Fenton oxidation of particulate terrestrial organic matter (TOM) samples and sequential POM/DOM fractionation

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Project
» EAGER: The camouflaging of terrigenous organic matter as marine organic matter through hydroxyl radical oxidation via the dark Fenton reaction (Fenton oxidation)

Contributors	Affiliation	Role
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Abstract
The export of terrestrial organic matter (TOM) to the ocean is broadly assumed to contribute minimally to the large amounts of marine organic matter. This has been largely due to the observed disappearance of stable carbon isotopic signatures (δ13C) of TOM that are typically <−25‰. As oceanic carbon has a very different δ13C value of ≥ −22‰, it is generally concluded that marine organic matter is derived from algae. Here, we present evidence from the oxidation of numerous particulate terrestrial samples showing that upon oxidation the δ13C becomes altered and a TOM with δ13C <−25‰ can be chemically converted into TOM with δ13C value ≥ −22‰. Presented are data of TOM samples after oxidation with hydrogen peroxide, after which the resultant suspension is separated into its particulate organic matter (POM) and dissolved organic matter (DOM) phases. This includes δ13C values and carbon percentages for POM and DOM fractions at different oxidation times. These data are important for developing an amendment to the global carbon cycle to account for the production of marine-like organic matter from abiotic TOM degradation.

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Coverage

Location: Eastern United States (Florida, Illinois, and Virginia)
Spatial Extent: **N**:41.3767 **E**:-76.5251 **S**:26.6834 **W**:-88.1121

Methods & Sampling

Hillsborough Soil: a riverbank soil of the Hillsborough River (Florida). The river arises from the Green Swamp, also known as the “Heart of the Floridan Aquifer”, and flows 60 miles to an outlet in the city of Tampa on Hillsborough Bay. Its watershed was formerly covered by a rich, old-growth forest of Bald Cypress, Longleaf

Pine, and Sand Live Oak. After decades of logging, the watershed's cover has shifted to recently grown Water Ash and Water Locust trees. The soil was collected on 02 April 2019 at coordinates 28° 05′ 16.8″ N and 82° 20′ 56.3″ W. After removal of large debris, the soil was homogenized, sieved, oven-dried at 105 °C, and stored in the dark to prevent degradation during storage.

Elliott Soil: a standardized fertile prairie soil purchased from the International Humic Substances Society (IHSS). This sample was obtained from an undisturbed area on the grounds of the Joliet Army Ammunition Plant near Joliet, Illinois, currently managed by the US Forest Service as the Midewin National Tallgrass Prairie Reserve. It is a poorly drained soil on moraines and till plains having loess or silty clay loam glacial till.

Pahokee Peat: a standardized peat soil purchased from the IHSS. It is an agricultural soil of the Florida Everglades obtained from the University of Florida Belle Glade Research Station. This is a poorly drained soil formed by organic deposits from freshwater marshes accumulating over limestone bedrock.

Great Dismal Swamp Peat: a peat from a blackwater wetland in Virginia that has high iron loadings. Its hydric soils are formed under repeated saturation, long enough to develop anaerobic conditions in the upper horizons. The peat is formed by fast accumulation of carbon and slow decomposition yielding an organic-rich peat (Sleeter et al., 2017).

Elemental and Isotopic Characterization: Samples were prepared for total organic carbon (TOC) and isotopic composition (δ13C) analysis by wrapping weighed amounts of sample in tin capsules. Analysis was performed using a Thermo-Scientific Flash EA instrument (combustion at 1010 °C) equipped with a thermal conductivity detector and a Delta V Plus isotope-ratio mass spectrometer. The instrument's performance is validated daily by analysis of standards (mentioned below). TOC and δ13C values were obtained in duplicate (technical replicates). TOC values were obtained after calibration with the isotopic standards below. Carbon peak integrations are done automatically by the instrument and peak areas are related to C amounts using calibration curves in Excel. δ13C values determined by the isotope-ratio mass spectrometer and computed by its software were peak-size-corrected and scale-corrected (in Excel using calibration curves) using laboratory and authentic reference standards (glutamic acid: δ13C = −13.90‰; USGS40: δ13C = −26.39‰; USGS41a: δ13C = +36.55‰; and tyrosine: δ13C = −24.90‰). δ13C results are reported in delta notation relative to that of Vienna Pee Dee Belemnite.

Oxidation experiments. Oxidation of TOM samples was performed by suspending 1-4 g of dried material (105 °C for 12 h) in 10-20 mL of 1 M H_2O_2 (Fisher, 30%), with iron concentrations unperturbed from the native sample compositions. Control experiments were done similarly but with ultrapure water (18.2 MΩ·cm). Experiments were performed in acid-cleaned and pre-combusted 60 mL glass vials, which were kept open to the air to ensure constant aeration and steady gas release, avoiding pressure buildup. As the soil samples were largely insoluble in water, once the aqueous H_2O_2 was added to the soils, vials were sonicated for 30 minutes to ensure proper mixing and breakage of any formed clumps. The formed suspensions were let react for 48 h at room temperature in a shaking incubator (vials were covered with a large KimWipe). Then, the vials were frozen at -80 °C (to quench the oxidation) and the liquid was removed by freeze-drying (with the freeze drier maintaining temperature of -60 to -80 °C). Then, new 10-20 mL of peroxide were added for another 48 hours.

Oxidation was performed for up to six consecutive 48-hour cycles, for a total of 288 hours. Samples were analyzed at 10 time points: 0, 12, 24, 36, 48, 96, 144, 192, 240, and 288 hours. The 12-, 24-, and 36-hour measurements were collected during the first oxidation cycle, while subsequent measurements corresponded to the completion of each 48-hour cycle. Oxidation times represent cumulative exposure to the oxidation treatment.

POM/DOM fractionation. After the suspensions were freeze-dried, the obtained OM was fractionated into POM and DOM via water-extraction: the OM residue was suspended in 20 mL of ultrapure water. Suspensions were sonicated for 30 min to ensure proper mixing and then placed on a shaking incubator. After 48 hours the suspensions were quantitatively transferred into pre-cleaned plastic falcon tubes. Following centrifugation, the supernatant liquid (containing the DOM) was decanted into a filter manifold (0.45 µm pre-combusted GFF) and then the remaining POM was resuspended in 20 mL water to wash the POM of any remaining DOM. The new suspension was centrifuged again, and the water wash was decanted into the filter manifold. The falcon tubes, containing the POM fraction, as well as the decanted and filtered DOM fractions, were freeze-dried.

The resultant DOM and POM powders were homogenized. Then, about 50 mg of each sample was digested with 1 mL of 20% HCl to remove refractory carbonates such as siderite (Larson et al., 2008). The acid was evaporated at 80 °C (O'Kelly, 2005) and samples were homogenized again prior to analysis.

Data Processing Description

Data was processed first by the instrument's software and then in Microsoft Excel.

BCO-DMO Curation Notes

This section documents curation actions performed prior to publication review with the submitter, and additional information relevant to understanding and reusing this dataset. It distinguishes changes made to the submitted (meta)data from unresolved issues and/or enhancements that improve future reuse and interoperability.

CURATION ACTIONS PERFORMED ON DATA

- Loaded TOM Fenton Oxidation POM-DOM fractionation BCO-DMO.xlsx (sheet1), header row 1, missing values "" and "nd" treated as null
- Renamed columns: Sample Name to sample_name, Oxidation Time, hours to oxidation_time_hours, POM d13C AVG to pom_d13c_avg, POM d13C STDEV to pom_d13c_stdev, POM C% AVG to pom_c_percent_avg, POM C% STDEV to pom_c_percent_stdev, DOM d13C AVG to dom_d13c_avg, DOM d13C STDEV to dom_d13c_stdev, DOM C% AVG to dom_c_percent_avg, DOM C% STDEV to dom_c_percent_stdev
- Output file as 1009219_v1_pom_dom_fenton_oxidation.csv

CURATION ACTIONS PERFORMED ON METADATA

- BCO-DMO's standard metadata entry and text formatting steps were performed. See: https://www.bco-dmo.org/how-to/standard-curation-edits
- Added detail about sampling times during the experiment

ISSUES POTENTIALLY IMPACTING REUSE

- No soil sampling dates or ranges are provided. The methods would benefit from clarification of the general dates/time periods of collection and description of collection methods in cases where samples were not purchased.
- Dataset values are derived (averaged) values, based on the observations. The complete data is not referenced or provided as part of this submission.

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Related Publications

Larson, T. E., Heikoop, J. M., Perkins, G., Chipera, S. J., & Hess, M. A. (2008). Pretreatment technique for siderite removal for organic carbon isotope and C:N ratio analysis in geological samples. Rapid Communications in Mass Spectrometry, 22(6), 865–872. Portico. https://doi.org/10.1002/rcm.3432
Methods

O'Kelly, B. C. (2005). Oven-Drying Characteristics of Soils of Different Origins. Drying Technology, 23(5), 1141–1149. https://doi.org/10.1081/drt-200059149
Methods

Sleeter, R., Sleeter, B. M., Williams, B., Hogan, D., Hawbaker, T., & Zhu, Z. (2017). A carbon balance model for the great dismal swamp ecosystem. Carbon Balance and Management, 12(1). https://doi.org/10.1186/s13021-017-0070-4
Methods

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Parameters

Parameter	Description	Units
sample_name	Name of the sample used for oxidation	unitless
oxidation_time_hours	Cumulative oxidation time in hours, including intermediate measurements at 12, 24, and 36 hours during the first 48-hour oxidation cycle and measurements at the completion of each subsequent 48-hour cycle, up to 288 hours.	hours
pom_d13c_avg	Stable carbon isotopic signature (δ13C) that is an average (AVG) of two technical replicates for the particulate organic matter (POM) fraction	per mille (‰)
pom_d13c_stdev	Standard deviation (STDEV) of the stable carbon isotopic signature (δ13C) of two technical replicates of the particulate organic matter (POM) fraction	per mille (‰)
pom_c_percent_avg	Amount of carbon that is an average (AVG) of two technical replicates for the particulate organic matter (POM) fraction	percentage (%)
pom_c_percent_stdev	Standard deviation (STDEV) of the amount of carbon in two technical replicates of the particulate organic matter (POM) fraction	percentage (%)
dom_d13c_avg	Stable carbon isotopic signature (δ13C) that is an average (AVG) of two technical replicates for the dissolved organic matter (DOM) fraction	per mille (‰)
dom_d13c_stdev	Standard deviation (STDEV) of the stable carbon isotopic signature (δ13C) of two technical replicates of the dissolved organic matter (DOM) fraction	per mille (‰)
dom_c_percent_avg	Amount of carbon that is an average (AVG) of two technical replicates for the dissolved organic matter (DOM) fraction	percentage (%)
dom_c_percent_stdev	Standard deviation (STDEV) of the amount of carbon in two technical replicates of the dissolved organic matter (DOM) fraction	percentage (%)

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Instruments

Dataset-specific Instrument Name	centrifuge
Generic Instrument Name	Centrifuge
Dataset-specific Description	Following centrifugation, the supernatant liquid (containing the DOM) was decanted into a filter manifold (0.45 µm pre-combusted GFF) and then the remaining POM was resuspended in 20 mL water to wash the POM of any remaining DOM. The new suspension was centrifuged again, and the water wash was decanted into the filter manifold. The falcon tubes, containing the POM fraction, as well as the decanted and filtered DM fractions, were freeze-dried.
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	oven
Generic Instrument Name	Drying Oven
Dataset-specific Description	After removal of large debris, the soil was homogenized, sieved, oven-dried at 105 °C, and stored in the dark to prevent degradation during storage.
Generic Instrument Description	a heated chamber for drying

Dataset-specific Instrument Name	Thermo-Scientific Flash EA instrument
Generic Instrument Name	Elemental Analyzer
Dataset-specific Description	Elemental and Isotopic Characterization. Samples were prepared for total organic carbon (TOC) and isotopic composition (δ13C) analysis by wrapping weighed amounts of sample in tin capsules. Analysis was performed using a Thermo-Scientific Flash EA instrument (combustion at 1010 °C) equipped with a thermal conductivity detector and a Delta V Plus isotope-ratio mass spectrometer. The instrument's performance is validated daily by analysis of standards (mentioned below). TOC and δ13C values were obtained in duplicate (technical replicates). TOC values were obtained after calibration with the isotopic standards below. Carbon peak integrations are done automatically by the instrument and peak areas are related to C amounts using calibration curves in Excel. δ13C values determined by the isotope-ratio mass spectrometer and computed by its software were peak-size-corrected and scale-corrected (in Excel using calibration curves) using laboratory and authentic reference standards (glutamic acid: δ13C = −13.90‰; USGS40: δ13C = −26.39‰; USGS41a: δ13C = +36.55‰; and tyrosine: δ13C = −24.90‰). δ13C results are reported in delta notation relative to that of Vienna Pee Dee Belemnite.
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	homogenizer
Generic Instrument Name	Homogenizer
Dataset-specific Description	After removal of large debris, the soil was homogenized, sieved, oven-dried at 105 °C, and stored in the dark to prevent degradation during storage.
Generic Instrument Description	A homogenizer is a piece of laboratory equipment used for the homogenization of various types of material, such as tissue, plant, food, soil, and many others.

Dataset-specific Instrument Name	shaking incubator
Generic Instrument Name	Shaker
Dataset-specific Description	The formed suspensions were let react for 48 h at room temperature in on a shaking incubator (vials were covered with a large KimWipe).
Generic Instrument Description	A Shaker is a piece of lab equipment used to mix, blend, or to agitate substances in tube(s) or flask(s) by shaking them, which is mainly used in the fields of chemistry and biology. A shaker contains an oscillating board which is used to place the flasks, beakers, test tubes, etc.

Dataset-specific Instrument Name	Delta V Plus isotope-ratio mass spectrometer
Generic Instrument Name	Thermo Fisher Scientific DELTA V Plus isotope ratio mass spectrometer
Dataset-specific Description	Elemental and Isotopic Characterization. Samples were prepared for total organic carbon (TOC) and isotopic composition (δ13C) analysis by wrapping weighed amounts of sample in tin capsules. Analysis was performed using a Thermo-Scientific Flash EA instrument (combustion at 1010 °C) equipped with a thermal conductivity detector and a Delta V Plus isotope-ratio mass spectrometer. The instrument's performance is validated daily by analysis of standards (mentioned below). TOC and δ13C values were obtained in duplicate (technical replicates). TOC values were obtained after calibration with the isotopic standards below. Carbon peak integrations are done automatically by the instrument and peak areas are related to C amounts using calibration curves in Excel. δ13C values determined by the isotope-ratio mass spectrometer and computed by its software were peak-size-corrected and scale-corrected (in Excel using calibration curves) using laboratory and authentic reference standards (glutamic acid: δ13C = −13.90‰; USGS40: δ13C = −26.39‰; USGS41a: δ13C = +36.55‰; and tyrosine: δ13C = −24.90‰). δ13C results are reported in delta notation relative to that of Vienna Pee Dee Belemnite.
Generic Instrument Description	The Thermo Scientific DELTA V Plus is an isotope ratio mass spectrometer designed to measure isotopic, elemental and molecular ratios of organic and inorganic compounds. The DELTA V Plus is an enhanced model of the DELTA V series of isotope ratio mass spectrometers, which can be upgraded from the DELTA V Advantage. The DELTA V Plus can be operated in Continuous Flow or Dual Inlet mode and can accommodate up to 10 collectors, ensuring flexibility to cover many applications. The DELTA V Plus is controlled by an automated, integrated Isodat software suite. A magnet, whose pole faces determine the free flight space for the ions, eliminates the traditional flight tube. The magnet is designed for fast mass switching which is further supported by a fast jump control between consecutive measurements of multiple gases within one run. The sample gas is introduced at ground potential, eliminating the need for insulation of the flow path, ensuring 100 percent transfer into the ion source. The amplifiers register ion beams up to 50 V. The DELTA V Plus has refined optics, enabling greater ion transmission than the DELTA V Advantage. It has a sensitivity of 800 molecules per ion (M/I) in Dual Inlet mode and 1100 M/I in Continuous Flow mode. It has a system stability of < 10 ppm and an effective magnetic detection radius of 191 nm. It has a mass range of 1 - 96 Dalton at 3 kV.

Dataset-specific Instrument Name	sonicated
Generic Instrument Name	ultrasonic cell disrupter (sonicator)
Dataset-specific Description	As the soil samples were largely insoluble in water, once the aqueous H2O2 was added to the soils, vials were sonicated for 30 minutes to ensure proper mixing and breakage of any formed clumps.
Generic Instrument Description	Instrument that applies sound energy to agitate particles in a sample.

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Project Information

EAGER: The camouflaging of terrigenous organic matter as marine organic matter through hydroxyl radical oxidation via the dark Fenton reaction (Fenton oxidation)

NSF Award Abstract:
Organic carbon in the ocean is made-up of materials delivered by riverine runoff from land and marine sources. However, even though a large amount of land-derived organic carbon enters the ocean from rivers, most carbon in the ocean appears to be from marine sources. This has led scientists to conclude that land-derived carbon is not transported far into the ocean. This EAGER project aims to test this assumption. The team of scientists will examine whether chemical reactions alter the composition of land-derived organic carbon in a way that makes it look like marine organic carbon. If this proves true, the results could explain why land-derived organic carbon is difficult to identify in the ocean and could lead to a reconsideration of present carbon budgets and models. The scientists will perform experiments using land-derived carbon collected from major river systems throughout the world. Samples will be introduced to reactive oxygen species (mainly hydroxyl radicals) and iron in the dark under conditions that occur in nature. Reaction rates and changes in the composition of the organic matter will be monitored during and following the experiments. This EAGER project provides research training and valuable professional development experience for an early career researcher who has not received prior support from NSF. Undergraduate students enrolled in STEM and REU programs at the lead institutions will participate in the research.

This EAGER project examines the hypothesis that hydroxyl radicals generated during dark Fenton reactions react with terrigenous organic matter to produce organic matter that is compositionally and isotopically similar to marine organic matter. The PIs will test this hypothesis using environmentally relevant concentrations of hydroxyl radical and terrestrial organic matter samples collected from several large-scale terrestrial riverine systems. The PIs will use multiple methods to characterize bulk organic matter (infrared/nuclear magnetic resonance (NMR) spectroscopy), its molecular composition (electrospray ionization Fourier Transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS), and stable isotope values of carbon and nitrogen (δ13C, δ15N) of dissolved and particulate organic matter pools before, during and following the experiments. This study explores an untested, but potentially transformative hypothesis that could alter existing paradigms about the fate of terrestrial organic matter in the ocean. Results from this study could revise understanding of the contributions of terrigenous organic matter to the ocean carbon cycle. The project would provide research and professional development opportunities for an early career investigator who has not received prior NSF support (co-PI Goranov). Undergraduates enrolled in REU and STEM training programs at the PIs' home institutions would participate in the research.

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-2346285

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