ORGANIC CARBON REACTIVITY IN LAKE SUPERIOR

A PROJECT SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE UNIVERSITY OF MINNESOTA BY

MATTHEW MICHAEL KISTNER

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

SERGEI KATSEV

FEBRUARY 2013

© Matthew Michael Kistner 2013

Acknowledgements

I would like to thank my advisor, Sergei Katsev, for his advice and assistance throughout this project. I also want to thank my other committee members, Jay Austin and Nathan Johnson. The courses and discussions I had with them were a valuable part of my graduate education. I want to thank Jiying Li for her constant support, willingness to answer questions, and assistance with lab techniques. I also want to acknowledge fellow students, Arthur Aaberg, Brian Beck, Julia Halbur, and David Miklesh, for their help on this project and others. I want to thank Josef Werne for the use of his lab and Sarah Grosshuesch for instructing me on lab techniques. Captain Mike King, the crew of the *R/V Blue Heron*, and marine technician Jason Agnich, provided assistance during sample collection. I also want to acknowledge Sean Crowe and Robert Sterner for providing some of the sediment cores. Sediment cores were split and logged at the Limnological Research Center, Department of Geology and Geophysics, University of Minnesota-Twin Cities with the help of Anders Noren and Kristina Brady.

This research was funded by the NSF Chemical Oceanography (OCE)-0961720 grant, University of Minnesota Duluth start-up funds to my advisor Sergei Katsev, and a teaching assistantship from the Department of Physics at the University of Minnesota-Duluth.

Abstract

To investigate carbon reactivity in Lake Superior, we collected sediment cores from eight locations across the lake. The sampling locations represent a broad range of bay and open water stations with depths ranging from 8 to 318 meters. Sediment profiles were determined for total organic carbon and ²¹⁰Pb. These profiles were combined with previous data on oxygen uptake rates to calculate effective carbon reactivity. Effective carbon reactivity was compared with marine and lacustrine systems around the globe.

Sediment carbon profiles were determined using carbon coulometry. In Lake Superior, total carbon concentration at the sediment water interface ranged from 1.7-4.8% and at depth (~20-25cm) it ranged from 1.1-2.5%. Sediment age profiles were determined using ²¹⁰Pb. The top ~10cm of Lake Superior sediment cores record approximately the last 200 years of sediment accumulation.

Effective carbon reactivity in Lake Superior was found to decrease with depth at a rate that could be described similarly to the power law (the so called Middelburg law) documented in marine environments, but with several significant differences. In Lake Superior, the carbon reactivity (k) decreases with time (t) according to

$$\log(k) = (-1.19 \pm 0.16) \log(t) - (0.09 \pm 0.31).$$

Carbon reactivity was also found to be higher and to decrease faster in oxic sediments than in anoxic sediments. No clear differences in carbon reactivity could be seen between cold temperate and warm tropical large lakes. This suggests that, over long time scales, the presence of oxygen may be more important for carbon mineralization rates than temperature.

Acknowledgements	i
Abstract	ii
Table of Contents	iii
List of Tables	iv
List of Figures	iv
Introduction	1
Background	3
Methods Sampling and Sample Preparation Carbon Analysis ²¹⁰ Pb Analysis Rate Calculations	
Results	14
Discussion	19
Conclusions	21
References	
Appendix	24
Lake Superior Carbon Data	25
Tropical Lakes Carbon Data	

Table of Contents

List of Tables

Table 1	Sampling locations
Table 2	Summary of reactivity vs. time relationships

List of Figures

Figure 1	Sampling locations in Lake Superior
Figure 2	Total carbon profiles – Lake Superior
Figure 3	Carbon profiles – Tropical Lakes
Figure 4	Sediment Age Profiles
Figure 5	Reactivity calculated by two different approaches
Figure 6	Carbon reactivity vs. age - Lake Superior
Figure 7	Carbon reactivity vs. age - Tropical Lakes
Figure 8	Carbon reactivity vs. age - Global
Figure 9	Carbon reactivity vs. age - Oxic vs. Anoxic Sediments-Global
Figure 10	Carbon reactivity vs. age - Oxic vs. Anoxic Sediments -Lake Superior
Figure 11	Carbon reactivity vs. age – Anoxic Sediments

Introduction

Better understanding of the rates and control factors of organic carbon mineralization in lacustrine environments is important for quantifying both global (Tranvik et al. 2009) and local carbon budgets. Improved estimates of the carbon budget can have important consequences in examining the relationship between the carbon cycle and a changing global climate.

Lakes comprise roughly 2% of the Earth's surface area, compared with 71% covered by oceans, but annually bury over 40% of the carbon buried in the oceans (Dean and Gorham 1998). Large lakes represent a significant fraction of the total lake area (Herdendorf 1982). A better understanding of the carbon burial in large lakes will help quantify the magnitude of carbon sequestration in inland waters. It is also important to understand how the carbon mineralization processes in large lakes compare with those in marine environments. The organic carbon in inland lakes comes from both terrestrial and marine sources. In large lakes, we are able to sample sufficiently far from shore in order to obtain predominantly autochthonous carbon. The contribution of terrigenous carbon in Lake Superior remains less than 17% throughout the year (Zigah et al. 2011). This provides for a better comparison with marine environments. In addition, quantifying the rate at which the effective carbon reactivity decreases with time after carbon deposition into the sediment may help in the reconstruction of paleolimnological records of carbon deposition. This would allow the diagenetic signal to be subtracted from the observed record of organic carbon preserved in the sediment.

Lake Superior is the world's largest lake by surface area. The carbon budget in

Lake Superior is poorly constrained (Sterner 2010), including the contribution of sediments to carbon burial and recycling (Li et al. 2012). The sediment data set currently available is subject to a geographic bias with more sampling in the western arm of the lake due to its proximity to Duluth, Minnesota (McManus et al. 2003).

In this study we collected and analyzed sediment cores from across the lake at a variety of depths and distances from shore in order to better constrain the sedimentary carbon values within Lake Superior (Figure 1). This data was then used to compare carbon reactivities in Lake Superior with those in other lakes, including large tropical lakes, and the global ocean.



Figure 1. Sampling locations in Lake Superior (Figure modified from Li 2011)

Background

Preservation of organic matter in sediment can be controlled by a number of biological, physical, and chemical factors (Paropkari et al. 1992). The processes that control organic matter preservation have been the target of numerous studies, yet the direct control mechanisms remain unclear (Hartnett et al. 1998). The studies of these processes in lakes have been less extensive and more fragmented than similar studies in marine environments (Sobek et al. 2009). Model estimates have suggested the importance of lakes as carbon sinks on regional and global scales (Kortelainen et al. 2004), and lacustrine sediments represent an important sink in the global carbon cycle (Dean and Gorham 1998).

Two potential controls on the preservation of organic matter in sediment include temperature and bottom water oxygen concentration/oxygen exposure time. Einsele et al. (2001), for example, found an increase in carbon burial rates corresponding with warmer and wetter climates. Sobek et al. (2009) found similar burial efficiencies of organic carbon in freshwater and marine systems; however, they also found that bottom water temperature had a "discernible effect on OC mineralization" which would imply climate change will have an effect on the role of lakes in the global carbon cycle. Hartnett et al. (1998) found a strong correlation between organic matter preservation and oxygen exposure time in continental margin sediments, which are considered to be one of the primary places of organic carbon burial in the oceans.

Middelburg (1989) proposed "a simple rate model for organic matter decomposition in marine sediments" and found that it held over time scales spanning eight orders of magnitude, based on dated cores and lab experiments. The reactivity of organic matter is characterized with a first order reaction rate constant k [year⁻¹], which links the rate of organic carbon degradation R [mol cm⁻³ y⁻¹] with the organic carbon concentration C [mol cm⁻³]. The Middelburg rate model suggested that the reactivity k decreased following a power law dependence on time t [year]:

$$\log(k) = -0.95 \, \log(t) - 0.81. \tag{1}$$

This model suggests that there is a continuous decrease in the first-order decay constant (k) over time and that the changing oxic state of the sediment down core has limited effect on the rate of change of reactivity (Middelburg 1989).

Middelburg et al. 1993 suggests that the rate of decomposition varies because of the origin and composition of the organic matter and environmental conditions and acknowledges the difficulty in establishing direct relationships between these factors and mineralization rates.

The goal of this project is to better constrain carbon concentrations across Lake Superior, to calculate carbon reactivity rates, and compare them with other sedimentary environments around the world.

The specific objectives are:

- Use coulometry to characterize organic carbon distributions in Lake Superior sediments. Compare sediments from different locations and characterize spatial variability.
- Calculate effective C reactivity. Characterize the decrease in C reactivity with aging of sediment organic matter.

4

• Compare the obtained relationships to those in other sedimentary environments, such as tropical large lakes and the global ocean.

Methods

Sampling and Sample Preparation

Eight sediment cores were collected on six University of Minnesota research cruises (*R/V Blue Heron*) on Lake Superior throughout 2009-2011. All Lake Superior sediment cores were collected using an Ocean Instruments MC-400 multi-corer. Lake Malawi cores were collected by Sergei Katsev using a multi-corer and the Lake Matano core was collected by S. A. Crowe using a gravity corer.

This multi-corer retrieves four cores (9.4 cm I.D. polycarbonate coring tubes) simultaneously with a maximum penetration depth of 34.5cm. The lake floor was monitored using a Knudsen Model 320/R echosounder to select spatially homogenous sampling sites and to avoid sampling previously disturbed sediment. Sediment cores were stored at 4°C until processing. This temperature represents the bottom water temperature of Lake Superior during the period of sampling (Li et al. 2012). Core sample resolution was determined based on preliminary oxygen profiles conducted on board and historical data. Oxygen concentration profiles were measured using a Unisense microelectrode on a separate core from the same multi-corer when possible (Li et al. 2012). Core sample resolution ranged from 0.1-0.5 cm at the top of the core to 5 cm below 20 cm (Appendix). Following subsampling, samples from discrete intervals were frozen at -18°C until further analysis. (Table 1)

Core	<u>Lake</u>	Water Depth (m)	<u>Latitude</u>	Longitude
BB_July11	Lake Superior	8	48 41.5 N	88 23.85 W
CM_Apr11	Lake Superior	239	48 03.04 N	87 47.74 W
ED_Sep10	Lake Superior	318	47 31.53 N	87 07.49 W
EM_Jun10	Lake Superior	229	47 33.38 N	86 35.76 W
FWM_Jun09	Lake Superior	170	47 02.90 N	91 14.97 W
IR_Apr11	Lake Superior	233	47 58.40 N	88 28.10 W
KW_Jun10	Lake Superior	84	47 09.85 N	88 05.32 W
NI_Jul11	Lake Superior	27	48 56.0 N	88 00.0W
CD_Jan12 ¹	Lake Malawi	650	11 16.78 S	34 21.73 E
S2_Jan12 ²	Lake Malawi	110	13 45.72 S	34 39.55 E
Matano_Jan10 ³	Lake Matano	65	02 28.0 S	121 17.0 E

Table 1. Sampling locations

¹Anoxic throughout sediment core (S. Katsev pers. comm.)

²Oxygen penetration depth <0.5mm (S. Katsev pers. comm.)

³Low oxygen in bottom water, appeared bioturbated in top 0.5-1 cm (S. Katsev pers. comm.)

Carbon Analysis

In the laboratory, the samples for carbon analysis were freeze dried, ground, and then baked at 60°C overnight. All samples were analyzed for total carbon (TC) and selected samples were analyzed for total inorganic carbon (TIC) using a UIC Inc. CM150 Total Carbon Analyzer. The CM150 uses coulometry to determine TC/TIC and can provide TOC by difference. The CM150 "measures the absolute mass amount of carbon dioxide resulting from sample combustion or acidification" (UIC Inc.). Total carbon analysis is performed by combusting the samples at 950°C. Total inorganic carbon



analysis is performed by acidifying the samples with 5mL of 2N HCl. (Figures 2-3)

a) Open Water Cores



b) Bay Cores

Figure 2. Total carbon profiles - Lake Superior



Figure 3. Carbon profiles – Tropical Lakes

²¹⁰Pb Analysis

Sediment cores were dated by analyzing ²¹⁰Pb activity. These analyses were performed by the Flett Research Laboratory at the University of Manitoba and the St. Croix Research Station laboratory operated by the Science Museum of Minnesota. The analyzing laboratory performed bulk density determinations and sediment age and accumulation rate calculations using a Constant Rate of Supply (CRS) model (Appleby and Oldfield 1978). Although the CRS model may result in underestimation of the sediment age as a result of Pb particle transport by bioturbation, the bioturbation depth in deep Lake Superior sediment does not exceed 2cm (Li et al. 2012) and absolute errors resulting from using this model should not exceed 5-20 years (T.C. Johnson, pers. comm.), depending on location. As C and Pb particles are transported by the same bioturbation processes, the relative significance of these errors for our results should be even smaller. Burial velocities U (cm yr⁻¹) were calculated from the obtained age vs. depth relationship (Figure 4) as a function of depth x as

$$U = \frac{dx}{dt}.$$
 (2)

Burial velocities for Lake Superior stations BB (0.17 cm/yr) and NI (0.17 cm/yr) were estimated from Evans 1980 and for station ED (0.012 cm/yr) from Kemp et al. 1978 (Li 2011).



a) Lake Superior



b)Tropical Lakes

Figure 4. Sediment age profiles

Rate Calculations

Carbon mineralization rates and effective carbon reactivity were calculated using the method outlined in Li et al. 2012.

Within the oxic zone, we used oxygen consumption rates as an approximation for carbon mineralization rates

$$R_{O_2} = k\xi C \tag{3}$$

Here, *k* is reactivity, ξ (g cm⁻³) is equal to (1- ϕ) ρ where ϕ is the porosity and ρ (g cm⁻³) is the density of the dry sediment, and C is the molar concentration of carbon (mol g⁻¹). In anoxic sediment, carbon mineralization is limited by carbon availability instead of the availability of oxidants. This allows us to write the carbon mineralization rate as

$$R_c = k\xi C \tag{4}$$

Rearranging the equations for carbon mineralization rates (Eq. 3 and Eq. 4) gives us carbon reactivity in the oxic zone as

$$k = \frac{R_{O_2}}{\xi C} \tag{5}$$

where R_{O_2} represents the rate of oxygen consumption per volume and can be calculated (Li et al. 2012) from

$$R_{O_2} = -\frac{dF_{O_2}}{dx} \tag{6}$$

where F_{O_2} is the oxygen flux. Oxygen flux profiles were calculated by Jiying Li (J. Li, pers. comm.; Li et al. 2012; Li 2011).

The reactivity calculation in the anoxic zone relies on a local steady state assumption, i.e. that the local changes in C concentration with depth, at a given depth in the sediment and below the bioturbation zone, are due to C mineralization rather than historic variations in C loadings to the sediment. Using this assumption and the sediment carbon profile, Equation 4 can be rewritten as

$$R_C = -\xi U \frac{dC}{dx} \tag{7}$$

Here, U (cm yr⁻¹) is the advection (burial) velocity. The carbon reactivity in the anoxic zone can then be calculated from Equations 4 and 7 as

$$k = \frac{R_C}{\xi C} = -\frac{U}{C} \frac{dC}{dx}$$
(8)

For the models in this paper, oxygen penetration depth (OPD) was used as the boundary for determining which approach (equation 5 or 8) to use when calculating carbon reactivity. Another approach would be to use the depth of bioturbation as the transition point. A comparison of these two approaches for several Lake Superior stations is shown in Figure 5. It shows that the two methods produce similar results.



a) Lake Superior Station CM



b) Lake Superior Station EM



c) Lake Superior Station FWM



e) Lake Superior Station KW

Figure 5. Reactivity calculated by two different approaches

Results

The total carbon content of Lake Superior sediment ranges from 1.7 to 4.8% at the sediment-water interface and it ranged from 1.1 to 2.5% at depth (~20-25cm) (Figure 2). Total inorganic carbon values were below the detection limit of the coulometer, which was consistent with previous studies (Zigah et al. 2011). Therefore, total carbon values were used to represent total organic carbon values for Lake Superior.

The total carbon content of the sediments from tropical large lakes that we analyzed was found to decrease less down core. In Lake Malawi, sediment carbon content ranged from 4.0 to 4.5% at the sediment water interface and at depth (~20-25cm) it was around 3.5%. Lake Matano sediment showed a TC value of 6.5% at the sediment water interface and 4.3% at depth (~15cm). Total inorganic carbon values of these tropical large lakes was found to be 0.0-0.4% with a general trend of increasing down core. Total organic carbon content of these tropical lakes is presented in Figure 3.

Carbon reactivity in Lake Superior was found to be higher than documented in marine environments (Figure 6). It was also found to decrease at an accelerated rate when compared to marine environments (Middelburg 1989, Middelburg et al. 1993). In Lake Superior, the carbon reactivity (k) decreases with time (t) according to

$$\log(k) = (-1.19 \pm 0.16) \, \log(t) - (0.09 \pm 0.31). \tag{9}$$

(95% confidence intervals in parentheses)



Figure 6. Carbon reactivity vs. age - Lake Superior

In large tropical lakes, Lake Matano (Indonesia) and Lake Malawi (East Africa) (Figure 7), the carbon reactivity (k) decreases with time (t) according to

$$\log(k) = (-0.41 \pm 0.26) \, \log(t) - (1.72 \pm 0.40). \tag{10}$$

(95% confidence intervals in parentheses)



Figure 7. Carbon reactivity vs. age – Tropical Lakes

A comparison of carbon mineralization rates from the three environments (Lake Superior, tropical lakes, marine) is presented in Figure 8.

A comparison was also made between oxic and anoxic sediments of both tropical and cold large lakes (Figure 9). In oxic sediment, the carbon reactivity (k) decreases with time (t) according to

$$\log(k) = (-1.02 \pm 0.21) \, \log(t) + (0.01 \pm 0.32) \,. \tag{11}$$

(95% confidence intervals in parentheses)

In anoxic sediment, the carbon reactivity (k) decreases with time (t) according to

$$\log(k) = (-0.63 \pm 0.16) \, \log(t) - (1.50 \pm 0.32) \,. \tag{12}$$

(95% confidence intervals in parentheses)



Figure 8. Carbon reactivity vs. age - Global



Figure 9. Carbon reactivity vs. age – Oxic vs. Anoxic Sediments-Global

In an attempt to isolate the effects of oxic condition from the effects of temperature, the data from Lake Superior was separated into oxic and anoxic sections (Figure 10). In Lake Superior oxic sediment, the carbon reactivity (k) decreases with time (t) according to

$$\log(k) = (-1.09 \pm 0.19) \log(t) + (0.16 \pm 0.31).$$
 (13)
(95% confidence intervals in parentheses)

In Lake Superior anoxic sediment, the carbon reactivity (k) decreases with time (t) according to

$$\log(k) = (-0.66 \pm 0.25) \, \log(t) - (1.50 \pm 0.56). \tag{14}$$

(95% confidence intervals in parentheses)



Figure 10. Carbon reactivity vs. age – Oxic vs. Anoxic Sediments-Lake Superior

Data Set	Sample Size	Slope	Slope 95% Confidence Limits	Intercept	Intercept 95% Confidence Limits
Middelburg	140	-0.95		-0.81	
Lake Superior All Data	115	-1.19	+/-0.16	-0.09	+/-0.31
Lake Malawi Lake Matano All Data	50	-0.41	+/-0.26	-1.72	+/-0.40
All Lakes Oxic Sediment	48	-1.02	+/-0.21	0.01	+/-0.32
All Lakes Anoxic Sediment	117	-0.63	+/-0.16	-1.50	+/-0.32
Lake Superior Oxic Sediment	48	-1.09	+/-0.19	-0.16	+/-0.31
Lake Superior Anoxic Sediment	67	-0.66	+/-0.25	-1.50	+/-0.56

 Table 2. Summary of reactivity vs. time relationships

Discussion

One goal of this project was to collect sediment cores from across Lake Superior at a wide variety of depths. We analyzed cores from eight locations (five deep water and three bays). These stations produce sediment cores that are visually distinct, with varying depths of oxygen penetration, as well as other geochemical parameters (Li 2011). The carbon profiles of these cores were similar in shape and order of magnitude for all stations.

Another goal of this project was to determine a relationship between effective carbon reactivity and the aging of sediment organic matter for Lake Superior and compare this with other large lakes as well as a previously established power law for marine organic matter. In Lake Superior, when data from oxic sediments and anoxic sediments are combined, the carbon reactivity (k) decreases with time (t) according to

$$\log(k) = (-1.19 \pm 0.16) \ \log(t) - (0.09 \pm 0.31).$$
(15)

This compares with the Middelburg power law for marine environments

$$\log(k) = -0.95 \, \log(t) - 0.81. \tag{16}$$

The Middelburg power law for the marine environment has a slope and intercept that both fall outside the 95% confidence interval for the Lake Superior data. Though confidence intervals were not reported for the Middelburg power law, measurements from Lake Superior suggest that organic material may degrade at a faster rate in Lake Superior when compared with the marine environment.

Comparison of the calculated carbon reactivities from oxic vs. anoxic sediments suggests that the presence of oxygen is an important factor on the rate of carbon degradation and may limit the applicability of a universal power law to model carbon degradation. The calculated regressions of carbon reactivity vs. time for oxic and anoxic sediments are statistically different as determined by ANCOVA (p=0.002). Additionally, comparing the carbon reactivity in oxic vs. anoxic sediment on a global and local (Lake Superior) scales, shows that lake temperature has little effect on the decay rate. This can especially be seen in the minimal amount of variation between equations 12 and 14 and in Figure 11.

The greater importance of oxygen presence suggests that over long time scales, the effect of temperature on carbon degradation may be minimal; therefore, the impact of climate change on the burial of organic matter may be smaller than previously suggested.



Figure 11 Carbon reactivity vs. age – Anoxic Sediments

Further research is necessary to better understand the effects of oxygen and temperature on organic carbon mineralization in lacustrine sediment. Assembling a larger and more diverse data set is crucial to advancing this goal. Additional data over a wider age range (i.e.: sediment traps and long cores) as well as a larger number of samples from temperate and tropical lakes would be beneficial.

Conclusions

In conclusion, this project expanded both the quantity and spatial expanse of sedimentary carbon data in Lake Superior. It also provides models of carbon reactivity over time for both Lake Superior and some tropical lakes. These equations can provide additional insight when performing lacustrine paleoproductivity investigations and may provide insight to implications of climate change on the global carbon cycle.

References

- Appleby, P. G., and F. Oldfield. 1978. The calculation of lead-210 dates assuming a constant rate of supply of unsupported ²¹⁰Pb to the sediment. Catena. **5**:1-8.
- Dean, W. E., and E. Gorham. 1998. Magnitude and significance of carbon burial in lakes, reservoirs, and peatlands. Geology. 26:535-538.
- Einsele, G., J. Yan, and M. Hinderer. 2001. Atmospheric carbon burial in modern lake basins and its significance for the global carbon budget. Global and Planetary change. **30**:167-195.
- Hartnett, H. E., R. G. Keil, J. I. Hedges, and A. H. Devol. 1998. Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. Nature. 391:572-575.
- Herdendorf, C. E., 1982. Large Lakes of the World. Journal of Great Lakes Research. **8**:379-412.
- Kortelainen, P., H. Pajunen, M. Rantakari, and M. Saarnisto. 2004. A large carbon pool and small sink in boreal Holocene lake sediments. Global Change Biology.
 10:1648-1653.
- Li, J.. 2011. Diagenesis and sediment-water exchanges in organic-poor sediments of Lake Superior. M. Sc. thesis. University of Minnesota.
- Li, J., S. A. Crowe, D. Miklesh, M. Kistner, D. E. Canfield, and S. Katsev. 2012. Carbon mineralization and oxygen dynamics in sediments with deep oxygen penetration, Lake Superior. Limnol. and Oceanogr. 57:1634-1650.

- Middelburg, J. J.. 1989 A simple rate model for organic matter deposition in marine sediments. Geochimica et Cosmochina Acta. **53**:1577-1581.
- Middelburg, J.J. T. Vlug., and F. J. W. A. van der Nat. 1993. Organic matter mineralization in marine systems. Global and Planetary Change. **8**:47-58.
- Paropkari, A. L., C. P. Babu, and A. Mascarenhas. 1992. A critical evaluation of depositional parameters controlling the variability of organic carbon in Arabian Sea sediments. Marine Geology. 107:213-226.
- Sobek, S., E. Durisch-Kaiser, R. Zurbrügg, N. Wongfun, M. Wessels, N. Pasche, and B.
 Wehrli. 2009. Organic carbon burial efficiency in lake sediments controlled by oxygen exposure time and sediment source. Limnol. Oceanogr. 54:2243-2254.
- Sterner, R. W.. 2010. In situ-measured primary production in Lake Superior. Journal of Great Lakes Research. 36:139-149.
- Tranvik, L.J., A. Downing, J. B. Cotner, S. A. Loiselle, R. G. Striegl, T. J. Ballatore, P.
 Dillon, K. Finlay, K. Fortino, L. B. Knoll, P. L. Kortelainen, T. Kutser, S. Larsen, I.
 Laurion, D. M. Leech, S. L. McCallister, D. M. McKnight, J. M. Melack, E.
 Overholt, J. A. Porter, Y. Prairie, W. H. Renwick, F. Roland, B.S. Sherman, D. W.
 Schindler, S. Sobek, A. Tremblay, M. J. Vanni, A. M. Verschoor, E. von
 Wachenfeldt, and G. A. Weyhenmeyer. 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnol. Oceanogr. 54:2298-2314.
- Zigah, P. K., E.C. Minor, J. P. Werne, and S.L. McCallister. 2011. Radiocarbon and stable isotopic insights into provenance and cycling of carbon in Lake Superior. Limnol. Oceanogr. 56:867-886.

Appendix

Lake Superior Carbon Data

Core	Average Depth (cm)	Total Carbon (%)
LS_BB	-0.25	1.7424
LS_BB	-0.75	1.6928
LS_BB	-1.5	1.6438
LS_BB	-2.5	1.6116
LS_BB	-3.5	1.5816
LS_BB	-4.5	1.6262
LS_BB	-5.5	1.5577
LS_BB	-6.5	1.5145
LS_BB	-7.5	1.3801
LS_BB	-9	1.2868
LS_BB	-11	1.2631
LS_BB	-13.5	1.2518
LS_BB	-16.5	1.2305
LS_BB	-19.5	1.2411
LS_BB	-23	1.0727
LS_CM	-0.05	3.9906
LS_CM	-0.3	3.8524
LS_CM	-0.75	3.6772
LS_CM	-1.5	3.554
LS_CM	-2.5	3.299
LS_CM	-3.5	2.954
LS_CM	-4.5	2.6275
LS_CM	-5.5	2.5258
LS_CM	-6.5	2.4354
LS_CM	-7.5	2.3019
LS_CM	-8.5	2.2168
LS_CM	-9.5	2.1851
LS_CM	-10.5	2.1525
LS_CM	-11.5	2.1104
LS_CM	-13	2.102
LS_CM	-15	1.7899
LS_CM	-17.5	1.8422
LS_CM	-20.5	1.9807
LS_ED	-0.25	4.8125
LS_ED	-0.75	4.9038
LS_ED	-1.5	4.6395
LS_ED	-2.5	4.0672

LS_ED	-3.5	3.6246
LS_ED	-4.5	3.084
LS_ED	-5.5	2.9518
LS_ED	-6.5	2.7866
LS_ED	-7.5	2.614
LS_ED	-8.5	2.346
LS_ED	-9.5	2.5389
LS_ED	-11	2.1659
LS_ED	-13.5	2.0997
LS_ED	-16.5	2.2837
LS_ED	-19.5	2.8864
LS_ED	-23	2.472
LS_EM	-0.75	4.3131
LS_EM	-1.5	4.1577
LS_EM	-2.5	3.9754
LS_EM	-3.5	3.6699
LS_EM	-4.5	3.4758
LS_EM	-6	3.0537
LS_EM	-8	2.6097
LS_EM	-10.5	2.4748
LS_EM	-13.5	2.5773
LS_EM	-16.5	2.4312
LS_EM	-19.5	2.1798
LS_EM	-23	2.3162
LS_FWM	-0.5	2.6532
LS_FWM	-1.5	2.3974
LS_FWM	-2.5	1.7064
LS_FWM	-3.5	1.4226
LS_FWM	-4.5	1.724
LS_FWM	-6.5	2.7214
LS_FWM	-8.5	2.4337
LS_FWM	-10.5	2.0097
LS_FWM	-13.5	1.865
LS_FWM	-18	1.6997
LS_FWM	-22	1.8974
LS_IR	-0.05	3.6101
LS_IR	-0.15	2.3397
LS_IR	-0.35	3.4338
LS_IR	-0.75	3.3512

LS_IR	-1.5	3.2273
LS_IR	-2.5	3.0679
LS_IR	-3.5	2.9909
LS_IR	-4.5	2.914
LS_IR	-5.5	2.9332
LS_IR	-6.5	2.9295
LS_IR	-8	2.8904
LS_IR	-10.5	2.5734
LS_IR	-13.5	2.5063
LS_IR	-16.5	2.5072
LS_IR	-19.5	2.3912
LS_KW	-0.25	3.856
LS_KW	-0.75	3.5915
LS_KW	-1.5	3.0341
LS_KW	-2.5	2.5844
LS_KW	-3.5	2.2409
LS_KW	-4.5	2.3783
LS_KW	-6	2.2135
LS_KW	-8	1.6488
LS_KW	-10.5	1.6748
LS_KW	-13.5	1.823
LS_KW	-16.5	2.2232
LS_KW	-19.5	2.1075
LS_KW	-23	2.1038
LS_NI	-0.25	1.7282
LS_NI	-0.75	1.7273
LS_NI	-1.5	1.6164
LS_NI	-2.5	1.539
LS_NI	-3.5	1.4392
LS_NI	-4.5	1.4376
LS_NI	-5.5	1.4624
LS_NI	-6.5	1.3468
LS_NI	-7.5	1.508
LS_NI	-9	1.3817
LS_NI	-11	1.4034
LS_NI	-13.5	1.3142
LS_NI	-16.5	1.1311
LS_NI	-19.5	1.1449
LS_NI	-23	1.0663

Tropical Lakes Carbon Data

Core	Average	Total	Total Inorganic	Total Organic
	Depth (cm)	Carbon (%)	Carbon (%)	Carbon (%)
Malawi_CD	-0.25	4.0266	0.0176	4.009
Malawi_CD	-0.75	3.9923	0.015	3.9773
Malawi_CD	-1.25	4.0879	0.0077	4.0802
Malawi_CD	-1.75	3.9703	0.0112	3.9591
Malawi_CD	-2.25	3.9441	0.0143	3.9298
Malawi_CD	-2.75	3.9118	0.0138	3.898
Malawi_CD	-3.5	3.7723	0.0107	3.7616
Malawi_CD	-4.5	3.5793	0.011	3.5683
Malawi_CD	-6	3.5837	0.0118	3.5719
Malawi_CD	-8	3.4878	0.0116	3.4762
Malawi_CD	-10.5	3.6027	0.0102	3.5925
Malawi_CD	-13.5	3.6377	0.0236	3.6141
Malawi_CD	-19.5	3.6545	0.0483	3.6062
Malawi_CD	-23	3.399	0.0472	3.3518
Malawi_CD	-28	4.898	0.2883	4.6097
Malawi_S2	-0.25	4.4691	0.0049	4.4642
Malawi_S2	-0.75	4.3581	0.0054	4.3527
Malawi_S2	-1.25	4.6073	0.0111	4.5962
Malawi_S2	-1.75	4.7089	0.0139	4.695
Malawi_S2	-2.25	5.1237	0.0152	5.1085
Malawi_S2	-2.75	4.9619	0.0073	4.9546
Malawi_S2	-3.5	4.6708	0.0127	4.6581
Malawi_S2	-4.5	5.4463	0.0113	5.435
Malawi_S2	-6	5.4779	0.0567	5.4212
Malawi_S2	-8	5.7857	0.0117	5.774
Malawi_S2	-10.5	4.2712	0.0695	4.2017
Malawi_S2	-13.5	4.8137	0.3764	4.4373
Malawi_S2	-16.5	4.9886	0.3062	4.6824
Malawi_S2	-19.5	4.0627	0.0341	4.0286
Malawi_S2	-23	3.4736	0.0534	3.4202
Matano_0110	-0.25	6.5175	0.0848	6.4327
Matano_0110	-0.75	6.0533	0.0831	5.9702
Matano_0110	-1.25	5.9305	0.0888	5.8417
Matano_0110	-1.75	5.484	0.099	5.385
Matano_0110	-2.25	5.4278	0.1062	5.3216
Matano_0110	-2.75	5.3723	0.154	5.2183

Matano_0110	-3.25	5.234	0.1043	5.1297
Matano_0110	-3.75	5.3073	0.0715	5.2358
Matano_0110	-4.25	5.0423	0.1056	4.9367
Matano_0110	-4.75	5.1574	0.0931	5.0643
Matano_0110	-5.5	5.0765	0.1351	4.9414
Matano_0110	-6.5	4.8438	0.0959	4.7479
Matano_0110	-7.5	4.5984	0.1246	4.4738
Matano_0110	-8.5	4.6084	0.1478	4.4606
Matano_0110	-9.5	4.5383	0.1339	4.4044
Matano_0110	-10.5	4.4338	0.1496	4.2842
Matano_0110	-11.5	4.3188	0.153	4.1658
Matano_0110	-12.5	4.3444	0.2601	4.0843
Matano_0110	-13.5	4.2405	0.2088	4.0317
Matano_0110	-14.5	4.3969	0.1884	4.2085