Elemental and isoptopic composition of sediment and biomass from the Carpinteria Salt March sampled in 2020 and 2021

Website: https://www.bco-dmo.org/dataset/938709
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Project
» Carbon Storage in Mangrove Ecosystems via Abiotic Sulfurization (Mangroves OS)

Contributors	Affiliation	Role
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Abstract
Here we provide data that help to evaluate organic matter sulfurization and pyrite formation in a salt marsh in California. We collected six sediment cores from three habitat types at Carpinteria Salt Marsh Reserve (34.41336°N, 119.84365°W) in July 2020. One core was used to establish dry bulk density, while the other was reserved for geochemical measurements. Both cores were kept at -20°C until analysis could be carried out. We provide elemental concentrations (organic C/N/S, Fe, pyrite) and isotopic compositions (δ13C, δ34S) of important carbon, iron and sulfur sediment pools. Additional biomass samples were collected between 2020 and 2023 and were also analyzed for elemental (C/N/S) and isotopic compositions (δ13C, δ34S). Data will be useful for those interested in assessing organic matter sulfurization and pyrite formation in blue carbon ecosystems such as mangroves, seagrass meadows and salt marshes. Data will also be informative for researchers investigating organic and inorganic sulfur cycling. Samples were collected by Lena Capece and Morgan Raven, data were interpreted by Lena Capece and Morgan Raven.

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Coverage

Location: UC Carpinteria Salt Marsh Reserve located in Carpinteria, CA
Spatial Extent: **N**:34.40329 **E**:-119.53802 **S**:34.40052 **W**:-119.53929
Temporal Extent: 2020-07-01 - 2021-01-16

Methods & Sampling

We collected six sediment cores from three habitat types at Carpinteria Salt Marsh Reserve (34.41336°N, 119.84365°W) in July 2020. One core was used to establish dry bulk density, while the other was reserved for geochemical measurements. Both cores were kept at -20°C until analysis could be carried out. We provide elemental concentrations (organic C/N/S, Fe, pyrite) and isotopic compositions ($\delta^{13}C$, $\delta^{34}S$) of important carbon, iron and sulfur sediment pools. Additional biomass samples were collected between 2020 and 2023 and were also analyzed for elemental (C/N/S) and isotopic compositions ($\delta^{13}C$, $\delta^{34}S$).

Data Processing Description

To isolate major carbon and sulfur pools, a ~1 g aliquot of the freeze dried sample from each sediment interval was subjected to two sequential microwave extractions (MARS-6, CEM, 70°C for 15 minutes) using a 9:1 dichloromethane: methanol solution to isolate lipids and elemental S. Solvent-extracted solids were rinsed with 0.7N NaCl solution, ultra-pure water, freeze dried and then acid fumigated to remove carbonates for 12 hrs with a 6N HCl solution. A 500-mg subsample of the same microwave-extracted solid residue was then subjected to a strong acid hydrolysis (6N HCl, 60°C, 2 hrs) to extract acid-volatile sulfur (AVS, operationally defined as iron monosulfides) following Canfield et al. 1986 and Raven et al. 2019b. The remaining solid residue underwent a chromium (II) chloride extraction at 60°C for 2 hours to isolate chromium reducible sulfur (CRS, operationally defined as pyrite) following Canfield et al. 1986. The leftover solid residue following the CRS extraction contains highly hydrolysis-resistant OM that we refer to as protokerogen (Burdige 2007; Raven et al. 2019b).

Subsamples of primary producer biomass (n=9) from CSMR (Ulva spp., Juamea carnosa, and Salicornia pacifica) underwent two separate chemical extractions in order to isolate important carbon and sulfur pools for x-ray absorbance spectroscopy (XAS). Briefly, ~1 g of each rinsed and freeze-dried biomass type underwent an acid hydrolysis with 1N hydrochloric acid for 2 hours at room temperature to ensure the removal of sulfate from the biomass.

The oxidation state and bonding environment of organic sulfur (OS) in both strongly acid-hydrolyzed (post-CRS extraction, which we refer to as protokerogen) sediments and mild acid-hydrolyzed (1N acid hydrolysis discussed above) whole biomass samples were characterized using synchrotron x-ray absorption spectroscopy (XAS). Sulfur K-edge XAS spectra were obtained at the Stanford Synchrotron Radiation Lightsource (SSRL) on beam line 14–3 using a spot size of 0.5 mm2 and a Si(111) ($\Phi = 90$) double crystal monochromator calibrated to the thiol pre-edge peak of thiosulfate at 2472.02 eV. For analysis, samples were adhered onto Saint Gobain M60 S-free polyester tape and covered with 5 µm SPEX 3520 polypropylene XRF film. Spectra were averaged and normalized in the SIXPACK (Webb 2005) software package using a K-edge E0 of 2473 and pre-edge and post-edge linear normalization ranges of -20 to -7 and 35 to 70 eV, respectively. The relative abundance (%) of individual sulfur species were determined in sediments and biomass samples using least squares fitting and a set of OS standards (Raven et al. 2021a). The relative abundances of different sulfur species were then used to determine the percentage of reduced (disulfide, monosulfide, aromatic) and oxidized (sulfoxide, sulfone/sulfonate, sulfate ester) sulfur in slightly acid hydrolyzed biomass and strongly acidified sediment.

BCO-DMO Processing Description

* Adjusted parameter names to comply with database requirements

Problem Description

There is missing data for some measurements due to detection limits or sample mishandling.

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Data Files

File
938709_v1_geochemistry.csv(Comma Separated Values (.csv), 7.76 KB)   MD5:81df47f4d868fe48b6993d69f76e4411   Primary data file for dataset ID 938709, version 1

Related Publications

Burdige, D. J. (2007). Preservation of Organic Matter in Marine Sediments: Controls, Mechanisms, and an Imbalance in Sediment Organic Carbon Budgets? Chemical Reviews, 107(2), 467–485. https://doi.org/10.1021/cr050347q
Methods

Canfield, D. E., Raiswell, R., Westrich, J. T., Reaves, C. M., & Berner, R. A. (1986). The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. Chemical Geology, 54(1-2), 149–155. doi:10.1016/0009-2541(86)90078-1
Methods

Fry, B., Silva, S. R., Kendall, C., & Anderson, R. K. (2002). Oxygen isotope corrections for online δ34S analysis. Rapid Communications in Mass Spectrometry, 16(9), 854–858. Portico. https://doi.org/10.1002/rcm.651
Methods

Jeitner, T. M. (2014). Optimized ferrozine-based assay for dissolved iron. Analytical Biochemistry, 454, 36–37. https://doi.org/10.1016/j.ab.2014.02.026
Methods

Phillips, A. A., Ulloa, I., Hyde, E., Agnich, J., Sharpnack, L., O'Malley, K. G., Webb, S. M., Schreiner, K. M., Sheik, C. S., Katsev, S., & Raven, M. R. (2023). Organic sulfur from source to sink in low-sulfate Lake Superior. Limnology and Oceanography, 68(12), 2716–2732. Portico. https://doi.org/10.1002/lno.12454
Methods

Poulton, S. W., & Canfield, D. E. (2005). Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates. Chemical Geology, 214(3-4), 209–221. doi:10.1016/j.chemgeo.2004.09.003
Methods

R Core Team (2022). R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. https://www.R-project.org/. R version 4.2.2 (2022-10-31)
Software

Raven, M. R., Fike, D. A., Gomes, M. L., & Webb, S. M. (2019). Chemical and Isotopic Evidence for Organic Matter Sulfurization in Redox Gradients Around Mangrove Roots. Frontiers in Earth Science, 7. https://doi.org/10.3389/feart.2019.00098
Methods

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

Webb, S. M. (2005). SIXPack a Graphical User Interface for XAS Analysis Using IFEFFIT. Physica Scripta, 1011. doi:10.1238/physica.topical.115a01011 https://doi.org/10.1238/Physica.Topical.115a01011
Methods

Parameters

Parameter	Description	Units
collection_date	sample collection date	unitless

latitude	latitude of sample location, south is negative	decimal degrees
longitude	longitude of sample location, west is negative	decimal degrees
type	sediment or type of biomass	unitless
location	where sample was taken	unitless
depth	sampling depth	meters (m)
depth_bin	depth description (surface, intermediate, deep)	unitless
habitat	habitat description of sample (algal, veg, unveg)	unitless
OC	organic carbon	weight percent carbon (wt. %C)
CPK	protokerogen organic carbon	weight percent carbon (wt. %C)
OS	C/N ratio total organic matter (mol/mol)	unitless
SPK	C/N ratio protokerogen organic matter	unitless
CN	organic sulfur	weight percent sulfur (wt. %S)
CNPK	protokerogen organic sulfur	weight percent sulfur (wt. %S)
SC	S/C ratio ratio total organic matter (mol/mol)	unitless
SCPK	S/C ratio protokerogen organic matter	unitless
pyrite	concentration of pyrite measured as the CRS pool	weight percent sulfur (wt. %S)
FeCRS	iron in the CRS pool	weight percent iron (wt. %Fe)
FeHR	iron in the CRS pool	weight percent iron (wt. %Fe)
d13C_OC	carbon isotope composition of organic carbon	per mille (‰)

d13C_PK	carbon isotope composition of protokerogen organic carbon	per mille (‰)
d34S_OS	sulfur isotope composition of organic sulfur	per mille (‰)
d34S_PK	sulfur isotope composition of protokerogen organic sulfur	per mille (‰)
d34S_pyrite	sulfur isotope composition of pyrite as CRS	per mille (‰)
CH	calculated hydrolyzable organic carbon	weight percent carbon (wt. %C)
offset	isotopic offset between d34S_pyrite and d34S_PK	unitless

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Instruments

Dataset-specific Instrument Name	MARS-6 microwave CEM
Generic Instrument Name	Accelerated Solvent Extractor
Dataset-specific Description	MARS-6 microwave CEM to extract lipids from sediments
Generic Instrument Description	Accelerated solvent extraction (ASE) is a method for extracting various chemicals from a complex solid or semisolid sample matrix. The process uses high temperature and pressure, which results in the extraction taking less time and requiring less solvent, and possibly also giving better analyte recovery, than traditional methods that use less extreme conditions.

Dataset-specific Instrument Name	Elementar vario ISOTOPE select elemental analyzer interfaced to a Nu Horizon isotope ratio mass spectrometer
Generic Instrument Name	Elemental Analyzer
Dataset-specific Description	Elementar vario ISOTOPE select elemental analyzer interfaced to a Nu Horizon isotope ratio mass spectrometer to measure CNS and δ13C
Generic Instrument Description	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.

Dataset-specific Instrument Name	Metrosep A Supp 5-100/4.0 column and Metrohm 930 Compact IC Flex
Generic Instrument Name	Ion Chromatograph
Dataset-specific Description	Metrosep A Supp 5-100/4.0 column and Metrohm 930 Compact IC Flex to measure CRS
Generic Instrument Description	Ion chromatography is a form of liquid chromatography that measures concentrations of ionic species by separating them based on their interaction with a resin. Ionic species separate differently depending on species type and size. Ion chromatographs are able to measure concentrations of major anions, such as fluoride, chloride, nitrate, nitrite, and sulfate, as well as major cations such as lithium, sodium, ammonium, potassium, calcium, and magnesium in the parts-per-billion (ppb) range. (from http://serc.carleton.edu/microbelife/research_methods/biogeochemical/ic....)

Dataset-specific Instrument Name	Thermo Scientific Delta V Plus Isotope Ratio Mass Spectrometer (IRMS) via Conflo IV
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	Thermo Scientific Delta V Plus Isotope Ratio Mass Spectrometer (IRMS) via Conflo IV to measure δ34S
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	Genesys 150 UV-Vis Spectrophotometer
Generic Instrument Name	Spectrophotometer
Dataset-specific Description	Genesys 150 UV-Vis Spectrophotometer to measure iron extracts
Generic Instrument Description	An instrument used to measure the relative absorption of electromagnetic radiation of different wavelengths in the near infra-red, visible and ultraviolet wavebands by samples.

Project Information

Carbon Storage in Mangrove Ecosystems via Abiotic Sulfurization (Mangroves OS)

Website: http://ravennoiselab.com

Coverage: Floridian and Caribbean mangroves; Californian salt mashes

NSF abstract:

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Mangrove forest sediments are important hotspots of organic carbon preservation, and they have the potential to sequester substantial amounts of atmospheric CO2. Currently, however, is it not fully understood why these environments are able to bury so much organic carbon, or how they will respond to future changes in sea level, land use, and climate. This project will investigate a mechanism that may help explain this carbon burial: organic matter sulfurization, the transformation and effective 'pickling' of sedimentary organic matter by sulfide. Its central aim is to understand what controls the extent of sulfurization in mangrove sediments, and to estimate the contribution of organic matter sulfurization to sediment carbon storage in different parts of the environment. By providing some of the first constraints on how, when, and where organic matter sulfurization happens in mangroves, the results of this work will guide decisionmakers managing coastal watersheds and carbon stocks in the face of land use, climate and sea level change. As part of this work, four undergraduate students and one PhD student at UC Santa Barbara will gain field and research experience. And, in collaboration with local groups associated with the field site, the team will produce a season of 'Ocean Solutions' podcast episodes related to conservation and human impacts of Caribbean mangroves.

The overarching goal of this project is to understand how microbial sulfur cycling affects organic matter preservation in vegetated coastal sediments, which have substantial leverage to impact the global carbon cycle on decadal to millennial timescales. It specifically investigates organic matter sulfurization, which can transform fresh, easily respired organic matter into recalcitrant, polymerized carbon stocks with long-term preservation potential. Although organic matter sulfurization is known to occur in mangrove sediments, the scale of its impact is essentially unknown. A pair of field expeditions will be conducted at a mangrove forest on the southwestern coast of Florida. In the first field season, geochemical profiles will be used to quantify organic matter sulfurization in sediments and its relationships with carbon storage, iron mineralogy, and the characteristics of sedimentary organic matter inputs. In the second field season, cyclic voltammetry will be used to target redox dynamics at the millimeter scale. Laboratory experiments will be conducted to test the susceptibility of various local organic matter sources to sulfurization and characterize their sulfurized forms. Throughout, the project applies a holistic approach to sedimentary organic matter by characterizing the dissolved, lipid, protein/carbohydrate, and proto-kerogen pools with isotopic and spectroscopic techniques. This work will yield a first quantitative, mechanistic framework for predicting the extent of organic matter sulfurization in coastal vegetated habitats and its likely response to changes in ecology, land use, or sea level.

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.

Funding

Funding Source	Award
NSF Division of Earth Sciences (NSF EAR)	EAR-2053163