

# All discrete TA/DIC samples from 2008-2012 collected from Bowdoin Buoy Mooring in the Lower Harpswell Sound, Casco Bay, Maine from 2011-2012

**Website:** <https://www.bco-dmo.org/dataset/546283>

**Version:** 26 Jan 2015

**Version Date:** 2015-01-26

## Project

» [River and sediment-modulated stress in planktonic and early settlement \*Mya arenaria\*](#) (OA stress in *Mya arenaria*)

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## Dataset Description

This data set includes all discrete TA/DIC samples from 2008-2012 collected in Casco Bay, Maine.

## Methods & Sampling

### Sample Collection

Discrete samples were collected from Niskin bottles or surface buckets in the estuary, and transferred to sample bottles through silicone tubing to prevent bubbling. Samples for pH, total alkalinity (TALK), and dissolved inorganic carbon (DIC) were transferred without bubbling into 60-ml glass BOD bottles with greased stoppers. These were filled to leave less than 1% headspace in the bottle, preserved with 0.1 ml of saturated mercuric chloride solution, and immediately cooled. Samples for TALK and DIC were generally stored for several weeks before analysis, allowing for settling of particulate material, with the supernatant sample drawn for analysis. DIC was measured first from each sample bottle, followed sequentially by pH and TALK.

### Temperature and Salinity Measurement

Temperature and salinity were measured in situ with either a SBE-37 thermosalinograph (Sea-Bird Electronics, Bellevue, WA) deployed as part of a profiling package (conductivity accuracy +/- 0.0003 S/m, temperature accuracy +/- 0.002 degrees C), or measured in situ with a handheld meter (YSI, Yellow Springs, Ohio) with a manufacturer-stated accuracy +/- 0.2 degrees C and +/- 1.0 uS.

### DIC Analysis

DIC of unfiltered water was determined using an automated analyzer built by Apollo SciTech (Bogart, GA). Immediately after opening the sample bottle, a digital syringe withdrew a small amount of sample (0.5 mL),

acidified it with 10% phosphoric acid and subsequently measured the evolved CO<sub>2</sub> with a Li-Cor 6262 non-dispersive infrared gas analyzer (similar to the method described by Cai and Wang 1998). Certified seawater reference materials from Dr. A. Dickson were used to determine DIC concentration by preparing a calibration curve covering the range of DIC from 200-2000 umol/kg (Dickson et al., 2003), with a resulting precision ranging from 0.05-0.5% (or 0.1-10 umol/kg), with an average of ~0.1% (2 umol/kg).

### TAlk and pH Analysis

TAlk and pH of unfiltered water were simultaneously measured by the same instrument, and thus pH and TAlk measurements are both based on the same pH electrode. The pH electrode used in the TAlk titration (Orion 3-Star, Thermo Fisher Inc.) was calibrated using three low ionic strength pH buffers certified on the U.S. National Bureau of Standards (NBS) scale to +/- 0.01, and the initial reading before the addition of acid titrant was taken as the sample pH<sub>NBS</sub> (pH on the NBS scale, hereafter simply referred to as pH).

TAlk was measured by Gran titration (Gran 1952) with 0.1N HCl using an automated titrator. This method adds an initial aliquot of acid to the sample in an open cell, generally lowering the sample pH<sub>NBS</sub> below 3.8, and then adds subsequent aliquots of titrant until the pH<sub>NBS</sub> changes linearly with the volume of acid added. The TAlk endpoint is then obtained from linear regression of the change of pH<sub>NBS</sub> against the volume of acid added, according to a Gran transformation:

$$GF = (v + V_0)/V_0 * 10^{(-pH)}$$

where GF is the resulting Gran Function, v is the volume of acid added to the sample, V<sub>0</sub> is the original sample volume, and pH is the pH value (in this case, on the NBS scale) measured after each successive addition of volume v. Multiple analyses of the Dickson reference material resulted in a calculated precision of this method of about 0.1% (or ~ +/- 2 umol/kg). The accuracy of the TAlk automated system, also calibrated with multiple batches of the Dickson CRM as discussed above, was +/- 3-4 umol/kg.

### References:

Cai, W.-J. and Wang, Y. 1998. The chemistry, fluxes and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. *Limnology and Oceanography* 43: 657-668.

Dickson, A.G., Afghan, J.D. and G.C. Anderson. 2003. Reference materials for oceanic CO<sub>2</sub> analysis: a method for the certification of total alkalinity. *Marine Chemistry* 80: 185-197. doi:[10.1016/S0304-4203\(02\)00133-0](https://doi.org/10.1016/S0304-4203(02)00133-0)

Gran, G. 1952. Determination of the equivalence point in potentiometric Titrations, Part II, *Analyst* 77: 661-671. doi:[10.1039/AN9527700661](https://doi.org/10.1039/AN9527700661)

### Data Processing Description

BCO-DMO replaced '-9999' with 'nd' to indicate 'no data' and added ISO\_DateTime.UTC column.

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### Data Files

File
<b>Bowdoin_buoy_discrete.csv</b> (Comma Separated Values (.csv), 15.66 KB) MD5:ee92829434da9c3d5d25abdb0585d6e5
Primary data file for dataset ID 546283

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### Parameters

Parameter	Description	Units
date	Month/day/year of sampling; UTC.	mm/dd/yy
month	2-digit month of sampling.	mm (01 to 12)
day	2-digit day of month of sampling.	dd (01 to 31)
year	4-digit year of sampling.	YYYY
time	Time (UTC), in hours and minutes; 24-hour clock.	HHMM
lat	Latitude; positive values = North.	decimal degrees
lon	Longitude; positive values = East.	decimal degrees
temp	Temperature.	degrees Celsius
sal	Salinity in PSU. The Sea-Bird and YSI use S/m and uS respectively to measure conductivity and then from that measurement they are converted to PSU.	PSU
depth	Sample depth.	meters
DIC	Dissolved Inorganic Carbon (DIC) concentration.	micromoles per kilogram (umol/kg)
TA	Total alkalinity.	micromoles per kilogram (umol/kg)
pH	pH-insitu-calculated	pH on the NBS scale
ISO_DateTime.UTC	Date and Time (UTC) formatted to ISO 8601 standard.	YYYY-MM-DDTHH:MM:SS[.xx]Z

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## Instruments

<b>Dataset-specific Instrument Name</b>	bucket
<b>Generic Instrument Name</b>	bucket
<b>Dataset-specific Description</b>	Discrete samples were collected from Niskin bottles or surface buckets in the estuary, and transferred to sample bottles through silicone tubing to prevent bubbling.
<b>Generic Instrument Description</b>	A bucket used to collect surface sea water samples.

<b>Dataset-specific Instrument Name</b>	DIC Automated Analyzer
<b>Generic Instrument Name</b>	Elemental Analyzer
<b>Dataset-specific Description</b>	DIC of unfiltered water was determined using an automated analyzer built by Apollo SciTech (Bogart, GA). (More information: <a href="http://www.apolloscitech.com/DIC.htm">http://www.apolloscitech.com/DIC.htm</a> )
<b>Generic Instrument Description</b>	Instruments that quantify carbon, nitrogen and sometimes other elements by combusting the sample at very high temperature and assaying the resulting gaseous oxides. Usually used for samples including organic material.

<b>Dataset-specific Instrument Name</b>	LI-COR LI-6262
<b>Generic Instrument Name</b>	LI-COR LI-6262 Gas Analyzer
<b>Dataset-specific Description</b>	Immediately after opening the sample bottle, a digital syringe withdrew a small amount of sample (0.5 mL), acidified it with 10% phosphoric acid and subsequently measured the evolved CO <sub>2</sub> with a Li-Cor 6262 non-dispersive infrared gas analyzer (similar to the method described by Cai and Wang 1998).
<b>Generic Instrument Description</b>	The LI-6262 CO <sub>2</sub> /H <sub>2</sub> O Gas Analyzer measures CO <sub>2</sub> flux in the environment. It was manufactured by LI-COR Biosciences Inc. (licor.com) from 1990 through 2005 and serial Numbers for this model have the prefix of IRG3-XXXX. The LI-6262 is a differential, non-dispersive, infrared (NDIR) gas analyzer. The CO <sub>2</sub> and H <sub>2</sub> O measurements are based on the difference in absorption of infrared (IR) radiation passing through two gas sampling cells. The reference cell is used for a gas of known CO <sub>2</sub> or H <sub>2</sub> O concentration, and the sample cell is used for a gas of unknown concentration. Infrared radiation is transmitted through both cell paths, and the output of the analyzer is proportional to the difference in absorption between the two (LI-6262 CO <sub>2</sub> /H <sub>2</sub> O Analyzer Operating and Service Manual, Publication Number 9003-59, March, 1996, pg 18).

<b>Dataset-specific Instrument Name</b>	Niskin bottle
<b>Generic Instrument Name</b>	Niskin bottle
<b>Dataset-specific Description</b>	Discrete samples were collected from Niskin bottles or surface buckets in the estuary, and transferred to sample bottles through silicone tubing to prevent bubbling.
<b>Generic Instrument Description</b>	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.

<b>Dataset-specific Instrument Name</b>	pH Sensor
<b>Generic Instrument Name</b>	pH Sensor
<b>Dataset-specific Description</b>	TAlk and pH of unfiltered water were simultaneously measured by the same instrument, and thus pH and TAlk measurements are both based on the same pH electrode. The pH electrode used in the TAlk titration was an Orion 3-Star (Thermo Fisher Inc.).
<b>Generic Instrument Description</b>	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 <sup>+</sup> ) or basic (less H <sup>+</sup> ).

<b>Dataset-specific Instrument Name</b>	SBE-37 Thermosalinograph
<b>Generic Instrument Name</b>	Thermosalinograph
<b>Dataset-specific Description</b>	Temperature and salinity was measured in situ with either a SBE-37 thermosalinograph (Sea-Bird Electronics, Bellevue, WA) deployed as part of a profiling package (conductivity accuracy +/- 0.0003 S/m, temperature accuracy +/- 0.002 degrees C), or measured in situ with a handheld meter (YSI, Yellow Springs, Ohio) with a manufacturer-stated accuracy +/- 0.2 degrees C and +/- 1.0 uS.
<b>Generic Instrument Description</b>	A thermosalinograph (TSG) is used to obtain a continuous record of sea surface temperature and salinity. On many research vessels the TSG is integrated into the ship's underway seawater sampling system and reported with the underway or alongtrack data.

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## Deployments

### Mooring\_D0205

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/546294">https://www.bco-dmo.org/deployment/546294</a>
<b>Platform</b>	Bowdoin Buoy
<b>Start Date</b>	2011-03-09
<b>End Date</b>	2012-03-08

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## Project Information

### **River and sediment-modulated stress in planktonic and early settlement *Mya arenaria* (OA stress in *Mya arenaria*)**

**Coverage:** Gulf of Maine: Kennebec River, Casco Bay

*Extracted from the NSF award abstract:*

Estuaries are productive, complex and have great economic value by virtue of their fisheries, ecosystem services and recreation potential. They are typically less buffered to acid than open oceans due to the combined effects of acid production during heterotrophy and acidic inputs from both land and atmosphere. Within estuaries, it is important to understand how varying acid burdens impact living resources, particularly those that provide ecosystem services and/or generate income as fisheries. The bivalve *Mya arenaria*, the focal species of this proposed research, is one such resource that sustains a valuable coastal fishery while providing service via its filtration capacity. Because *Mya* shells are constructed from a relatively soluble form of calcium carbonate (aragonite), and the clams often inhabit eutrophic waters, they may be particularly vulnerable as pH declines. Planktonic larvae and benthic juveniles are critical life stages -- even small reductions in their abundances could substantially decrease adult populations.

This proposed research addresses four distinct hypotheses concerning the roles of riverine and sediment interactions on the viability of larval and juvenile *Mya*. Research activities include the following.

1. Fieldwork will evaluate the spatial and seasonal changes in aragonite saturation state within the Kennebec River Estuary and Casco Bay. Seasonal sampling will be coupled with high-frequency sampling during the annual *Mya* spawn to observe and document the effect of lowered aragonite saturation state on the health status of larval *Mya*.
2. Using larval *Mya*, laboratory experiments will mimic the aragonite saturation state observed in Casco Bay during the high-frequency cruises. Metamorphic change (veligers, pediveligers, and metamorphosed juveniles), growth rate, and survivorship of *Mya* will be evaluated as a function of aragonite saturation state.
3. Spatially intensive daily cohort monitoring of the intertidal mud flats in Falmouth, Maine, will establish the link between changes in abundance of settling juveniles and aragonite saturation state during the period of *Mya* set. Cohort monitoring of settling *Mya* will be examined in reference to sediment pH and aragonite saturation state in nearby deposits to ascertain if sediment saturation state is a primary settlement cue for transitioning larvae.
4. A diagnostic model will be developed for the shellfish management community that can be used to detect aragonite saturation state of the water column. The model would run on routine oceanographic measurements (salinity, temperature, oxygen and chlorophyll fluorescence).

The chemical consequences of increasing atmospheric CO<sub>2</sub> and resulting hydrolysis of carbonic acid is well understood and resultant ocean acidification has been accurately predicted with the current generation of global circulation models. These predictions have accelerated research into the effects of ocean acidification on marine organisms, particularly those with CaCO<sub>3</sub> exoskeletons. Estuarine waters are far less buffered than oceans, are subject to a variety of acid loadings, and are quite possibly acidifying at a faster rate than the open ocean. Yet, these regions have been largely ignored in 'acidification' research. Effects of acidification on calcifying organisms are similar regardless of whether of acid origin -- atmospheric exchange, net heterotrophy, or discharge of acidic river water. Likewise, each of these acid fluxes is being perturbed via anthropogenic activity (e.g. fossil fuel use, deforestation, agriculture). The proposed research will further

understanding of the combined and cumulative impacts of varied acid burdens on calcifying organisms in coastal waters.

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## Funding

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-0961825</a>

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