Organic alkalinity data from estuary transects in Coastal Gulf of Maine (Pleasant, Maine; St. John, New Brunswick) in May and October of 2018 and 2019

Website: https://www.bco-dmo.org/dataset/918545
Data Type: Other Field Results
Version: 1
Version Date: 2024-01-25

Project
» Collaborative Research: Organic Alkalinity: Impacts of the [OTHER] Alkalinity on Estuary and Coastal Ocean Chemistry (organic alkalinity)

Contributors	Affiliation	Role
Hunt, Christopher	University of New Hampshire (UNH)	Principal Investigator
York, Amber D.	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract
Four organic alkalinity estuary transects, in May and October of 2018 and 2019, were completed in the Pleasant (Maine, USA) and St. John (New Brunswick, Canada) estuaries. Discrete samples were collected at intervals of salinity along each estuary. An underway measurements system was also operated during each transect (see "Related Datasets" section). Discrete samples were analyzed via a number of methods described below. Underway measurements were collected using the procedures described in Hunt et al. (2013). Organic alkalinity is a poorly understood component of the estuarine and coastal ocean acid-base system. This lack of understanding makes assessment of ocean acidification vulnerability and inorganic carbon dynamics more difficult. However, the methods used to quantify organic alkalinity and its effects on the acid-base system are not standardized. In this work we examined several approaches for the measurement of organic alkalinity, and their application to inorganic carbon dynamics.

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Coverage

Location: Coastal Gulf of Maine: Pleasant (Maine, USA) and St. John (New Brunswick, CA)
Spatial Extent: **N**:45.941 **E**:-66.001 **S**:44.48 **W**:-67.764
Temporal Extent: 2018-05-15 - 2019-10-24

Dataset Description

This project was a collaboration between Dr. Christopher W. Hunt and Dr. Joseph Salisbury (of the University of New Hampshire) and Dr. Xuewu Liu and Dr. Robert H. Byrne (of the University of South Florida).

Methods & Sampling

Sampling was conducted during day trips on Pleasant (Maine, USA) and St. John (New Brunswick, CA) estuaries in May and October 2018 and 2019.

* See "Related Datasets" section for access to the related Underway Data described below.

Sample Collection:

Four surveys were conducted of both the Pleasant and St. John estuaries, in May and October 2018, and again in May and October 2019 in order to assess potential differences in estuary conditions between spring and fall seasons. Estuary samples were collected during single-day surveys on small vessels in each system, departing from Addison Maine for Pleasant estuary surveys and from St. John, New Brunswick, for St. John surveys. Estuary water was continuously pumped to an underway measurement system, which recorded location, salinity(Seabird SBE-45), water temperature (Seabird SBE-45), and the partial pressure of carbon dioxide (pCO2) among other parameters. Surveys were started on the incoming tide and lasted through high tide and into the ebb tide. At intervals determined from the underway salinity, surface water was captured for discrete sample collection. During the October 2017 and May 2018 surveys a Niskin bottle was lowered overboard by hand; during the later surveys a 10-liter high-density polyethylene (HDPE) carboy was rinsed and filled from the outflow of the underway system, then tightly capped until samples were drawn from a spout at the bottom of the carboy. River endmember samples were collected from above the final downstream dam on each river. For the Pleasant, this dam formed a physical tidal barrier, and the transition from river to estuary was immediate. For the St. John the closest site was in Fredericton New Brunswick, a location over 120 km from the estuary mouth along the river's course. For both endmember sites, a plastic bucket was lowered from the center of a bridge over the river, rinsed three times with river water, and samples were collected as described above. The temperature and conductivity of samples were measured directly from the bucket with a handheld meter (YSI, Yellow Springs, Ohio).

Water from the Niskin or carboy was transferred without bubbling into individual, previously-flushed borosilicate glass BOD bottles: 500 mL for alkalinity and pHT analyses, and 300 mL for inorganic carbon (DIC) analysis. All bottles had greased stoppers and positive closure mechanisms, were filled to leave less than 1% headspace in the bottle, and were preserved with saturated mercuric chloride solution. Samples for silicate and phosphate analysis were filtered using a plastic syringe and 0.2 μm cartridge filter into acid-washed and previously-rinsed 50 mL HDPE vials and preserved with chloroform. Samples for DOC were filtered as was done for the nutrients into acid-washed and previously-rinsed 30 mL HDPE bottles. All samples were immediately placed on ice. Alkalinity, pH, and DIC samples were refrigerated until analysis; nutrient and DOC samples were frozen until analysis.

Instruments:

Discrete sample salinity was measured with a Guildline Portasal salinometer (Guildline, Smiths Falls Canada). The pHT of samples above pHT 7.0 was measured spectrophotometrically with meta-cresol purple (mCP), using 10 cm pathlength cylindrical glass cells and an Agilent Technologies Cary 8454 UV-Vis spectrometer. The same instrument was used to verify the response slope of a combination glass pH electrode (Metrohm EcoTode Plus). For samples of pHT less than 7.0, and therefore outside the working range of mCP, the initial electrode mV reading and zero-pHT intercept potential (E0) value determined from the AlkGran1 titration were used to calculate the pHT of the untitrated sample. DOC was measured with an uncertainty of 1.5 μmol kg-1 using a Shimadzu high temperature catalytic oxidation analyzer with chemiluminescent detection. Nutrients including phosphate and silicate were analyzed using a SmartChem automated analyzer (Westco Scientific) according to standard colorimetric methods. The resulting measurement uncertainties were 0.8 μmol kg-1 and 0.25 μmol kg-1, respectively (Strickland and Parsons 1972). DIC was measured by acidifying each sample in a custom-built gas extraction system and measuring the evolved CO2 with a Picarro G5131-I cavity ringdown spectrometer (Picarro, Santa Clara CA).

Alkalinity Titrations
Total alkalinity and organic alkalinity titrations were conducted using a custom-built apparatus similar to that presented in Cai et al. (1998). This system performed several successive titrations on the same water sample. The total alkalinity was measured by Gran titration (AlkGran1) , followed by the carbonate-free alkalinity that was also measured using the Gran titration approach (AlkGran2), and finally the carbonate-free alkalinity was measured according to an endpoint approach at pHT 4.5 (Alk4.5). Samples were initially titrated from the initial pHT (pHi) to a pHT of 3.5, bubbled with nitrogen, then titrated to pHT 3.0 (AlkGran1). CO2-free NaOH was then added to return the sample to an alkaline pHi. The sample was then titrated to pHT 3.0 (AlkGran2). This process was then repeated, with the final titration ending at pHT 4.5 (Alk4.5).

NaOH titrations
We generally followed the methods presented by Cai et al. (1998), Song et al. (2020), and Kerr et al. (2023a) to estimate both organic functional group concentrations (XTi) and corresponding acid dissociation constants (pKai). Briefly, a sample was acidified to pHT 3.0 via Gran titration (AlkGran1), then automatically titrated stepwise under nitrogen with small additions of CO2-free NaOH from pHT 3.0 to pHT 8.5 or 10, resulting in several hundred sequential NaOH additions.

BCO-DMO Processing Description

* Sheet 1 of file "Hunt et al Organic Alkalinity Data.xlsx" was imported into the BCO-DMO data system with values "n/m" as missing data values.
** Missing data values are displayed differently based on the file format you download. They are blank in csv files, "NaN" in MatLab files, etc.

* Column names adjusted to conform to BCO-DMO naming conventions designed to support broad re-use by a variety of research tools and scripting languages. [Only numbers, letters, and underscores. Can not start with a number]

* ISO_DateTime_UTC in ISO 8601 format added as a colunn.

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Data Files

File
918545_v1_organic-alkalinity.csv (Comma Separated Values (.csv), 14.33 KB)   MD5:a913f947cc1049bb7d6c32a2edb5c8de   Primary data file for dataset ID 918545, version 1

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Supplemental Files

File
Whole-pH titration files and model fitting routine   filename: Whole-pH_Titration.zip (ZIP Archive (ZIP), 191.99 KB)   MD5:023a4134607bdb59f6c04b853de69483   This .zip package contains 65 individual whole-pH titration files (.txt). There is one file for every sample in this dataset this dataset. XT/Korg value is also included.   This package also contains two matlab .m files: model_XT_OrgK_HCl.m - Matlab function for performing the whole-pH fitting. Note that the model fitting routine will not reproduce exactly the same K and XT values as those listed in the Discrete Data file (.txt) (and will not return exactly the same values upon multiple runs of the program on the same data file).   %Program to analyze whole-pH titration data for organic alkalinity   %written by Chris Hunt, University of New Hampshire, chunt@unh.edu   % [sam]=function_calc_OrgAlk_pKa_HCl   [sam_file,datadir] = uigetfile('*.txt');   ---   sumsq_calc.m -This is a supporting function called by model_XT_OrgK_HCl.m (matlab)   function [sumsq] = sumsq_calc(inputs,mass_acid,H,ST,KS,Z,mass,acid_c,FT,KH)

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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

Hinckley, Jessica A., "The Non-Conservative Behavior of Organic Alkalinity in Simulated Gulf of Maine Estuary Mixing" (2021). Master's Theses and Capstones. 1512. https://scholars.unh.edu/thesis/1512
Results

Hunt, C. W., Salisbury, J. E., & Vandemark, D. (2013). CO2 Input Dynamics and Air–Sea Exchange in a Large New England Estuary. Estuaries and Coasts, 37(5), 1078–1091. https://doi.org/10.1007/s12237-013-9749-2
Methods

Hunt, C.W., Salisbury, J.E., Liu, X., and R.H. Byrne. 2023. Estuary Organic Alkalinity Distributions, Characteristics, and Application to Carbonate System Calculations (in prep).
Results

Hunt, Christopher, "Alkalinity and Buffering in Estuarine, Coastal and Shelf Waters" (2021). Doctoral Dissertations. 2623. https://scholars.unh.edu/dissertation/2623
Results

Kerr, D. E., Turner, C., Grey, A., Keogh, J., Brown, P. J., & Kelleher, B. P. (2023). OrgAlkCalc: Estimation of organic alkalinity quantities and acid-base properties with proof of concept in Dublin Bay. Marine Chemistry, 251, 104234. https://doi.org/10.1016/j.marchem.2023.104234
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

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Related Datasets

IsRelatedTo

Hunt, C. (2024) **Underway data from estuary transects in Coastal Gulf of Maine (Pleasant, Maine; St. John, New Brunswick) in May and October of 2018 and 2019.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2024-01-26 doi:10.26008/1912/bco-dmo.918590.1 [view at BCO-DMO]
Relationship Description: Data collected from the same estuary transects, in May and October of 2018 and 2019, completed in the Pleasant (Maine, USA) and St. John (New Brunswick, Canada) estuaries.

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Parameters

Parameter	Description	Units
ID	Sample identification number for each estuary transect	unitless
Collection_Date	Collection Date (mm/dd/yyyy)	unitless
Collection_Time	Collection Time, in Universal Time (i.e. Greenwich Mean Time)	unitless
ISO_DateTime_UTC	Collection DateTime in ISO 8601 format	unitless
Latitude	Station Latitude, south is negative	decimal degrees
Longitude	Station Longitude, west is negative	decimal degrees
Salinity	Sample salinity measured by the Guildline PortaSal	unitless
In_Situ_Water_Temperature	Sample temperature measured by the Seabird SBE-45	degrees Celcius
pHT	pH on the Total Scale, measured at 25 degrees Celcius	unitless (total scale)
pH_Method	mCP=spectrophotometrically using meta-cresol purple, Electrode=via potentiometric pH electrode	unitless
pCO2	Partial Pressure of carbon dioxide in estuary water equilibrated with atmospheric air	microatmospheres
DOC	Dissolved Organic Carbon	micromoles carbon per liter
T_Alk	Total alkalinity from initial Gran titration	micromoles per kilogram
DIC	Dissolved Inorganic Carbon	micromoles per kilogram
OrgAlk_from_Endpoint_Titration	Organic Alkalinity at pH 4.5 from titration of carbonate-free sample	micromoles per kilogram
OrgAlk_from_Second_Gran_Titration	Organic Alkalinity from Second Gran titration of carbonate-free sample	micromoles per kilogram
SiO2	Silicate concentration	micromoles per liter
PO4	Phosphate concentration	micromoles per liter
X1T	Modeled concentration of first organic functional group	moles per kilogram
K1org	Modeled dissociation constant of first organic functional group	unitless
X2T	Modeled concentration of second organic functional group	moles per kilogram
K2org	Modeled dissociation constant of second organic functional group	unitless
X3T	Modeled concentration of third organic functional group	moles per kilogram
K3org	Modeled dissociation constant of third organic functional group	unitless

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Instruments

Dataset-specific Instrument Name	SmartChem automated analyzer (Westco Scientific)
Generic Instrument Name	Discrete Analyzer
Generic Instrument Description	Discrete analyzers utilize discrete reaction wells to mix and develop the colorimetric reaction, allowing for a wide variety of assays to be performed from one sample. These instruments are ideal for drinking water, wastewater, soil testing, environmental and university or research applications where multiple assays and high throughput are required.

Dataset-specific Instrument Name	
Generic Instrument Name	Niskin bottle
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	pH electrode (Metrohm EcoTode Plus)
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	Guildline Portasal salinometer (Guildline, Smiths Falls Canada)
Generic Instrument Name	Salinometer
Dataset-specific Description	Discrete sample salinity was measured with a Guildline Portasal salinometer (Guildline, Smiths Falls Canada).
Generic Instrument Description	A salinometer is a device designed to measure the salinity, or dissolved salt content, of a solution.

Dataset-specific Instrument Name	
Generic Instrument Name	Sea-Bird SBE 45 MicroTSG Thermosalinograph
Dataset-specific Description	. Estuary water was continuously pumped to an underway measurement system, which recorded location, salinity(Seabird SBE-45), water temperature (Seabird SBE-45), and the partial pressure of carbon dioxide (pCO2) among other parameters.
Generic Instrument Description	A small externally powered, high-accuracy instrument, designed for shipboard determination of sea surface (pumped-water) conductivity and temperature. It is constructed of plastic and titanium to ensure long life with minimum maintenance. It may optionally be interfaced to an external SBE 38 hull temperature sensor. Sea Bird SBE 45 MicroTSG (Thermosalinograph)

Dataset-specific Instrument Name	Shimadzu high temperature catalytic oxidation analyzer with chemiluminescent detection
Generic Instrument Name	Shimadzu TOC-L Analyzer
Dataset-specific Description	DOC was measured with an uncertainty of 1.5 µmol kg-1 using a Shimadzu high temperature catalytic oxidation analyzer with chemiluminescent detection.
Generic Instrument Description	A Shimadzu TOC-L Analyzer measures DOC by high temperature combustion method. Developed by Shimadzu, the 680 degree C combustion catalytic oxidation method is now used worldwide. One of its most important features is the capacity to efficiently oxidize hard-to-decompose organic compounds, including insoluble and macromolecular organic compounds. The 680 degree C combustion catalytic oxidation method has been adopted for the TOC-L series. http://www.shimadzu.com/an/toc/lab/toc-l2.html

Dataset-specific Instrument Name	Agilent Technologies Cary 8454 UV-Vis spectrometer
Generic Instrument Name	Spectrometer
Generic Instrument Description	A spectrometer is an optical instrument used to measure properties of light over a specific portion of the electromagnetic spectrum.

Dataset-specific Instrument Name	Picarro G5131-I cavity ringdown spectrometer (Picarro, Santa Clara CA)
Generic Instrument Name	Spectrometer
Generic Instrument Description	A spectrometer is an optical instrument used to measure properties of light over a specific portion of the electromagnetic spectrum.

Dataset-specific Instrument Name	handheld meter (YSI, Yellow Springs, Ohio).
Generic Instrument Name	Thermosalinograph
Generic Instrument Description	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.

Project Information

Collaborative Research: Organic Alkalinity: Impacts of the [OTHER] Alkalinity on Estuary and Coastal Ocean Chemistry (organic alkalinity)

Coverage: Laboratory Research and Florida, New Hampshire, Maine

NSF Award Abstact:

Estuaries are bodies of water formed where rivers meet the ocean, and are important ecosystems that provide protected environments and abundant food for fish and shellfish to reproduce. Many estuary systems are under pressure by changing atmospheric and oceanic conditions, as well as impacts on the rivers that empty into them. Scientists from the University of New Hampshire and the University of South Florida propose that the total alkalinity of some coastal systems, influenced by river runoff, may contain a large fraction of organic acids that have been previously ignored and may play a role in the acid-base chemistry of the estuary. This project would focus on understanding the organic and inorganic acid-base chemistry in estuaries. The project will support a PhD student and several undergraduate students, as well as high school interns from minority communities, broadening participation in the ocean sciences. Also, the monitoring and outreach capacity of a regional wild fishery conservation group will be enhanced, allowing the public to be more fully informed on the effect of ongoing estuarine changes on fisheries.

This project will be a comparison study of two estuary-plume systems to examine the exact buffering impact of organic alkalinity on the acid-base properties of coastal systems. The Pleasant (Maine) and St. John (Canada) estuaries represent extremes of river acid-base systems, where the Pleasant is comprised mostly of organic alkalinity and the St. John has a small organic alkalinity fraction. It is hypothesized by these scientists that some coastal regions may experience organic alkalinity as the dominant alkalinity factor in the total alkalinity distribution. This would mean that organic alkalinity would be the dominant factor affecting system pH, pCO2 (partial pressure of carbon dioxide), and the saturation index of aragonite. By doing this river endmember study into organic alkalinity of these two systems, these scientists will provide the tools for the entire oceanographic community to assess the buffering capability of organic alkalinity in other coastal systems and how the systems are likely to respond to acidification.

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1658321
NSF Division of Ocean Sciences (NSF OCE)	OCE-1658377