# Discrete bottle sample measurements for carbonate chemistry from samples collected in the Sage Lot Pond salt marsh tidal creek in Waquoit Bay, MA from 2012 to 2015

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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 from samples collected in the Sage Lot Pond salt marsh tidal creek in Waquoit Bay, MA from 2012 to 2015.

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# Coverage

**Spatial Extent**: Lat:41.5546 Lon:-70.5071 **Temporal Extent**: 2012-04-09 - 2015-12-16

### Methods & Sampling

Samples were collected from the Sage Lot Pond salt marsh tidal creek in Waquoit Bay, MA at approx. 41.5546N, 70.5071W.

Discrete bottle samples were collected at ~30 cm above the bottom of the tidal creek every 1-2 h at the sampling site using a peristaltic or diaphragm pump for periods of a full tidal cycle (~12-14 h). DIC collection and analysis followed standard best practice procedures outlined by Dickson et al. (2007). Samples were collected through purgeable capsule filters with 0.45  $\mu$ m pore size (Farrwest Environmental Supply, Texas, USA) into 250 mL borosilicate bottles, poisoned with 100 uL saturated mercuric chloride, sealed with a glass stopper coated with APIEZON® – L grease, and se- cured with a rubber band.

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 CO2 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  $\sim \pm 2.0 \ \mu$ mol kg-1.

TA was measured with an Apollo SciTech alkalinity auto-titrator (Model AS-ALK2), 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 instrument was about  $\pm$  2.0 µmol kg-1.

An EXO2 Multiparameter Sonde (YSI Inc., Yellow Springs, OH) was submerged in the tidal creek to measure temperature and salinity. 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  $\pm$  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:** 

- modified parameter names (replaced spaces with underscores; removed units of measurement);
- formatted date/time to ISO format;
- replaced blanks with "nd" ("no data)".

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# **Data Files**

```
File

bottle.csv(Comma Separated Values (.csv), 10.18 KB)

MD5:d4d25db9ab42495bbe51003f814c134c
```

Primary data file for dataset ID 768577

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# **Related Publications**

Chu, S. N., Wang, Z. A., Gonneea, M. E., Kroeger, K. D., & Ganju, N. K. (2018). Deciphering the dynamics of inorganic carbon export from intertidal salt marshes using high-frequency measurements. Marine Chemistry, 206, 7–18. doi:<u>10.1016/j.marchem.2018.08.005</u> *Results* 

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 <u>https://hdl.handle.net/11329/249</u> *Methods* 

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 <u>https://doi.org/10.3133/tm1D3</u> *Methods*  Wang, Z. A., & Cai, W.-J. (2004). Carbon dioxide degassing and inorganic carbon export from a marshdominated estuary (the Duplin River): A marsh CO2pump. Limnology and Oceanography, 49(2), 341–354. doi:<u>10.4319/lo.2004.49.2.0341</u> *Methods* 

Wang, Z. A., Kroeger, K. D., Ganju, N. K., Gonneea, M. E., & Chu, S. N. (2016). Intertidal salt marshes as an important source of inorganic carbon to the coastal ocean. Limnology and Oceanography, 61(5), 1916–1931. doi:10.1002/lno.10347

Results

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## Parameters

Parameter	Description	Units
ISO_DateTime_UTC	Date and time (UTC) formatted to ISO 8601 standard. Format: yyyy-mm-ddTHH:MM:SS	unitless
DIC	Dissolved inorganic carbon (DIC)	micromoles per kilogram (umol kg-1)
ТА	Total alkalinity	micromoles per kilogram (umol kg-1)
TEMPERATURE	Water temperature	degrees Celsius
SALINITY	Water salinity	practical salinity scale

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# 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	Apollo SciTech alkalinity auto-titrator (Model AS-ALK2)	
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	ORION 3 Star pH meter
Generic Instrument Name	Benchtop pH Meter
Generic Instrument Description	An instrument consisting of an electronic voltmeter and pH-responsive electrode that gives a direct conversion of voltage differences to differences of pH at the measurement temperature. (McGraw-Hill Dictionary of Scientific and Technical Terms) This instrument does not map to the NERC instrument vocabulary term for 'pH Sensor' which measures values in the water column. Benchtop models are typically employed for stationary lab applications.

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	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	EXO2 Multiparameter Sonde (YSI Inc., Yellow Springs, OH)
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.

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# **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 composition (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.

# Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1459521</u>

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