# Depth profiles of pore water constituents from sediment cores collected on the Louisiana Shelf of the Northern Gulf of Mexico during November 2020 on R/V Savannah cruise SAV-20-07

Website: https://www.bco-dmo.org/dataset/904417 Data Type: Cruise Results Version: 1 Version Date: 2023-07-18

### Project

» <u>Importance of Riverine Discharge on the Benthic Flux of Alkalinity to Continental Margins</u> (NGoM Benthic Alk Flux)

Contributors	Affiliation	Role
Taillefert, Martial	Georgia Institute of Technology (GA Tech)	Principal Investigator
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## Abstract

This data set reports depth profiles of pore water concentrations of dissolved inorganic carbon (DIC), orthophosphate (PO43-), ammonium (NH4+), total alkalinity (TA), carbon isotopic fractionation of DIC (13C-DIC), dissolved manganese (Mnd), dissolved calcium (Cad), reduced iron (Fe(II)), total dissolved Fe (Fed), and dissolved Fe(III) (Fe(III)d) by the difference of total dissolved Fe and Fe(II). These pore water data were obtained from sediment cores collected at five different stations on the Louisiana Shelf on the Northern Gulf of Mexico during the week of November 3-6, 2020 using an MC-800 multi-corer. These stations extend from the middle of the shelf offshore from Cocodrie, LA to the mouth of the Mississippi River North West Pass. All cores were processed within a few hours after collection. The field sampling was conducted during R/V Savannah cruise SAV-20-07. The pore waters were first extracted by slicing sediment cores of < 25 centimeters (cm) long and centrifugation of the pore waters under N2 atmosphere to avoid air contamination. Pore waters were then immediately filtered through 0.22-micrometer (um) PSE syringe filters under N2 atmosphere and either analyzed immediately onboard (Fe speciation, orthophosphate, DIC), preserved acidified with hydrochloric acid at 4 degrees Celsius (Cad, Mnd), frozen (ammonium), or preserved at 4 degrees Celsius after addition of HgCl2 (TA) until analysis. In addition, samples for TA and carbon isotopic analyses were preserved in glass bottles, whereas other samples were preserved in polypropylene containers. DIC was analyzed by flow injection analysis (Hall and Aller, 1992), orthophosphate, ammonium, and Fe speciation by spectrophotometry (Murphy and Riley, 1962; Strickland and Parsons, 1972; Stookey, 1970), TA by Gran titration (Gran, 1952), the carbon isotopic signature by isotope ratio mass spectrometry (Wang et al, 2018), and Mnd and Cad by ICP-MS (Magette et al., 2023 In preparation). "nd" in the spreadsheet is provided when samples were not analyzed for these species ("nd" = not determined).

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## Coverage

Spatial Extent: N:28.913378 E:-89.599387 S:28.603532 W:-90.304053 Temporal Extent: 2020-11-03 - 2020-11-06

### Methods & Sampling

Sediments were collected and pore waters were extracted within 30 minutes after sampling. Pore waters were obtained by centrifugation at 3000 rotations per minute (rpm) for less than 10 minutes after slicing the cores in a sealed anaerobic two-hands bag flushed three times with UHP N2 gas. Pore waters were immediately filtered onto 0.22-micrometer ( $\mu$ m) Whatman 25-millimeter (mm) Acrodisc syringe filters (PES membrane) and either preserved until analysis or analyzed immediately onboard the ship. Samples were preserved at 4° Celsius after acidification (dissolved Ca, dissolved Mn, NH4+) or addition of HgCl2 ( $\delta$ 13C-DIC, TA), dispensed directly into reagents for analysis (Fe(II), total dissolved Fe,  $\Sigma$ PO43-), or analyzed immediately (DIC). Sealed borosilicate glass vials were used for TA and  $\delta$ 13C-DIC as recommended (Dickson et al., 2007; Wang et al., 2018).

NH4+ was measured spectrophotometrically by the indophenol blue method (Strickland and Parsons, 1972), total dissolved Fe and Fe(II) were measured spectrophotometrically by the ferrozine method after the addition or not of hydroxylamine (Stookey, 1970). ΣΡΟ43- was measured spectrophotometrically using the molybdateblue method after natural color correction to avoid interferences from dissolved silica and sulfides (Murphy and Riley, 1962). DIC was measured by flow injection analysis with conductivity detection after spiking samples with 10 millimoles (mM) ZnCl2 to prevent dissolved sulfide interferences (Hall and Aller, 1992). TA was measured by acid titration in an open-cell with continuous pH measurements (Dickson et al., 2007; Rassmann et al., 2016). δ13C-DIC was measured using an isotope ratio mass spectrometer with high-performance liquid chromatography preparation module for gas samples (Brandes, 2009; Wang et al., 2018). Finally, dissolved Ca and dissolved Mn were measured by ICP-MS with collision cell to prevent argon interferences. Internal standards were used to correct for the drift of the instrument, quality control blanks, standard checks, and certified seawater references were run several times during each run to control accuracy and reproducibility. All calibrations were conducted with at least five standards prepared in a 0.54 molar (M) NaCl matrix prior to each series of measurements. Blanks and quality control checks were run routinely during each analysis. Finally, calibrations sensitivities were compared routinely to ensure accuracy of the methods. For DIC analyses, Dickson DIC certified seawater samples were run routinely during analyses to validate the accuracy of the method. Errors of all reported concentrations represent the analytical error propagated from calibration curves, dilution, and instrumental drift.

#### Instruments:

Sediment cores were collected with a MC-800 multi-corer (Ocean Instruments). Core barrels of 10 cm inner diameter and 75 cm long were used to collect sediments. Aldrich two-glove atmospheric bags were used to control the atmosphere during pore water extraction and centrifugation with an ELMI CM-7S clinical centrifuge. All spectrophotometric measurements were conducted with a Beckman Coulter DU 720 UV-vis spectrophotometer. DIC measurements were conducted with an in-house system consisting of a Dynamax peristaltic pump, Rheodyne injection valve, Amber Science conductivity detector, and Analytical Instruments, Inc. LCC-100 integrator with computer control. TA measurements were obtained with a computer-controlled Metrohm 877 Titrino plus. 613C-DIC measurements were conducted with a Thermo Electron SurveyorLite autosampler, a Surveyor MS HPLC pump, and a LC Isolink interface coupled to a Thermo Scientific Delta V plus stable isotope mass spectrometer. Finally, Finally, Cad and Mnd measurements were conducted with an Agilent 7900e ICP-MS with SPS4 Autosampler.

#### **Known Issues or Problems:**

"nd" in the dataset is provided when the chemical species was not determined, typically because pore water volumes were too small to be able to conduct all analyses in the same sample. All data sets provided have been analytically validated via the procedures described above.

#### **Data Processing Description**

#### **Data Processing:**

Spectrophotometric measurements were recorded on paper forms specifically designed for each analysis and digitized to process the data. DIC, TA,  $\delta$ 13C-DIC, and ICP-MS data were acquired by computers. DIC chromatographic data were integrated using Matlab-based software developed in-house (Bristow and Taillefert, 2008). TA,  $\delta$ 13C-DIC, and ICP-MS data were processed through Excel macro spreadsheet routines developed for each of these analyses.

In the data file, standard deviations of either duplicate analyses or analytical error are provided with each parameter.

#### **BCO-DMO Processing:**

- imported original file named "GOM Fall2020 PoreWaterData BCO-DMO.xlsx" into the BCO-DMO system;
- added "Date" column from the separate "Year", "Month", and "Day" columns;
- renamed fields to comply with BCO-DMO naming conventions;
- named the final file "904417\_v1\_pore\_water\_fall2020.csv".

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## **Related Publications**

Brandes, J. A. (2009). Rapid and precise δ13C measurement of dissolved inorganic carbon in natural waters using liquid chromatography coupled to an isotope-ratio mass spectrometer. Limnology and Oceanography: Methods, 7(11), 730–739. Portico. https://doi.org/10.4319/lom.2009.7.730 Methods

Bristow, G., & Taillefert, M. (2008). VOLTINT: A Matlab®-based program for semi-automated processing of geochemical data acquired by voltammetry. Computers & Geosciences, 34(2), 153–162. doi:<u>10.1016/j.cageo.2007.01.005</u> *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 <u>https://isbnsearch.org/isbn/1-897176-07-4</u> *Methods* 

Hall, P. . J., & Aller, R. C. (1992). Rapid, small-volume, flow injection analysis for total CO2, and NH4+ in marine and freshwaters. Limnology and Oceanography, 37(5), 1113–1119. doi:<u>10.4319/lo.1992.37.5.1113</u> *Methods* 

Murphy, J., & Riley, J. P. (1962). A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta, 27, 31–36. doi:10.1016/s0003-2670(00)88444-5 <a href="https://doi.org/10.1016/S0003-2670(00)88444-5">https://doi.org/10.1016/S0003-2670(00)88444-5</a> *Methods* 

Rassmann, J., Lansard, B., Pozzato, L., & Rabouille, C. (2016). Carbonate chemistry in sediment porewaters of the Rhone River delta driven by early diagenesis (northwestern Mediterranean). Biogeosciences, 13(18), 5379–5394. doi:<u>10.5194/bg-13-5379-2016</u> *Methods* 

Stookey, L. L. (1970). Ferrozine---a new spectrophotometric reagent for iron. Analytical Chemistry, 42(7), 779–781. doi:<u>10.1021/ac60289a016</u> *Methods* 

Strickland, J. D. H. and Parsons, T. R. (1972). A Practical Hand Book of Seawater Analysis. Fisheries Research Board of Canada Bulletin 157, 2nd Edition, 310 p. *Methods* 

Wang, H., Hu, X., Rabalais, N. N., & Brandes, J. (2018). Drivers of Oxygen Consumption in the Northern Gulf of Mexico Hypoxic Waters—A Stable Carbon Isotope Perspective. Geophysical Research Letters, 45(19). Portico. https://doi.org/10.1029/2018gl078571 <u>https://doi.org/10.1029/2018GL078571</u> *Methods* 

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## **Related Datasets**

#### IsRelatedTo

Taillefert, M. (2023) **Electrochemical data from sediment cores collected on the Louisiana Shelf of the Northern Gulf of Mexico during November 2020 on R/V Savannah cruise SAV-20-07.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2023-07-20 http://lod.bco-dmo.org/id/dataset/904782 [view at BCO-DMO]

Relationship Description: The electrochemical depth profiles were obtained in separate sediment cores, yet from the same cast as the pore water dataset.

# Parameters

Parameter Description		Units	
Year	4-digit year when samples were collected	unitless	
Month	Month when samples were collected	unitless	
Day	Day of month when samples were collected	unitless	
Date	Date when samples were collected	unitless	
Collection_Type	Type of sample collection (porewater)	unitless	
Station	Station identifier	unitless	
Lon	Longitude where samples were collected; negative values = West	decimal degrees	
Lat	Latitude where samples were collected; positive values = North	decimal degrees	
sample_ID	Sample ID number	unitless	
Sediment_depth_cm	Sediment depth	centimeters (cm)	
DIC	Dissolved inorganic carbon (DIC)	millimoles per liter (mM)	
sd_DIC	Standard deviation of DIC	millimoles per liter (mM)	
PO4	Orthophosphate (PO4)	micromoles per liter (uM)	
sd_PO4	sd_PO4 Standard deviation of PO4		
NH4	Ammonium (NH4)		
sd_NH4	NH4 Standard deviation of NH4		
ТА	Total alkalinity (TA)	millimoles per liter (mM)	
sd_TA	Standard deviation of TA	millimoles per liter (mM)	
d13C_DIC	The carbon isotopic fractionation of DIC (d13-DIC)	per mil (‰)	
sd_d13C_DIC	Standard deviation of d13C_DIC	per mil (‰)	
Mnd	Dissolved manganese (Mn)	micromoles per liter (uM)	
sd_Mnd	Standard deviation of Mnd	micromoles per liter (uM)	
Cad	Dissolved calcium (Ca)	millimoles per liter (mM)	
sd_Cad	Standard deviation of Cad	millimoles per liter (mM)	
Fe_II	e_II Reduced iron (Fe(II))		
sd_Fe_II	d_Fe_II Standard deviation of Fe_II		
Fed	Total dissolved iron (Fe)	micromoles per liter (uM)	
sd_Fed	ed Standard deviation of Fed		
Fe_III_d	Dissolved Fe(III); the difference of Fed and Fe_II	micromoles per liter (uM)	
sd_Fe_III_d Standard deviation of Fe_III_d		micromoles per liter (uM)	

# Instruments

Dataset-specific Instrument Name	Metrohm 877 Titrino plus	
Generic Instrument Name	Automatic titrator	
Dataset-specific Description	TA measurements were obtained with a computer-controlled Metrohm 877 Titrino plus.	
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	ELMI CM-7S centrifuge
Generic Instrument Name	Centrifuge
Dataset-specific Description	Aldrich two-glove atmospheric bags were used to control the atmosphere during pore water extraction and centrifugation with an ELMI CM-7S clinical centrifuge.
Generic Instrument Description	A machine with a rapidly rotating container that applies centrifugal force to its contents, typically to separate fluids of different densities (e.g., cream from milk) or liquids from solids.

Dataset- specific Instrument Name	Agilent 7900e ICP-MS
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset- specific Description	Dissolved Ca and dissolved Mn measurements were conducted with an Agilent 7900e ICP-MS with SPS4 Autosampler.
Generic Instrument Description	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

Dataset- specific Instrument Name	ICP-MS
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Generic Instrument Description	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

Dataset- specific Instrument Name	Thermo Scientific Delta V plus stable isotope mass spectrometer
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset- specific Description	$\delta$ 13C-DIC measurements were conducted with a Thermo Electron SurveyorLite autosampler, a Surveyor MS HPLC pump, and a LC Isolink interface coupled to a Thermo Scientific Delta V plus stable isotope mass spectrometer.
Generic Instrument Description	The Isotope-ratio Mass Spectrometer is a particular type of mass spectrometer used to measure the relative abundance of isotopes in a given sample (e.g. VG Prism II Isotope Ratio Mass-Spectrometer).

Dataset- specific Instrument Name	Thermo Electron SurveyorLite autosampler
Generic Instrument Name	Laboratory Autosampler
Dataset- specific Description	δ13C-DIC measurements were conducted with a Thermo Electron SurveyorLite autosampler, a Surveyor MS HPLC pump, and a LC Isolink interface coupled to a Thermo Scientific Delta V plus stable isotope mass spectrometer.
Generic Instrument Description	Laboratory apparatus that automatically introduces one or more samples with a predetermined volume or mass into an analytical instrument.

Dataset-specific Instrument Name	SPS4 Autosampler	
Generic Instrument Name		
Dataset-specific Description	Dissolved Ca and dissolved Mn measurements were conducted with an Agilent 7900e ICP-MS with SPS4 Autosampler.	
Generic Instrument Description	Laboratory apparatus that automatically introduces one or more samples with a predetermined volume or mass into an analytical instrument.	

Dataset- specific Instrument Name	MC-800 multi-corer
Generic Instrument Name	Multi Corer
Dataset- specific Description	Sediment cores were collected with an MC-800 multi-corer (Ocean Instruments). Core barrels of 10 centimeters (cm) inner diameter and 75 cm long were used to collect sediments.
Generic Instrument Description	The Multi Corer is a benthic coring device used to collect multiple, simultaneous, undisturbed sediment/water samples from the seafloor. Multiple coring tubes with varying sampling capacity depending on tube dimensions are mounted in a frame designed to sample the deep ocean seafloor. For more information, see Barnett et al. (1984) in Oceanologica Acta, 7, pp. 399-408.

Dataset-specific Instrument Name	Beckman Coulter DU 720 UV-vis spectrophotometer	
Generic Instrument Name Spectrometer		
Dataset-specific Description	All spectrophotometric measurements were conducted with a Beckman Coulter DU 720 UV-vis spectrophotometer.	
Generic Instrument Description	A spectrometer is an optical instrument used to measure properties of light over a specific portion of the electromagnetic spectrum.	

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## Deployments

SA	V-	20	-07

Website	https://www.bco-dmo.org/deployment/904422
Platform	R/V Savannah
Start Date	2020-10-23
End Date	2020-11-21
Description	See more information at R2R: <u>https://www.rvdata.us/search/cruise/SAV-20-07</u>

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## **Project Information**

Importance of Riverine Discharge on the Benthic Flux of Alkalinity to Continental Margins (NGoM Benthic Alk Flux)

#### NSF Award Abstract

Ocean acidification is the process that lowers the pH of the ocean over time due to uptake of atmospheric carbon dioxide. This project investigates how chemical reactions in marine sediments exposed to high riverine sediment loads influence ocean acidification in coastal waters. Although we know that ocean acidification affects marine life and commercial fisheries in coastal waters, little is known about how acidification processes in the water column are influenced by reactions occurring in sediments on the sea floor. The role of large sediment deposits from rivers in these processes has also never been investigated. This study will be conducted in the Mississippi River and Gulf of Mexico. The Mississippi River transports a high sediment load to the continental shelf in the Gulf of Mexico and plays an important role in the economy of the southern coast of the United States. Results from this study will be useful to the oceanographic community for increasing understanding of ocean acidification processes in delta and shelf environments. It will also benefit decision makers interested in predicting the role of sediments on the nutrient -rich Louisiana shelf for discharge control purposes. This project also has an important educational component by training undergraduate, graduate, and postdoctoral students, providing experiences at sea for undergraduates, and conducting outreach activities with K-12 students.

The geochemical and microbiological processes responsible for the transformation of particles deposited on the seafloor will be characterized near the Mississippi River mouth and along the nearby continental slope. The release of acids (CO2) and bases (alkalinity) from the sediment will be quantified using autonomous instruments deployed on the seafloor to determine whether sediments contribute to the acidity of the surrounding water column or instead provide bases to buffer the water column from atmospheric CO2 inputs. As the Mississippi River discharge during the later Winter and Spring provides much more sediment to the coastal zone compared to the rest of the year, research cruises will be taken twice a year to determine how seasonal variations in riverine discharge affect the release of acids and bases into the water column. Mathematical models will then be used to predict the effect of seasonal variations on acids or bases release to

the water column. This study will therefore provide a quantitative understanding of the role of large sediment depositions to the seafloor on sediment geochemical and microbiological processes and their feedback to the overlying waters. Simultaneously, a large data set will be generated and used to calibrate mathematical models and better characterize benthic-pelagic interactions. Such efforts are needed to predict how continental margins respond to constantly increasing stress from anthropogenic activities.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

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## Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1948914

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