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

Website: https://www.bco-dmo.org/dataset/904782
Data Type: Cruise Results
Version: 1
Version Date: 2023-07-20

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

Contributors	Affiliation	Role
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Abstract

This data set reports sediment depth profiles of dissolved O2, Mn2+, Fe2+, and total dissolved sulfide (SH2S) concentrations, as well as pH and current intensities of organic-Fe(III) complexes and aqueous clusters of FeS (FeS(aq)) that cannot be quantified directly. These data were obtained by profiling intact sediment cores using voltammetric and pH microelectrodes deployed on a computer-operated micromanipulator. Sediment cores were 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 depth profiles were started within 30 minutes after collection. The field sampling was conducted during R/V Savannah cruise SAV-20-07.

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Coverage

Spatial Extent: **N**:28.9134 **E**:-89.5994 **S**:28.6035 **W**:-90.3041
Temporal Extent: 2020-11-03 - 2020-11-06

Methods & Sampling

Intact sediments were collected and brought inside the ship's laboratory for profiling within 30 minutes after sampling. Each sediment core was profiled with a single non-invasive mercury/gold (Hg/Au) voltammetric microelectrode deployed on a computer-controlled micromanipulator along with an M-414 combination pH mini-electrode (Microelectrodes, Inc.). Dissolved oxygen (O2(aq)), manganese (Mn2+), iron (Fe2+), organic-Fe(III) complexes (Org-Fe(III)), aqueous clusters of FeS (FeS(aq)), thiosulfate (S2O32-), and total dissolved sulfide (SH2S = H2S + HS- + S(0) + Sx2-) were detected voltammetrically using either linear sweep voltammetry (LSV) for O2(aq) or cathodic square-wave voltammetry (CSWV) for the other species (Luther et al., 2008).

Each voltammetric microelectrode was fabricated in-house and prepared by polishing the 100-micrometer (μm) gold tip to a mirror-like surface with diamond pastes of different sizes (15, 6, 1, and ¼ μm, Buehler Inc.), electroplating a liquid mercury layer on the Au surface at -0.2 volts (V) for 4 minutes, and calibrating for Mn^{2+} in degassed seawater according to previously published methods (Brendel and Luther, 1995). Voltammetric microelectrode quality was determined before calibration by measuring $O_2(aq)$ in a fully aerated 0.54 molar (M) NaCl solution by LSV. Dissolved oxygen is reduced to water at the electrode surface in two steps of two-electron transfer with the formation of hydrogen peroxide (H_2O_2) as intermediate species. As a result, good electrodes should produce two linear sweep waves of the same shape and current intensity. Electrodes that passed this quality test were calibrated for deployment in the sediment cores. Mn^{2+} calibrations were obtained by CSWV using at least five standard additions of a 0.1 M Mn^{2+} stock to a 0.54 M NaCl solution degassed with UHP N_2 before calibration. Dissolved oxygen measured by LSV was calibrated ex situ in the overlying waters of sediment cores collected during the same cast by Winkler titration. Dissolved Fe^{2+} and $SH^{-}S$ were quantified by the pilot ion method using Mn^{2+} as the pilot ion (Luther et al., 2008; Tercier-Weber and Taillefert, 2009). Org-Fe(III) and FeS(aq) cannot be quantified by these methods and are reported in current intensities. Finally, the pH on the total scale was determined by measuring the temperature and electrode potential of both samples and a TRIS buffer in NaCl 0.54 M, then using the Nernst equation to calculate the pH of the samples (Skoog and Leary, 1996). Errors of all reported concentrations and current intensities represent the standard deviation of at least three replicate measurements at each depth in the sediment core.

Instruments:
Sediment cores were collected with an MC-800 multi-corer (Ocean Instruments). Core barrels of 10-centimeter (cm) inner diameter and 75 cm long were used to collect sediments. A DLK-70 Electrochemical analyzer with electrode stand (STAND-1) and EX-MAN-1 micromanipulator (Analytical Instrument Systems, Inc.) was used for all electrochemical analyses, including voltammetric scans and potential measurements at the pH minielectrode.

Known Issues or Problems:
"nd" in the data set is provided when the chemical species were not determined, typically because of electrochemical noise issues on the ship, or because the electrochemical technique was not applied (e.g., the CSWV technique was not applied in the overlying waters). All data sets provided have been analytically validated using the procedures described above.

Data Processing Description

Data Processing:
Voltammetric data were integrated using Voltint, an Matlab-based software developed in-house to identify and quantify the waves (O_2, H_2O_2) by LSV or peaks ($S_2O_3^{2-}$, $SH^{-}S$, Mn^{2+}, Fe^{2+}, Org-Fe(III), FeS(aq)) by CSWV (Bristow and Taillefert, 2008). As H_2O_2 is produced by reduction of $O_2(aq)$ at the electrode surface, it is not considered a species that is measurable in situ and is not reported in the data set. The potential of the pH mini-electrode is collected independently before the voltammetric scans and reported in the header of each scan. It is extracted from the headers by Voltint. The filename, potential, current, and surface area of each voltammetric peak quantified in the CSWV files as well as the filename, and potential of the pH mini-electrodes are automatically saved in two different files that can be processed further. The filename, potential, and limiting current of the $O_2(aq)$ and H_2O_2 waves quantified in the LSV scans are saved in a third file that can be processed further. Finally, a Matlab-based software was written to calculate the mean and standard deviation of the currents (and surface area for CSWV data) at each depth in the profiles before quantification of O_2 by external calibrations and the other species by the pilot ion method. The Matlab-based software also calculates the average and standard deviation of the pH measurements at each depth.

In the data file, standard deviations of the mean of at least triplicate electrochemical measurements are provided with each parameter.

BCO-DMO Processing:
- imported original file named "GOM_Fall2020_VoltammetryData_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 "904782_v1_electrochemical_data.csv".

Related Publications

Brendel, P. J., & Luther, G. W. I. (1995). Development of a Gold Amalgam Voltammetric Microelectrode for the Determination of Dissolved Fe, Mn, O2, and S(-II) in Porewaters of Marine and Freshwater Sediments. Environmental Science & Technology, 29(3), 751–761. doi:10.1021/es00003a024
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:10.1016/j.cageo.2007.01.005
Methods

Luther, G. W., Glazer, B. T., Ma, S., Trouwborst, R. E., Moore, T. S., Metzger, E., … Brendel, P. J. (2008). Use of voltammetric solid-state (micro)electrodes for studying biogeochemical processes: Laboratory measurements to real time measurements with an in situ electrochemical analyzer (ISEA). Marine Chemistry, 108(3-4), 221–235. doi:10.1016/j.marchem.2007.03.002
Methods

Skoog, D. A., Holler, F. J., & Nieman, T. A. (1998). Principles of instrumental analysis (5th ed., Ser. Saunders golden sunburst series). Saunders College Publ. https://isbnsearch.org/isbn/9780030233432
Methods

Taillefert, M., Bono, A. B., & Luther, G. W. (2000). Reactivity of Freshly Formed Fe(III) in Synthetic Solutions and (Pore)Waters: Voltammetric Evidence of an Aging Process. Environmental Science & Technology, 34(11), 2169–2177. https://doi.org/10.1021/es990120a https://doi.org/10.1021/ES990120A
Methods

Tercier-Waeber, M.-L., & Taillefert, M. (2008). Remote in situ voltammetric techniques to characterize the biogeochemical cycling of trace metals in aquatic systems. J. Environ. Monit., 10(1), 30–54. https://doi.org/10.1039/b714439n https://doi.org/10.1039/B714439N
Methods

Theberge, S. M., & Luther III, G. W. (1997). Aquatic Geochemistry, 3(3), 191–211. https://doi.org/10.1023/a:1009648026806
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Related Datasets

IsRelatedTo

Taillefert, M. (2023) **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.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2023-07-18 http://lod.bco-dmo.org/id/dataset/904417 [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.

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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 (Voltammetry)	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
Sediment_depth	Sediment depth	centimeters (cm)
pH	pH	unitless (pH scale)
O2	Dissolved oxygen	micrometers (uM)
sd_O2	Standard deviation of O2	micrometers (uM)
Mn_II	Reduced manganese (Mn2+)	micrometers (uM)
sd_Mn_II	Standard deviation of Mn_II	micrometers (uM)
Fe_II	Electrochemical labile reduced iron (Fe2+)	micrometers (uM)
sd_Fe_II	Standard deviation of Fe_II	micrometers (uM)
SH2S	Total dissolved sulfides	micrometers (uM)
sd_SH2S	Standard deviation of SH2S	micrometers (uM)
S2O3	Thiosulfate (S2O32-)	micrometers (uM)
sd_S2O3	Standard deviation of S2O3	micrometers (uM)
Org_Fe_III	Organic Fe(III) complexes	nanoampere (nA)
sd_Org_Fe_III	Standard deviation of Org_Fe_III	nanoampere (nA)
FeS_aq	Aqueous clusters of FeS	nanoampere (nA)
sd_FeS_aq	Standard deviation of FeS_aq	nanoampere (nA)

Instruments

Dataset-specific Instrument Name	EX-MAN-1 micromanipulator (Analytical Instrument Systems, Inc.)
Generic Instrument Name	micromanipulator
Dataset-specific Description	A DLK-70 Electrochemical analyzer with electrode stand (STAND-1) and EX-MAN-1 micromanipulator (Analytical Instrument Systems, Inc.) was used for all electrochemical analyses, including voltammetric scans and potential measurements at the pH minielectrode.
Generic Instrument Description	A micromanipulator is an apparatus used to physically interact with a sample under a microscope.

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	pH microelectrodes
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	DLK-70 Electrochemical analyzer with electrode stand
Generic Instrument Name	Voltammetry Analyzers
Dataset-specific Description	A DLK-70 Electrochemical analyzer with electrode stand (STAND-1) and EX-MAN-1 micromanipulator (Analytical Instrument Systems, Inc.) was used for all electrochemical analyses, including voltammetric scans and potential measurements at the pH minielectrode.
Generic Instrument Description	Instruments that obtain information about an analyte by applying a potential and measuring the current produced in the analyte.

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Deployments

SAV-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: https://www.rvdata.us/search/cruise/SAV-20-07

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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 (CO_2) 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 CO_2 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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