAlk	Organic alkalinity	micromoles per kilogram (umol kg-1)
DOC	Dissolved organic carbon	micromoles per kilogram (umol kg-1)
pH	Water pH	unitless
Temp	Water temperature	degrees Celsius
Sal	Water salinity	practical salinity scale
Elevation	Water elevation (North American Vertical Datum of 1988 or NAVD88)	meters
ISO_DateTime_UTC	Date and time (UTC) in ISO 8601 format: yyyy-mm-ddTHH:MM:SSZ	unitless

Instruments

Dataset-specific Instrument Name	Apollo SciTech DIC auto-analyzer (Model AS-C3)
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 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	
Generic Instrument Name	Automatic titrator
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	LI-COR 7000 infrared analyzer
Generic Instrument Name	LI-COR LI-7000 Gas Analyzer
Generic Instrument Description	The LI-7000 CO2/H2O Gas Analyzer is a high performance, dual cell, differential gas analyzer. It was designed to expand on the capabilities of the LI-6262 CO2/ H2O Gas Analyzer. A dichroic beam splitter at the end of the optical path provides radiation to two separate detectors, one filtered to detect radiation absorption of CO2 and the other to detect absorption by H2O. The two separate detectors measure infrared absorption by CO2 and H2O in the same gas stream. The LI-7000 CO2/ H2O Gas Analyzer is a differential analyzer, in which a known concentration (which can be zero) gas is put in the reference cell, and an unknown gas is put in the sample cell.

Dataset-specific Instrument Name	ORION 3 Star pH electrode and pH meter
Generic Instrument Name	pH Sensor
Generic Instrument Description	An instrument that measures the hydrogen ion activity in solutions. The overall concentration of hydrogen ions is inversely related to its pH. The pH scale ranges from 0 to 14 and indicates whether acidic (more H+) or basic (less H+).

Dataset-specific Instrument Name	Peristaltic or diaphragm pump
Generic Instrument Name	Pump
Generic Instrument Description	A pump is a device that moves fluids (liquids or gases), or sometimes slurries, by mechanical action. Pumps can be classified into three major groups according to the method they use to move the fluid: direct lift, displacement, and gravity pumps

Dataset-specific Instrument Name	Agilent 8454 UV-visible spectrophotometer
Generic Instrument Name	Spectrophotometer
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	O.I. Analytical Aurora 1030C Autoanalyzer
Generic Instrument Name	Total Organic Carbon Analyzer
Generic Instrument Description	A unit that accurately determines the carbon concentrations of organic compounds typically by detecting and measuring its combustion product (CO2). See description document at: http://bcodata.whoi.edu/LaurentianGreatLakes_Chemistry/bs116.pdf

Dataset-specific Instrument Name	YSI EXO2 Sonde
Generic Instrument Name	YSI EXO multiparameter water quality sondes
Generic Instrument Description	Comprehensive multi-parameter, water-quality monitoring sondes designed for long-term monitoring, profiling and spot sampling. The EXO sondes are split into several categories: EXO1 Sonde, EXO2 Sonde, EXO3 Sonde. Each category has a slightly different design purpose with the the EXO2 and EXO3 containing more sensor ports than the EXO1. Data are collected using up to four user-replaceable sensors and an integral pressure transducer. Users communicate with the sonde via a field cable to an EXO Handheld, via Bluetooth wireless connection to a PC, or a USB connection to a PC. Typical parameter specifications for relevant sensors include dissolved oxygen with ranges of 0-50 mg/l, with a resolution of +/- 0.1 mg/l, an accuracy of 1 percent of reading for values between 0-20 mg/l and an accuracy of +/- 5 percent of reading for values 20-50 mg/l. Temp ranges are from -5 to +50 degC, with an accuracy of +/- 0.001 degC. Conductivity has a range of 0-200 mS/cm, with an accuracy of +/-0.5 percent of reading + 0.001 mS/cm and a resolution of 0.0001 - 0.01 mS/cm.

Project Information

Collaborative Research: The Paradox of Salt Marshes as a Source of Alkalinity and Low pH, High Carbon Dioxide Water to the Ocean: A First In-depth Study of A Diminishing Source (Salt Marsh Paradox)

Coverage: Sage Lot Pond salt marsh tidal creek in Waquoit Bay, MA at approx. 41.5546N, -70.5071W

NSF Award Abstract:
Carbon production in vegetated coastal systems such as marshes is among the highest in the biosphere. Resolving carbon production from marshes and assessing their impacts on coastal carbon cycling are critical to determining the long-term impacts of global change such as ocean acidification and eutrophication. In this project, researchers will use new methods to improve the assessment of carbon production from salt marshes. The overarching goals are to understand the role of coastal wetlands in altering carbonate chemistry, alkalinity, and carbon budgets of the coastal ocean, as well as their capacity to buffer against anthropogenically driven chemical changes, such as ocean acidification. This project will involve training for undergraduate, graduate, and postdoctoral researchers, and will provide educational opportunities for students from a local Native American tribe.

Tidal water, after exchange with intertidal salt marshes, contains higher total alkalinity (TA), higher carbon dioxide, but lower pH. These highly productive, vegetated wetlands are deemed to export both alkalinity and dissolved inorganic carbon (DIC) to the ocean. This creates an apppartent paradox in that salt marshes are both an acidifying and alkalizing source to the ocean. Limited studies suggest that marsh DIC and alkalinity export fluxes may be a significant player in regional and global carbon budgets, but the current estimates are

still far too uncertain to be conclusive. Unfortunately, tidal marsh ecosystems have dramatically diminished in the recent past, and are likely to diminish further due to sea level rise, land development, eutrophication, and other anthropogenic pressures. To assess the potential impacts of this future change, it is imperative to understand its current status and accurately evaluate its significatce to other parts of the carbon cycle. Similarly, little is know about the distinct sources of DIC and alkalinity being exported from marshes via tidal exchange, although aerobic and various anaerobic respiration processes have been indicated. In this study, researchers will undertake an in-depth study using new methods to vastly improve export fluxes from intertidal salt marshes through tidal exchange over minutes to annual scales, characterize and evaluate the compostiion (carbonate versus non-carbonate alkalinity) of marsh exported TA, the role and significance of the DOC pool in altering carbonate chemistry and export fluxes, identify sources of DIC being exported in tidal water, and investigate how marsh export of TA and DIC impacts carbonate chemistry and the carbon and alkalinity budgets in coastal waters.

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