2010 Project Abstract
For the Period Ending June 30, 2013

PROJECT TITLE: Quantifying Carbon Burial in Healthy Minnesota Wetlands
PROJECT MANAGER: James Cotner
AFFILIATION: University of Minnesota-Twin Cities
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FUNDING SOURCE: Environment and Natural Resources Trust Fund
LEGAL CITATION: M.L. 2010, Chp. 362, Sec. 2, Subd. 3g

APPROPRIATION AMOUNT: $144,000

Overall Project Outcome and Results:

We examined the potential for shallow lakes to mitigate carbon dioxide release from fossil fuels. The CO_2 concentration in the atmosphere is increasing and it is a greenhouse gas that has been strongly connected to climate change on Earth. The state of Minnesota emits over 150 million metric tons of CO_2 annually due to fossil fuel burning and a stated goal is to stabilize releases at 1990 levels. Reaching this goal will require both minimizing sources and maximizing sinks such as lakes.

To determine how much CO_2 is removed from the atmosphere by shallow lakes, we collected sediment samples from over 100 lakes throughout the state, determined how much organic carbon resides in the sediments and determined the burial rate using a new method that is based on ^{210}Pb dating. Our goals were to identify important variables that facilitate carbon burial and to estimate burial rates for the entire state. We found that shallow lakes bury organic carbon at very high rates compared to other landscape features and that effective burial is facilitated by high rates of productivity that occurs in these systems; anaerobic (no oxygen) conditions, when they occur, particularly in the wintertime under the ice, also facilitate increased carbon burial. Although burial represents a large quantity of carbon, about 6 Tg per year (or 6 million metric tons), the State of Minnesota releases about 150 million metric tons of carbon per year through the burning of fossil fuels.

In addition to the scientific results of our work, this project has helped train 10 undergraduate students from both the University of St. Thomas and University of Minnesota, two graduate students at the University of Minnesota and one post-doctoral fellow for two years.

More information on the results of this project can be found in our final project report.

Project Results Use and Dissemination

The results from this project have been incorporated into materials for use in the class room at St. Thomas and University of Minnesota. Cotner and Zimmer have used material from this project in lectures they have given locally, nationally and internationally (Sweden, Brazil, Japan). At the recent Ecological Society of America annual meeting, members of our team presented 11 posters and/or oral presentations that were very well received. We also organized a special session on terrestrial-aquatic linkages that had a strong focus on carbon burial. This was an extremely well-attended session at this international meeting. Also, 6 members of our group (Cotner, Zimmer, Hobbs and Ramstack-Hobbs, Herwig, and Hanson) presented results from this project at a Shallow Lakes Workshop that we helped organize in Fergus Falls this past August. This workshop was completely full and was attended by resource managers from throughout the state. Cotner has also been presenting some of this work through informal education talks that he has been giving in the past 18 months to various groups (mostly senior citizens) in the Twin Cities area. He has given approximately 20 presentations that have focused on marine and freshwater resources. Lastly, we have published three papers in the scientific literature based on results from this and a related project funded through the National Science Foundation. We have four other papers that are either currently being reviewed or that will be submitted by June 2014.

Environment and Natural Resources Trust Fund (ENRTF)
2010 Work Program-Final Report

Date of Report: 9 Dec 2013
Final report
Date of Work Program Approval:
Project Completion Date: 30 June 2013

I. PROJECT TITLE: 220G – 2010 - Quantifying Carbon Burial in Healthy Minnesota Wetlands

Project Manager: James Cotner
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Location: This project is focused on the entire state, but we will sample lakes in the six shaded study areas shown in Figure 1, representing five of Minnesota's ecoregions. This will allow us to integrate our results over the entire state.

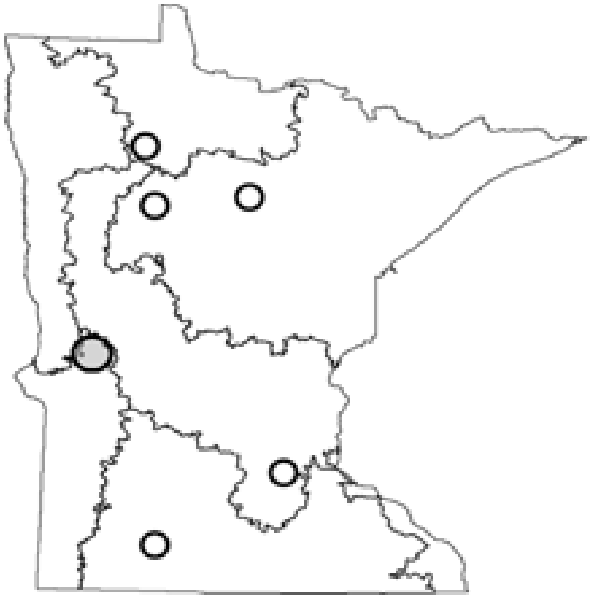

Figure 1. The location of the proposed project. The shaded grey circle shows the location of our NSF work on 13 lakes in western MN. Hollow circles show the location of additional lakes to be studied with LCCMR funds, as well as additional lakes in the western Minnesota study area. Lines represent boundaries of Minnesota's seven ecoregions. The scope of the project includes the entire state but efforts will be focused on lakes in various ecoregions.

Total ENRTF Project Budget:	**ENRTF Appropriation**	**$144,000**
	Minus Amount Spent:	**$143,917**
	Equal Balance:	**$83**

Legal Citation: M.L. 2010, Chp. 362, Sec. 2, Subd. 3g

Appropriation Language:
$144,000 is from the trust fund to the Board of Regents of the University of Minnesota to determine the potential for carbon sequestration in Minnesota's shallow lakes and wetlands. This appropriation is available until June 30, 2013, by which time the project must be completed and final products delivered.

II. FINAL PROJECT SUMMARY AND RESULTS:

We examined the potential for shallow lakes to mitigate carbon dioxide release from fossil fuels. The CO_2 concentration in the atmosphere is increasing and it is a greenhouse gas that has been strongly connected to climate change on Earth. The state of Minnesota emits over 150 million metric tons of CO_2 annually due to fossil fuel burning and a stated goal is to stabilize releases at 1990 levels. Reaching this goal will require both minimizing sources and maximizing sinks such as lakes.

To determine how much CO_2 is removed from the atmosphere by shallow lakes, we collected sediment samples from over 100 lakes throughout the state, determined how much organic carbon resides in the sediments and determined the burial rate using a new method that is based on ^{210}Pb dating. Our goals were to identify important variables that facilitate carbon burial and to estimate burial rates for the entire state. We found that shallow lakes bury organic carbon at very high rates compared to other landscape features and that effective burial is facilitated by high rates of productivity that occurs in these systems; anaerobic (no oxygen) conditions, when they occur, particularly in the wintertime under the ice, also facilitate increased carbon burial. Although burial represents a large quantity of carbon, about 6 Tg per year (or 6 million metric tons), the State of Minnesota releases about 150 million metric tons of carbon per year through the burning of fossil fuels.

In addition to the scientific results of our work, this project has helped train 10 undergraduate students from both the University of St. Thomas and University of Minnesota, two graduate students at the University of Minnesota and one post-doctoral fellow for two years.

Project Results Use and Dissemination
The results from this project have been incorporated into materials for use in the class room at St. Thomas and University of Minnesota. Cotner and Zimmer have used material from this project in lectures they have given locally, nationally and internationally (Sweden, Brazil, Japan). At the recent Ecological Society of America annual meeting, members of our team presented 11 posters and/or oral presentations that were very well received. We also organized a special session on terrestrial-aquatic linkages that had a strong focus on carbon burial. This was an extremely well-attended

session at this international meeting. Also, 6 members of our group (Cotner, Zimmer, Hobbs and Ramstack-Hobbs, Herwig, and Hanson) presented results from this project at a Shallow Lakes Workshop that we helped organize in Fergus Falls this past August. This workshop was completely full and was attended by resource managers from throughout the state. Cotner has also been presenting some of this work through informal education talks that he has been giving in the past 18 months to various groups (mostly senior citizens) in the Twin Cities area. He has given approximately 20 presentations that have focused on marine and freshwater resources. Lastly, we have published three papers in the scientific literature based on results from this and a related project funded through the National Science Foundation. We have four other papers that are either currently being reviewed or that will be submitted by June 2014.

III. PROGRESS SUMMARY AS OF:

15 Aug 2013

In the last few months of this project, we have continued to make progress in terms of understanding the burial of organic carbon in Prairie Pothole lakes and wetlands as well as shallow lakes throughout the entire state of Minnesota. As mentioned in our last report, we planned a special session at the annual Ecological Society of America Meeting that was held here in Minneapolis in August. There were over 15 talks and posters presented related to our topic of ‘Terrestrial-aquatic linkages of nutrients and carbon’. In general, there was a great deal of excitement for the session and it was extremely well-attended. Another important accomplishment in the last period of our funding was that the L&O Methods paper that we submitted was accepted and is now published: http://aslo.org/lomethods/free/2013/0316.pdf. Three other papers are either currently being reviewed or are in various stages of preparation for submission to journals.

One of the key overall outcomes of our research is that carbon dynamics are incredibly similar among shallow lakes in clear (macrophyte-dominated) and turbid (phytoplankton-dominated) states. We did not expect this when we began our research. This argues that despite vast differences in community composition, ecosystem-scale processes are very similar. Relatedly, another important result that came out of this work is that shallow lakes bury a great deal of organic carbon into their sediments. We found that lakes throughout the state bury, on average, more than 100 grams of organic carbon per square meter per year and that the burial actually differs very little in different regions of the state and among lakes in different states (turbid or clear). These values are quite high but in the range of values that others have observed in other parts of the world. What it means is that these shallow lakes are extremely effective in removing CO_2 from the atmosphere and putting that CO_2 into the sediments where it can remain for a very long period of time, perhaps hundreds to thousands of years. Therefore, an important management outcome is that it is certainly reasonable to take advantage of these systems for removing CO_2 from the atmosphere. If we assume that about 23% of the total land area of Minnesota is covered by freshwaters with similar burial properties, that means that about 6 Tg (10^{12} grams or 6 million metric tons) of CO_2 are buried in our shallow lakes annually. This is a very large amount of carbon, but to help put it in context, this is about 4% of the total amount of CO_2 released in the state by burning fossil fuels. It is nonetheless an important value for managers to be aware of as we likely could increase burial by a factor of 2 or more.

31 December 2012
During this past quarter, we have made considerable progress on our LCCMR project. As we had proposed, a great deal of progress has been made towards estimating the rate at which organic carbon is accumulating in the sediments of each of our study lakes (80 in total). We have refined a method allowing us to acquire an estimate for each individual lake. This method is novel and represents a significant contribution to the scientific community. A manuscript of this method has been submitted to the peer-reviewed journal Limnology and Ocenaography Methods (Hobbs et al.). While the manuscript was being prepared, sediment samples were being analyzed for ^{210}Pb to implement this new method into our study. This analysis is near completion and we can move to final stage of the project, which is comparing these carbon burial rates to landscape and in-lake data to ascertain possible drivers of burial to Minnesota wetlands. Furthermore, this analysis will allow us to determine whether these systems act as relevant C-sinks in the context of carbon trading legislation and markets.

Hobbs (project post-doc), Cotner and Zimmer have also organized a session at the upcoming Ecological Society of America Annual Meeting to be held in Minneapolis August 2013. This session will focus on measuring the movement of nutrients and carbon from terrestrial to aquatic ecosystems through time and space. Work from this project will feature prominently in this session of invited talks by internationally recognized scientists.

Published papers:
Hobbs, WO, DR Engstrom, SP Scottler, KD Zimmer, and JB Cotner. "Estimating Modern Carbon Burial Rates in Lakes Using a Single Sediment Sample." LIMNOLOGY AND OCEANOGRAPHY-METHODS 11 (2013): doi:10.4319/lom.2013.11.316.

Theissen, Kevin M, William O Hobbs, Joy M Ramstack Hobbs, Kyle D Zimmer, Leah M Domine, James B Cotner, and Shinya Sugita. "The Altered Ecology of Lake Christina: A Record of Regime Shifts, Land-use Change, and Management From a Temperate Shallow Lake." Sci Total Environ 433 (2012): doi:10.1016/j.scitotenv.2012.06.068.

30 June 2012
During this quarter, we prepared and analyzed hundreds of samples collected through the study for analyses of organic carbon and nitrogen. We are currently using these data and data from additional lakes made available to us from Dr. Dan Engstrom (St. Croix Watershed Research Station) to calibrate the data from our lakes. We are in the process of developing two manuscripts that should be submitted in the next 6-8 months describing a new technique for estimating carbon burial in lakes. This is an important development because it will allow more estimates of carbon burial from many lakes in Minnesota and elsewhere. The second manuscript will make estimates of carbon burial from the across the entire state using the lakes we sampled in this study.

31 December 2011

Prior to field work this summer, a new microprofiling system for the measurement of oxygen, pH, and sulfides in the lake surface sediments was acquired with additional in-kind funds for use during the 2011 field campaign. This sensitive instrument allows us to directly measure the penetration of oxygen into the sediments at the sub-millimeter scale in a short (~10cm) sediment core, which is important for calculating the efficiency of C-burial in the lake sediments. Over 70 lakes were sampled this past summer and fall; all field work has now been completed for this project. Combined with the lakes sampled in 2010 there are a total of 85 shallow lakes across the 5 ecoregions represented in our dataset. The microprofiling system was set-up in semi-permanent lab spaces while in the field and used to collect data on 78 lakes (with triplicate profiles measured for each sediment core). Eight undergraduates were trained in field and lab methods during the field season.

30 June 2011

During this quarter, we hired the post-doctoral fellow (Dr. Will Hobbs) that will be conducting the research on shallow lakes this summer and into the fall. This spring he procured a new instrument that will be used for characterizing the sediments in five different ecoregions of the state. Initial cores were collected to begin to characterize the penetration of dissolved oxygen into the sediments, a key parameter that is related to burial of organic carbon in these sediments. The cores are also being analyzed for carbon content by undergraduate students at the University of St Thomas. Later yet this summer, lakes in all five of the ecoregions will be sampled by collecting cores and removing sub-samples for determination of the quantity of organic carbon and dissolved oxygen present. In some of our NSF-supported research in the western Minnesota ecoregion, we have found that dissolved oxygen levels are an important parameter to degradation of organic matter that occurs in the water column but we do not know yet if this is an important parameter that has an important impact on degradation of material once it is buried in the sediments. We will use ^{210}Pb to characterize the burial rates of carbon in these cores.

31 December 2010

We spent this period establishing collaborations with the Minnesota DNR, recruiting and hiring personnel, and collecting initial sediment cores for estimating carbon burial. We successfully recruited a postdoctoral associate (Dr. Will Hobbs) for this project this past fall, and he will begin working on the grant this spring. We also recruited a University of St. Thomas undergraduate who will begin working on sediment cores in January. A collaborative agreement has also been established between the University of Minnesota and the University of St Thomas to manage the funds. We also established our collaboration with Mark Hanson and Brian Herwig of the Minnesota DNR to share data being collected with their LCCMR grant (Cotner and Zimmer are collaborators on the Hanson LCCMR grant). We will collect and use surface sediment cores to estimate carbon burial rates in the 127 lakes being sampled in the Hanson LCCMR project, and the DNR data will allow us to identify variables influencing carbon burial rates in Minnesota shallow lakes (watershed land use, lake depth, abundance of fish, etc.). We began collecting sediment cores this past fall from 18 lakes, and these samples will be processed this winter. With Dr. Hobbs on board, coring will continue next spring. In summary, the first six months on this project were spent hiring, working out sampling and analytical logistics, and establishing collaborations. At this point, we have not spent any of our allocated funds, but we will begin to spend our funds in January of 2011.

Amendment Request (05/19/11):
This summer we will collect sediment samples from lakes in all five ecoregions. One of the key variables that affects organic matter degradation in sediments that we have examined as part of our NSF study is the amount of time that organic carbon is exposed to oxygen in the water before it is ultimately buried into anoxic sediments. In order to determine the time of oxygen exposure, one needs to know the age of the sediments at various depths (which we are already determining) and how deep into the sediments dissolved oxygen penetrates. It is this latter variable that we will be able to measure precisely with the instrumentation that we plan to purchase. Previously, we had planned to assume that the penetration depth would be relatively uniform across the five ecoregions but given that there are profound differences in the amount of organic matter as well as the density of the sediments, we expect that there could be large differences in this parameter. With permission from the LCCMR, we would move $5546 from our 'Supplies' portion of our budget into the 'Capital equipment over $3500' category. It should be noted that this expenditure will cover about one-third of the cost of the equipment we will purchase. The remainder of funds will come from our NSF funds and from another professor's funds at the University of Minnesota who intends to use this equipment when we are not using it. The instrumentation we will purchase is a microelectrode system that includes several dissolved oxygen sensors, a micromanipulator for moving the sensor through the sediments and software for interpreting the measurements.
Amendment Approved: 05/19/2011

IV. OUTLINE OF FINAL PROJECT RESULTS*:*

RESULT 1: Estimate the statewide potential for shallow lakes to bury carbon in their sediments, and calculate the statewide potential for shallow lakes to serve as carbon credits.

Description: We estimated both temporal and spatial variability in carbon storage in shallow lakes, scaling estimates of carbon storage in individual lakes to estimates for Minnesota's ecoregions, and estimated the potential for Minnesota's shallow lakes to remove carbon and develop estimates of carbon credits in the carbon trading market.

Summary Budget Information for Result 1:

ENRTF Budget:	**$144,000**
Amount Spent:	**$143,917**
Balance:	**$83**

Deliverable	Completion Date	Budget

1. *Identify variables driving carbon storage in each ecoregion and provide an estimate of carbon buried for individual lakes in each ecoregion, total burial for each ecoregion, as well as statewide burial of carbon in shallow lakes*	30 Jun 2012	$84,550
2. *Convert estimates of carbon burial by shallow lakes into estimates of potential carbon credits for each ecoregion and the entire state.*	30 Jun 2013	$59,450

Result Completion Date: *30 June 2013*

Result Status as of *31 December 2010*:

We successfully recruited a postdoctoral associate (Dr. Will Hobbs) for this project this past fall, and he will begin working on the grant this spring. Dr. Hobbs has an extensive history of collecting sediment cores from lakes, and also has experience working in shallow lakes in Minnesota. We also recruited a University of St Thomas undergraduate research assistant who also has experience working on lake sediment

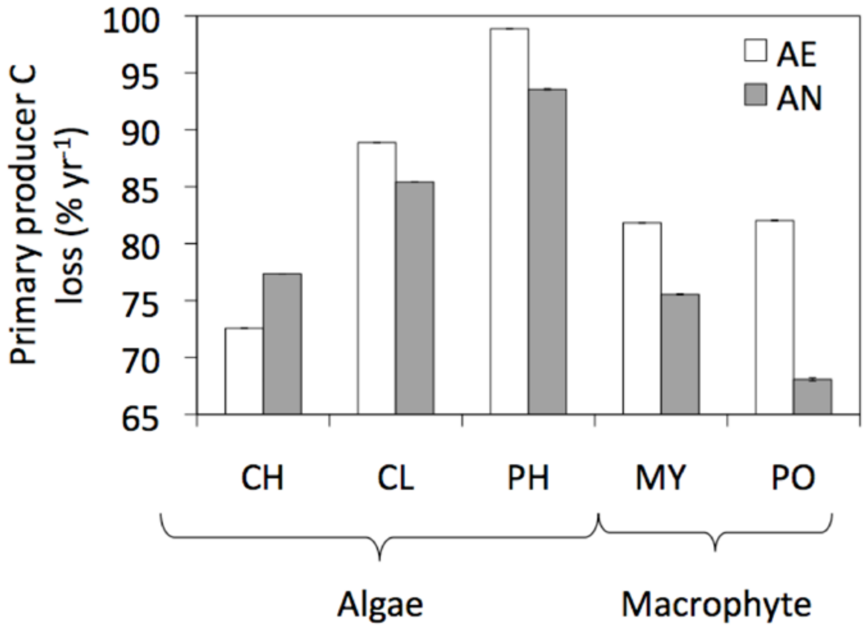

Figure 2. The percentage of organic carbon loss in different types of plants found in shallow lakes in the western ecoregion of Minnesota (CH-Chara; CL- Cladophora; PH-phytoplankton; MY-Myriophyllum; PO- Potomogeton. Note that, with the exception of Chara, all of the plants decomposed at faster rates, i.e., higher loss rates, under aerobic-oxygenated conditions.

cores, and he will begin working on the project in January.

We also established our collaboration with Mark Hanson and Brian Herwig of the Minnesota DNR to share data being collected with their LCCMR grant. The PIs on this LCCMR grant (Cotner and Zimmer) are also collaborators on the Hanson LCCMR grant, which made the collaboration and coordination between the two projects much easier to establish. Hanson has provided us with the location of the 127 shallow lakes they are studying in five different regions of the state. We have already collected cores from 18 of the lakes and will collect surface sediment cores from additional lakes over the next two years and analyze them for concentrations of inorganic carbon, organic carbon, nitrogen, and phosphorus. We will also measure dissolved oxygen levels in the cores to calculate carbon burial efficiency. The cores will be ^{210}Pb dated, allowing us to estimate carbon burial rates and efficiency in all 127 shallow lakes. Using data collected by Hanson on abundance of fish, algae, aquatic plants, nutrient levels, and watershed features, we will then determine the primary drivers of recent carbon burial in Minnesota shallow lakes.

We collected initial sediment cores from 12 lakes in the Alexandria study area and 6 lakes in the Twin Cities Metropolitan area this past fall. Now that Dr, Hobbs is on board, these cores will be analyzed this winter and more cores will be collected this spring. Collection of cores from the other 115 lakes will begin in earnest this spring, and we expect to core half the lakes this summer and the other half in summer of 2012.

Our first six months on this project were spent on hiring, logistics, and establishing collaborations. Thus, we have spent only $2,500 of the allocated funds from LCCMR, but the activity on this project will increase significantly in January of 2011.

Result Status as of *30 June 2011*:
To identify variables that contribute to organic carbon burial in survey lakes, we will be collecting cores from all 5 ecoregions this summer to (a) measure the quantity of organic carbon buried in short cores and also to determine how far dissolved oxygen penetrates into the sediments in each of the regions. Similar work that is being performed by us as part of our related NSF study has demonstrated that the amount of dissolved oxygen exposure of organic matter can play an important role in determining how quickly the organic matter degrades (Fig. 2). These data demonstrated that different plants typically degraded faster when oxygen was present with one exception (Chara sp.). Relatedly, as part of our joint project with DNR-Fisheries, we have quantified the plant and chlorophyll biomass in all of the lakes that we will be sampling this year and have found that the plant biomass varies quite substantially from 0 to 7.7 kg per m^2. This large amount of variation is important, because we expect that macrophyte plant biomass should be an important variable in organic carbon burial.

We have also quantified organic carbon burial rates in some of these western Minnesota shallow lakes and presently our results indicate that organic carbon burial rates have increased by a factor of 2-5 since European settlement in this region of Minnesota (Fig. 3). We suspect that this increase is due to a number of factors but land clearing and more recently, intensive use of inorganic fertilizers are suspected to be important contributors. Also of note is the fact that clear (macrophyte-dominated) and turbid (phytoplankton-dominated) do not appear to differ significantly in the quantity of carbon buried, but it should be noted that we do not know how long these lakes have been in their current conditions, i.e., a lake that is presently turbid may have been clear in the past.

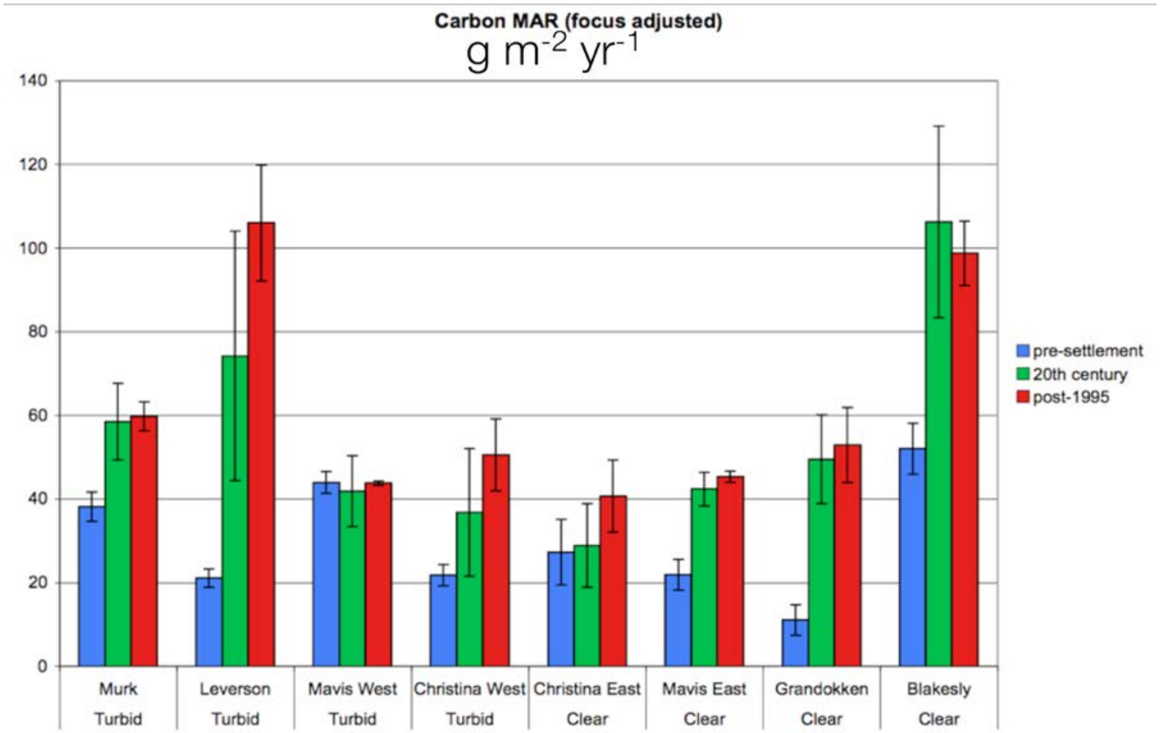

Fig. 3. Organic carbon burial rates in the western Minnesota ecoregion. Burial rates were estimated from dated (^{210}Pb) cores during different periods: pre-settlement (blue bars), 20th Century (green bars) and only in the last 15 years (red bars). These comparisons do not suggest that wetlands that are currently turbid (dominated by phytoplankton) or clear (dominated by macrophytes) bury organic carbon differently.

Result Status as of *31 December 2011*:

We had hypothesized that dissolved oxygen exposure would be an important variable determining how much organic carbon is buried in the shallow lakes across the state. Therefore, we measured how far oxygen penetrates into sediments in each of the ecoregions as discussed above (in more than 70 lakes). Surprisingly, there was little variation in the depth to which oxygen penetrates (Fig. 4). But this does not necessarily mean that the exposure time of oxygen does not have an effect on carbon burial rates because there could be significant variation in the exposure time due to differences in burial rates. Presently, we are continuing analyses of samples that were collected this past fall (measuring organic carbon content and 210-Pb) to better estimate burial rates. Subsequently we will model oxygen exposure times across the state to determine how large the differences are in the different eco-regions and if it matters to organic carbon burial.

The figure below shows the resolution and amount of data attained from each lake. Results showed that regardless of the location of the lake or the ecological regime it is currently in (turbid or clear water), the penetration of oxygen into the sediments was on average 3.6 ± 1.8 mm. Further data analysis is required to determine whether there are significant subtle differences amongst each of our study regions.

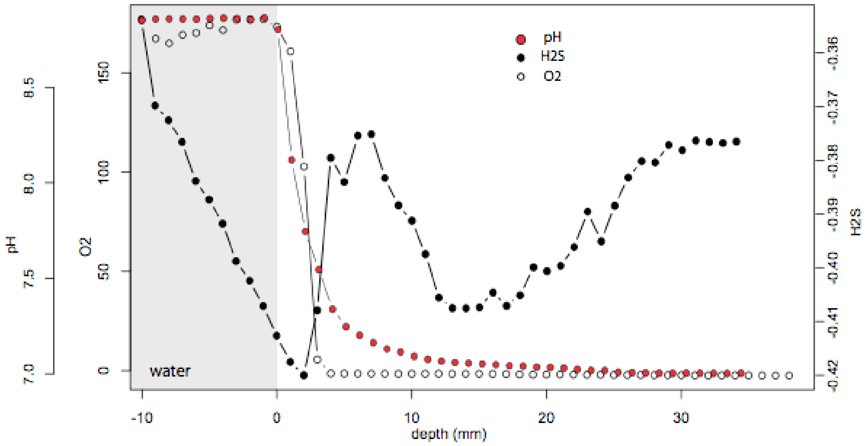

Figure 4: Lower Pigeon Lake in the Chippewa National Forest. Depth on the x-axis represents depth into the lake sediment, where 0 mm is the sediment-water interface. Oxygen is completely consumed by a depth of 2.5mm and pH decreases by over a unit and a half across the same interval.

Following the oxygen and pH measurements, the sediment cores were sub-sampled at 0.5 cm resolution in the field. Sediments were transported back to the University of Minnesota, weighed and freeze-dried, and dry bulk density was calculated for each interval. Currently, ~90% of the samples are dried and awaiting further analysis. Four undergraduate students working in co-PI Zimmer’s lab have been pulverizing the sediment samples in preparation for elemental C and N analysis. Surface sediments from a subset of the lakes have been analyzed for 210-Pb activity, as a means to estimate the sediment accumulation rate in the lake using a model of radioactive decay. Currently, this approach is being refined, with scientists at the St. Croix Watershed Research Station, to enable us to estimate the sediment accumulation rate in each of our study lakes.

Result Status as of *30 June 2012*:

All sediment samples have now been freeze-dried and sub-samples have been pulverized for the analysis of organic C. Pulverizing the samples ensures that a homogenous and accurate representative sample is taken. Hobbs (project post-doc) has now prepared (acidified and packed in analysis containers) a number of samples for each lake in order to show changes in the organic C concentration in the upper lake sediments (see Figure 5). This is important for the calculation of organic carbon burial rates. Samples are being analyzed in the lab of co-PI Zimmer and are near completion. Additional samples will be analyzed to assure quality control and accuracy of results. In order to estimate the rate of organic C deposition and burial in the lakes, a dataset of previously dated lake sediment cores from D.E. Engstrom (St. Croix Watershed Research Station) has been used to refine an accurate approach to using surface sediment radioisotopic lead activities as a means of assessing the modern (last 10 years) sedimentation rates for all 85 lakes in our dataset. This approach represents a significant advance in the science of dating and measuring lake sedimentation which will enable us to be able to estimate organic carbon burial much easier and in many more lakes. Composite sediment samples from each lake are now being compiled in order to incorporate the last 10 years of sedimentation. These composite samples will then be analyzed for lead activity and used in conjunction with the organic C concentrations to give a modern C-burial rate for each lake. Finally, the supplemental dataset of physical, biological, and chemical monitoring data for the lakes is near completion. This dataset will enable us to statistically compare the C-burial rates to a large number of lake variables to elucidate the dominant controls on C-burial.

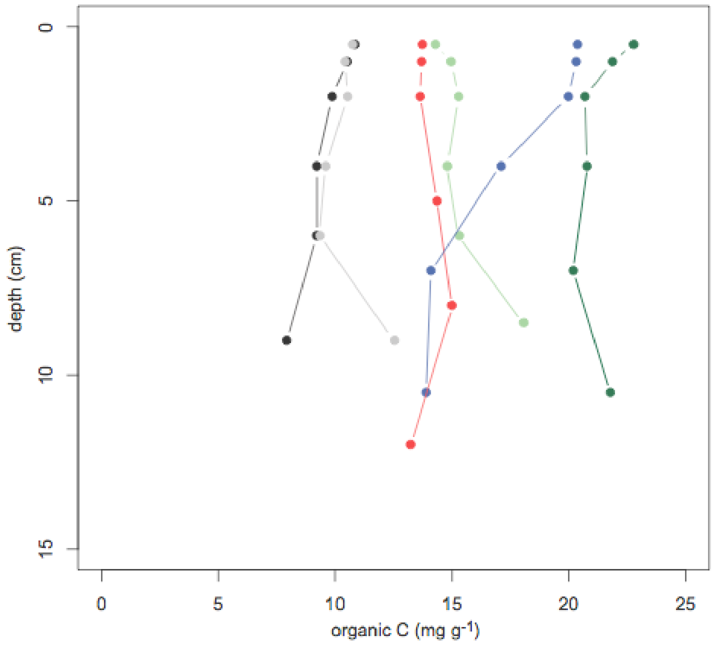

Figure 5: Organic C profiles in the surface sediments (0 cm being the sediment-water interface) from a number of lakes in western MN.

Result Status as of *31 December 2012*:

We have completed most of the sample collection and analyses and are in the process of synthesizing the analyses. As mentioned above, we have completed a manuscript describing a new method that we developed for estimating organic carbon burial rates from surface sediment samples and a manuscript describing this method has been submitted for publication (Figure 6). We will now apply this method to the 80 different lakes that we have samples from to estimate lake-specific organic carbon burial rates and scale those results up for regional and state-wide estimates. In addition, the supplemental dataset of physical, biological, and chemical monitoring data for the lakes is completed so we will now be able to compare the C-burial rates to a large number of lake variables to elucidate the dominant controls on C-burial. This approach will allow us not only to understand these processes on a lake-by-lake and regional perspective, but by better understanding these mechanisms, we will be able to predict burial rates in many other lakes.

Result Status as of ***30 June 2013*****:** As discussed above, we have used this method for estimating burial to arrive at mean burial rates in shallow lakes that are about 120 g C m^{-2} yr^{-1} (Figure 7). If we scale these measurements up to the entire state of Minnesota, it means that shallow lakes bury about 6 Tg (or 6 million metric tons) of carbon per year. This is about 4% of the total amount of carbon dioxide produced in the state per year through the burning of fossil fuels, not a huge percentage but it could nonetheless be managed in order to remove it more effectively. Some of our work also shows that low oxygen conditions may enable more effective carbon burial so that eutrophication of our freshwaters may enable more effective carbon burial. Although we do not advocate increased eutrophication of freshwaters, it is happening anyways, so this is one way where it may actually be a benefit.

Final Report Summary: 30 June 2013

We have found that shallow lakes bury organic carbon at very high rates compared to other landscape features. Effective burial is facilitated by high rates of productivity that occurs in these systems; anaerobic (no oxygen) conditions, when they occur, particularly in the winter time under the ice, also facilitates increased carbon burial. Although burial represents a large quantity of carbon, about 6 Tg per year (or 6 million metric tons), the State of Minnesota releases about 150 million metric tons of carbon per year through the burning of fossil fuels.

In addition to the scientific results of our work, this project has helped train numerous students (both undergraduate and graduate), technicians and post-doctoral fellows. Over 10 undergraduate students from both the University of St. Thomas and University of Minnesota were directly or indirectly (via funding for a related National Science Foundation project) supported on this project. Two graduate students at the University of Minnesota benefitted from this LCCMR project and the funding on this project supported a post-doctoral fellow for two years.

V. TOTAL ENRTF PROJECT BUDGET:

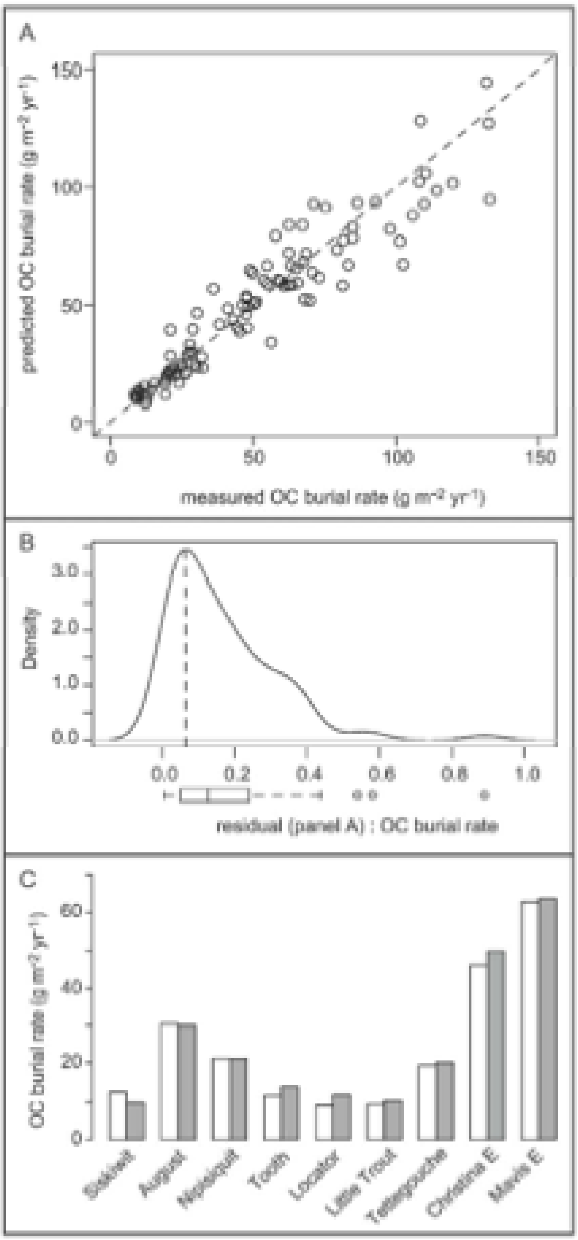

Figure 6. A scatterplot of the estimated OC burial rates using the surface-sample approach against the measured values based on fully-dated cores over a 10-year period, adjusted for sediment focusing. (B) The density probability of the residuals from the 1:1 line of plot (A), expressed as a percentage of the measured value with the highest probable error shown as a dashed line. (C) Repeat sediment cores were collected and independently analyzed in 9 of the lakes (4 to 10 years apart); OC burial rates of the repeat samples (grey bars) are calculated using the surface-sample approach.

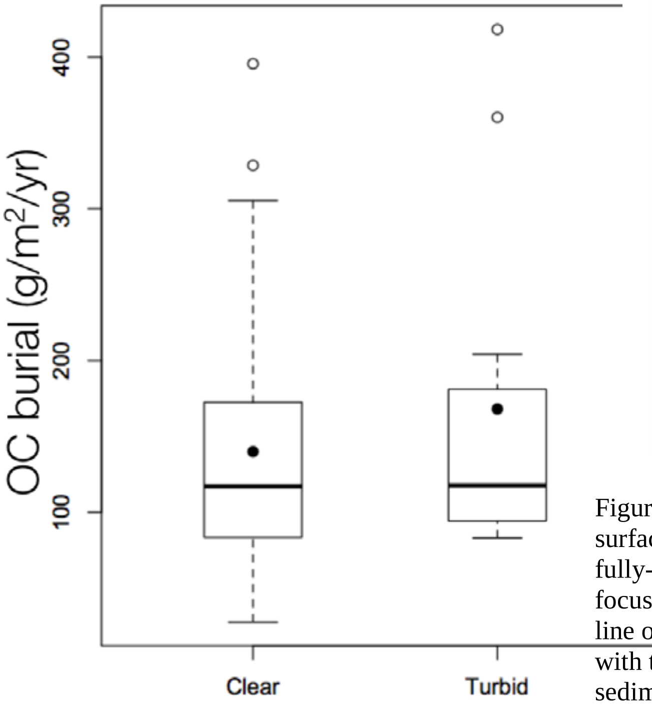

Figure 7. Median and variation (quartiles, mean and standard [illegible]) values for organic carbon burial in shallow lakes throughout the state of Minnesota.

Personnel: $ 115,425

Post-doctoral fellow was paid 100% time to do the following: 1) Assess temporal variability in organic carbon burial rates in lake sediment cores taken throughout the state of Minnesota; 2) Assess variation in different regions of the state in terms of organic carbon burial; and 3) Determine the potential for carbon credits to be traded via a cap and trade system using Minnesota's shallow lakes.

Contracts: $15,000

This funding was used to support Dr. Kyle Zimmer's (University of St. Thomas) efforts on the project. Most of this funding will support travel and supply expenses.

Equipment/Tools/Supplies: $ 10,120

These funds were used primarily for supplies used in collection and processing of sample cores collected throughout the state of Minnesota. In addition to cores collected and processed for the NSF funded work, we collected cores and surface sediment samples from lakes in the other ecoregions (Figure 1). These funds enabled the collection, processing and analyses associated with these other regions such as: total organic carbon estimates and some stable isotope measurements.

Acquisition (Fee Title or Permanent Easements): $

Travel: $3,455

These funds were used to collect cores and surface sediment samples from shallow lakes throughout the state of Minnesota (Figure 1).

Additional Budget Items: $

TOTAL ENRTF PROJECT BUDGET: $144,000

Explanation of Capital Expenditures Greater Than $3,500:

Although we did not have any capital expenditures in our original budget, we requested and got approval to purchase a microprobe system for measuring dissolved oxygen concentrations in sediments (see results in Fig. 4). The cost to this project was $5,546 and the total cost of the instrument was approximately $15,000, with one-third of the remaining cost coming from our NSF-supported work on mechanisms contributing to carbon burial in Minnesota shallow lakes and the other one-third coming from a colleague in University of Minnesota's Department of Ecology, Evolution and Behavior (Dr. Jacques Finlay) who also used this instrument.

VI. PROJECT STRATEGY:

A. Project Partners: Dr. Kyle Zimmer (University of St. Thomas: $15,000)

B. Project Impact and Long-term Strategy: This work needed to be done to (a) help Minnesota take advantage of remaining wetlands in future carbon trading, and (b) to leverage funds to help protect those wetlands.

C. Other Funds Proposed to be Spent during the Project Period: National Science Foundation

$443,474 to Cotner; Total award $1,212,103. Clarification: There are five scientists from two universities (University of St. Thomas [including Zimmer] and University of Minnesota-Twin Cities), and one research institute (Science Museum of Minnesota/St. Croix Watershed Research Station) funded through this NSF project. Of the >$1.2 million of total funding, Cotner received $443,474 to fund research that was related to, but not overlapping, with the work program outlined here. Much of the remaining work that is being funded by NSF is focused on interactions between climate variability and organic matter burial in the past. This work helped in the LCCMR project in that it helped us project organic matter burial in shallow lakes into the future.

D. Spending HIstory: *$143,917*

VII. DISSEMINATION: The results from this project have been incorporated into materials for use in the class room at St. Thomas and University of Minnesota. Cotner and Zimmer have used material from this project in lectures they have given locally, nationally and internationally (Sweden, Brazil, Japan). At the recent Ecological Society of America annual meeting, members of our team presented 11 posters and/or oral presentations that were very well received. We also organized a special session on terrestrial-aquatic linkages that had a strong focus on carbon burial. This was an extremely well-attended session at this international meeting. Also, 6 members of our group (Cotner, Zimmer, Hobbs and Ramstack-Hobbs, Herwig, and Hanson) presented results from this project at a Shallow Lakes Workshop that we helped organize in Fergus Falls this past August. This workshop was completely full and was attended by resource managers from throughout the state. Cotner has also been presenting some of this work through informal education talks that he has been giving in the past 18 months to various groups (mostly senior citizens) in the Twin Cities area. He has given approximately 20 presentations that have focused on marine and freshwater resources. Lastly, we have published three papers in the scientific literature based on results from this and a related project funded through the National Science Foundation. We have four other papers that are either currently being reviewed or that will be submitted by June 2014.

VIII. REPORTING REQUIREMENTS: Periodic work program progress reports will be submitted not later than 31 Dec 2010, 30 Jun 2011, 31 Dec 2011, 30 Jun 2012, 31 Dec 2012, 30 Jun 2013. A final work program report and associated products will be submitted between June 30 and August 1, 2013 as requested by the LCCMR.

Supplementary Documents:

We have included copies of two of the scientific papers that have been published from the results of this project.

Hobbs, WO, DR Engstrom, SP Scottler, KD Zimmer, and JB Cotner. "Estimating Modern Carbon Burial Rates in Lakes Using a Single Sediment Sample." LIMNOLOGY AND OCEANOGRAPHY-METHODS 11 (2013): doi:10.4319/lom.2013.11.316.

Theissen, Kevin M, William O Hobbs, Joy M Ramstack Hobbs, Kyle D Zimmer, Leah M Domine, James B Cotner, and Shinya Sugita. "The Altered Ecology of Lake Christina: A Record of Regime Shifts, Land-use Change, and Management From a Temperate Shallow Lake." Sci Total Environ 433 (2012): doi:10.1016/j.scitotenv.2012.06.068.

Final Attachment A: Budget Detail for 2010 Projects - Summary and a Budget page for each partner (if applicable)

Project Title: *Quantifying Carbon Burial in Healthy Minnesota Wetlands*

Project Manager Name: *James Cotner*

Trust Fund Appropriation: $ *144,000*

1) See list of non-eligible expenses, do not include any of these items in your budget sheet

2) Remove any budget item lines not applicable

2010 Trust Fund Budget	**Revised Result 1 Budget: (05/19/2011)**	**Amount Spent or Encumbered (6/30/13)**	**Balance (6/30/13)**	**TOTAL BUDGET**	**TOTAL BALANCE**
	Estimate the statewide potential for shallow lakes to bury carbon in their sediments, and calculate the statewide potential for shallow lakes to serve as	*143,917*	*83*	**144,000**	**83**
BUDGET ITEM					
PERSONNEL: wages and benefits					
Post-doctoral fellow (100% time for 2 years; 19% fringe benefits)	84,550	84,550	0	84,550	0
Technician (17% time for 3 years; 37% fringe benefits)	25,876	25,876	0	25,876	0
Undergraduate researchers	5,000	4,917	83	5,000	83
Contracts	15,000	15,000	0	15,000	0
Professional/technical					
Other contracts					
Other direct operating costs					
Non-capital Equipment / Tools					
Office equipment & computers - NOT ALLOWED unless unique to the project					
Capital equipment over $3,500	5,546	5,546	0	5,546	0
Land acquisition					
Easement acquisition					
Professional Services for Acq.					
Printing					
Supplies ***(filters, lab chemicals for analyses and other supplies)***	4,574	4,574	0	4,574	0
Travel expenses in Minnesota	3,454	3,454	0	3,454	0
Travel outside Minnesota					
Other					
Total	**$144,000**	**$143,917**	**$83**	**$144,000**	**$83**

Science of the Total Environment 433 (2012) 336–346

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The altered ecology of Lake Christina: A record of regime shifts, land-use change, and management from a temperate shallow lake

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ABSTRACT

We collected two sediment cores and modern submerged aquatic plants and phytoplankton from two sub-basins of Lake Christina, a large shallow lake in west-central Minnesota, and used stable isotopic and elemental proxies from sedimentary organic matter to explore questions about the pre- and post-settlement ecology of the lake. The two morphologically distinct sub-basins vary in their sensitivities to internal and external perturbations offering different paleoecological information. The record from the shallower and much larger western sub-basin reflects its strong response to internal processes, while the smaller and deeper eastern sub-basin record primarily reflects external processes including important post-settlement land-use changes in the area. A significant increase in organic carbon accumulation (3–4 times pre-settlement rates) and long-term trends in δ^{13}C, organic carbon to nitrogen ratios (C/N), and biogenic silica concentrations shows that primary production has increased and the lake has become increasingly phytoplankton-dominated in the post-settlement period. Significant shifts in δ^{15}N values reflect land-clearing and agricultural practices in the region and support the idea that nutrient inputs have played an important role in triggering changes in the trophic status of the lake. Our examination of hydroclimatic data for the region over the last century suggests that natural forcings on lake ecology have diminished in their importance as human management of the lake increased in the mid-1900s. In the last 50 years, three chemical biomanipulations have temporarily shifted the lake from the turbid, algal-dominated condition into a desired clear water regime. Two of our proxies (δ^{13}C and BSi) measured from the higher resolution eastern basin record responded significantly to these known regime shifts.

1. Introduction

Due to their significance to the global carbon cycle and the growing exploration of alternative stable regime theory, there is interest in developing historical reconstructions from shallow lake sediments (e.g. (Downing et al., 2008; Scheffer et al., 1993)). Efforts have been made to apply multiple biological and geochemical proxies from these records to address questions about the influence of human settlement and the longer-term controls on the ecology of shallow lakes. In two recent papers, Sayer et al. (2010a) and Sayer et al. (2010b) examined both modern and sedimentary remains of macrophyte and phytoplankton communities from shallow English lakes to examine modern dynamics and historical records and their implications for future ecological changes in the lakes. Schelske et al. (1999) successfully used diatom benthic/planktonic ratios and carbon to nitrogen ratios (C/N) in sedimentary organic matter from a core taken from Lake Apopka, a large, shallow lake (mean depth 1.7 m) in Florida to identify a known stable regime transition that occurred in 1947. Lake Apopka and three other shallow lakes were later studied by Kenney et al. (2010), who found that statistical analysis of C/N, biogenic silica (BSi), and total phosphorus results from sediment cores was a more effective means of identifying past sources of organic matter and interpreting whether the lakes were in a clear or turbid regime over the past two centuries. Others have used C and N stable isotopes (Das et al., 2008; Jinglu et al., 2007), chironomid assemblages (Brodersen et al., 2001), and diatoms and pollen (Vermaire and Gregory-Eaves, 2008) to track changes in the abundance of macrophytes and in the trophic status of shallow lakes. The overwhelming majority of lakes investigated in these studies have shown a clear post-settlement (or more recent) shift to algal dominance and/or loss of macrophyte diversity that is largely the result of human influence.

An improved understanding of the paleoecology of shallow lake systems is desirable as we consider how to best manage them. Recent

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work on shallow lake dynamics has revealed that shallow lakes can fluctuate between various alternative regimes, including two end members: a clear-water regime dominated by aquatic macrophytes with little phytoplankton abundance, or a turbid-water regime dominated by phytoplankton (Scheffer et al., 1993; Scheffer and van Nes, 2007). Shallow lakes are often the critical habitat for waterfowl and there is empirical evidence that shallow lakes and wetlands with rich macrophyte communities normally support diverse communities of waterfowl (Hanson and Butler, 1994a; Wallsten and Forsgren, 1989). The recent work also highlights the significance of shallow lakes and wetlands as natural carbon sinks (e.g. Cole et al., 2007; Euliss et al., 2006) and the ecosystem state of the lake may be important to its carbon burial potential. Here we use ^{210}Pb age-dated lake sediment core records from two morphologically-distinct basins in Lake Christina, a relatively large shallow lake in west-central Minnesota. Lake Christina has been both heavily managed and extensively monitored over the past 40–50 years. Analyzing sediment cores from both the large shallow basin and the smaller deep basin of the lake in conjunction with historical information allowed us to address the following questions: 1) How does the post-settlement ecology of the lake compare with pre-settlement conditions?, 2) What impacts have human activity such as land-clearing and regional agriculture had on Lake Christina's condition and how do these influences compare with the influence of historical climate trends?, 3) Do our proxies respond to known stable regime shifts that were forced as part of management efforts for the lake? To address these questions we measured BSi in sediment cores and C and N elemental and stable isotopic values in cores and modern plants collected from two sub-basins in the lake and calculated carbon accumulation rates for approximately the past two centuries. Our findings reveal marked ecological changes in Lake Christina following settlement of the region. Interestingly, these changes were manifested differently in the sedimentary records of the two sub-basins. We first discuss modern Lake Christina and its known history before explaining the multi-proxy methods we used and the high-resolution results we obtained for the past two centuries and lower resolution results that extend to nearly the past millennium.

2. Methods

2.1. Site description

Lake Christina (46.09° N, 95.74° W), is a shallow (mean depth 1.5 m; 80% of lake has depth of 1.2 m), eutrophic lake in west-central Minnesota that sits in calcareous glacial till (Fig. 1). The lake is relatively large (16.1 km^2) and can be separated into two distinct sub-basins; a large western sub-basin with fairly uniform morphology and depth (nearly all ~1.2 m) which is connected by a narrow stretch of water to a much smaller and deeper eastern sub-basin (max. depth 4.3 m is located here). While both of these basins might be lumped together as "shallow", there are important differences in the physical, chemical, and biological processes in each. Monitoring of Lake Christina over the past three decades has shown that the east basin has notably higher levels of surface water primary production in most years and a somewhat distinct pattern of change when compared to the west basin (Fig. 2A). This is likely due to the differences in depth and morphology between the two basins. Ongoing monitoring of several small shallow lakes near Lake Christina reveals that even minor differences in depth can have important implications on lake mixing. For example, temperature and dissolved oxygen data we collected during late summer 2010 from a small shallow lake basin of 1.5 m depth (a slightly greater depth than the west basin of Christina) shows a continually well-mixed water column. In contrast, a similar basin that is just 1.2 m deeper (2.7 m depth) is stratified for the majority of the same period (Fig. 2 B–E).

Lake Christina is primarily a groundwater fed lake with inflow rates ranging from 0.6 to 1 $m^3\ s^{-1}$ and an average of 0.7 $m^3\ s^{-1}$ over a 17 year monitoring period (1982–99). Surface water flow is estimated at half the groundwater flow into the lake (Minnesota Department of Natural Resources). Lake pH ranges from 7.6 to 9.5 and a $CaCO_3$ alkalinity of 190–290 mg L^{-1} as measured during 1987–88 (Hanson et al., 1990). Lake sediments have high concentrations of calcium carbonate due to this water chemistry and can be especially high during the warm season when primary productivity causes whiting events. Lake Christina lies within the Prairie Pothole Region, a large (nearly 900,000 km^2) area that includes millions of shallow lakes and wetlands. The lake is nationally recognized as a prime area for waterfowl production and is one of the only 40 lakes in Minnesota that has been designated a Wildlife Management Lake. As part of the management effort, Lake Christina has been periodically restored from a less desirable, phytoplankton-dominated condition that greatly reduced the waterfowl activity to a preferred clear water condition through three biomanipulations in the past 45 years. These treatments resulted in significant water quality improvements, re-establishment of macrophytes, and the return of waterfowl and associated invertebrates to the lake (Hanson and Butler, 1994a,b; Hobbs et al., in press). In the first half of the 1900s, Lake Christina was likely in a clear regime based on the observation of very high numbers of waterfowl which peaked in the late 1930s and early 1940s (Ordal, 1966). In 1937, a dam was constructed on the western basin outlet, increasing lake water depth by 0.25–0.75 m over the next decade (Hobbs et al., in press). By 1959 conditions had deteriorated, leaving the lake with a <25 cm transparency, very few macrophytes, and a dramatic reduction in waterfowl. In 1965 the lake was treated with the chemical toxaphene and macrophyte abundance increased sharply (Hobbs et al., in press). However, by the late 1970s clarity had decreased and by the early 1980s it was again turbid leading to another biomanipulation with the chemical rotenone in 1987 (Hanson and Butler, 1994a,b). This pattern of macrophyte recovery and eventual return to turbid phytoplankton-dominated conditions was repeated again over the next decade leading to another biomanipulation using rotenone in 2003 (Hobbs et al., in press). This known history of the trophic status of the lake provided an opportunity to examine the response of geochemical proxies (δ^{13}C, C/N, δ^{15}N, and BSi) to regime shifts in the lake. Because these biomanipulations have only been effective over periods of several years, but not in the long-term, a pump station was recently installed (Nov. 2010) with the goal of maintaining a low water level that is beneficial to the growth of macrophytes.

2.2. Modern plant sample collection and analyses

During July 2006, phytoplankton samples were collected from Lake Christina's western basin by filtering water through an 80 μm mesh to remove zooplankton, and then filtered onto pre-combusted Whatman GF/F filters with a 0.7 μm nominal pore size. Filters were dried and stored desiccated until time of analysis. Submerged aquatic macrophytes have been collected from the lake since 1947, with annual sampling since 1980. Plant abundance estimates were compiled from weighted rake tows that included at least 35 stations on the lake (Hansel-Welch et al., 2003). Macrophytes were also collected for elemental and stable isotopic analysis. Samples were collected by hand, frozen, and immediately transferred to the laboratory for analysis. In the laboratory, macrophytes were separated by species (*Myriophyllum sibiricum* and *Stuckenia pectinata*), rinsed, washed with dilute acid to remove any precipitated inorganic C, dried and ground. Each macrophyte sample was weighed and wrapped in a tin capsule, then stored in a dessicator for analysis. C and N concentrations and stable isotopic values of phytoplankton and macrophytes were measured using an isotope ratio mass spectrometer at the Colorado Plateau Analytical Laboratory. Accuracy of δ^{13}C was +0.21‰.

2.3. Core collection and geochemical analyses

A 1.4 m core was collected from the eastern sub-basin of the lake in January, 2006 (EB-06) and both a 1.2 m core and a 0.79 m core

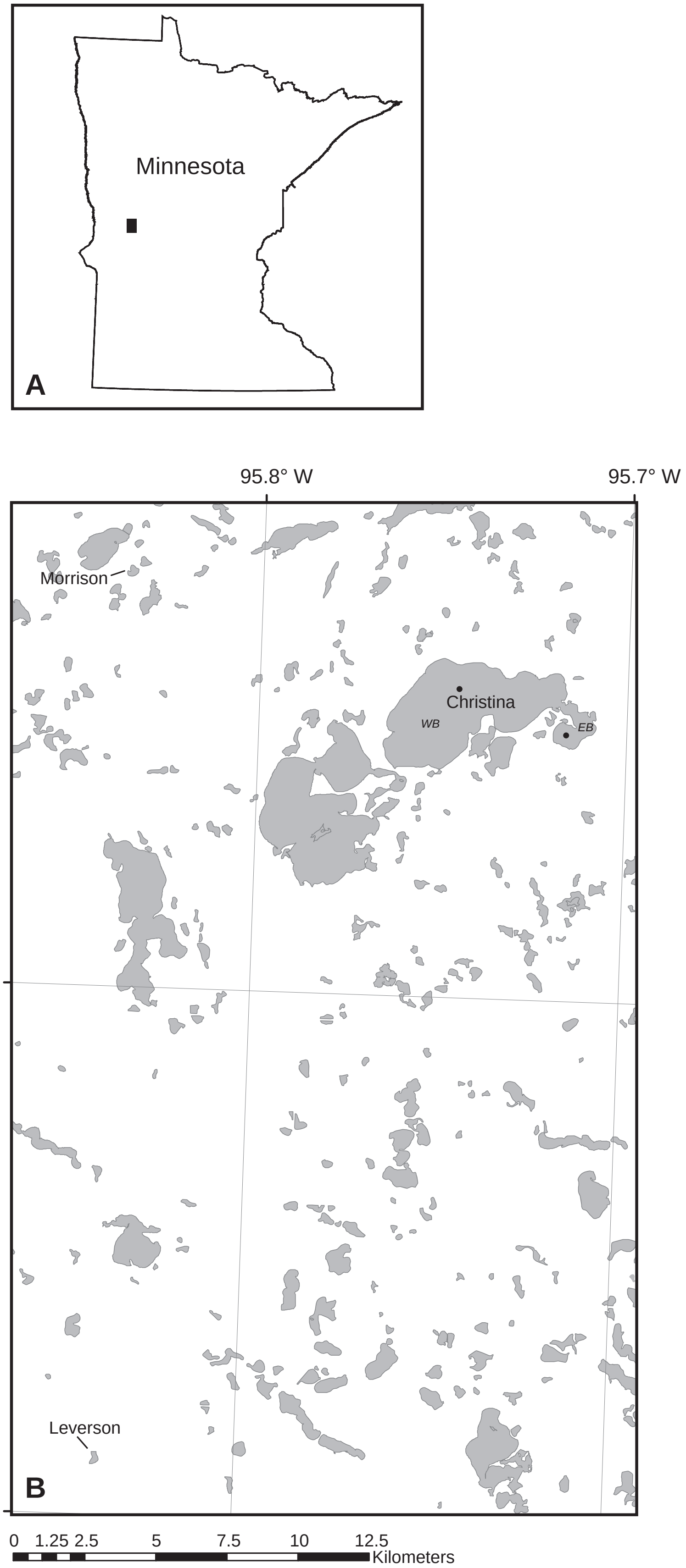

Fig. 1. Site map of Lake Christina. (A) State map of Minnesota showing the approximate location of the study area with a black square. (B) Regional map of Lake Christina and the two small shallow lakes (Leverson and Morrison) discussed in the text. The two closed circles indicate coring sites on Lake Christina, and the two lake sub-basins (East basin and West basin) are indicated with the text "EB" and "WB" respectively.

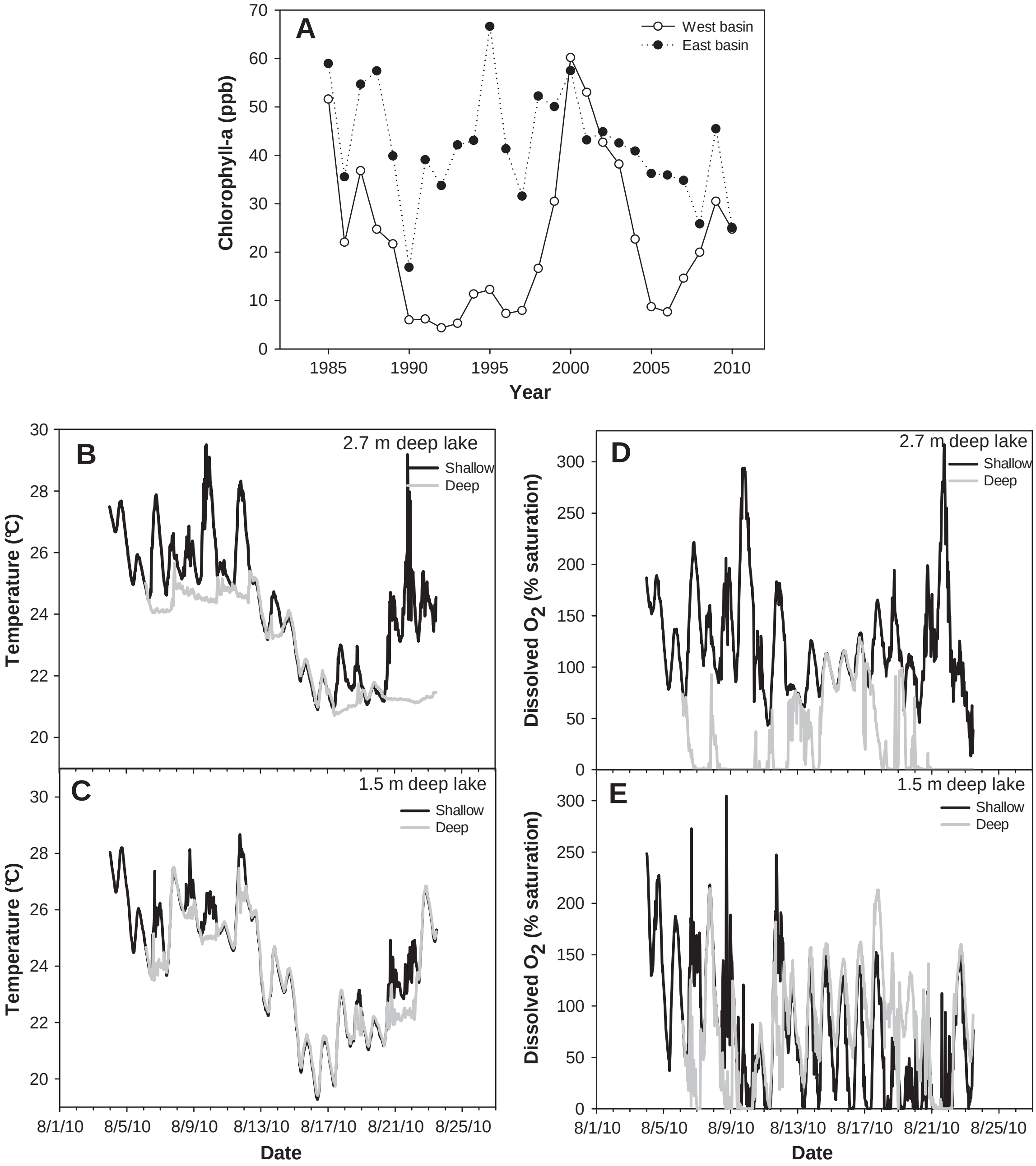

Fig. 2. (A) Chlorophyll-a data collected from the west (open circles) and east (closed circles) basins of Lake Christina from 1985 to 2010. (B–E) Temperature and dissolved O_2 data collected during August 2010, using multi-probe sondes in Lakes Morrison and Leverson, shallow west-central MN lakes. Temperature and dissolved O_2 data from Lake Morrison (2.7 m deep) (B, D) compared to Lake Leverson (1.5 m deep) (C, E). In each panel, the black line represents a near-surface measurement and the gray line represents a measurement near the deepest part of the water column.

were collected from the eastern and western sub-basins during October, 2008 (EB-08 and WB-08). All cores were collected using a piston coring device, and care was taken to preserve the sediment–water interface. Cores were kept in cold storage (~4 °C) until they were sub-sampled. Cores were dominated by homogeneous tan to light brown carbonate-rich silt. There was no indication of fine-scale bedding or other sedimentary structures in the cores. However, well-preserved fossil ostracods were abundant throughout the cores.

EB-06 and WB-08 were sub-sampled for bulk sedimentary organic matter (SOM) at 1 and 0.25 cm intervals, respectively, in the Geology Laboratory at the University of St. Thomas (UST). Samples were dried at 60 °C, ground, weighed, and treated with 6% sulfurous acid to remove all carbonate phases (Verardo et al., 1990). Samples were analyzed for total organic carbon (TOC), total nitrogen (TN), $\delta^{13}C$, and $\delta^{15}N$ using a Carlo Erba NA1500 elemental analyzer/Conflo II device coupled with a Finnigan Delta Plus mass spectrometer in the Stable Isotope Laboratory at Stanford University. The C/N, $\delta^{13}C$, and $\delta^{15}N$ values of SOM and the accumulation rates of organic carbon (OC MAR) are widely known for their utility in identifying sources of organic matter and detecting changes in paleoproductivity (e.g. (Meyers, 1997)). Published values for phytoplankton sources of organic matter in lakes have both low C/N and $\delta^{13}C$ (avgs. 7, −27‰). Macrophytes and terrestrial plants can have $\delta^{13}C$ values that span a large range but they tend to have higher C/N values, thus a combination of the two proxies can be used to identify the general sources of organic matter (Meyers, 1997). Organic C/N (atomic) values were calculated based on TOC and TN results. All $\delta^{13}C$ values are expressed relative to the Pee Dee Belemnite (PDB) standard and all $\delta^{15}N$ values are expressed relative to atmospheric N_2.

Approximately 5% of unknowns were replicated yielding average standard deviations of 0.480% for TOC, 0.113% for TN, 0.119‰ for $\delta^{13}C$, and 0.314‰ for $\delta^{15}N$. Assuming the organic carbon can be linked to autochthonous processes, the organic carbon mass accumulation rate (OC MAR) is a reliable indicator of primary production in a lake. We calculated the OC MAR using [TOC] (mg g^{-1}) multiplied by the sediment accumulation rate (g m^{-2} yr^{-1}) for each sediment interval.

Subsamples from Cores EB-08 and WB-08 were measured for biogenic silica at the St. Croix Watershed Research Station. The analysis of BSi in sediments provides a quantification of the total accumulation of siliceous algal fossils (diatoms and chrysophyte cysts). We used a modified wet alkali digestion method from DeMaster (1991) on approximately 30 mg of freeze-dried sediment (Conley and Schelske, 2001). Sediments were digested in a 1% Na_2CO_3 solution, while in a shaking water bath at 85 °C, and aliquots were removed at 3, 4, and 5 h for analysis of dissolved Si. This method allows for the sequential digestion and separation of BSi and the aluminosilicate fraction. The concentration of dissolved silica (as H_4SiO_4) in the extract was then analyzed using the heteropoly blue method (Clescerl et al., 1999) with a flow-injection analysis auto-analyzer (Lachat Quikchem 8000). The percent relative standard deviation amongst method triplicate samples, which were run on 10% of the sediment intervals, was <5%.

2.4. ^{210}Pb and other age dating methods

In order to construct an accurate age chronology for the cores, ^{210}Pb activity was measured through its granddaughter product ^{210}Po at 18, 23, and 15 intervals downcore in the EB-06, EB-08, and WB-08 cores respectively. Po isotopes were distilled from 0.5 to 3.0 g dry sediment at 550 °C after they were pre-treated with concentrated HCl and plated directly onto silver planchets from a 0.5 N HCl solution (modified from Eakins and Morrison, 1978). Activity was measured for $1–6\times10^5$ s with ion-implanted surface barrier detectors and an Ortec alpha spectroscopy system. Unsupported ^{210}Pb was then calculated by subtracting supported activity from the total activity measured at each level; supported ^{210}Pb was estimated from the asymptotic activity at depth (the mean of the lowermost samples in a core). Dates and sedimentation rates were determined according to the constant rate of supply model with confidence intervals calculated by first-order error analysis of counting uncertainty (Appleby, 2001). Lake Christina EB-06 core dates have an uncertainty of less than ±6 yrs back to the time of settlement of the region and the dating remains fairly precise back to the early 1800s (±13 years at 1826). WB-08 core dates have an uncertainty of less than ±8.5 yrs for the last century but are somewhat less precise for the mid-late 1800s (±15 years at 1881). ^{210}Pb age models are shown in Fig. 3. The age models were made by linear interpolation between the individual ^{210}Pb age dates for each core.

In order to determine the age of core material older than ^{210}Pb age-dating allows, we obtained one ^{14}C age date from the EB-06 core. Bulk sediment samples from lakes can be especially prone to problems with old sources of carbon that can result in erroneous age dates. With this in mind, seeds of *Carex* spp. (sedge) which grow along the lake margins were carefully separated from a bulk sediment sample at 104–105 cm depth in the core and sent to Beta-Analytic Laboratories where they were further treated and analyzed by Accelerator Mass Spectrometry. The resulting radiocarbon date was calibrated using the INTCAL04 database (Reimer et al., 2004) giving a calibrated age of 980±40 yr B.P. or approximately 1030 A.D. (Accession # Beta 244773).

2.5. Data transformations and statistics

In order to best compare select sedimentary data (BSi concentrations, $\delta^{13}C$ values) with independent historical datasets (Palmer Drought Severity Index, Lake Christina Plant abundance), smoothing and linear detrending techniques were applied to account for differences in sampling resolution between datasets and to reduce the influence of non-relevant trends. Data transformations (detrending and smoothing) and statistics (correlations) were done using Sigmaplot (Systat software).

3. Results

3.1. Geochemical results from eastern and western basin core samples for the last 200 years

Fig. 4 illustrates the correlation of C/N and $\delta^{13}C$ values in SOM samples representing the past 200 years from both the east ($n=135$, $r=0.604$, $P=<0.0001$) and west ($n=83$, $r=0.982$, $P=<0.0001$) basins of Lake Christina. C/N is a well-established indicator of various plant sources of OM and the good correlation suggests that both indicators are largely driven by changes in the sources of OM. The somewhat weaker correlation between these indicators in eastern basin SOM suggests the possibility of a more complex response, perhaps owing to both changes in the source material and in primary production. Downcore records spanning the last 150–200 years from the eastern and western basins of Lake Christina are presented in Fig. 5. Eastern basin TOC ranged from 8 to 12% with a long-term trend of declining values towards present. However, in the last 40 years this trend reversed and TOC increased from ~8.5% to nearly 12%. TN ranged from 1 to 2% and followed a pattern similar to TOC. Western basin TOC ranged from 3 to 14% with a long-term trend of increasing values towards the present. This trend was interrupted briefly in the early 1940s. TN ranged from 0.3 to 1.8% and again followed a pattern similar to TOC. Eastern basin C/N values were fairly stable for the majority of the last 200 years, rising slightly (~8.8–9.3) from 1800 to the early 1960s. However, values then declined sharply from 9.3 to 7.9 in the last 40 years of the record. Western basin C/N values spanned a wider range varying from 8.5 to 14.2. C/N values were generally higher, varying between ~11 and 14 in the earlier part of the record. The latter half of the record showed a steady long-term decrease in values since the early 1920s. The lowest C/N values (~8.5–9) occurred in the most recent part of the record.

In the eastern basin, organic carbon mass accumulation rates (OC MAR) ranged between 2.5 and 13.3 mg cm^{-2} yr^{-1}. These rates rose slightly from 2.5 to 3 mg cm^{-2} yr^{-1} from the early to late 1800s and then began to rise sharply in the early 1900s up to the highest rates (9.1–13.3 mg cm^{-2} yr^{-1}; roughly 4–5 times the pre-settlement rates) in the late 1950s and early sixties (Fig. 5A). MARs dropped somewhat in the late 60s and early 70s and varied between 4.5 and 7.7 mg cm^{-2} yr^{-1}. Western basin OC MARs were generally much slower than in the eastern basin and ranged from approximately 0.5 to 3.5 mg cm^{-2} yr^{-1} (Fig. 5B). Values rose slightly from ~1 mg cm^{-2} yr^{-1}around the time of settlement to ~1.5 mg cm^{-2} yr^{-1} by 1931. Rates then decreased below 1 mg cm^{-2} yr^{-1} and stayed relatively low over much of the next forty years. OC MAR then rose sharply after 1968, going from 0.5 mg cm^{-2} yr^{-1} to the highest rate of 3.58 mg cm^{-2} yr^{-1} in 2007.

In the period since settlement, eastern basin $\delta^{13}C$ values showed several rapid changes of approximately 1‰ and a rapid shift of greater than 2.5‰ to the lowest $\delta^{13}C$ values in the record from the late 1960s to the early 1990s. Since ~1993 values have remained stable at about −23.5‰. Western basin $\delta^{13}C$ values were both isotopically heavier and spanned a wider range. The trends in the record of $\delta^{13}C$ were very similar to those for C/N; with generally higher values (varying between 10 and 15‰) in the earlier part of the record, followed by a long-term decrease in values since the early 1920s. The lowest $\delta^{13}C$ values (−17 to −19‰) occurred in the most recent part of the record. From the time of settlement, eastern basin $\delta^{15}N$ values first showed a large increase of ~4‰, followed by a decrease of 2‰ to the present starting in the late 1960s. West basin $\delta^{15}N$ values

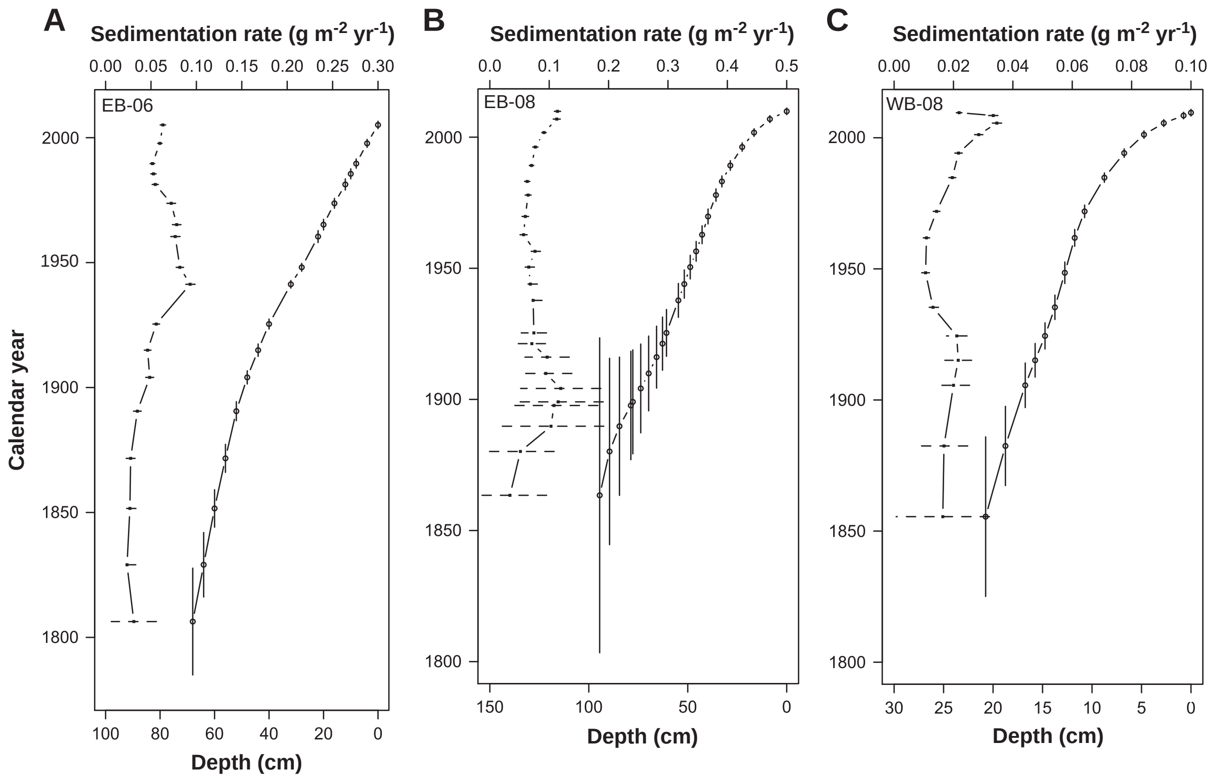

Fig. 3. ^{210}Pb age-dating results for the three sediment cores used in this study. (A) Line plot with open circles shows each of the determined ^{210}Pb ages versus depth in the EB-06 core. Dating errors are indicated with vertical error bars. Line plot with small dots shows the calculated sedimentation rate and dashed horizontal lines show associated error. (B) Same for core EB-08; (C) Same for core WB-08.

showed a subtle increase from the earliest part of the record to the early 1920s. From the 1920s to the present values decreased by ~2‰ (from ~0.5 to −1.5‰) to the present.

Our records of BSi concentrations extend from the early 1800s and the early 1940s in the eastern and western basins, respectively. In the eastern basin, concentrations rose from 3 to 5% from 1850 to the early 1870 s before rising sharply to ~8% near the time of settlement. BSi concentrations were fairly stable over the next 30 years and then jumped to nearly 13% between 1913 and 1919. BSi then fell to ~6% over the next two decades. Since the late 1930s, BSi has varied between 6 and 9% and the timing of these changes has closely followed three known lake management efforts (Fig. 5A). In the western basin BSi gradually increased from 6.5 to 8.5% from the early 1950s to 1994. This was followed by a sharp drop of ~1.5% over the next 12 years. In the upper most few years of the record, BSi rose sharply reaching the highest recorded value of 9.8% at the most recent sampled interval.

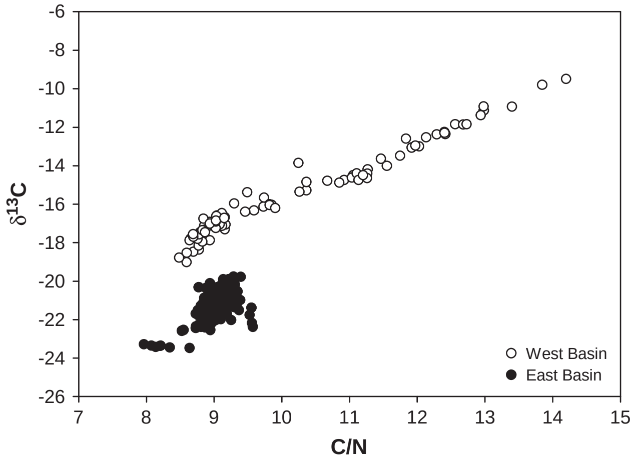

Fig. 4. Crossplot showing the correlation of δ^{13}C and C/N of sedimentary organic matter measured at the same depths in the western ($n=83$, $r=0.982$, $P=<0.0001$) and eastern ($n=135$, $r=0.604$, $P=<0.0001$) sub-basins of Lake Christina.

3.2. Elemental and stable isotopic results from western basin modern plant samples and comparison with downcore SOM results

Modern phytoplankton from the western basin of Lake Christina has δ^{13}C values ranging from −14 to −15.5‰ and C/N values ranging from 9.5 to 11. In contrast submerged aquatic macrophytes have both higher δ^{13}C values (ranging from −9 to −12‰) and C/N values (from 20 to 29). Phytoplankton and macrophytes plot into distinctly different regions on a crossplot of their C/N and δ^{13}C values (Fig. 6). On the crossplot western basin C/N and δ^{13}C values for SOM samples spanning nearly the past two centuries form a clear, long-term linear trend with significantly higher values in the earlier part of that record (prior to and near the time of settlement) that are closer to the composition of modern macrophytes in the lake. However, by the mid-twentieth century (see year 1943 in Fig. 6) western basin SOM values had become nearly identical to modern phytoplankton values. The trend towards lower values continues up to the present with values that are lower than those recorded in modern lake phytoplankton, but consistent with those generally reported in the published literature for phytoplankton in other lake systems (Meyers, 1997). C/N and δ^{13}C values from all of the eastern basin SOM samples are lower than both western basin SOM and phytoplankton sources as measured in samples from the modern lake.

3.3. Geochemical results from eastern basin over the last 1000 years

Core EB-06 provides a longer view of pre-settlement trends for the eastern basin (Fig. 7). This approximately 1000-year record shows

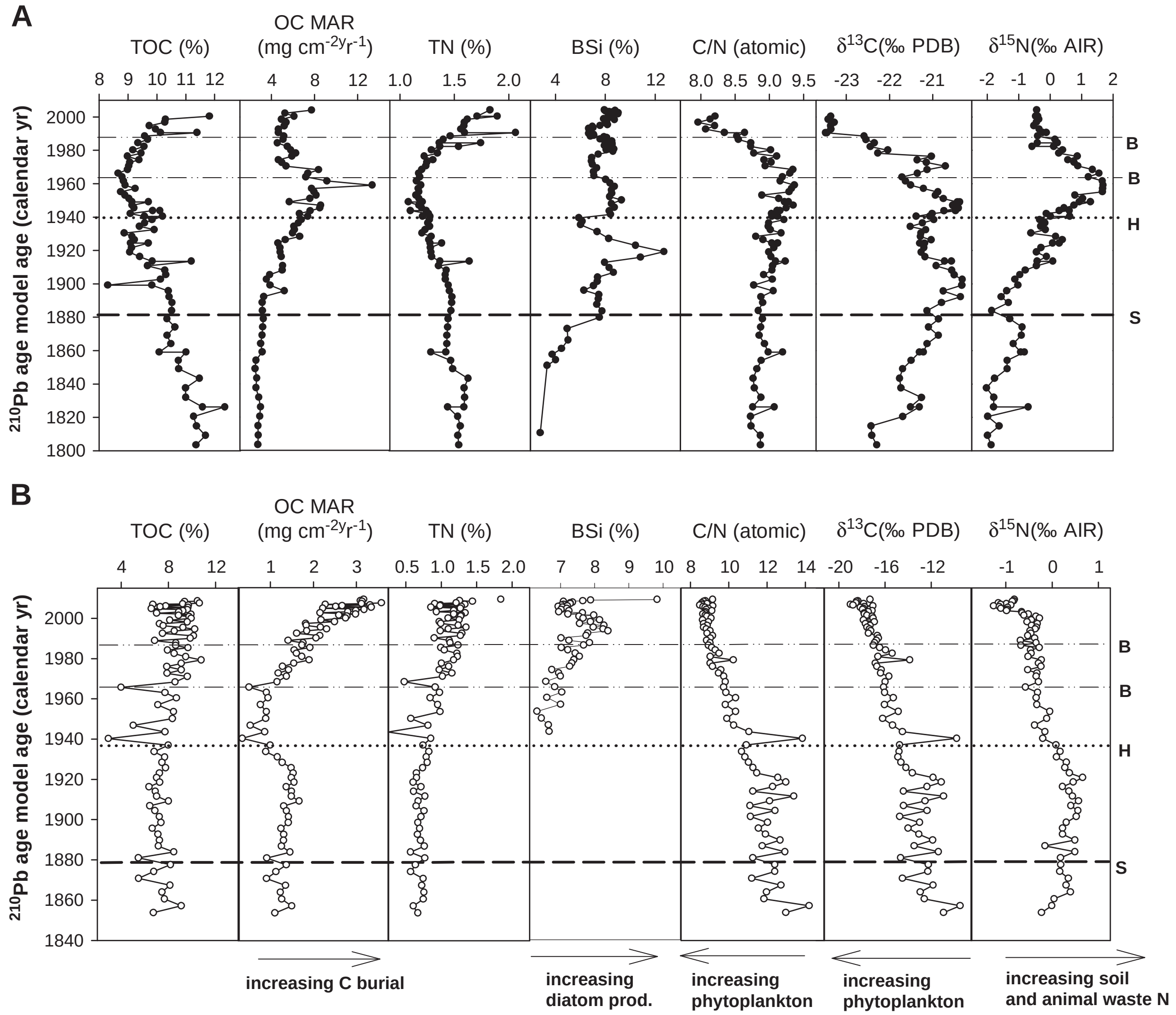

Fig. 5. Historical downcore records of elemental and stable isotopic information for (A) the eastern basin (core EB-06) and (B) the western basin (core WB-08). Total organic carbon (TOC), total nitrogen (TN), and biogenic silica (BSi) are all presented as concentrations (weight%). Organic carbon accumulation (OC MAR), C/N, and carbon and nitrogen isotopic data ($\delta^{13}C$, $\delta^{15}N$) are given as well. The dashed line with an "S" represents the time of European settlement (~1880), while the dotted line with "H" and the two dot-dash lines labeled with "B" represent the time of a known hydrological change (dam construction) and two chemical biomanipulations of the lake respectively.

how anomalous the post-settlement period has been relative to earlier times. TOC values were highest in the oldest part of the record (~14%) and then gradually trended towards lower values over the rest of the record, reaching values of <9% in the early 1900s before a sharp reversal towards higher TOC values in the last 40 years. TN values (ranging from ~1 to 2%) followed the same trends, but changed even more than TOC, nearly doubling in the last 40 years. C/N values ranged from 7.9 to 9.5. Values were stable through most of the record and varied notably in just three short intervals: one centered on about 800 yr BP, the second centered on ~650 yr BP, and the last in the most recent 40 years. $\delta^{13}C$ values varied from ~−20‰ to −23.5‰, rising and falling by 1–2‰ over a few multi-century periods before a large and rapid decline to the lowest values occurred in the last 40 years of the record. Eastern basin $\delta^{15}N$ values gradually decreased by approximately 2‰ (from ~0 to −2‰) from the earliest part of the record until about 200 yrs BP. They then rose gradually by about 1‰ prior to the sharp changes of the post-settlement period.

4. Discussion

Based on the downcore elemental and isotopic results and the burial rates we obtained, Lake Christina has generally been trending towards more phytoplankton production and organic C burial since the time of human settlement. Yet the records from the eastern and western sub-basins of the lake differ significantly in terms of the magnitude and timing of geochemical changes, reflecting site-specific responses. We suspect that many of the observed differences in the records from the two sub-basins are explained by their differing morphological characteristics. To briefly restate these differences, the western basin is comparatively quite large, of uniform depth throughout, and well-mixed. In contrast, the eastern basin is much smaller, has a deeper and more variable profile, and is stratified during at least part of the year. Although similar land-use changes occurred around both sub-basins after settlement, sediment focusing in the eastern basin resulted in a more enhanced response to these changes than in the western basin. On the other hand, the western basin responded more significantly to internal changes (such as changes to plant communities) than the eastern basin.

The large linear decline in both C/N and $\delta^{13}C$ values of SOM suggests that the plant communities in the shallower western basin have changed most dramatically, going from a macrophyte-dominated system in the mid-1800s, to one with an ever-increasing phytoplankton presence towards the present (Fig. 6). In contrast, the deeper eastern basin has continuously had a more significant phytoplankton presence

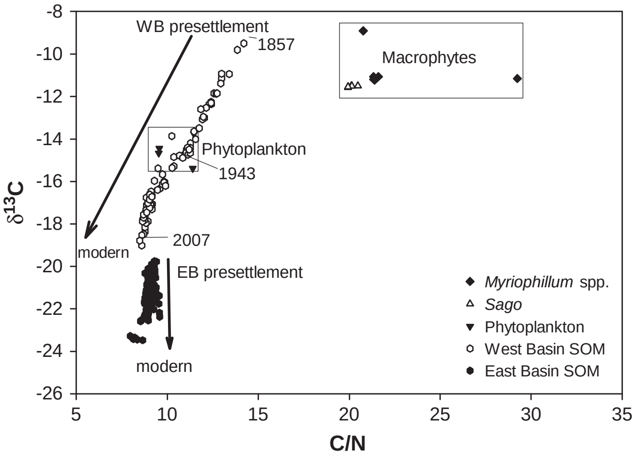

Fig. 6. Crossplot showing the geochemical relationship of SOM from each of the Lake Christina sub-basins to modern plants in the lake. The arrows show the trends in the geochemistry ($\delta^{13}C$ and C/N) of SOM from both of the sub-basins that occurred from pre-settlement to modern time. $\delta^{13}C$ and C/N values from west basin SOM samples dated to 1857, 1943, and 2007 are indicated to show the steady linear progression from C/N and $\delta^{13}C$ values in the earliest part of the dataset that are more closely associated with modern macrophytes (1857) to values that are typical of modern phytoplankton (reached by 1943), and finally to very recent values (2007) that are lower than those of the modern plants we made measurements on.

over this time span. The generally elevated C/N and $\delta^{13}C$ in the western basin relative to the eastern basin are likely the result of the shallow water conditions in the western basin which would tend to favor macrophyte production there (e.g. Scheffer et al., 1992). Interannual to decadal-scale variability is clearly more discernable in the eastern basin record. This is especially noticeable in the $\delta^{13}C$ and BSi records from the eastern basin where several rapid changes occurred during post-settlement time (Fig. 5A). The difference in the resolution of the two records is most likely due to the slower sedimentation rate in the western basin.

Both basins showed a significant increase in carbon burial rates (OC MAR) since the time of settlement, increasing by a factor of 3–4. The increased burial was likely the result of both increased terrestrial input to the lakes as a result of land-clearing for agriculture as well as increased primary production as nutrient supply to the lake increased (Hobbs et al., in press). The generally higher C burial rates in the eastern basin are most likely the result of sediment focusing into the small, deeper area of the eastern basin from which the core was collected. The rise in eastern basin burial rates that began shortly after settlement and ran until the early 1960s is most likely due to land-clearing, development and increased terrestrial input. This inference is supported by a more subtle rise in C/N values that spans the same period (Fig. 5A). The western basin was clearly less affected by these external changes and burial rates remained stable. The small but notable drop in western basin burial rates during the early to middle part of the twentieth century suggests a corresponding decrease in primary production beginning approximately at the onset of the "dust bowl" years of drought (~1933–1940) that affected this area (Fig. 5B). Historical aerial photographs of the lake and the character of the sediment indicate that the lake never dried out so it is unlikely that this was simply the result of desiccation and erosion under drought conditions. However, a number of the elemental proxies (BSi, TOC, and TN) were also at their lowest concentrations during this period, supporting our inference that primary production was reduced in the western basin. In contrast, the sharp rise in western basin burial rates from the 1960s to present was accompanied by increases in each of these proxies, signaling a sharp increase in production (Fig. 5B).

One of the important findings of this research is the anomalous post-settlement changes in the N-cycle of the lake and surrounding watershed that are indicated by significant $\delta^{15}N$ shifts, particularly in the eastern basin (Fig. 7). West-central MN is and has been an active agricultural region since the time of settlement and the vast majority of the land surrounding lake Christina is rural cultivated farmland. With this in mind, we believe that the explanation for the rise in $\delta^{15}N$ seen in the eastern basin record is the onset of significant inputs of eroded soil OM, human wastewater, and livestock waste inputs during the decades following settlement. All are isotopically heavy nitrate $\delta^{15}N$ sources (soil OM: 4–9‰, wastes: 10–22‰; (Heaton, 1986)) that are regularly detected in Minnesota lakes (Komor and Anderson, 1993) and there are animal feedlots within the lake watershed. The western basin record, showed little change in $\delta^{15}N$ in the decades immediately following settlement because it primarily responded to internal processes rather than external landscape changes. An alternative explanation for the post-settlement increase in $\delta^{15}N$ is that denitrification increased after settlement as a result of the observed increase in OC burial and the onset of lower dissolved O_2 levels in the deeper eastern basin. During denitrification, an isotopic fractionation occurs with ^{14}N preferentially taken up in the N_2 gas phase, resulting in residual nitrate that is enriched in ^{15}N and increased $\delta^{15}N$ values (Mariotti et al., 1982). In contrast, the well-mixed western basin never consistently

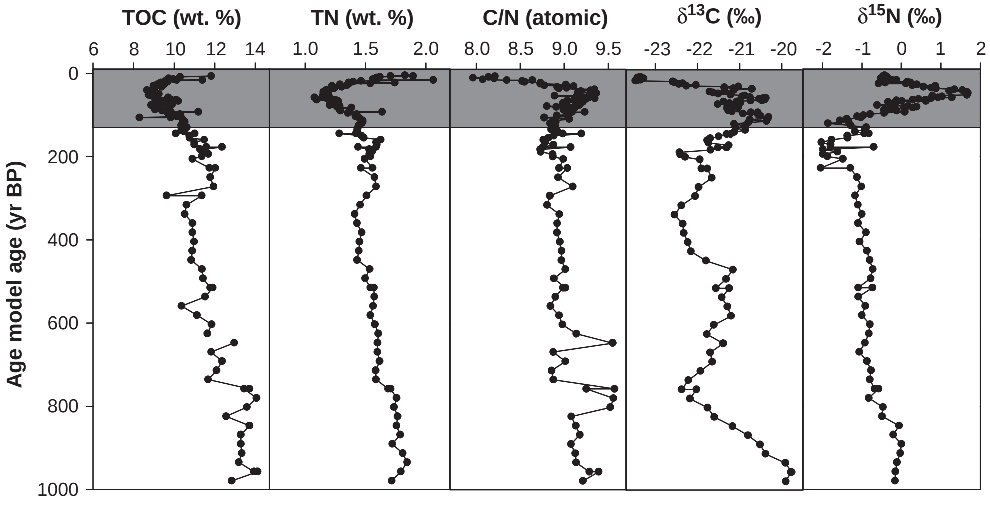

Fig. 7. Downcore records of TOC, TN, C/N, $\delta^{13}C$, and $\delta^{15}N$ for approximately the last 1000 years from the East basin of Lake Christina (core EB-06). Total organic carbon (TOC) and total nitrogen (TN) are presented as concentrations (weight%). C/N, and carbon and nitrogen isotopic data ($\delta^{13}C$, $\delta^{15}N$) are given as well. The shaded area is the post-settlement period.

developed the conditions required for denitrification and accordingly δ^{15}N values in SOM changed little after settlement (Fig. 5B). Both the post-1960 δ^{15}N decrease seen in the eastern basin record and the post-1920 decrease in the western basin record likely reflect the growing influence of fertilizer N with lower values than other sources (ranging from −4 to +4‰; Heaton, 1986). Assuming that the eastern basin δ^{15}N values are primarily driven by changing N sources (and not denitrification), the post-1960 decrease seen in the eastern basin record reflects a relatively greater input of fertilizer N over the inputs of isotopically heavier soil OM, human, and animal wastes into the lake over time. Indeed, records for Douglas County, where the majority of the lake lies show that total land within the county used for farming peaked in 1935 at ~93% before steadily declining and reaching a low of 63% by 1992 (Douglas County Land and Resource Mgmt. Dept., 1998). Moreover, the majority of the lost farmland was in dairy farming and other livestock operations. Douglas County land-use data collected between 1978 and 1992 show this steady decrease with the number of dairy farms decreasing by 47%, cattle farms by 36%, hog farms by 64%, and the number of poultry farms by 66% (Douglas County Land and Resource Management Department, 1998).

Climate is another important factor for us to consider as a possible driver for changing lake ecology and regime shifts in shallow lakes. We compared eastern basin δ^{13}C values and Palmer Drought Severity Index (PDSI) data for West Central Minnesota (Cook et al., 1999) over the past century. As discussed above, the δ^{13}C values are in large part an indicator of the source of organic material. Eastern basin values are more appropriate to consider since the higher sedimentation rate at the core site allows for greater resolution of interannual to decadal trends. The PDSI is an established hydroclimatic metric that integrates parameters that reflect the availability of water moving through the subsurface to the water table (Palmer, 1965). PDSI values reflect the magnitude and duration of departures from regional mean conditions (Alley, 1984). Eastern basin δ^{13}C values were negatively correlated with the PDSI during the earlier half of the record (Fig. 8, years 1896–1937; $n=15$, $r=-0.539$, $p=0.0379$). That is, during periods of more arid conditions in west central MN, δ^{13}C was higher than normal, and when conditions were wetter δ^{13}C was somewhat lower than normal. However, by the mid-1960s the records show a weaker relationship with no statistically significant correlation (Fig. 8, years 1939–2001; $n=32$, $r=0.234$, $p=0.179$). We hypothesize that the change was stimulated by a greater human influence on the lake system starting in the late 1930s with the construction of the dam on the lake. Prior to the 1937 installation of the dam, when the climate became wetter and lake level became higher (as indicated by positive PDSI values) this was more favorable to algae (as indicated by negative δ^{13}C values) and when the climate became drier and lake became level lower (as indicated by negative PDSI values) this was somewhat more favorable to macrophytes (as indicated by positive δ^{13}C values). One way that climate might influence shallow lakes is through its influence on lake water depth (Scheffer and van Nes, 2007). Shallower lakes have greater light at the bottom and allow macrophytes to grow through to the surface and avoid the effects of shading by phytoplankton (Scheffer et al., 1992). In contrast, high water levels can lead to a sharp reduction in macrophytes and a shift to the turbid regime (Engel and Nichols, 1994; Wallsten and Forsgren, 1989). In 1937 the dam was constructed and it is reasonable to assume that climatic influence on lake water depth was at least somewhat diminished. Our reconstruction shows that between the late 1930s and the early 1960s the δ^{13}C record was still out of phase with the PDSI record, but not to the same extent suggesting a slightly weakening link. By the mid-1960s when the first biomanipulation was done, any relationship between the PDSI and δ^{13}C became less clear suggesting an even weaker link between regional hydroclimatic influences and lake vegetation. A recent investigation of the Lake Christina plant community response to various environmental factors during the period 1985–1998 showed that water depth was the weakest of these factors, although changes in water depth were minimal during the study period (Hansel-Welch et al., 2003).

Using our data as an indicator of source material, we can evaluate the potential of our proxies to identify known regime changes in the lake through the earlier two of the regime shifts. In particular, the eastern basin BSi and δ^{13}C records show a response to the known state transitions in Lake Christina from the mid-1950s towards the present (Fig. 9). Since these datasets were each sampled at different time intervals, we compared ~2 year average values. We found a statistically significant negative correlation between plant abundance and BSi concentrations ($n=19$, $r=-0.51$, $p=0.013$) over a 44 year time period (1957–2001) and a slightly weaker positive correlation between plant abundance and δ^{13}C values over a 30 year period (1957–1987; $n=13$, $r=0.44$, $p=0.066$). Prior to the 1965 treatment when plant abundance was clearly declining, δ^{13}C shifted towards

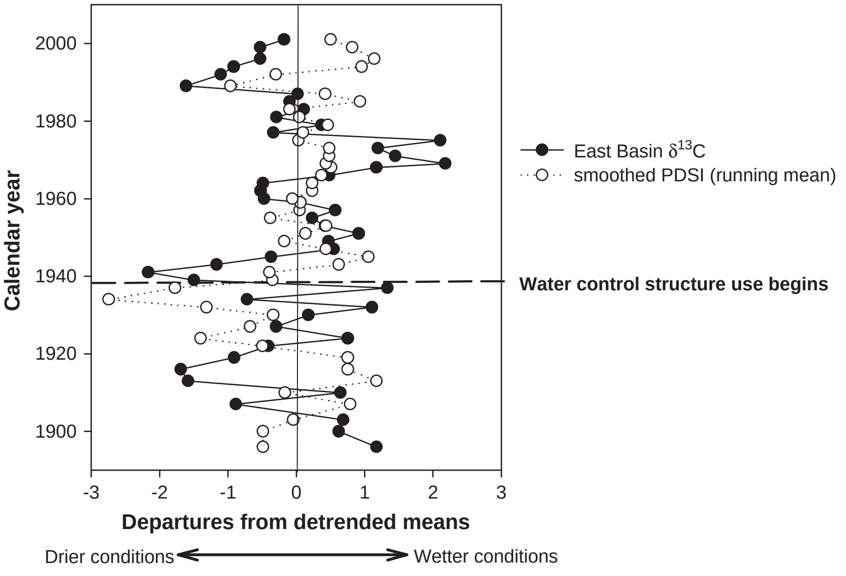

Fig. 8. Comparison of East basin δ^{13}C values and the Palmer Drought Severity Index (PDSI) for West-Central MN. PDSI data were smoothed at a time span comparable to sediment sampling intervals (~2 years). The East basin δ^{13}C was detrended in two parts to remove significant linear decreases in values both prior to 1937 and after 1960. Both records are expressed as departures from mean values. For the PDSI, positive values correspond to wetter than average conditions and negative values correspond to drier than average conditions. For δ^{13}C, positive values are more consistent with macrophyte sources of OM, while negative values are more consistent with phytoplankton.

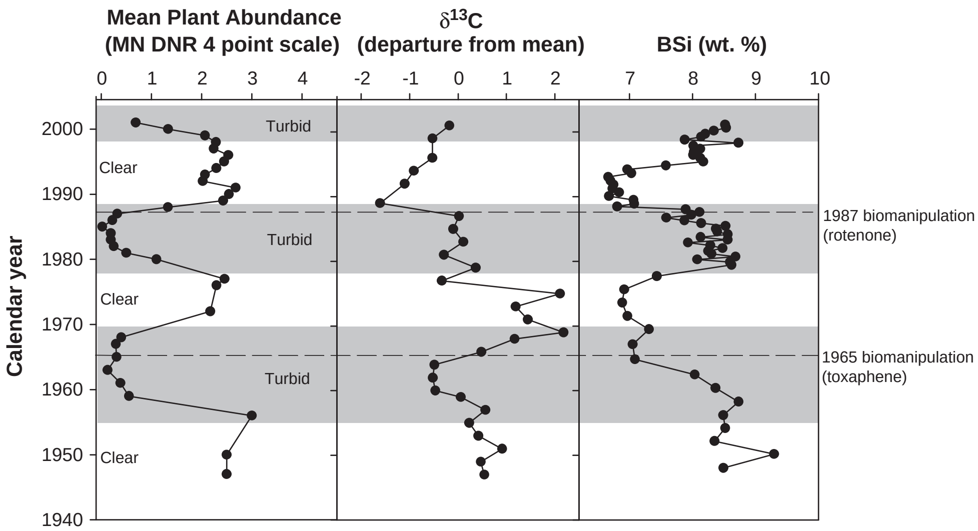

Fig. 9. Comparison of mean plant abundance as measured by the Minnesota DNR (Carlson et al., unpubl.), eastern basin δ^{13}C departures from the 1943–2001 mean values, and eastern basin BSi concentrations. In the 4-point scale used by the Minnesota DNR, 0–1 = 'Rare', 1–2 = Sparse, 2–3 = Abundant and 3–4 = 'Lush'. Shaded areas represent known periods of turbid water regime, white areas represent clear water regime.

more negative values, signaling a stronger influence of phytoplankton source material. After the biomanipulation when plant abundance sharply increased, δ^{13}C values increased and BSi concentration decreased, suggesting a somewhat stronger input of macrophyte material and reduced phytoplankton input. Again during the mid-1970s and early 1980s when plant abundance dropped sharply and turbid conditions set in, δ^{13}C followed suit with a decrease while the BSi concentration increased. After the 1987 biomanipulation of the lake plants again recovered, and BSi concentration decreased. A shift in δ^{13}C also occurred, but it was towards more negative values that are more consistent with phytoplankton rather than macrophytes. A possible explanation for the negative δ^{13}C shift may be found in lake management efforts that followed the 1987 biomanipulation. In the winter of 1987, the use of a large aeration system was initiated in the deepest part of the eastern basin in order to keep predatory fish alive. Use of this system continued for three years (T. Carlson, pers. comm.). Mixing of the water column during the aeration process would have re-circulated a ^{13}C-depleted pool of DIC (from degrading plant materials in deeper waters, e.g. McKenzie, 1985) into the surface waters, resulting in the observed sharp decrease in the δ^{13}C of SOM. We find the response of δ^{13}C and BSi to the biomanipulations to be compelling and we suspect that with further work these proxies might be useful indicators of past regime shifts in high-resolution sedimentary records from shallow lakes.

Our results show that Lake Christina has clearly become a more eutrophic lake in the time since settlement and especially since the mid-1900s when active management of the lake began. The biomanipulations have been effective in returning the lake to a desired clear water condition in the short run, but as eutrophication has progressed, management of the lake has become more difficult. This was made evident by the results of the most recent biomanipulation in 2003, the effects of which appear to have been especially short-lived as the lake has once again shifted to the turbid regime. Our proxy records show a lake that appears to be firmly locked into this condition with only brief shifts into the clear regime forced by lake management efforts.

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LIMNOLOGY
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Estimating modern carbon burial rates in lakes using a single sediment sample

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Abstract

The rate of organic carbon (OC) burial in inland waters is an important flux in the global C-cycle. Here we provide methodological improvements that offer a rapid and accurate assessment of modern OC burial rates in lakes from a single surface-sediment sample. Using a 93 lake dataset of reliably dated sediment cores (OC burial of 9 to 318 g m^{-2} y^{-1}), we demonstrate the applicability of this approach in a variety of lake types. We validate our estimated rates of OC burial against (1) measured whole-lake accumulation from the sum of multiple area-weighted sediment cores, (2) single central-basin cores adjusted for sediment focusing, and (3) duplicate sediment cores taken in multiple locations and at different times (4-10 years apart) in 9 lakes. Our single-sample estimates, which were in good agreement with measured values, suggest a within-lake variability of 4 g m^{-2} y^{-1} and have a small inter-lake error of only 6.5%. The applicability of this approach to other lakes and regions requires knowledge of (1) atmospheric ^{210}Pb flux, (2) an estimate of supported ^{210}Pb activity, and (3) some understanding of typical sedimentation rates in the study lakes. This approach provides an accurate assessment of OC burial, with increased potential for greater spatial coverage in inland waters and improved ability to address questions focused on terrestrial–aquatic exchanges of organic carbon.

Roughly 10% of the carbon that enters inland aquatic ecosystems from the land is permanently buried (Cole et al. 2007), which yields rates of organic carbon (OC) sequestration comparable with or even higher than in marine sediments and terrestrial soils (Gudasz et al. 2010). The spatial extent, rates, and efficiencies at which inland waters bury OC are therefore relevant to the discussion of the global C-cycle. Indeed, there has been considerable attention paid to estimating long-term rates of OC burial and storage in lakes (Dean and Gorham 1998; Einsele et al. 2001; Cole et al. 2007; Downing et al. 2008; Sobek et al. 2009; Anderson et al. 2009; Heathcote and Downing 2012; Mackay et al. 2012). However, considerable spatial heterogeneity exists among lakes and geographic regions, and improvements that refine the rate and magnitude of OC burial across lake types and regions are needed.

Previous estimates of OC burial in aquatic ecosystems have generally relied upon ^{210}Pb-dated lake-sediment cores (e.g., Sobek et al. 2009 and Heathcote and Downing 2012). As a result, the characterization of OC burial in inland waters is limited by the number of lake cores that are reliably dated, constraining large spatial surveys of lakes. In addition to the effort and cost required to date individual sediment cores, accurately assessing the lake-wide rate of OC burial is limited by sediment focusing—the spatial redistribution of fine-grained sediments by wave and current action. Focusing contributes a great deal of spatial heterogeneity to the accumulation of geochemical constituents across the depositional basin (Likens and Davis 1975; Lehman 1975; Blais and Kalff 1995; Mackay et al. 2012). As a result, proper estimation of whole-lake sedimentation rates generally requires multiple sediment cores covering the entire depositional basin (Swain et al. 1992; Rippey et al. 2008; Engstrom and Rose 2013) or the adjustment of a single central core based on the atmospheric flux of

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^{210}Pb (Rippey and Douglas 2004; Engstrom 2005). Methods that improve our ability to rapidly and accurately estimate OC burial rates over large spatial scales therefore are particularly important to understanding the role inland waters play in the global C-cycle.

Here, we present a method that allows for the rapid and accurate assessment of modern (last ~ 10 y) whole-lake OC-burial rates using a single sediment sample from the near-center of a lake basin and which accounts for sediment focusing to the sample site. We incorporate the earlier work of Binford and Brenner (1986), who formulated an approach to estimate the trophic state of a lake based similarly on the degree of ^{210}Pb dilution in the surface sediments. We demonstrate—by validation against conventional measures of whole-lake OC burial—the applicability of this method in a variety of lake types covering a large range of size and depth, and show how this approach furthers our understanding of the transport, focusing, and burial of OC and atmospheric ^{210}Pb.

Materials and procedures

Study sites

This method was developed using sediment cores from 93 lakes located throughout Minnesota and northern Wisconsin and upper Michigan, USA over the period of 1996–2010 (Table 1). The lakes are situated across several ecoregions as defined by land use, soil type, landforms, and natural vegeta-

Table 1. Study sites across Minnesota and northern Wisconsin and Michigan used in the analysis. Ecoregions are WCBP–Western Corn Belt Plains, NGP–Northern Glaciated Plains, NCHF–North Central Hardwood Forest, and NLF– Northern Lakes and Forests.

Lake	Ecoregion	County	Latitude	Longitude	Lake maximum depth (m)	Lake area (km^2)	Cumulative dry mass (g/cm^2)[*]	210Pb activity (Bq g^{-1})[†]	% organic matter (10 y mean)	Lake sediment focus factor	Measured whole-lake OC burial $(\text{g C m}^{-2}\text{y}^{-1})$	Predicted single-sample OC burial $(\text{gC m}^{-2}\text{ yr}^{-1})$
Bass	WCBP	Faribault, Minn.	43.81666667	–94.08083333	6.1	0.80	1.80	0.24	13.3	1.99	48	44
Dunns	NCHF	Meeker, Minn.	45.15555556	–94.42944444	6.1	0.63	2.99	0.15	19.2	3.73	86	105
Fish	NCHF	Dakota, Minn.	44.82222222	–93.16416667	10.2	0.13	3.26	0.28	13.2	2.70	56	38
Hook	WCBP	McLeod, Minn.	44.95465	–94.340176	5.5	1.33	3.18	0.20	26.7	4.04	133	107
Bean	NLF	Lake, Minn.	44.0713241	–95.37360592	7.9	0.13	1.49	0.14	17.0	1.54	75	98
Emily	WCBP	McLeod, Minn.	44.957383	–94.325687	1.6	0.40	1.00	0.23	31.3	1.16	114	101
Emily Peter	NCHF	Le Sueur, Minn.	44.311021	–93.922272	11.3	1.21	4.54	0.19	21.5	5.27	85	94
Fox	NGP	Martin, Minn.	43.67549896	–94.6989975	6.1	2.11	2.77	0.13	14.4	1.47	98	90
Greenleaf	NCHF	Le Sueur, Minn.	44.3972	–93.6267	5.8	1.22	6.30	0.15	19.7	4.78	110	106
Luce	NCHF	Carver, Minn.	44.964807	–93.781129	2.0	0.09	0.83	0.26	21.0	1.19	55	58
Lady Slipper	WCBP	Lyon, Minn.	44.5714	–95.629	3.4	1.16	1.48	0.16	14.5	1.59	55	71
Round	NLF	Itasca, Minn.	47.213207	–93.35848	4.9	0.40	5.36	0.22	20.2	5.21	102	77
Smith	NCHF	Wright, Minn.	45.079034	–94.126167	1.3	0.91	0.90	0.22	37.8	1.01	132	127
E.Bah	NGP	Douglas, Minn.	46.00365	–95.7635	3.0	0.16	0.93	0.25	20.8	1.17	59	59
Little Turtle	NGP	Grant, Minn.	45.88441667	–95.84591667	5.2	0.10	1.09	0.40	28.4	2.54	51	53
Beaver	WCBP	Steele, Minn.	43.89194444	–93.34911111	8.2	0.39	2.68	0.28	14.9	3.14	45	43
Diamond	NCHF	Kandiyohi, Minn.	45.18333	–94.8389	8.2	6.50	0.71	0.38	20.5	1.81	21	34
Duck	NCHF	Blue Earth, Minn.	44.21805556	–93.81555556	7.6	1.18	1.18	0.18	18.7	1.05	101	81
George B.E.	NCHF	Blue Earth, Minn.	44.98472222	–92.88361111	8.5	0.35	1.50	0.27	18.2	2.35	48	53
George Kandi	NCHF	Kandiyohi, Minn.	45.23333333	–94.98361111	9.8	0.92	0.80	0.41	18.8	1.99	28	32
Henderson	NCHF	Kandiyohi, Minn.	45.2307	–94.9929	17.4	0.30	0.40	0.76	30.0	2.11	27	25
Kreighle	NCHF	Stearns, Minn.	45.57916667	–94.47802778	20.1	0.51	0.21	0.60	47.1	1.03	36	33
Long	NCHF	Kandiyohi, Minn.	45.32583333	–94.87	13.7	1.33	0.38	0.53	20.6	1.60	21	23
Richardson	NCHF	Meeker, Minn.	45.15888889	–94.43941667	14.3	0.48	4.85	0.16	12.6	3.96	81	67
Stahls	NCHF	McLeod, Minn.	44.95416667	–94.41833333	11.3	0.55	1.58	0.30	26.3	2.33	71	68
Clear	WCBP	Sibley, Minn.	44.455292	–94.514751	2.4	2.00	0.63	0.11	18.8	0.30	109	109
Lura	WCBP	Blue Earth, Minn.	43.875687	–94.015914	2.8	5.26	1.85	0.20	16.0	1.58	65	64
Buffalo	WCBP	Murray, Minn.	44.07741667	–95.57903333	2.7	0.50	1.93	0.11	15.2	1.17	108	112
Edwards	NCHF	Pope, Minn.	45.50948333	–95.46865	2.8	0.57	0.89	0.27	23.0	1.27	73	63
Gil-Bret	NCHF	Pope, Minn.	45.42958333	–95.35815	2.2	0.10	1.18	0.24	21.4	2.12	49	67
Island	NGP	Lyon, Minn.	44.38283333	–96.00991667	2.3	0.65	1.56	0.20	19.9	1.81	62	76
Little Lower Elk	NCHF	Grant, Minn.	45.93336667	–95.80955	4.0	0.52	0.83	0.29	21.4	1.45	47	52
Lone Tree	WCBP	Yellow Medicine, Minn.	44.68958333	–95.44535	2.7	0.33	1.40	0.16	16.7	1.12	85	83
Malachy	NGP	Swift, Minn.	45.36806667	–95.67901667	1.1	0.13	1.15	0.20	16.4	1.27	62	61
Nelson	NCHF	Pope, Minn.	45.52386667	–95.4443	3.9	1.10	0.95	0.24	19.4	1.46	61	60
Ohsrund	NGP	Grant, Minn.	45.79721667	–96.04708333	2.0	0.76	1.13	0.23	18.3	1.44	63	61
Oak	NGP	Lincoln, Minn.	44.5367	–96.24246667	3.0	0.40	0.82	0.19	16.1	1.13	59	62
Round - Pope	NCHF	Pope, Minn.	45.5571	–95.27426667	3.5	0.79	1.19	0.22	16.0	1.96	70	57
Steep Bank	NGP	Lincoln, Minn.	44.53901667	–96.32761667	1.7	0.76	2.10	0.12	12.7	1.58	81	85
Slotseye	NCHF	Grant, Minn.	46.06308333	–95.84256667	3.8	0.10	1.04	0.28	19.4	1.73	50	52
Solem	NCHF	Douglas, Minn.	45.80981667	–95.63943333	3.7	0.15	0.69	0.40	26.7	1.54	41	45
Turtle A	NGP	Grant, Minn.	45.8859	–95.83581667	4.9	0.25	3.23	0.13	12.8	2.47	68	80
Turtle B	NGP	Grant, Minn.	45.88355	–95.83758333	8.5	1.78	3.82	0.16	14.3	3.38	65	74
Wolf	NLF	Lake, Minn.	43.85691667	–95.08986111	0.7	0.48	3.33	0.08	15.3	1.63	132	162
Hjermsted A	NGP	Murray, Minn.	44.17258333	–95.97130556	0.9	0.28	2.24	0.11	13.8	1.20	106	96
Skunk	NCHF	Grant, Minn.	45.15908	–95.05273	1.2	0.07	0.20	0.21	39.4	0.57	71	93
Murk	NCHF	Douglas, Minn.	45.1201	–95.07285	2.5	0.16	0.66	0.24	22.2	0.92	68	65
Mavis West	NCHF	Otter Tail, Minn.	46.26367	–96.0516	4.3	0.14	0.50	0.29	19.2	1.16	68	52
Mavis East	NCHF	Otter Tail, Minn.	46.0956	–96.04243	3.8	0.22	0.31	0.26	28.5	0.95	63	75
Leverson	NGP	Grant, Minn.	45.01778	–95.06203	1.3	0.08	3.68	0.12	17.2	2.04	120	114

Continued…

Table 1. Continued

Lake	Ecoregion	County	Latitude	Longitude	Lake maximum depth (m)	Lake area (km^2)	Cumulative dry mass (g/cm^2)*	210Pb activity (Bq g^{-1})†	% organic matter (10 y mean)	Lake sediment focus factor	Measured whole-lake OC burial (g C m^{-2} y^{-1})	Predicted single-sample OC burial (gC m^{-2} yr^{-1})
Grandokken	NCHF	Douglas, Minn.	46.027	–95.14308	1.9	0.02	0.23	0.37	40.4	0.87	59	59
Frolund	NCHF	Pope, Minn.	45.08212	–95.53333	1.9	0.06	0.91	0.30	27.9	1.66	63	67
Blakesley	NCHF	Grant, Minn.	45.14057	–95.04053	2.0	0.03	1.11	0.27	38.8	1.42	110	108
Morrison	NCHF	Otter Tail, Minn.	46.131115	–95.892983	2.5	0.20	0.95	0.20	25.7	1.12	93	95
Org	NCHF	Douglas, Minn.	45.05857	–95.09078	3.3	0.03	1.43	0.21	24.4	1.76	67	87
Pisa	NGP	Stevens, Minn.	45.04808	–95.05515	1.3	0.10	0.80	0.31	28.5	0.96	83	64
Bellevue	NCHF	Grant, Minn.	45.09948	–95.02497	3.0	0.12	0.44	0.33	19.9	1.25	43	41
Christina E	NCHF	Douglas, Minn.	46.084006	–95.690649	4.3	2.00	0.87	0.40	27.0	1.61	46	51
Christina W	NCHF	Douglas, Minn.	46.098365	–95.742881	1.3	16.19	0.28	0.25	21.2	0.49	54	45
Tettegouche	NLF	Lake, Minn.	47.3449135	–91.2686615	4.6	0.27	0.25	2.04	44.8	2.25	19	19
Siskiwit	NLF	Keweenaw, Mich.	48.0005271	–88.7956283	45.1	16.35	0.27	2.06	23.4	1.89	13	10
Rainy	NLF	St. Louis/Koochiching, Minn.	48.539183	–92.8291833	49.1	233.80	0.34	0.82	13.3	1.15	14	15
Kabetogama	NLF	St. Louis, Minn.	48.4557667	–92.95295	24.4	97.26	0.33	0.85	24.7	1.27	29	26
Lac La Croix	NLF	St. Louis, Minn.	48.3611226	–92.1751029	51.2	55.47	0.14	1.50	20.6	1.14	13	11
Namakan	NLF	St. Louis, Minn.	48.4338	–92.702267	45.7	48.24	0.60	0.78	15.3	2.49	15	18
Moskey Basin, Lake Superior	NLF	Keweenaw, Mich.	48.068972	–88.5663986	NA	NA	0.84	0.98	13.8	2.40	19	13
Ahmik	NLF	Keweenaw, Mich.	48.14787	–88.54153	2.6	0.10	0.45	0.90	43.3	1.96	44	45
Harvey	NLF	Keweenaw, Mich.	48.05067	–88.79602	4.3	0.55	0.21	0.46	39.7	0.50	79	76
Richie	NLF	Keweenaw, Mich.	48.04092	–88.70236	10.5	2.16	0.32	1.21	24.1	1.76	19	18
Outer	NLF	Ashland, Wisc.	47.004173	–90.4597519	0.8	0.22	0.51	2.47	49.4	3.62	24	18
Beaver	NLF	Alger	46.56524	–86.34362	9.2	3.10	0.23	1.93	45.6	1.73	23	20
Grand Sable	NLF	Alger	46.641305	–86.0357166	19.2	2.55	0.52	1.27	11.6	2.51	12	9
Florence	NCHF	Leelanau, Mich.	45.010527	–86.1198853	7.3	0.26	0.09	2.15	56.5	1.60	21	21
Manitou	NCHF	Leelanau, Mich.	45.12693	–86.0237	13.1	1.04	0.46	1.25	34.5	2.05	30	25
Shell	NCHF	Leelanau, Mich.	44.9477137	–85.9000603	4.0	0.41	0.12	0.86	47.2	1.65	30	48
Bass	NCHF	Leelanau, Mich.	44.9231008	–85.884445	7.9	0.35	0.55	2.26	66.8	5.83	25	28
Peary	NLF	St. Louis, Minn.	48.52423	–92.77164	4.6	0.45	0.16	0.60	28.3	0.48	29	36
Ek	NLF	St. Louis, Minn.	48.46975	–92.836	5.8	0.37	0.17	1.62	45.1	1.21	25	23
Cruiser	NLF	St. Louis, Minn.	48.49753	–92.80225	27.7	0.47	0.24	1.28	31.8	1.16	26	22
Swamp	NLF	St. Louis, Minn.	47.951333	–89.858083	5.8	1.44	0.12	1.07	52.7	0.88	38	40
Speckled Trout	NLF	Cook, Minn.	47.95	–89.8463	6.4	0.26	0.24	1.89	51.7	2.39	22	24
August	NLF	Lake, Minn.	47.762531	–91.608573	5.8	0.90	0.23	0.89	29.5	1.06	31	29
Intermediate	NLF	Keweenaw, Mich.	48.0304239	–88.7283577	6.7	70.80	0.44	0.97	26.8	1.22	32	25
Whittlesey	NLF	Keweenaw, Mich.	48.0058915	–88.707158	7.6	65.00	0.32	1.09	27.8	1.45	26	23
Little Trout	NLF	St. Louis, Minn.	48.396615	–92.522264	29.0	1.10	0.19	1.84	24.2	1.52	9	11
Locator	NLF	St. Louis, Minn.	48.540272	–93.005386	15.8	0.54	0.06	2.91	44.9	1.41	9	10
Nipisiquit	NLF	Lake, Minn.	47.355569	–91.247845	5.5	0.24	0.12	1.57	38.1	1.33	21	20
Tooth	NLF	St. Louis, Minn.	48.397123	–92.642813	13.1	0.24	0.08	2.71	49.2	1.45	12	12
Wallace	NLF	Keweenaw, Mich.	48.057148	–88.627924	3.0	0.05	0.18	0.63	39.9	0.64	47	53
Mukooda	NLF	St. Louis, Minn.	48.334024	–92.488719	23.8	3.13	0.15	2.31	32.4	1.55	11	11
Ryan	NLF	St. Louis, Minn.	48.518566	–92.706795	5.2	0.15	0.20	1.24	43.6	1.24	29	30
Kjostad	NLF	St. Louis, Minn.	48.109206	–92.606389	15.2	1.68	0.13	2.37	41.6	1.97	14	15
Dunnigan	NLF	Lake, Minn.	47.70722	–91.630521	4.3	0.33	0.25	2.02	58.3	1.01	24	24

*Cumulative dry mass of lake sediment equivalent to ~ 10 years accumulation.

†Total unsupported decay corrected ^{210}Pb activity corresponding to regional cumulative dry mass values (0.2 g cm^{-2}, northern Minn. Lakes, and 0.9 g cm^{-2}, southern Minn. lakes).

tion (Omernik 1987). From south to north, the lakes are in the Western Corn Belt Plains (WCBP), Northern Glaciated Plains (NGP), North Central Hardwood Forest (NCHF), and Northern Lakes and Forests (NLF). The WCBP and NGP are cultivated, heavily agricultural landscapes with NGP having marginally more pasture. The NCHF is a transitional landscape with cultivated, pasture, urban, and forested regions, whereas NLF is overwhelmingly forested with coniferous and deciduous vegetation. The region's many glacial lakes follow a gradient of nutrient enrichment from north to south, because of differences in land use, vegetation, soil conditions, and lake size (Heiskary and Wilson 2008). In general, lakes in the south (WCBP and NGP) are shallower and eutrophic to hypereutrophic, whereas lakes in NLF are deep and oligotrophic to mesotrophic. In our study, maximum lake depths ranged from 0.65 m to 51.2 m, and lake surface-areas range from 0.02 km^2 to 234 km^2. Two additional lakes, Dunnigan and Kjostad, were cored at multiple locations (12 and 14 sites, respectively) as part of an earlier study of atmospheric mercury deposition to northern Minnesota (Swain et al. 1992; Engstrom et al. 1994). The latter two lakes were chosen for analysis of carbon burial based on their contrasting morphometry and size (Fig. 1). Given the range of lakes used in validating this method, we feel it is broadly applicable to many temperate lake types and sizes.

Sediment core collection

This method relies on the retrieval of undisturbed lake sediment cores with an intact sediment-water interface. In our validation of the method, we use a piston-type corer (Wright 1991) with a 2.75-cm polycarbonate core barrel operated from the lake surface by Mg-alloy drive rods. Cores were sectioned vertically in the field at 0.5 or 1 cm increments for the uppermost sediments (and more coarsely at depth), and stored in polypropylene jars for subsequent analysis of water and organic content and ^{210}Pb dating.

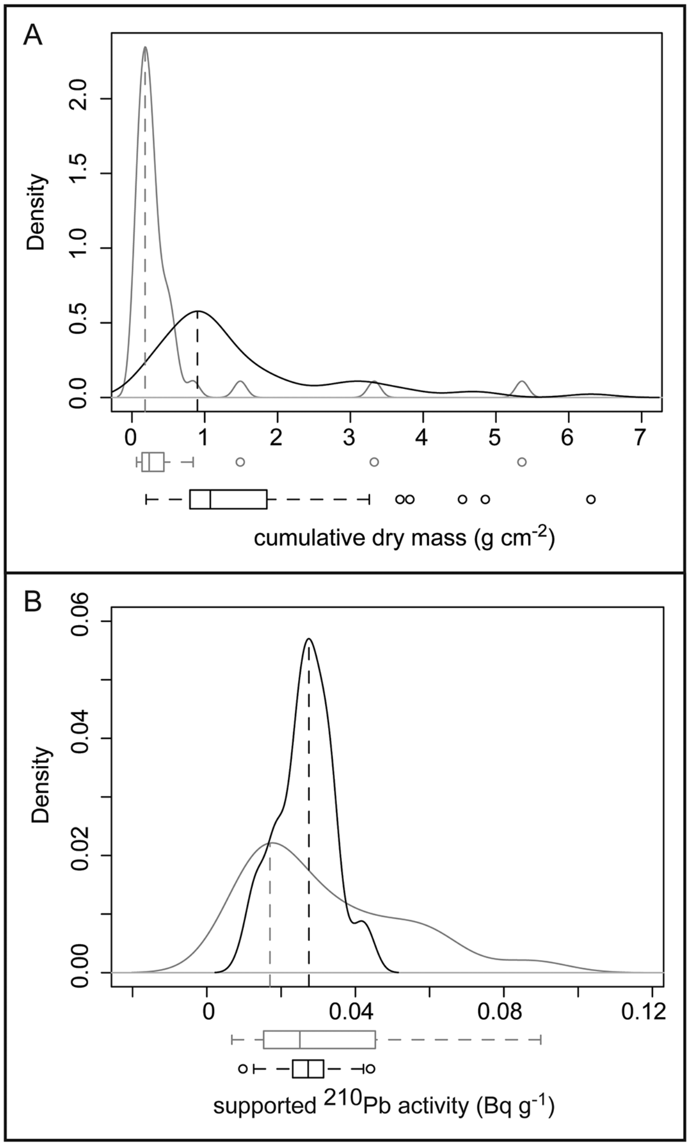

Fig. 1. The probability density functions of northern forested (gray) and southern agricultural (black) Minnesota lakes for (A) the cumulative dry mass of sediment, which corresponds to ~10-years accumulation, and (B) the supported ^{210}Pb activity in the lakes used in our dataset. Dashed lines represent the most probable values for northern and southern lakes, respectively: 0.2 g cm^{-2} and 0.9 g cm^{-2} cumulative dry mass, and 0.019 Bq g^{-1} and 0.028 Bq g^{-1} supported ^{210}Pb. Data are also summarized below each density plot with a boxplot showing the median and quartiles.

Gravity coring methods (Glew et al. 2001; Renberg and Hansson 2008) would be equally suitable for retrieval of short cores with an intact sediment-water interface, and operationally superior to piston coring if only surface sediments are needed. If the study goal is solely to quantify recent OC burial, an integrated surface interval representing ~10 years can be homogenized in the field (see methods below). However, we recommend subsampling at 0.5-1.0 cm, in the eventuality that greater temporal resolution or further analysis may be warranted in the future.

Organic carbon

The organic fraction of the lake sediments (%OM) was quantified through combustion at 550°C (Heiri et al. 2001) and the percent OC calculated using the equation, %OC = %OM • (12/30) from Rosén et al. (2010). Sediment organic carbon can also be measured directly with a dedicated carbon analyzer, which avoids interferences from other hydrated sedimentary materials (e.g., clays) and is more accurate.

Lead-210 dating

This method, for use on surface sediments, was developed using fully detailed chronologies from 93 sediment cores, established by conventional ^{210}Pb dating. Selected sediment samples (15-25 per core) were analyzed for ^{210}Po, the granddaughter product of ^{210}Pb, by α spectrometry and isotope dilution with ^{209}Po. Samples were pretreated with concentrated HCl and the Po isotopes distilled at high temperature (500°C) and plated directly onto silver planchets (Eakins and Morrison 1978). Activity was measured for 1-7 days with an Ortec α spectrometry system. The mean supported (background) activity for each core was derived from the asymptotic activity at depth and subtracted from total activity to calculated unsupported (excess) ^{210}Pb. Dates and sediment accumulation rates were established for each core using the constant rate of supply (c.r.s.) model (Appleby and Oldfield 1978).

For validation of the surface-sample method, we numerically integrated data representing the most recent ~10 years of accumulation post hoc based on the full-core dating and cumulative sediment dry mass. The decay-corrected ^{210}Pb activity of this integrated interval ($^{210}\mathrm{Pb}_{\mathrm{site}}'$) was calculated according to

$$^{210}\mathrm{Pb}_{\mathrm{site}}' = {}^{210}\mathrm{Pb}_{\mathrm{site}} \bullet e^{\left(k \bullet \frac{t}{2}\right)} \qquad \text{(Eq. 1)}$$

where $^{210}\mathrm{Pb}_{\mathrm{site}}$ is the measured unsupported ^{210}Pb, k is the ^{210}Pb decay constant (0.03114 y^{-1}), and t is the estimated age at the base of the integrated sediment interval, calculated using modeled sediment accumulation rates. We chose a 10-year integration period in part to overcome short-term variability in burial rates and an undue influence of early diagenetic alteration of recently deposited sediments (OC mineralization). This diagenetic loss of OC occurs largely within the first 5 years of deposition (Gälman et al. 2008). Conversely, the 10-year integration period is short enough that the lakes have likely not experienced dramatic changes affecting OC production (e.g., eutrophication; Heathcote and Downing 2012). It also necessitates a relatively small decay correction (17%), which limits the error associated with estimating sediment age for undated surface cores.

Our use of fully dated cores to validate the surface-sample method provided information that would not normally be available in any subsequent study applying this method to undated lakes. In particular, we knew a priori sediment cumulative dry mass corresponding to 10 years as well as supported ^{210}Pb established from core depths > 150 years of age. In the absence of sedimentation rates for the lakes under investigation, dating from a small number of similar lakes from the same region could be used to estimate a suitable cumulative dry mass corresponding to ~ 10 years. We emulate this approach in our validation of the method by establishing a representative 10-year cumulative dry mass for northern Minnesota lakes (Northern Lakes and Forest ecoregion) and southern lakes (Northern Great Plains, Western Corn Belt Plains, and North Central Hardwood Forest ecoregions). Using a probability density function to describe the cumulative dry mass for the two regions yielded a value of 0.2 g cm^{-2} for northern lakes and 0.9 g cm^{-2} for southern lakes (Fig. 1). In doing so, the resulting error associated with ^{210}Pb decay correction for 90% of the lakes in our dataset was < 23% for northern lakes and < 14% for southern lakes. We suggest that this information can be used for small glacially formed lakes in similar ecoregions.

Regional estimates of supported ^{210}Pb can also come from other lakes if ^{210}Pb is measured by α spectrometry. Supported ^{210}Pb is typically a small portion of total ^{210}Pb in recently deposited sediments, 3 ± 2% for northern lakes and 14 ± 6% for southern lakes in our dataset. Using the probability density function to describe regional supported ^{210}Pb gave activities of 0.02 Bq g^{-1} for northern lakes and 0.03 Bq g^{-1} for southern lakes (Fig. 1). Alternatively, supported ^{210}Pb (as well as total ^{210}Pb) can be measured directly by γ spectrometry (as ^{214}Pb or ^{214}Bi) (Appleby 2001).

Calculations

The mean lake-wide burial (flux) of organic carbon in the sediments of a lake, $F(OC)_L$ (g m^{-2} y^{-1}) is equal to the concentration of organic carbon in the surface sediments $[OC_S]$ (g • g^{-1}) multiplied by the sediment mass accumulation rate at the sampling site R_S (g m^{-2} y^{-1}) and a correction term for sediment focusing ($1/ff_{OC}$):

$$F(OC_L) = [OC_S] \bullet R_S \bullet \frac{1}{ff_{OC}} \qquad \text{(Eq. 2)}$$

Focusing is defined here as the ratio of the site-specific rate of OC burial to the rate for the lake as a whole and can be approximated by the focusing factor for ^{210}Pb,

$$ff_{^{210}Pb} = \frac{F\left(^{210}Pb_{site}\right)}{F\left(^{210}Pb_{atm}\right)} \qquad \text{(Eq. 3)}$$

where $F(^{210}Pb_{site})$ is the site-specific flux of unsupported (excess) ^{210}Pb and $F(^{210}Pb_{atm})$ is the atmospheric flux of excess ^{210}Pb (both Bq m^{-2} y^{-1}). Combining Eqs. 2 and 3, and decay-correcting for 10 years of accumulation using Eq. 1, then rearranging terms,

$$F(OC_L) = [OC_S] \bullet F\left(^{210}Pb_{atm}\right) \Big/ \frac{F\left(^{210}Pb_{site}'\right)}{R_S} \qquad \text{(Eq. 4)}$$

we note that $F(^{210}Pb_{site}')/R_S$ equals the decay-corrected activity (concentration) of excess ^{210}Pb in surface sediments at the sample site $[^{210}Pb_S]$ (Bq g^{-1}), and thus

$$F(OC_L) = \frac{[OC_S]}{\left[^{210}Pb_S\right]} \bullet F\left(^{210}Pb_{atm}\right) \qquad \text{(Eq. 5)}$$

In this derivation, the mean lake-wide burial of organic carbon is simply the ratio of organic carbon to ^{210}Pb measured in a surface sediment sample multiplied by the atmospheric flux of ^{210}Pb for the region in which the lake is located.

The same equation (Eq. 5) was originally proposed by Binford and Brenner (1986) to estimate the trophic state of a lake based on the degree of ^{210}Pb dilution by organic matter in surface sediments. What these authors did not highlight at the time is that this simple model actually accounts for sediment focusing and that the resulting flux approximates a lake-wide average, rather than a core-specific value. This outcome is incredibly powerful because it removes a major impediment to comparing sediment fluxes among lakes based on the analysis of a single-core—that is, the spatial variation in sediment deposition across a lake basin.

There are several critical assumptions inherent in this model, which are discussed at length in a subsequent critique (Benoit and Hemond 1988) and response (Binford and Brenner 1988) to the original publication. Most important among these are that (1) the atmospheric flux of ^{210}Pb is known with some level of certainty, (2) organic matter (or any sediment constituent of interest) is focused to about the same degree as ^{210}Pb, and (3) direct atmospheric deposition is the primary source of ^{210}Pb to the lake. We review these assumptions in detail, and present study results supporting them elsewhere in the paper.

Assessment and discussion

Multiple-core validation, whole-lake accumulation

Whole-lake OC burial rates were assessed in detail for two lakes (Dunnigan and Kjostad; Fig. 2) using an area-weighted approach based on multiple sediment cores (12 and 14 cores, respectively). The cores, collected as part of an earlier study on mercury loading to northern Minnesota lakes (Swain et al. 1992; Engstrom et al 1994), were assigned depositional areas of the lake basin based on nearest-neighbor topology and summed to the OC accumulation (the product of OC concentration and sedimentation rate) for the whole lake (Fig. 2). The resulting OC burial rates were significantly different between the lakes ($P = 0.01$; Fig. 2C), with Dunnigan showing higher lake-wide values than Kjostad, but lower within-lake variability. These differences were largely explicable in terms of basin size and morphometry. Dunnigan Lake occupies a small (0.33 km^2), shallow, flat-bottomed basin with a single area of sediment deposition and a proportionally small catchment (0.46 km^2). The sediment focus factors for the core sites range from

0.62 to 1.24, whereas the range of OC accumulation rates was 16 to 34 g m^{-2} y^{-1}. In contrast, Kjostad Lake has a more complex morphology, with two depositional basins separated by an island, and a large catchment (9.85 km^2). The sediment focus factors range from 0.28 to 1.98, and the range of OC accumulation for the core sites was 1.8 to 33 g m^{-2} y^{-1}. The whole-lake accumulation of OC was 20 g m^{-2} y^{-1} for Dunnigan and 12 g m^{-2} y^{-1} for Kjostad (Fig. 2D).

These whole lake, multiple-core rates can be used to assess the accuracy of OC burial rates determined from a single dated core in the center of the main depositional basin corrected for sediment focusing to the core site. As discussed previously, the focusing correction for each lake is calculated as the ratio of unsupported ^{210}Pb flux measured at the core site to the measured atmospheric fallout for the region. In the case of Minnesota lakes, there are two National Atmospheric Deposition Program (NADP) sites where the annual atmospheric ^{210}Pb flux is known for a 27-month period (2003-2005), one in the northeastern part of the state (MN16, Marcell Experimental Forest; 211 Bq m^{-2} y^{-1}; 47.531°N, 93.469°W) and another in the southwest (MN27, Lamberton; 181 Bq m^{-2} y^{-1}; 44.237°N, 95.301°W) (Lamborg et al. 2012). Using a single core from the central location, the resulting OC burial rates were very comparable to the whole-lake rates calculated using multiple cores (Fig. 2D; Dunnigan, 24 g m^{-2} y^{-1}; Kjostad, 14 g m^{-2} y^{-1}). Thus a single, well-dated sediment core from the central area of the lake basin can, when focusing-corrected, provide a reliable measure of whole-lake OC accumulation.

Finally, the OC burial data from the multiple-core lakes provided a first-order appraisal of the accuracy of calculating modern OC burial rates from single surface samples. Using the same core locations as the focus-corrected single-core sites and integrating surface samples representing a cumulative dry mass of 0.2 g cm^{-2} (Minn. northern lakes) or approximately 10 years of sediment accumulation, we found very similar OC burial rates compared with the measured whole-lake values (Fig. 2D; Dunnigan, 24 g m^{-2} y^{-1}; Kjostad, 15 g m^{-2} y^{-1}). This result is also encouraging as it supports our assumption that sediment focusing is accounted for, because of the fact that OC and ^{210}Pb are focused in a similar manner. Indeed, there was a similar ratio of OC : ^{210}Pb (g Bq^{-1}) at multiple sites across the main depositional area of the two lake basins. We found that this ratio varied (expressed as 2 standard errors relative to the mean) by 9% in Dunnigan Lake and by 26% in Kjostad Lake, the latter being higher as it reflects two depositional basins.

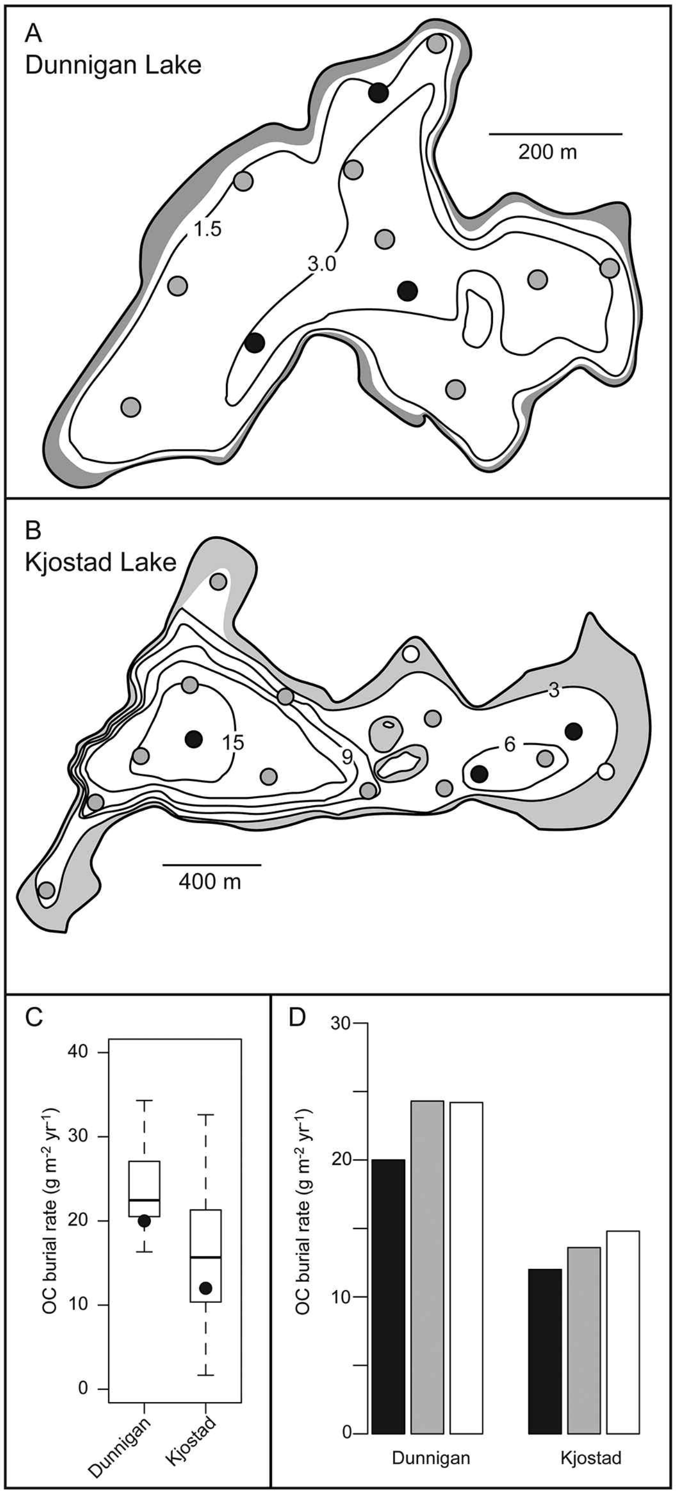

Fig. 2. Multiple sediment-core locations in two morphologically distinct lake basins in the Superior National Forest, Minnesota: (A) Dunnigan Lake with a simple, single basin and (B) Kjostad Lake, Minnesota, with two depositional basins and an island. In both (A) and (B), black circles show the locations of cores dated in detail, gray circles are coarsely dated cores, and white circles are cores not included as they fall in the erosional zone of the lake (gray shaded area) (from Engstrom et al. 1994). Bathymetry contours are in meters. (C) A box plot of OC burial rates for each lake showing the median (black line), quartiles, and a significant difference in mean (black circle) burial rates between the lakes. (D) A bar plot of whole lake OC burial rates calculated by area-weighted accumulation of multiple cores (black), a single sediment core from the central part of the basin, dated in detail and adjusted for sediment focusing (gray), and the predicted burial using the surface-sample approach (white).

Single core validation, whole-core accumulation

Using our dataset of 93 lakes, we compared OC burial rates in fully dated single cores with burial rates estimated by the surface-sample approach. The modern OC burial rate across the lakes, adjusted by ^{210}Pb flux for sediment focusing, varied from 9 to 318 g m^{-2} y^{-1} (Fig. 3A). Regional estimates of cumulative dry mass for northern and southern lakes, surface ^{210}Pb activities (decay-corrected to 10 y) and OC concentrations were used to calculate modern OC burial rates according to Eq. 5 (Fig. 3A). These single-sample estimates do a very reliable job of describing whole-core OC burial measured for each lake. This validation step relies on common parameters between the predicted and observed values, however the derivation of both ^{210}Pb$_{atm}$ and ^{210}Pb$_{site}$ is sufficiently different so as not to consider the comparison of OC burial rates a circular relationship. The observed whole-core values of modern OC burial rely on (1) a measured whole-core ^{210}Pb inventory to derive ^{210}Pb flux, which is used to explicitly correct for sediment focusing; (2) a site-specific sediment accumulation derived from the c.r.s model; (3) a ^{210}Pb$_{site}$ which is decay-corrected using site-specific accumulation. The predicted single-sample estimates rely on (1) a regional ^{210}Pb$_{atm}$ and make no assumptions about site-specific ^{210}Pb flux to the core site; (2) a regional estimate of modern (~10 y) cumulative dry mass accumulation; (3) a regional decay correction ^{210}Pb$_{site}$. We therefore feel that there are sufficient differences between how the OC burial values are derived that this validation step demonstrates single-samples can reliably estimate whole-core OC burial. Based on the residuals of the estimated values from the 1:1 line as a percentage of the measured OC burial, we estimated a % error for OC burial from the surface-sample approach. The probability density distribution of the residuals suggested that 6.5% is a suitable inter-lake predictive error, where the 75th percentile was 24% error (Fig. 3c).

As an additional validation of the surface-sample approach, we re-cored and independently analyzed nine of the original study lakes (Fig. 3). The sediments from the additional lakes were collected in the vicinity of the original core site, somewhere near the center of the depositional basin, as is common practice. The OC burial rates for the repeat cores were calculated using our Eq. 5 (Fig. 3). This cross-validation of the estimated OC burial values yielded a root mean square error of prediction of 1.9 g m^{-2} y^{-1}. We therefore conclude that single surface-sediment samples can be used to provide reliable estimates of whole-core OC burial.

Method assumptions and applicability

Our surface-sample approach, originally proposed by Binford and Brenner (1986) to assess trophic state, requires the acceptance of a number of assumptions (Benoit and Hemond 1988). Whereas some concerns have been addressed (Binford and Brenner 1988), a lack of data at the time prevented explicit validation for the main assumptions. Here, we revisit some of these original concerns and defend the assumptions made in using a single sediment sample.

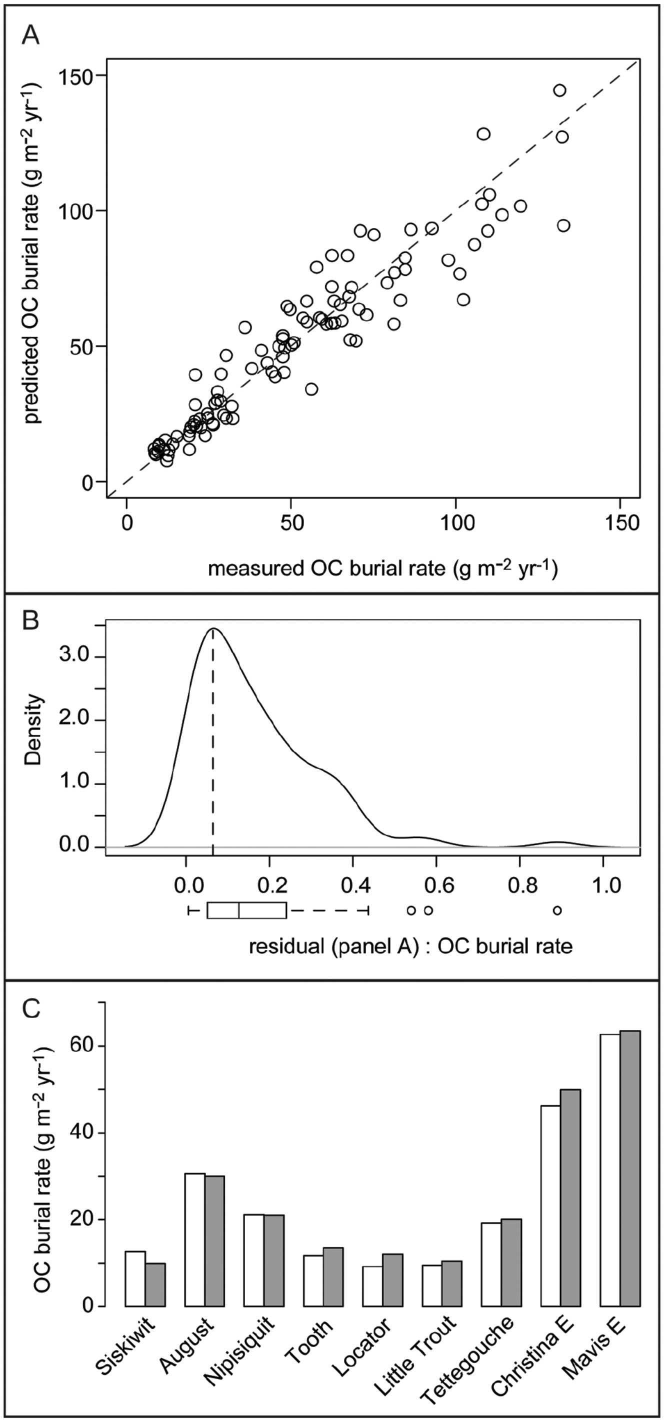

Fig. 3. (A) A scatterplot of the estimated OC burial rates using the surface-sample approach against the measured values based on fully dated cores over a 10-y period, adjusted for sediment focusing. (B) The density probability of the residuals from the 1:1 line of plot (A), expressed as a percentage of the measured value with the highest probable error shown as a dashed line. A boxplot of the data are shown below the probability plot, where the 75th percentile is 24% error (C). Repeat sediment cores were collected and independently analyzed in 9 of the lakes (4 to 10 years apart); OC burial rates of the repeat samples (gray bars) are calculated using the surface-sample approach.

A key condition of Binford and Brenner's (1986) formulation was the use of an estimated global average for the atmospheric ^{210}Pb flux, a value of 185 Bq m^{-2} y^{-1} (Turekian et al. 1977; Appleby and Oldfield 1983; Binford and Brenner 1988; Preiss et al. 1996). The range of published atmospheric ^{210}Pb fluxes spans almost an order of magnitude (30–200 Bq m^{-2} y^{-1}) and is a function of available landmass, climatic factors, and orographic influence. Whereas we now have a better understanding of the spatial variation of atmospheric ^{210}Pb flux in the Northern Hemisphere (Graustein and Turekian 1986; Binford and Brenner 1988; Preiss et al. 1996; Appleby 2008; Baskaran 2011; Lamborg et al. 2012), these data remain incomplete for many other parts of the world. Specific to our study, we have atmospheric ^{210}Pb flux measured from two sites in northeastern and southwestern Minnesota (Lamborg et al. 2012). In the absence of site-specific deposition data, an educated estimate based on published values is defendable in the Northern Hemisphere, acknowledging that there appears to be a west to east increase in fallout over the mid-latitudes of the major continents (Appleby 2008). Studies in polar and Southern Hemisphere regions should employ published values for these areas; because the smaller available land mass and high-latitude aridity will limit ^{222}Rn emanation and ^{210}Pb fallout (Appleby et al. 1995; Appleby 2008; Ribeiro Guevara et al. 2003). In the absence of published deposition data, ^{210}Pb-dated cores on a lake (or multiple lakes) in the region of interest can provide a robust estimate of the regional atmospheric ^{210}Pb flux (Fitzgerald et al. 2005). We caution against establishing ^{210}Pb flux from multiple soil profiles (Nozaki et al. 1978; Benoit and Hemond 1988), as it introduces uncertainty associated with local ^{210}Pb scavenging by terrestrial vegetation (Stankwitz et al. 2012) as well as down-slope redistribution of ^{210}Pb within the catchment.

A second assumption is that ^{210}Pb sedimentation should be linearly proportional to atmospheric deposition in order for the method to accurately describe sedimentation. This concern is based primarily on the understanding that sediment is focused within a lake basin, which affects the total ^{210}Pb inventory at the core site. We discussed earlier our contention that no additional correction is needed for focusing because it is explicitly included in the calculation (Eq. 5). Furthermore, results from our two multiple-core lakes demonstrated that the OC : ^{210}Pb ratio across the depositional basin remains relatively uniform because OC and ^{210}Pb are focused in a similar manner. Similar focusing likely results from the association of ^{210}Pb with fine-grained sediment particles, including organic seston. However, OC from littoral production and particulate carbon from terrestrial sources might focus differently than ^{210}Pb because of spatially non-uniform loading, especially in complex lake basins with multiple embayments (Bindler et al. 2001; Engstrom and Rose 2013). Nonetheless, the relative uniformity of OC:^{210}Pb ratios noted above suggests that both constituents are redistributed to the depositional region of a lake in roughly the same proportions.

A final assumption is that nonatmospheric inputs of ^{210}Pb to the lake are negligible. This condition is generally true except in cases where catchment erosion rates are very high and the soil residence time of ^{210}Pb is short relative to its half-life (22 y). It is evident to us from studies within Minnesota and elsewhere that the overwhelming input of ^{210}Pb to lakes is atmospheric (Binford and Brenner 1988; Engstrom et al. 1994; Schottler et al. 2010). We do acknowledge that in lake systems with significant fluvial inputs the delivery of ^{210}Pb from the catchment may be significant and the retention of ^{210}Pb inputs may be incomplete (Cornett et al. 1984; Benoit and Hemond 1987). However, none of the lakes in our dataset represent systems that we would consider to have significant fluvial inputs, nor do they have very short hydraulic residence times (e.g., Dunnigan and Kjostad lakes have a residence time of 5 years; Swain et al. 1992). As the dataset of lakes used in this study covers a broad range of morphometric and trophic conditions over several biogeoclimatic zones (Table 1), we conclude that the surface-sample approach is broadly applicable to many temperate lake types and sizes.

Comments and recommendations

The obvious appeal of estimating modern OC burial using a single sediment sample is the increased efficiency and decreased cost of sample collection and analysis with greater potential spatial coverage. Applying this technique to large datasets provides a clearer picture of the spatial trends of OC burial in inland waters, whereas single-lake studies are more susceptible to the spatial variability that exists from lake to lake. This approach also allows a more accurate definition of spatial variability and the error associated with measuring OC burial in lakes. The within-lake variability (standard deviation) from our multiple core studies was ~4 g m^{-2} y^{-1}, while regionally an estimate of error for the method was 6.5%.

This method is broadly applicable to different lake types and offers a more accurate assessment of the role inland waters play in the global carbon cycle (*sensu* Cole et al. 2007; Tranvik et al 2009). As an example, there is a growing global dataset on OC burial as a function of lake area, which suggests smaller lakes bury more OC (Fig. 4). We find that this relationship holds when this dataset is populated with our results, providing confidence on the applicability of this method to large regional studies. The broader application of this method requires (1) measured or published data of atmospheric ^{210}Pb flux, (2) analysis of supported ^{210} Pb by γ spectrometry or a regional estimate of supported ^{210}Pb from cores previously dated by α spectrometry, and (3) an understanding of typical sedimentation rates in lakes from the study region to establish a realistic cumulative dry mass over which to integrate the sample (representing ~ 10 y). For many regions, these ancillary data already exist in the literature. In addition to clarifying the role of inland waters in the global C-cycle, this technique applied over large spatial gradients of land-use and water quality will allow us to address questions on the role that terrestrial–aquatic linkages play in the sequestration of OC by inland waters.

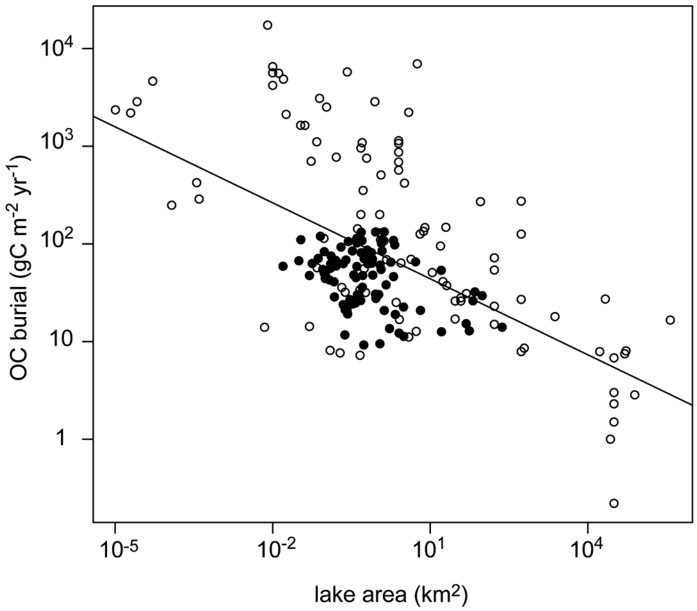

Fig. 4. A scatterplot of OC burial as a function of lake area for n = 193 lakes and reservoirs throughout the globe, including those from this study (solid circles) (Mulholland and Elwood 1982; Sobek et al. 2009; Downing et al. 2008; Heathcote and Downing 2012). A statistically significant linear model fit is shown with an adjusted r^2 of 0.33 and df = 189.

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