

Sulfur speciation of sediment and biomass from the Carpinteria Salt Marsh sampled in 2020 and 2021

Website: <https://www.bco-dmo.org/dataset/938382>

Data Type: Other Field Results

Version: 1

Version Date: 2024-09-30

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 data on the speciation of sulfur in acid hydrolysis resistant organic matter and biomass samples. Data will be useful for those interested in assessing organic matter sulfurization in blue carbon ecosystems such as mangroves, seagrass meadows and salt marshes. Data will also be informative for researchers investigating organic 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:34.41336 E:-119.53802 S:34.40052 W:-119.84365

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 data on the speciation of sulfur in acid hydrolysis resistant organic matter and biomass samples.

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 carnososa*, 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 μ m 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
938382_v1_sulfur.csv (Comma Separated Values (.csv), 4.78 KB) MD5:bdbbb7a447892edc983947d13e90b4b1
Primary data file for dataset ID 938382, version 1

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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](https://doi.org/10.1016/0009-2541(86)90078-1)

Methods

Fry, B., Silva, S. R., Kendall, C., & Anderson, R. K. (2002). Oxygen isotope corrections for online $\delta^{34}\text{S}$ 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](https://doi.org/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) [2022_R_v4.2.2](#)

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](https://doi.org/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

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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
habitat	type of habitat where sample was taken	unitless
depth	core depth of sample	cm
disulfide	relative abundance of organic disulfides in samples determined following XAS	fraction as a decimal
monosulfide	relative abundance of organic monosulfides in samples determined following XAS	fraction as a decimal
aromatic	relative abundance of aromatics in samples determined following XAS	fraction as a decimal
sulfoxide	relative abundance of sulfoxides in samples determined following XAS	fraction as a decimal
sulfonate	relative abundance of sulfonates in samples determined following XAS	fraction as a decimal
sulfate_ester	relative abundance of sulfate esters in samples determined following XAS	fraction as a decimal
chi_sq	results of statistical analyses carried out in Sixpack that detail the goodness of the fit of standard spectra to sample spectra determined following XAS	unitless
reduced	sum of reduced species	fraction as a decimal
oxidized	sum of oxidized species	fraction as a decimal

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Project Information

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

Website: <http://ravennoiselab.com>

Coverage: Floridian and Caribbean mangroves; Californian salt marshes

NSF Award Abstract:

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-kерogen 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.

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Funding

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

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