TEMPORAL NETWORK INVESTIGATIONS INTO THE LIFE CYCLE OF TERRESTRIAL DISSOLVED ORGANIC MATTER

Shannon Stephens, Dr. Aleksander Goranov, Dr. Kyle Lambert
Old Dominion University

Abstract

Dissolved organic matter found in ocean contributing waterways, such as rivers and swamps, is a key contributor to the global carbon cycle. Sunlight degradation of fluvial samples produce CO_2 and CH_4, causing significant carbon emissions with the remaining degradation by-products travelling into the ocean. While the processing of fluvial organic matter is vitally important for understanding the global biogeochemical cycles, it remains understudied on the chemical level. To resolve this knowledge gap, simulated solar irradiation was applied to nine fluvial samples taken from various American southeastern waterways and analyzed via a multitude of analytical platforms, including 15-Tesla Fourier transform – ion cyclotron resonance – mass spectrometry (FT-ICR-MS) for obtaining the molecular fingerprint of each sample, and NMR and X-ray spectroscopies for determining bulk structural composition. Each sample mixture contained a profusion of unique chemical species (~5000) corresponding to different molecular photo-degradation transformations. Herein we report, the use of a temporal graph model exploring these molecular transformations. Their connection with data from other analytical techniques allow for a proposal of an overall organic matter lifecycle framework allowing for large-scale planetary modeling of fluvial photo-degradation.

Introduction

Light-driven chemical reactions are fundamental to Earth's biogeochemistry within fluvial and oceanic waters. Dissolved organic matter (DOM) largely influences how aquatic environments absorb visible and ultraviolet (UV) light from the sun. This leads to subsequent effects on photosynthesis and enhances the activity of microbes, which leads to stimulated bacterial growth influencing the aquatic foods web.[1] The major contributor to DOM fluxes is terrestrial dissolved organic matter (tDOM), which are deposited into fluvial environments from land (e.g., soils) by hydrologic events (e.g., precipitation).

Quantitatively, on a global scale, about 2.90 Pg-C (10^{15} g carbon-equivalents) of tDOM are annually exported from land to rivers and only 0.48 Pg-C end up reaching the oceans. The apparent losses of tDOM largely occur due to its exposure to various degradative pathways driven by sunlight (photochemical degradation), microbes (bio-degradation), and minerals (Fenton-like degradation).[2–4] Considering that these degradative processes release massive amounts of carbon into the atmosphere (about 2.12 Pg-C, cite my paper from the link above), it is of high importance to understand the chemistry behind these processes. To examine the effects of sunlight on individual chemical species, previous studies have performed experiments to ascertain the specific reactions of these heterogeneous sample mixtures. Unfortunately, these studies are unable to combine a multitude of specific organic reactions and have primarily focused on smaller sample areas with more uniform water profiles such as wastewater sludge, lakes, or seas.[5–8]

Environmental samples are also difficult to analyze due to the multitude of chemical

Figure 1. Graphical map of project sample sites.

species within each one (generally estimated to reach hundreds of thousands of molecules in a sample), necessitating only bulk analysis of each sample. Such measurements yield a holistic snapshot of each sample, but the drawback is the inability to study the individual species. At present, the most powerful approach to resolve this extreme molecular complexity is by the use of ultrahigh resolution mass spectrometry (Fourier transform – ion cyclotron resonance – mass spectrometry, FT-ICR-MS), which can identify thousands of different molecular species in a sample.

The need to better understand the chemical transformations on a larger scale both with respect to sample type and reaction diversity and the emergence on data-driven analysis has provided excellent opportunities. Plamper and coworkers created a temporal network-based model that compiled previously photo-irradiation reactions with simulated sunlight on a previously created dataset from wastewater samples using Neo4j graph database and their own python interface. Their analysis provided us a baseline for our own experimental analysis.[9,10]

Methods

Nine terrestrial samples were previously collected from waterways of the American southeast (Figure 1) and subsequently underwent light exposure for 6 days via a SUNTEST CPS+ solar simulator with a daylight UV glass filter. The exposure time was chosen to simulate an equivalent of 26 days of natural sunlight a water sample would theoretically undergo while traveling from a fluvial source to the open ocean. Sampling sites were chosen based upon their contributions to their watershed and their accessibility. The chemical makeup of each sample was analyzed via a multitude of analytical platform, including FT-ICR-MS, liquid-state ^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy, ultraviolet-visible (UV-VIS) spectrophotometry, as well as bulk geochemical characterization (pH, conductivity, and salinity) both prior to and post irradiation. Each sample was found to be a mixture containing many unique chemical species (~5000). These analyses enumerate the organic transformations that the sample undergoes (e.g. carbon losses from oxidation via conversion into CO/CO_2 and subsequent removal into air) over the course of the simulated sunlight exposure.

Using our mass spectrometry data, we prepared a graphical database using Neo4j software and Plumper's python interface. Our database annotated each chemical species as a node and potential or predicted transformations were defined as the edges between them (Figure 2).[10]

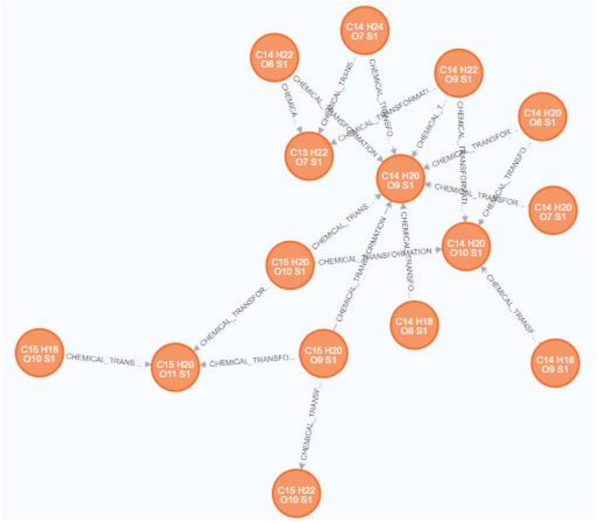


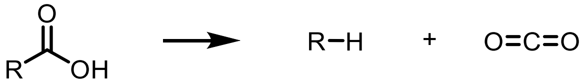
Figure 2. Neo4j graph database of Hillsborough sample, reduced to 15 compounds for clarity.

As part of our investigation, additional organic transformations were incorporated into the graph database system based upon previous literature and organic chemical intuition.

Results and Discussion

Initial PCA data analysis was performed to get a general overview of the chemical transformations of the samples (Figure 3). These findings indicate a continuum consisting of different samples with each having a unique chemical make-up but traveling the same life cycle continuum (shown by the blue arrow). This continuum can be thought of as a tDOM pathway in which each sample type undergoes the same journey but begins at different starting points. Another important finding was the correlation between PC1 score values and the quantity of chromophoric (light-absorbing) DOM. This indicates that if such continuum exists, chromophoric data from satellite imagingREF can be used to predict the photochemical degradation chemistry and quantitative CO2 production on a planetary scale.[11]

Our analysis here aims to connect the different analysis techniques employed on the samples to one another, further supporting the photochemical continuum hypothesis. Figure 4 reports the top ten chemical reaction types for each of the nine samples. For each sample with the exemption of the Ashepoo River, oxidations were the highest occurring reaction type (15%-39%). The Ashepoo River sample showed the highest occurring transformations as decarboxylation reactions (26%) (Scheme 1).



Scheme 1. Decarboxylation reaction example.

Interestingly, the Santa Fe River sample showed high levels of decarboxylation reactions as well (22%). The PCA analysis indicates that both samples' controls are located within the "Fresh tDOM" and fell into the "Minimally photo-transformed tDOM" category upon irradiation.

Further data analysis for this work is ongoing, but these initial analyses provide evidence of our continuum hypothesis.

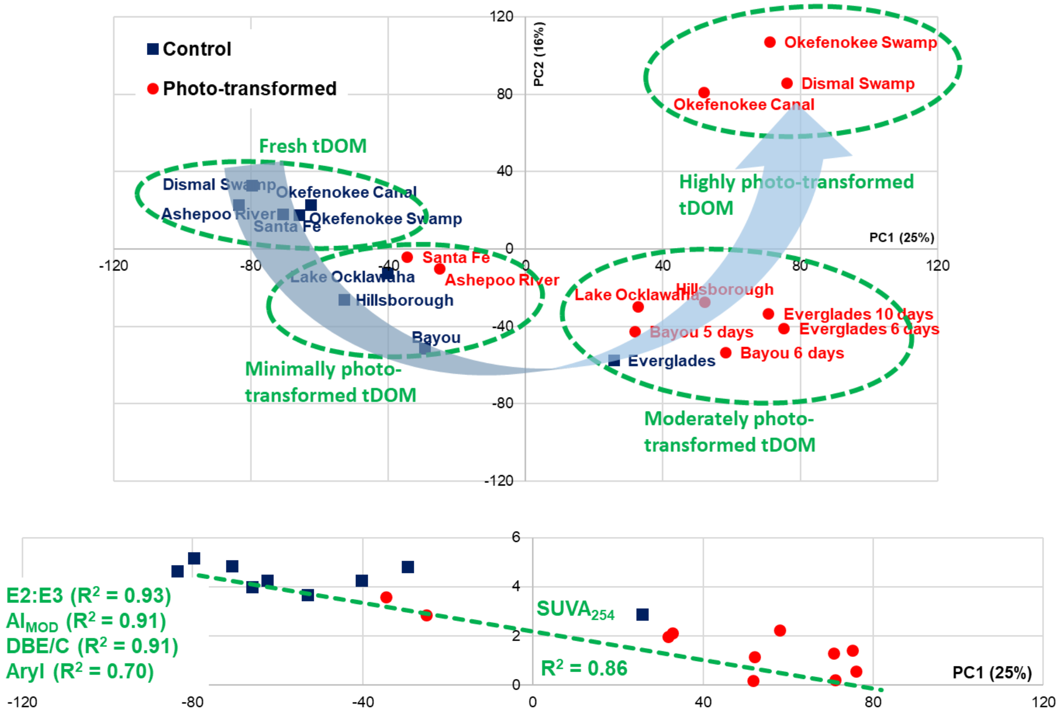


Figure 3. PCA analysis of American southeast fluvial samples (top).

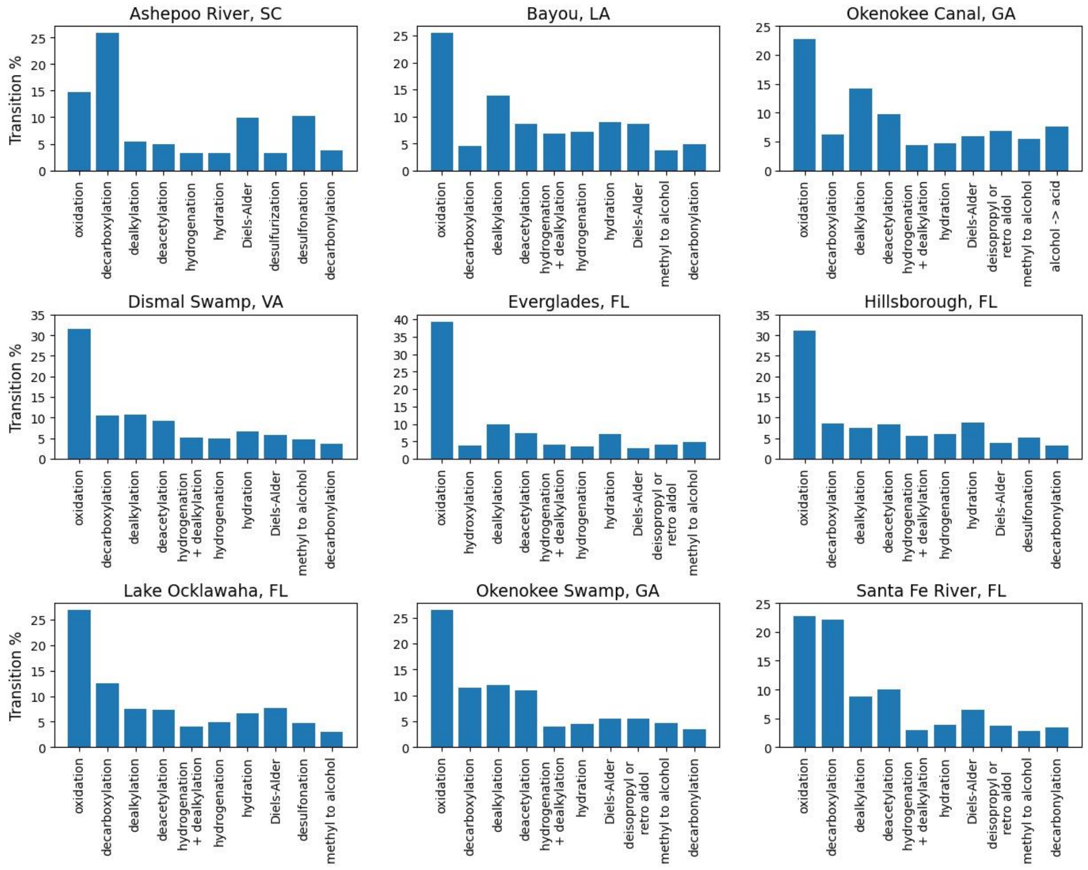


Figure 4. Top ten organic transformations for fluvial samples. The x-axis depicts the reaction type, y-axis is the percentage of the sample of each reaction type.

Conclusions

Coupling ultrahigh resolution FT-ICR-MS molecular characterization with neural network explorations allowed for exploring the track potential and predicted chemical transformations of tDOM, which are expected to occur in fluvial environments. While data analysis is ongoing, initial examination supports a hypothesis that fluvial tDOM samples undergo a singular life cycle continuum. Continuing work on this project will include making connections between the predicted chemical reactions from mass spectrometry data and linking it to additional analyses, namely ^{1}H NMR and X-ray spectroscopies. This will provide validation of the occurring photochemical reactions and enable their modeling on a global planetary scale in combination with chromophoric DOM data obtained from satellite remote sensing. Collectively, this work will provide a more accurate and quantitative picture of the photochemical degradation of tDOM and fluvial production of carbon emissions (e.g., CO_2) on a global planetary scale.

References

(1) Mopper, K.; Kieber, D.; Stubbins, A. *Marine Photochemistry of Organic Matter: Processes and Impacts - ScienceDirect*; 2015.

(2) Cole, J. J.; Prairie, Y. T.; Caraco, N. F.; McDowell, W. H.; Tranvik, L. J.; Striegl, R. G.; Duarte, C. M.; Kortelainen, P.; Downing, J. A.; Middelburg, J. J.; Melack, J. Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget. *Ecosystems* **2007**, *10*, 172–185.

(3) Drake, T. W.; Raymond, P. A.; Spencer, R. G. M. Terrestrial Carbon Inputs to Inland Waters: A Current Synthesis of Estimates and Uncertainty. *Limnology and Oceanography Letters* **2018**, *3*, 132–142.

(4) Tranvik, L. J.; Downing, J. A.; Cotner, J. B.; Loiselle, S. A.; Striegl, R. G.; Ballatore, T. J.; Dillon, P.; Finlay, K.; Fortino, K.; Knoll, L. B.; Kortelainen, P. L.; Kutser, T.; Larsen, Soren.; Laurion, I.; Leech, D. M.; McCallister, S. L.; McKnight, D. M.; Melack, J. M.; Overholt, E.; Porter, J. A.; Prairie, Y.; Renwick, W. H.; Roland, F.; Sherman, B. S.; Schindler, D. W.; Sobek, S.; Tremblay, A.; Vanni, M. J.; Verschoor, A. M.; von Wachenfeldt, E.; Weyhenmeyer, G. A. Lakes and Reservoirs as Regulators of Carbon Cycling and Climate. *Limnology and Oceanography* **2009**, *54*, 2298–2314.

(5) Hu, A.; Li, L.; Huang, Y.; Fu, Q.-L.; Wang, D.; Zhang, W. Photochemical Transformation Mechanisms of Dissolved Organic Matters (DOM) Derived from Different Bio-Stabilization Sludge. *Environment International* **2022**, *169*, 107534.

(6) Zhang, B.; Wang, X.; Fang, Z.; Wang, S.; Shan, C.; Wei, S.; Pan, B. Unravelling Molecular Transformation of Dissolved Effluent Organic Matter in UV/H2O2, UV/Persulfate, and UV/Chlorine Processes Based on FT-ICR-MS Analysis. *Water Research* **2021**, *199*, 117158.

(7) Stedmon, C. A.; Markager, S.; Tranvik, L.; Kronberg, L.; Slätis, T.; Martinsen, W. Photochemical Production of Ammonium and Transformation of Dissolved Organic Matter in the Baltic Sea. *Marine Chemistry* **2007**, *104*, 227–240.

(8) Zuo, Y.; Jones, R. D. Photochemistry of Natural Dissolved Organic Matter in Lake and Wetland Waters—Production of Carbon Monoxide. *Water Research* **1997**, *31*, 850–858.

(9) Plamper, P.; Lechtenfeld, O. J.; Herzsprung, P.; Groß, A. A Temporal Graph Model to Predict Chemical Transformations in Complex Dissolved Organic Matter. *Environ. Sci. Technol.* **2023**, *57*, 18116–18126.

(10) Neo4j Graph Database & Analytics. https://neo4j.com/.

(11) Kutser, T.; Pierson, D. C.; Kallio, K. Y.; Reinart, A.; Sobek, S. Mapping Lake CDOM by Satellite Remote Sensing. *Remote Sensing of Environment* **2005**, *94*, 535–540.