Effect of changing oxygen conditions on iron-bound organic carbon in lake sediment

Abstract Associations between iron and organic carbon play a critical role for carbon burial in marine sediments. However, the role of iron in freshwater organic carbon burial is poorly understood. This is a critical research gap, as reservoirs alone may bury more carbon than ocean sediments each year. Moreover, it remains unknown how the global trend of decreasing bottom-water oxygen concentrations in lakes and reservoirs may impact the preservation of iron-bound organic carbon. Low oxygen concentrations may cause reductive dissolution of iron-bound organic carbon complexes, releasing organic carbon into the water column and facilitating carbon export or mineralization. In this study, I will pair whole-ecosystem oxygenation experiments and laboratory incubations to quantify the importance of iron for organic carbon burial in sediments and the sensitivity of these interactions to changing water-column oxygen concentrations. Through this work, I will develop a better understanding of iron-bound organic carbon dynamics in freshwater ecosystems, helping to predict future carbon cycling dynamics in the face of global change.

Public Abstract Lakes are an important "sink" in the global carbon cycle: they take up carbon dioxide from the atmosphere through photosynthesis and bury this carbon in sediments, thereby limiting the accumulation of carbon dioxide (a greenhouse gas) in Earth's atmosphere. One of the primary factors that facilitates the preservation of carbon in sediments is "protection" of organic carbon by iron. However, changes in climate and land use are decreasing oxygen concentrations in many lakes around the world, which may decrease the strength of the protection that iron offers organic carbon. This would potentially allow more carbon to be released and transported downstream, increasing natural emissions of carbon dioxide to Earth's atmosphere and worsening anthropogenic climate change. In this study, I will pair whole-ecosystem experiments with small-scale incubations in the lab to determine what percentage of organic carbon in the sediment is bound to iron and how sensitive those associations are to changing oxygen concentrations. Through this work, I shed light on a potentially critical climate feedback, helping to predict and prepare for the trajectory of future climate change.

Motivation

Freshwater lakes and reservoirs (hereafter: "lakes") are globally important sinks of organic carbon, burying more carbon than ocean sediments each year (Dean and Gorham 1998; Downing et al. 2008; Knoll et al. 2013; Pacheco et al. 2014). However, the rate at which these waterbodies sequester carbon is predicted to change over time due to simultaneous changes in temperature and oxygen levels (Pacheco et al. 2014; Bartosiewicz et al. 2019). A thorough understanding of the factors that control carbon sequestration is essential to be able to predict the role of lakes in the global carbon cycle under interacting systems of global change.

Mineral associations with organic carbon are increasingly recognized as a critical way in which carbon is retained in soils and sediment (Mayer 1994; Kaiser and Guggenberger 2000; Lalonde et al. 2012; Hemingway et al. 2019). Associations between organic carbon and mineral surfaces (most notably iron; Fe) serve to stabilize organic carbon in the soil or sediment and protect it from

microbial mineralization. On a geologic time scale, mineral associations appear to be more influential than inherent organic carbon reactivity in promoting the preservation of organic carbon in soils and sediments (Torn et al. 1997; Hemingway et al. 2019). Studies across a broad range of (primarily marine) aquatic systems have found that 10–40% of the sediment organic carbon may be associated with iron (Lalonde et al. 2012; Shields et al. 2016). Despite the critical role that freshwater ecosystems play in global carbon cycling, comparably little research has been done on the importance of mineral associations with iron in these systems.

Associations between iron and organic carbon can be sensitive to the redox potential of the surrounding environment. During oxic (high oxygen) conditions, iron exists in surface sediments in a variety of forms, including iron-bound organic carbon. As the water column becomes anoxic (low oxygen), Fe(III) associated with organic carbon may be reduced to Fe(II), breaking apart the iron-bound organic carbon complex. This dissolution of iron-bound organic carbon under anoxic conditions releases both soluble iron and dissolved organic carbon into the surrounding water (O'Loughlin and Chin 2004). Restoration of oxic conditions can quickly (i.e., in a few minutes; Zak et al. 2004) reverse this process, as iron and organic carbon re-associate and precipitate back into the sediment.
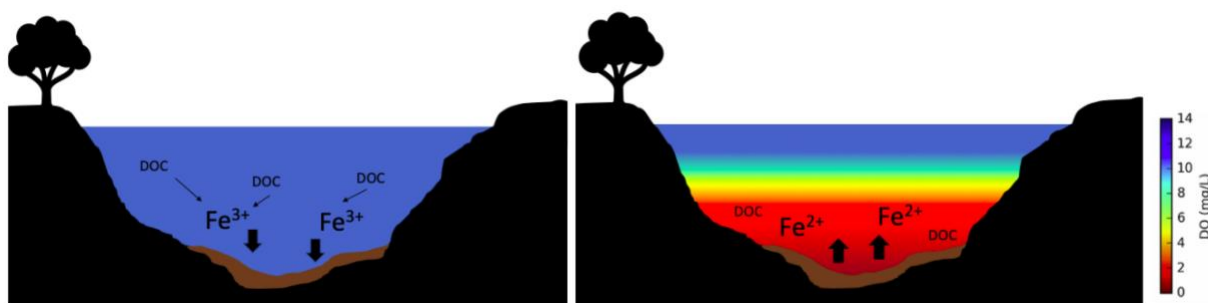

Figure 1: Co-precipitation and reductive dissolution of iron (Fe) and organic carbon complexes are predicted to play an important role in freshwater carbon cycling. Left: under oxic conditions, iron co-precipitates with dissolved organic carbon, sequestering the carbon in the sediment. Right: under anoxic conditions, iron is reduced, releasing organic carbon back into the water column.

Redox-sensitive association and dissolution of iron-bound organic carbon has been well demonstrated in both soils and marine sediment (Skoog and Arias-Esquivel 2009; Riedel et al. 2013; Bhattacharyya et al. 2018). However, relatively little research has been done on the importance of coupled biogeochemical cycles of iron and organic carbon in freshwater lakes, and what research has been done has yielded conflicting results (Lalonde et al. 2012; Brothers et al. 2014; Peter et al. 2016; Peter and Sobek 2018). More research is needed to determine the significance of iron-bound organic carbon and its sensitivity to oxygen concentrations in freshwater lakes.

Proposed work
In this study, I will use a combination of whole-ecosystem oxygenation experiments and sediment incubations to determine the significance of changing water column oxygen levels for iron-bound organic carbon and long-term carbon storage in sediments.

Effect of changing oxygen conditions on iron-bound organic carbon in lake sediment

I began working on this project during the summer of 2019 by comparing the amount of iron-bound organic carbon in sediments from Falling Creek and Beaverdam Reservoirs (FCR and BVR; Roanoke, VA, USA). FCR is equipped with a bottom-water oxygenation system that has been operated on a variable schedule for seven years, maintaining primarily oxic conditions. BVR serves as an unoxygenated reference and exhibits anoxic conditions from May to October. I found that a large percentage of sediment organic carbon was bound to iron in both reservoirs, and this percentage was significantly higher in FCR (μ = 35% of sediment organic carbon) than in BVR (μ = 31%). These results are noteworthy in two ways: first, the concentrations of iron-bound organic carbon in sediment reported here are higher than those reported in other lakes and most marine sediments (Lalonde et al. 2012; Peter and Sobek 2018), indicating that iron may play a more important role in carbon preservation in some iron-rich ecosystems than has been previously documented. Second, the fact that iron-bound organic carbon levels differed between reservoirs suggests that long-term trends in anoxia may decrease carbon sequestration in sediments. I originally intended to do another summer of whole-ecosystem experiments and lab incubations to confirm these findings in the summer of 2020. However, that work had to be postponed to 2021 due to the covid-19 pandemic.

This summer, I will conduct multiple whole-ecosystem oxygenation experiments in FCR to expand upon my results from 2019. Through a collaboration with the Western Virginia Water Authority, I will operate the oxygenation system on a variable schedule to experimentally determine how intermittent periods of oxic and anoxic conditions affect iron-bound organic carbon concentrations in sediment. To complement these whole-ecosystem results, I will also incubate sediment in the lab under variable oxygen conditions to test the isolated impacts of oxygen on iron-bound organic carbon in the absence of other drivers (e.g., temperature). In 2019, we observed high levels of variability in iron-bound organic carbon concentrations within each reservoir. Laboratory incubations will substantially reduce this variability, providing a clearer test of the effects of oxygen on iron-bound organic carbon. Conducting both whole-ecosystem and laboratory-based experiments is highly complementary, as whole-ecosystem work highlights the real-world importance of ecological changes, while laboratory incubations provide a detailed test of the mechanism behind those changes.

Broader Impact

This work will provide important insight to inform our understanding of how oxygen dynamics affect freshwater carbon processing, improving estimates of the global carbon cycle and generating valuable information for the management of lakes and reservoirs in the face of global change. Additionally, I will work with the Center for Communicating Science to share results broadly at events such as Science on Tap that draw in non-scientific audiences; I am already scheduled to give a science on tap talk in June 2021. Finally, I have an undergraduate mentee (Arpita Das) who I have worked with for the past two years, and she has accepted our offer to stay for the summer and work on this project. Through work on this project, Arpita will gain critical experience helping to design, execute, and analyze the results of this experiment, likely leading to co-authorship on the final manuscript.

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Estimated Budget

1. **64 Qt. containers**
   $11.98 each * 4 = **$47.92**
   Containers will be used to catch precipitating organic matter in FCR and BVR (two replicates in each reservoir). Containers will be suspended using existing anchors and buoys available for this project.
   Home Depot

2. **250 mL incubation bottles**
   $65.11 per case of 24 * 6 cases = **$390.66**
   Sediment will be incubated in the lab under three different oxygen treatments. Each treatment will have 33 replicates, to enable destructive sampling for iron-bound organic carbon concentrations over the course of the experiment. Therefore, a minimum of 99 bottles are needed for the experimental incubations.
   Corning Life Sciences

3. **Size 8 incubation bottle stoppers**
   $1.62 * 70 = **$113.40**
   Two-thirds of the sediment incubations will be anoxic at some point during the experiment and therefore need to be sealed using bottle stoppers: 2/3 * 99 = 66 stoppers needed at a minimum.
   Indigo instruments

4. **15 mL centrifuge tubes**
   $315.50 for 1 case (500 tubes)
   Three centrifuge tubes are needed for each iron-bound organic carbon extraction. Assuming 48 whole ecosystem samples and 99 incubation samples: (48 + 99) * 3 = 441 tubes are needed at minimum.
   Fisher scientific

Total: **$867.48**

Budget Justification

This project is partially supported by additional external funding which will provide transportation to and from the reservoir, coolers for sample incubation, monitoring of organic carbon and iron in both reservoirs throughout the summer, and the majority of the costs of external iron analysis. However, funding is requested to cover the items above, which are not directly related to this ongoing reservoir water quality monitoring.

Links are provided for each line item. However, due to shipping delays caused by the covid-19 pandemic and blockage of the Suez canal, we will need to be flexible in purchasing these items from whatever source can provide them in time for field and laboratory experiments.

Estimated Timeline

Phase 1: Completed work

June 2019–
February 2020

As discussed above, I collected and analyzed the initial samples for this project in 2019. The exciting results from that initial analysis motivated increased sampling in 2020, which had to be postponed to 2021 due to the covid-19 pandemic.

Phase 2a: Whole-ecosystem manipulations

June 2021–
September 2021

This summer, I am working with the Western Virginia Water Authority to conduct whole-ecosystem oxygen manipulation experiments. In 2019, we found that the oxygenated reservoir had generally higher concentrations of iron-bound organic carbon in sediment. By activating and deactivating the oxygenation system over weekly to monthly timescales this summer, we will expand upon those results by experimentally testing whether oxygen fluctuations lead to changes in iron bound organic matter in sediment.

Phase 2b: Laboratory incubations

June 2021–
July 2021

To compliment my whole-ecosystem work, I will also conduct small-scale sediment incubations. In 2019, we observed high levels of variability in iron-bound organic carbon concentrations within each reservoir. Laboratory incubations will substantially reduce this variability, providing a clearer test of the effects of oxygen on iron-bound organic carbon.

Phase 3: Writing and analysis

September 2021–
June 2022

Throughout next year, I will work with my undergraduate assistant to finish processing the samples from these experiments, analyze the resulting data, and write the final manuscript. I will aim to submit the manuscript for publication by June 2022.