

Changes in dissolved organic carbon, stable carbon isotopes, pH, condensed aromatic carbon, and carboxyl-rich alicyclic molecules during laboratory photo-irradiation of vanillin

Website: <https://www.bco-dmo.org/dataset/1009323>

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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)

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Abstract

Demystifying the fate of terrestrial dissolved organic matter (tDOM) in rivers and the export of tDOM degradation products to the ocean furthers our understanding of the global carbon cycle. It allows for more reliable predictions of carbon fluxes that affect our environment and ultimately, our climate. While massive amounts of tDOM are annually exported from land through rivers to the oceans (5.1 Pg-C), its contribution to the open ocean beyond continental margins appears to be small based on conventional parameters that supposedly track tDOM. Photochemistry and other oxidative processes can transform the major component of tDOM, lignin, into compounds resembling oceanic organic matter, as verified by traditional biomarker or isotopic methods. Therefore, tDOM inputs to the oceans may be camouflaged by oxidation processes such as sunlight oxidation and other oxidative processes. Here we test this idea in photochemical experiments with vanillin, a lignin biomarker model representing environmental tDOM. The vast majority (91%) of the identified molecular transformation products of vanillin are found in terrestrial or marine environments. With the assumption that vanillin is a good quantitative biomarker for tDOM, we provide a global estimate for the amounts of tDOM-derived photo-degradation by-products (0.203 Pg-C/year) that are exported to the global oceans in forms that appear marine-like ($\delta^{13}\text{C} \approx -22 \text{ ‰}$). The findings of this study are globally transformative as they indicate that lignin photo-oxidation may be a major source of DOM in both terrestrial and marine environments and that the flux of these products beyond coastal boundaries can sustain both the oceanic DOM turnover and sedimentation rates implying a terrestrial origin of oceanic dissolved and particulate/sedimentary organic matter. This dataset contains measurements of dissolved organic carbon concentration, stable carbon isotopic composition ($\delta^{13}\text{C}$), pH, condensed aromatic carbon concentration, and carboxyl-rich alicyclic molecule carbon concentration from these laboratory photo-irradiation experiments.

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Coverage

Location: Laboratory

Temporal Extent: 2019 - 2026

Methods & Sampling

Vanillin (Acros, 99%), a lignin monophenol, was chosen as a representative monomeric unit of lignin, a major component of tDOM (Opsahl and Benner, 1998). A solution of 20 mg-C of vanillin in 1 L ultrapure MilliQ water was prepared to serve as a stock solution in photochemical experiments. This concentration was chosen because it is representative to carbon contents in upstream terrestrial aquatic environments such as rivers and lakes (Gonsior et al., 2009).

Photo-irradiation. Approximately 350 mL of vanillin stock solution was aliquoted into a pre-combusted 500 mL quartz round-bottom flask capped with a pre-combusted glass cap. An aliquot of the stock solution was immediately wrapped with aluminum foil and stored at room temperature as a dark control. Another aliquot of the stock solution was frozen to evaluate the stability of the dark control at room temperature. Up to three 500 mL quartz flasks were placed in a flatbed SUNTEST CPS+ solar simulator equipped with a daylight UV glass filter (ATLAS Cat. No. 56052371, cutoff at ~290 nm) for simulating solar radiation outdoors. Irradiation was performed under controlled chamber air temperature of 35 °C in 24-hour cycles using power of 250 W/m² yielding ~21,600 kJ/m² per 24 hours. Flasks were irradiated for 24 hours and then opened for 30 minutes during which they were aerated and gently stirred. During this aeration step, a 20-, 40-, or 50-mL subsample was taken out for analyses. To keep the same total volume throughout the irradiation (350 mL), the same amount of ultrapure water was added back. Multiple irradiation experiments were performed to yield sufficient sample volumes for the different analytical methods employed for the characterization of the photo-products.

Dissolved organic carbon. Dissolved organic matter was quantified as dissolved organic carbon (DOC) equivalents (in mg-C/L) on a Shimadzu TOC-VCPH instrument following standard operating procedures. Briefly, samples were acidified and sparged with air for 3 minutes to remove any inorganic carbon species (dissolved CO, CO₂, HCO₃⁻, CO₃²⁻) or other dissolved volatile gases (e.g., CH₄). Then, samples were injected in a high temperature combustion reactor (720 °C) to oxidize the DOM to CO₂. Detection of CO₂ is achieved using a non-dispersive infrared detector. DOC concentrations were quantified using standard calibration curves made with potassium hydrogen phthalate (Nacalai Tesque, JIS special grade).

Stable carbon isotopic composition (δ¹³C). Photo-irradiated solutions of vanillin were aliquoted to Falcon® tubes that were pre-aged in 2 % (w/w) NaOH for one month to remove any leachable carbon. Samples were freeze-dried and resuspended in ultrapure water to yield concentrated solutions necessary for analysis on a spooling-wire microcombustion (SWiM) device (Sessions et al. 2005) interfaced with an isotope-ratio mass spectrometer (IRMS) to determine the ratio of ¹³C to ¹²C atoms expressed in a delta notation (δ¹³C) and referenced to Vienna Pee Dee Belemnite (Camin et al. 2025).

The SWiM system used has been employed previously to measure δ¹³C values of aqueous samples (Mohr et al. 2014). The SWiM interface is connected to a ThermoFinnigan DeltaPlus Advantage IRMS via an open split. Reference CO₂ is controlled using a Conflo III, and data are collected and analyzed using Isodat v3.0. Each analytical run begins with three pulses of standard CO₂ reference gas and ends with two pulses of standard CO₂ reference gas. Samples were injected in 1 μL aliquots, separated by 30 sec; 3 to 5 injections are made of each sample. All data are corrected assuming linear drift of the m/z 45/44 ratio over the duration of the run. Each run includes samples (unknowns) and standard dilution series of two laboratory reference materials (dextrose, -11.2‰, and nor-leucine, -27.7‰). Empty tube blanks containing ultrapure water are also measured. Directly measured blank δ¹³C values were smaller than values inferred from the dilution series, determined by the intersection of δ¹³C versus Area-1 for the two dilution series, which intersect at Area-1 and δ¹³C of the blank. All samples were subsequently blank-corrected using the intersection of these two lines.

pH. pH measurements were performed using a Thermo Orion Star Series benchtop conductivity meter on unirradiated and irradiated vanillin solutions. The pH meter was calibrated daily with pH 4.01 buffer solution (YSI 3821), pH 7.00 buffer solution (YSI 3822), and pH 10.00 buffer solution (YSI 3823).

Condensed aromatic carbon (ConAC). Exactly 40 mL of vanillin control and photochemically processed samples were freeze-dried. The obtained residue was redissolved in 2 mL of 1:1 methanol:water and transferred to 2-mL glass ampoules. The solvent was evaporated at 60 °C and the residue was mixed with 0.5 mL concentrated nitric acid (65 %). Ampoules were flame-sealing and then samples were digested in an oven at 160°C for 6 hours. After this thermal digestion, the nitric acid was evaporated at 70°C in a sand bath under a stream of ultrapure nitrogen. The residue was redissolved in 0.5 mL of 0.6 mol L⁻¹ H₃PO₄ and filtered through a 0.2 µm syringe filter (Thermo Scientific™ Titan3™ PTFE). Benzenepentacarboxylic acid (B5CA, C₁₁H₆O₁₀) and benzenhexacarboxylic acid (B6CA, C₁₂H₆O₁₂) were quantified using an Agilent 1100 high-performance liquid chromatography system (Wagner et al. 2017). Their concentrations were then converted to carbon concentrations (i.e., B6CAC and B5CAC) and used to estimate the ConAC content of the original sample prior to digestion by multiplying by a scaling factor of 7.04 (Bostick et al., 2018) followed by normalization to organic carbon content. The molar ratio of B6CA to B5CA was also calculated to serve as an indicator of the degree of condensation of ConAC.

Carboxyl-rich alicyclic molecules (CRAM). Carboxyl-rich alicyclic molecules (CRAM) were quantified using liquid-state ¹H NMR spectroscopy. Analyses were performed at room temperature (24.9 ± 0.1 °C) on a 400 MHz (9.4 Tesla) Bruker BioSpin AVANCE III spectrometer fitted with a double-resonance broadband inverse (BBI) probe at the College of Sciences Major Instrumentation Cluster (COSMIC) facility of Old Dominion University (Norfolk, VA). Instrument control and data processing were performed using the TopSpin software. Analyses were performed without pre-concentration (e.g., via solid-phase extraction) or filtering on aliquots of samples taken at different time points. Samples were prepared by mixing a 516-µL aliquot of the sample with 60 µL deuterated water (Acros Organics, 99.9% D, CAN RN 7789-20-0) to produce a 90:10 H₂O:D₂O solution necessary for obtaining a deuterium lock. Additionally, sodium 2,2,3,3-tetradeutero-3-trimethylsilylpropanoate was added (24 µL of 25 µM solution; Acros Organics, 98% D) to serve as an internal standard. Once all aliquots were added to an NMR tube, they were mixed using a vortex mixer. NMR tubes were pre-cleaned by soaking in aqua regia for 2+ weeks. Prior to use, each NMR tube is rinsed with ~250 mL of ultrapure water and dried at 60 °C to ensure no contamination.

One-dimensional (1D) quantitative ¹H spectra were acquired using the PEW5shapepr pulse program, which utilizes Perfect Echo - WATERGATE and shaped presaturation techniques for water suppression (Adams et al., 2013, Whitty et al., 2019). The employment of this pulse sequence results in quantitative spectra, with the water resonance at 4.7 ppm being suppressed. The relaxation delay (D1) employed for all quantitative analyses was 13.5 s, which was determined after an inversion-recovery experiment. For each individual sample the 90° excitation pulse width (P1) and transmitter offset (O1) were optimized to ensure quantitiveness of the signals. The obtained free-induction decay of 4096 summed transients was zero-filled to a 16k-sized dataset and apodized using a 10-Hz Lorentzian window function.

Additional Data

Additional spectroscopic and mass spectrometric data is available from the authors upon request.

Data Processing Description

Data were processed in Microsoft Excel.

NMR spectra were processed using the TopSpin software. First, spectra were calibrated, phased, and baseline-corrected. Then, spectra were integrated in the following regions: CH₃ (0.6 – 0.91 ppm), CRAM (0.91 – 3.15 ppm), HC-O-R (3.15 – 4.4 ppm), olefinic (5 – 6.5 ppm), aromatic (6.5 – 8.3 ppm), and CHO (8.3 – 10 ppm). Formate (~8.3 ppm), methanol (3.34 ppm), and acetate (~1.9 ppm) were also independently integrated following manual inspection of each spectrum. They were subtracted from the region they resonate at: for example, acetate (resonating at ~1.9 ppm) is removed from the CRAM region (0.91-3.15 ppm). The CRAM region range has been previously determined by McKee et al. 2024. All integrals were also corrected for minor background signals using blank correction obtained from the analysis of pure vanillin in ultrapure water.

To be able to use ¹H NMR data for dissolved organic matter analysis (which is done via DOC, i.e., on a C-basis), the integrals (which are on H-basis as they originate from ¹H spectra) were converted into C-basis integrals by multiplication with H/C molar ratios as following: 3 for CH₃, 1 for CRAM (McKee et al. 2024), 1.1 for HC-O-R (Decesari et al., 2007), 1 for olefinic, 0.4 for aromatic (Decesari et al. 2007), and 1 for CHO.

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 Data for BCO-DMO repository.xlsx (Sheet1, header row 1), using filename as resource name; set missing value sentinels to "", "nd", "ND", "N.D."
- Renamed columns: "Laboratory time, hours" to laboratory_time, "Measured [DOC], ppm-C" to measured_DOC, "Measured [DOC] Standard Deviation" to measured_DOC_std_dev, "d13C Standard Deviation" to d13C_std_dev, "pH Standard Deviation" to pH_std_dev, "Measured ConAC (ppm-C)" to measured_ConAC, "Measured ConAC Standard Deviation" to measured_ConAC_std_dev, "Measured CRAM (ppm-C)" to measured_CRAM, "Measured CRAM Standard Deviation" to measured_CRAM_std_dev (d13C and pH kept unchanged since names already matched targets)
- Output file as 1009323_v1_doc_degradation_incubation.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>
- Included information from instrument descriptions in the methods section
- Expanded parameter definitions for clarity

ISSUES POTENTIALLY IMPACTING REUSE

- Dataset values seem to be derived values, based on the observations. The complete data is not referenced or provided as part of this submission.
- Metadata does not state whether a dilution correction was applied to reported concentrations to account for the ultrapure water added back after each 30-minute aeration/subsampling step to maintain the 350 mL total volume, nor how such a correction would be calculated; metadata does not clarify whether the reported parameter values represent raw measured concentrations or values adjusted for this dilution effect.
- Metadata does not specify how many independent irradiation experiments (replicates) were conducted.

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Related Publications

Adams, R. W., Holroyd, C. M., Aguilar, J. A., Nilsson, M., & Morris, G. A. (2013). "Perfecting" WATERGATE: clean proton NMR spectra from aqueous solution. *Chem. Commun.*, 49(4), 358–360.

<https://doi.org/10.1039/c2cc37579f>

Methods

Bostick, K. W., Zimmerman, A. R., Wozniak, Andrew. S., Mitra, S., & Hatcher, P. G. (2018). Production and Composition of Pyrogenic Dissolved Organic Matter From a Logical Series of Laboratory-Generated Chars.

Frontiers in Earth Science, 6. <https://doi.org/10.3389/feart.2018.00043>

Methods

Camin, F., Besic, D., Brewer, Paul J., Allison, Colin E., Coplen, Tyler B., Dunn, Philip J. H., Gehre, M., Gröning, M., Meijer, Harro A. J., Hélie, J.-F., Iacumin, P., Kraft, R., Krajnc, B., Kümmel, S., Lee, S., Meija, J., Mester, Z., Mohn, J., Moossen, H., et al. (2025). Stable Isotope Reference Materials and Scale Definitions—Outcomes of the 2024 IAEA Experts Meeting. *Rapid Communications in Mass Spectrometry*, 39(14). Portico.

<https://doi.org/10.1002/rcm.10018>

Methods

Decesari, S., Mircea, M., Cavalli, F., Fuzzi, S., Moretti, F., Tagliavini, E., & Facchini, M. C. (2007). Source Attribution of Water-Soluble Organic Aerosol by Nuclear Magnetic Resonance Spectroscopy. *Environmental Science & Technology*, 41(7), 2479–2484. <https://doi.org/10.1021/es061711j>

Methods

Gonsior, M., Peake, B. M., Cooper, W. T., Podgorski, D., D'Andrilli, J., & Cooper, W. J. (2009). Photochemically Induced Changes in Dissolved Organic Matter Identified by Ultrahigh Resolution Fourier Transform Ion

Cyclotron Resonance Mass Spectrometry. Environmental Science & Technology, 43(3), 698–703.

<https://doi.org/10.1021/es8022804>

Methods

McKee, K., Abdulla, H., O'Reilly, L., & Walker, B. D. (2024). Cycling of labile and recalcitrant carboxyl-rich alicyclic molecules and carbohydrates in Baffin Bay. Nature Communications, 15(1).

<https://doi.org/10.1038/s41467-024-53132-5>

Methods

Mohr, W., Tang, T., Sattin, S. R., Bovee, R. J., & Pearson, A. (2014). Protein Stable Isotope Fingerprinting: Multidimensional Protein Chromatography Coupled to Stable Isotope-Ratio Mass Spectrometry. Analytical Chemistry, 86(17), 8514–8520. <https://doi.org/10.1021/ac502494b>

Methods

Opsahl, S., & Benner, R. (1998). Photochemical reactivity of dissolved lignin in river and ocean waters. Limnology and Oceanography, 43(6), 1297–1304. Portico. <https://doi.org/10.4319/lo.1998.43.6.1297>

Methods

Sessions, A. L., Sylva, S. P., & Hayes, J. M. (2005). Moving-Wire Device for Carbon Isotopic Analyses of Nanogram Quantities of Nonvolatile Organic Carbon. Analytical Chemistry, 77(20), 6519–6527.

<https://doi.org/10.1021/ac051251z>

Methods

Wagner, S., Brandes, J., Goranov, A. I., Drake, T. W., Spencer, R. G. M., & Stubbins, A. (2017). Online quantification and compound-specific stable isotopic analysis of black carbon in environmental matrices via liquid chromatography-isotope ratio mass spectrometry. Limnology and Oceanography: Methods, 15(12), 995–1006. doi:[10.1002/lom3.10219](https://doi.org/10.1002/lom3.10219)

Methods

Whitty, S. D., Waggoner, D. C., Cory, R. M., Kaplan, L. A., & Hatcher, P. G. (2019). Direct noninvasive ^1H NMR analysis of stream water DOM: Insights into the effects of lyophilization compared with whole water. Magnetic Resonance in Chemistry, 59(5), 540–553. Portico. <https://doi.org/10.1002/mrc.4935>

Methods

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Parameters

Parameter	Description	Units
laboratory_time	Time of irradiation; Cumulative duration of sample exposure recorded in 24-hour irradiation cycle increments	hours
measured_DOC	Measured Dissolved Organic Carbon	ppm-C
measured_DOC_std_dev	Standard Deviation of the Measured [DOC]	ppm-C
d13C	Stable carbon isotopic signature	‰
d13C_std_dev	Standard Deviation of the d13C	‰
pH	pH	unitless
pH_std_dev	Standard Deviation of the pH	unitless
measured_ConAC	Condensed aromatic carbon (ConAC) concentration	ppm-C
measured_ConAC_std_dev	Standard deviation of replicate ConAC measurements	ppm-C
measured_CRAM	Carboxyl-rich alicyclic molecule (CRAM) carbon concentration	ppm-C
measured_CRAM_std_dev	Standard deviation of replicate CRAM measurements	ppm-C

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Instruments

Dataset-specific Instrument Name	Thermo Orion Star Series benchtop conductivity meter
Generic Instrument Name	Benchtop pH Meter
Dataset-specific Description	pH measurements were performed using a Thermo Orion Star Series benchtop conductivity meter on unirradiated and irradiated vanillin solutions. The pH meter was calibrated daily with pH 4.01 buffer solution (YSI 3821), pH 7.00 buffer solution (YSI 3822), and pH 10.00 buffer solution (YSI 3823).
Generic Instrument Description	An instrument consisting of an electronic voltmeter and pH-responsive electrode that gives a direct conversion of voltage differences to differences of pH at the measurement temperature. (McGraw-Hill Dictionary of Scientific and Technical Terms) This instrument does not map to the NERC instrument vocabulary term for 'pH Sensor' which measures values in the water column. Benchtop models are typically employed for stationary lab applications.

Dataset-specific Instrument Name	oven
Generic Instrument Name	Drying Oven
Dataset-specific Description	Ampoules were flame-sealing and then samples were digested in an oven at 160°C for 6 hours.
Generic Instrument Description	a heated chamber for drying

Dataset-specific Instrument Name	Agilent 1100 high-performance liquid chromatography system
Generic Instrument Name	High-Performance Liquid Chromatograph
Dataset-specific Description	Benzenepentacarboxylic acid (B5CA, C ₁₁ H ₆ O ₁₀) and benzenhexacarboxylic acid (B6CA, C ₁₂ H ₆ O ₁₂) were quantified using an Agilent 1100 high-performance liquid chromatography system (Wagner et al. 2017).
Generic Instrument Description	A High-performance liquid chromatograph (HPLC) is a type of liquid chromatography used to separate compounds that are dissolved in solution. HPLC instruments consist of a reservoir of the mobile phase, a pump, an injector, a separation column, and a detector. Compounds are separated by high pressure pumping of the sample mixture onto a column packed with microspheres coated with the stationary phase. The different components in the mixture pass through the column at different rates due to differences in their partitioning behavior between the mobile liquid phase and the stationary phase.

Dataset-specific Instrument Name	flatbed SUNTEST CPS+ solar simulator
Generic Instrument Name	irradiation system
Dataset-specific Description	Up to three 500 mL quartz flasks were placed in a flatbed SUNTEST CPS+ solar simulator equipped with a daylight UV glass filter (ATLAS Cat. No. 56052371, cutoff at ~290 nm) for simulating solar radiation outdoors.
Generic Instrument Description	A system of instruments/devices that provide irradiation of materials. Irradiation is an energy transfer process during which a material entity receives energy through radiation.

Dataset-specific Instrument Name	spooling-wire microcombustion (SWiM) device interfaced with an isotope-ratio mass spectrometer (IRMS)
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	Samples were freeze-dried and resuspended in ultrapure water to yield concentrated solutions necessary for analysis on a spooling-wire microcombustion (SWiM) device (Sessions et al., 2005) interfaced with an isotope-ratio mass spectrometer (IRMS) to determine the ratio of ¹³ C to ¹² C atoms expressed in a delta notation (δ ¹³ C) and referenced to Vienna Pee Dee Belemnite (Camin et al. 2025).
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	Bruker BioSpin AVANCE III spectrometer
Generic Instrument Name	Nuclear Magnetic Resonance Spectrometers
Dataset-specific Description	Analyses were performed at room temperature (24.9 ± 0.1 °C) on a 400 MHz (9.4 Tesla) Bruker BioSpin AVANCE III spectrometer fitted with a double-resonance broadband inverse (BBI) probe at the College of Sciences Major Instrumentation Cluster (COSMIC) facility of Old Dominion University (Norfolk, VA).
Generic Instrument Description	Instruments that identify and quantify magnetically active chemical entities by subjecting a sample to orthogonal magnetic and electrical fields.

Dataset-specific Instrument Name	Shimadzu TOC-VCPH
Generic Instrument Name	Shimadzu Total Organic Carbon Analyzer TOC-VCPH
Dataset-specific Description	Dissolved organic matter was quantified as dissolved organic carbon (DOC) equivalents (in mg-C/L) on a Shimadzu TOC-VCPH instrument following standard operating procedures.
Generic Instrument Description	The Shimadzu Total Organic Carbon Analyzer TOC-VCPH is a PC-controlled, total organic carbon analyzer (high-sensitivity model), designed to measure total carbon (TC), inorganic carbon (IC), total organic carbon (TOC), and non-purgeable organic carbon (NPOC); an optional accessory enables the measurement of particulate organic carbon (POC) and total nitrogen (TN) as well. The instrument uses the 680 degrees Celsius combustion catalytic oxidation method to analyze aqueous samples, and optionally solid and gas samples.

Dataset-specific Instrument Name	vortex mixer
Generic Instrument Name	vortex mixer
Dataset-specific Description	Additionally, sodium 2,2,3,3-tetradeutero-3-trimethylsilylpropanoate was added (24 μ L of 25 μ M solution; Acros Organics, 98% D) to serve as an internal standard. Once all aliquots were added to an NMR tube, they were mixed using a vortex mixer.
Generic Instrument Description	A vortex mixer is an electrical rotator that blends or mixes substances or ingredients, in whirling or rotary motion, for homogenizing samples.

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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 ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) 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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