Lake of the Woods Nutrient Mass Balance, Phase I.

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Mark B. Edlund, Shawn P. Schottler, Daniel R. Engstrom

St. Croix Watershed Research Station
Science Museum of Minnesota
16910 152nd St N
Marine on St. Croix, MN 55047
medlund@smm.org

Euan D. Reavie
NRRI
University of Minnesota-Duluth
Duluth, MN 55811

Andrew M. Paterson
Ontario Ministry of the Environment
Doreset Environmental Science Centre
Dorset, Ontario, Canada P0A 1E0

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Nolan Baratono and Cary Hernandez
Minnesota Pollution Control Agency
Detroit Lakes, MN 56501

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Executive Summary

1) Sediment cores recovered from seven basins in southern Lake of the Woods in 2012 were analyzed to reconstruct a historical phosphorus budget for the southern lake from 1900-2011.

2) Sediment cores were subjected to multiple analyses including radioisotopic dating with Pb-210 to establish a date-depth relationship for each core, loss-on-ignition to determine major sediment constituents, biogenic silica to estimate historical diatom productivity, diatom communities to identify ecological changes and estimate historical water column total phosphorus (TP), extraction and determination of phosphorus (P) fractions, and extraction of fossil pigments to quantify the historical abundance of various algal groups.

3) Pre-damming sediments were between 17 and 30 cm deep depending on basin (Buffalo Bay is an outlier with pre-damming sediments only 7.5 cm deep), and sediments in all basins are predominantly inorganic (> 70% dry weight) and secondarily organic matter (typically 10-20% dry weight). Sedimentation rates in the cores have typically increased at least two-fold since damming.

4) Organic-P and NaOH-P were most abundant phosphorus fractions in Big Traverse 4, Little Traverse Bay, Sabaskong Bay, and Big Narrows. In contrast, HCl-P was the predominant P fraction in Big Traverse 3, Buffalo Bay, and deeper sediments of Little Traverse and Muskeg bays. In all cores the accumulation rates of sediment P and fractions increased 2- to 3-fold upcore to highest levels at the core surface. Although monitoring records suggest that P loading to the lake was highest in the 1960s and 1970s and has declined significantly since, P concentration and accumulation increases upcore to modern times. Key findings were that there is a large amount of labile P that increases in concentration and flux upcore and acts as an active pool of legacy P to fuel internal P loading to the lake.

5) Among the seven cores analyzed for diatoms, most showed significant upcore increases in historical diatom-inferred total phosphorus (DI-TP). All cores showed pre-damming TP concentrations in southern Lake of the Woods to be approximately 10 µg P/L. Cores from Muskeg, Big Narrows, and Big Traverse 4 showed increasing DI-TP upcore after 1900, whereas Big Traverse 3, Sabaskong, and Little Traverse had more marked increases in DI-TP after 1950. Most cores showed their highest DI-TP in the most recent sediments because of increasing abundance of eutrophic indicators such as the diatoms *Cyclostephanos dubius* and small *Stephanodiscus* species.
6) Biogenic silica (BSi) composed 2-6% dry weight of Lake of the Woods sediment, with markedly lower values in Buffalo Bay. Upcore increases in BSi were noted in near surface sediments of Big Traverse 3 and 4, and Muskeg bays, whereas Sabaskong, Little Traverse, and Big Narrows had longer trends of increasing weight percent BSi, mostly since the 1950s. When converted to accumulation rates, the flux of BSi increases toward the top of all cores.

7) Downcore concentrations of fossil algal pigments and derivatives were grouped by algal types or indicator value for each core. There are two primary patterns among pigment profiles from Lake of the Woods. Many sites including Big Traverse 3 and 4, Sabaskong, Muskeg, Little Traverse, and Big Narrows show a bimodal pattern of increasing pigment concentration since damming that peaks around 1970, followed by decreased concentrations in the 1980s, and then increased concentrations again in the last 15 years. This pattern is reflected in pigment profiles from most algal groups including diatoms (e.g., diatoxanthin), cyanobacteria (e.g. canthaxanthin, myxoxanthophyll), and general algal indicators (e.g. lutein-zeaxanthin).

8) Because of the large active pool of P that is present in Lake of the Woods, four whole basin, mass balance approaches and/or dynamic models were used to explore potential historical P loading scenarios to Lake of the Woods and historical in-lake nutrient dynamics. Key results of the models included, first, that phosphorus loading estimates for Lake of the Woods are estimated to be approximately 646 t P/yr before damming, which is nearly as high as current loading estimates. Second, burial rates of refractory P are increasing in Lake of the Woods compared to pre-damming levels. Third, there is a large pool of labile P that can only be accounted for if historical loading was larger (as documented by Hargan et al. 2011). Fourth, most of the models we tested indicate that the pool of active P was much larger in the past, and at its maximum size in the 1970s. Fifth, the active legacy pool is currently being depleted to support modern levels of productivity in Lake of the Woods (this could also be interpreted by invoking a large unaccounted P loading to the lake). Last, the rate at which the pool is being depleted varies among models, but generally shows the pool as being rapidly depleted since the 1970s.
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Introduction

The Lake of the Woods is a large multibasin lake located along the borders of Minnesota (USA), Ontario and Manitoba (Canada). The lake extends about 100 km from E to W and over 100 km from N to S. The largest portion of the lake is its southern basin, known as Big Traverse Bay, which has several secondary basins including Buffalo and Muskeg bays to the south and west, and Sabaskong Bay to the east. Moving northward in the direction of the lake's flow, it passes through Little Traverse Bay, before flowing through the Big Narrows to join outflow from several deeper basins in Canadian waters including Whitefish, Clearwater, Andrew, and Big Stone bays and flow from Shoal Lake. The lake discharges to the Winnipeg River at Kenora, Ontario, and its major inflow is the Rainy River, which enters the lake near Baudette, Minnesota into Four Mile Bay.

With the publication of the Lake of the Woods State of the Basin Report by a transboundary interagency group in 2009 (updated 2nd Ed., Lake of the Woods Sustainability Foundation 2014), and the Minnesota Pollution Control Agency's placement of the lake on the state's impaired list for nutrients and eutrophication indicators in 2008, the future of the lake became a high profile concern for the Ontario and Minnesota governments and the lake's diverse group of stakeholders. The Basin Report highlighted nutrients and their biological impacts – primarily a perceived increase in frequency and extent of cyanobacterial blooms – as a primary resource concern for the lake, although evidence from monitoring, including satellite imagery, is equivocal (Chen et al. 2007, 2009, Binding et al. 2011). Earlier research recommendations and data gaps suggested that improved coordination of monitoring efforts and the construction of a modern-day nutrient budget for the lake were logical first steps. Significant progress has been made in these respects, including the completion of two M.Sc. theses (K. Hargan, Trent University, ON, see also Hargan et al. 2011; J. Hadash, St. Cloud State University, MN), development of a BATHTUB model (Anderson et al. 2013), and a linked hydrodynamic trophic state model (Zhang et al. 2013), which have helped refine our understanding of P sources, internal loading, and variability in water quality among basins and years.

The Basin Report also laid out the critical need to put any monitoring data in a historical context through the use of traditional knowledge and paleolimnology. In our most well-studied lakes and rivers, traditional or historical monitoring data usually exist for only 30-50 years and are often discontinuous or subject to changing analytical and sampling technologies. This is the case for Lake of the Woods as well with sporadic water quality data only as far back as the 1960s. In contrast, the sediment record in lakes faithfully preserves biological, physical, and geochemical clues to a lake's history, and that history can be sampled at time scales of 10s to 1000s of years to decipher the environmental history of a lake.

Lake of the Woods (LoW) is known to have elevated nutrient P in comparison to other lakes within the Precambrian Shield, a strong N-S gradient of water quality (Pla et al. 2005), and is well-known for its extensive cyanobacterial blooms (Binding et al. 2011). While both of these characteristics have some historical precedence, resource managers
are faced with a complex system in Lake of the Woods. For example, monitored inputs of P loads from the Rainy River, the Lake of the Woods primary source of P, have decreased in the last 30 years as point source loadings have declined (Hargan et al. 2011). Yet comparison of monitored water quality variables between the 1980s and 2000s show little change in in-lake concentrations of most nutrients. Furthermore, paleoecological evidence in Canadian waters of the northern part of the lake record little change in diatom-inferred P values (Rühland et al. 2008, 2010, Hyatt et al. 2011), but paleolimnological evidence from a small bay in the southern lake basin shows increased eutrophic conditions (Reavie and Baratono 2007). In contrast, cyanobacterial blooms, especially in the southern basin, are perceived to be more frequent and of greater spatial coverage than in previous decades, suggesting that there may be a strong legacy effect of nutrient availability from sediments, or alternative mechanisms such as long-term changes in mixing and thermal structure may be fueling blooms. Research initiatives to increase the spatial and temporal frequency of water quality monitoring, employ satellite imagery, test for cyanobacterial toxins, develop a modern-day P budget for the lake, and to explore the importance of internal nutrient loading have led to key findings on the modern condition of the lake (summarized in Lake of the Woods Sustainability Foundation 2014). However, a long-term, historical perspective is required to address the disconnect between possible indicators of eutrophication in the face of decreased nutrient loading.

To address this problem, we must better understand the historical nature of nutrient dynamics in Lake of the Woods. Constructing a historical nutrient mass balance P model for LoW, using whole-basin reconstruction techniques, holds promise for the LoW. Historical techniques for estimating past P loading and dynamics have proven useful in other nutrient-enriched transboundary waters such as the Upper Mississippi River's Lake Pepin and Lake St. Croix (Edlund et al. 2009, Engstrom et al. 2009; Triplett et al. 2009). In both lakes, the diatoms indicated dramatic ecological changes in the last 200 years. Diatom-inferred P increased in both lakes following Euro-American settlement, with marked increases after 1950 A.D. Historical phosphorus mass balances indicated that P loading to each lake had increased rapidly after World War II in response to growing populations and increased point and nonpoint source loadings. Results of these paleolimnological approaches were instrumental in determining that both rivers suffer from nutrient impairment and that the Mississippi is further impaired for turbidity. Pre- and post-settlement nutrient levels and sedimentation rates guided federal and interstate agencies to develop nutrient and sedimentation targets and remediation policies. This project uses a similar approach to determine historical nutrient dynamics in Lake of the Woods.

For this study, we recovered and analyzed sediment cores from seven basins in southern Lake of the Woods and addressed these primary research questions:

1. How has P loading to LoW changed over the last 100 years?
2. How have biological communities (cyanobacteria and diatoms) changed over the last 100 years?
3. Are trends in biological communities, nutrient dynamics, and sedimentation related to changes in external nutrient loading?
4. Do trends in biological communities, nutrient dynamics, and sedimentation reflect legacy nutrient effects?

Methods

Lake-Sediment Coring and Analyses

Coring
Sediment cores were recovered from depositional basins from seven basins or bays in Lake of the Woods (Table 1). Cores were recovered using either a piston corer consisting of a 6.5 cm diameter polycarbonate tube outfitted with a piston and operated with rigid drive rods working from the ice surface (Wright 1991), or using an line-operated gravity corer deployed from an anchored boat. Piston cores ranged in length from 90 to 98 cm, and the gravity core collected from Buffalo Bay was 9.5 cm long. All cores were stabilized with Zorbitrol or sectioned immediately in the field in 0.5-cm increments to 10 cm depth using a vertical extrusion system. For piston cores, the core material was sealed in its polycarbonate tube and transported horizontally back to the laboratory for additional analyses and sectioning in 1-cm increments from 10 cm to 35 cm (to 60 cm for Sabaskong and Big Narrows cores).

Isotopic Dating and Geochemistry
Sediment cores were analyzed for $^{210}$Pb activity to determine age and sediment accumulation rates for the past 150 to 200 years. Lead-210 activity was measured from its daughter product, $^{210}$Po, which is considered to be in secular equilibrium with the parent isotope. Aliquots of freeze-dried sediment were spiked with a known quantity of $^{209}$Po as an internal yield tracer and the isotopes distilled at 550°C after treatment with concentrated HCl. Polonium isotopes were then directly plated onto silver planchets from a 0.5 N HCl solution. Activity was measured for 1-3 x 10^5 s using an Ortec alpha spectrometry system. Supported $^{210}$Pb was estimated by mean activity in the lowest core samples and subtracted from upcore activity to calculate unsupported $^{210}$Pb. Core dates and sedimentation rates were calculated using the constant rate of supply model (Appleby and Oldfield 1978, Appleby 2001). Dating and sedimentation errors represented first-order propagation of counting uncertainty (Binford 1990). For cores with uncharacteristic decay profiles, additional dating tools were used to measure supported $^{210}$Pb and identify the distribution of $^{137}$Cs in the core using gamma spectrometry.

Bulk-density (dry mass per volume of fresh sediment), water content, organic content, and carbonate content of sediments were determined by standard loss-on-ignition techniques (Dean 1974). Weighed sediment subsamples were dried at 105°C for 24 hr to determine water content and dry bulk density, then heated at 550°C and 1000°C to calculate organic and carbonate content from post-ignition weight loss, respectively.
These data were used in combination with $^{210}$Pb dating to calculate sedimentation rates (mg cm$^{-2}$ yr$^{-1}$) for each core.

Biogenic silica (BSi), a proxy for historical diatom and chrysophyte algal productivity, was measured using weighed subsamples (30 mg) from each primary core, which were digested for BSi analysis using 40 mL of 1% (w/v) Na$_2$CO$_3$ solution heated at 85°C in a reciprocating water bath for five hours (DeMaster 1979, Conley and Schelske 2001). A 0.5 g aliquot of supernatant was removed from each sample at 3, 4, and 5 hr. After cooling and neutralization with 4.5 g of 0.021N HCl solution, dissolved silica was measured colorimetrically on a Lachat QuikChem 8000 flow injection autoanalyzer as molybdate reactive silica (McKnight 1991).

Sediment phosphorus fractions were analyzed following the sequential extraction procedures in Engstrom (2005) and Engstrom and Wright (1984). Extracts were analyzed colorimetrically on a Lachat QuikChem 8000 flow injection autoanalyzer. Measured sediment P concentrations were also converted to flux using bulk sedimentation rates in each core. In addition to total phosphorus in cores, sediment fractions include the refractory forms HCl-P and Organic-P and labile forms NaOH-P and exchangeable P (Ex-P).

**Diatom and Pigment Analysis**

Diatoms were primarily analyzed under separate funding (Reavie et al. in prep.) but used in this study to provide estimates of historical water column total phosphorus concentrations. In short the analytical steps are as follows. Diatoms and chrysophyte cysts were prepared by placing a weighed subsample (approximately 50 mg) in a 50 cm$^3$ polycarbonate centrifuge tube and adding 2-5 drops of 10% v/v solution to dissolve carbonates. Organic material was subsequently oxidized by adding 10 ml of 30% H$_2$O$_2$ and heating for 3 hr in an 85°C water bath. After cooling the samples were centrifuged and rinsed 4-6 times with deionized water to remove oxidation byproducts. Material was then transferred into a Battarbee settling chamber (Battarbee 1973), which produces random distributions of siliceous microfossils on 18 mm diameter #1 coverglasses. Coverglasses were permanently attached to microscope slides using Zrax mounting medium (Ramstack et al. 2008). Diatoms were identified along measured random transects to the lowest taxonomic level under 1250X magnification (full immersion optics of NA>1.3). A minimum of 400 valves was counted in each sample. Identification of diatoms relied on floras and monographs such as Hustedt (1927-1966, 1930), Patrick and Reimer (1966, 1975), Krammer and Lange-Bertalot (1986-1991), Reavie and Smol (1998), Camburn and Charles (2000), and Fallu et al. (2000). All diatom counts were converted to percentage abundances by taxon; abundances are reported relative to total diatom counts in each sample. Counts were also converted to microfossil flux by taxon (diatom valves cm$^{-2}$ yr$^{-1}$).

A stratigraphy of predominant diatoms (species with greater than or equal to 5% relative abundance in one or more core depths) was plotted against core date. Relationships among diatom communities within the sediment core were explored using the unconstrained ordination method of Detrended Correspondence Analysis (DCA) and
constrained cluster analysis in the software package R (R Core Development Team 2012).

To estimate historical water column total phosphorus, a diatom calibration set constructed by Paterson et al. (2007) was applied to relative abundance data of downcore diatom assemblages using weighted averaging regression with inverse deshrinking. Details on model performance and reconstruction statistics are presented in Reavie et al. (in prep.).

Fossil pigments including carotenoids, chlorophylls, and their derivatives were extracted (4°C, dark, N₂) from freeze-dried sediments according to Leavitt et al. (1989), measured on a Hewlett-Packard model 1050 high performance liquid chromatography system, and are reported relative to total organic carbon (TOC; Hall et al. 1999).

**Modeling a Historical Phosphorus Budget**

Supporting data for modeling of historical phosphorus budgets came from several sources. Outflow rates to the Winnipeg River at Kenora were available from 1927-2008 and provided by Matt DeWolfe (lwcb.ca). Outflow at the Big Narrows was scaled based on supplemental data provided in Zhang et al. (2013) by comparing daily step outflow from 2000-2010 at the Big Narrows to Kenora. Phosphorus loadings from the Rainy River were assembled from 1962-2009 by Hargan et al. (2011). Lake area and lake volume by basin were taken from Zhang et al. (2013).

Four modeling approaches were applied to downcore data to understand historical nutrient dynamics and phosphorus loads to the Lake of the Woods:

- Model 1) Simple whole-lake mass balance
- Model 2) Whole-lake mass balance with active sediment layer
- Model 3) Two box dynamic model (best guess scenario)
- Model 4) Two box dynamic model (best fit scenario)

Each model is presented below with its conceptual basis, assumptions, and a discussion of its results, trends, potential shortcomings, and key findings. Models 3 and 4 were assembled and run using the software Stella 9.0 (*isee systems inc.*, Lebanon, NH).

**Results and Discussion**

**Sediment core records**

**Pb-210 inventory**

Most cores from Lake of the Woods showed monotonic exponential declines in ²¹⁰Pb inventories to supported depths (Fig. 1). Cores generally reached supported levels of ²¹⁰Pb around 25 to 35 cm depth, except for Buffalo Bay, where supported levels were reached at 7-8 cm. Supported ²¹⁰Pb levels ranged from 0.85 pCi/g (Muskeg Bay) to 1.28 pCi/g (Big Narrows). Using the c.r.s. model, a date-core depth relationship was established for each core site. Sediments dated to 1900 were found between 17 cm (Little Traverse) and
34 cm (Sabaskong Bay) downcore, except for Buffalo Bay. Buffalo Bay appears to have not begun accumulating lacustrine sediments until approximately 1900 (7.5 cm core depth), likely in response to damming at Kenora that raised Lake of the Woods water levels by approximately 1 m.

**Focus factors**
To understand whole basin depositional rates for various constituents including dry bulk sediment and phosphorus fractions, a "focusing factor" was calculated for each core using the method of Engstrom and Rose (2013) and Hobbs et al. (2013) to normalize for downcore fluxes among basins. Focus factors estimate the efficiency by which each depositional site integrates sediment within a basin. Focus factores varied among the core sites from 0.37 at Buffalo Bay to 1.68 in Sabaskong Bay (Table 2).

**Sedimentation rates**
Most cores showed general trends toward increasing sedimentation rates upcore with modern rates typically two-fold greater than pre-1900 rates (Fig. 1). Some cores had slightly greater increases in sedimentation rates including the Big Traverse Bay and Little Traverse Bay cores, with recent sedimentation nearly three times pre-1900 rates. Little Traverse and Muskeg bays had secondary increases in sedimentation rates since the 1970/80s, repsectively. Modern sedimentation rates varied from 0.06 (Big Traverse 4) to 0.12 g/cm² yr (Sabaskong Bay), whereas pre-damming rates ranged from less than 0.01 (Big Traverse 3) to 0.06 g/cm² yr in Muskeg Bay.

Sedimentation rates for individual basins were corrected for sediment focusing, the data pooled, and averaged among time intervals represented by approximately equal numbers of observations (5-year window back to 1990, decadal intervals to 1940, 20-year intervals to 1900, and pre-1900 samples grouped) to estimate whole lake sedimentation rates. Whole lake sedimentation rates increase from pre-damming rates of 0.265 kg/m² yr to an intial peak in the 1970s of 0.686 kg/m² yr, a slight decline in the 1980s and values of approximately 0.7 kg/m² yr since the 1980s (Fig. 3b).

**Loss-on-ignition**
Sediments at all cores sites were dominated by the inorganic fraction, which generally composed over 80% of the dry sediment weight (Fig. 1). Muskeg Bay had slightly lower amounts of inorganics (70-80%) and Buffalo Bay had a distinct shift in sediment composition below 6 cm depth, where carbonates increased in abundance to 40% below 8 cm depth. Except for Buffalo Bay, organics comprised the next predominant sediment constituent with most cores having 5 to 20% organics by dry weight. Carbonates made up less than 5% dry weight of all cores except for the deeper sediments (>6 cm) of Buffalo Bay.

**Sediment phosphorus fractions**
Total phosphorus in Lake of the Woods sediment ranged from 0.4 to over 1.0 mg P/g (Fig. 2). The organic-P and NaOH-P fractions were most abundant in Big Traverse 4, Little Traverse Bay, Sabaskong Bay, and Big Narrows. In contrast, HCl-P was a predominant P fraction in Big Traverse 3, Buffalo Bay, and deeper sediments of Little
Traverse and Muskeg bays. In all cores the accumulation rates of sediment P and fractions increased 2- to 3-fold upcore to highest levels at the core surface.

For each core, accumulation rates of sediment P fractions were corrected for sediment focusing factors, and the seven Lake of the Woods basins summed to estimate the southern basin whole lake accumulation of P and P fractions in sediments across time intervals (Fig. 4a). The P fractions were also separately treated as refractory (HCl-P, Org-P) or labile/exchangeable fractions (Ex-P, NaOH-P; Fig. 4a). Labile fractions are prevalent in all levels of Lake of the Woods sediments and flux has increased markedly in sediments deposited since 1970. Based on historical estimates of P loading from the Rainy River (Hargan et al. 2011) there has been significant declines in P loading since the mid 1970s to modern levels that are 2- to 3-fold less than loading estimates during the 1960s and early 1970s. However, there is no clear indication of decreased accumulation of P in the sediments in response to decreased loading.

Because burial of P is one of the primary mechanisms that removes P from a lake, we also estimated the historical or permanent burial of P, as well as recognize that a significant proportion of the labile fractions remained in an active pool of P that could be readily exchanged with the overlying waters. Sediments deposited before 1960 in Lake of the Woods are deeper than 12-20 cm depending on core site, and we surmised that all P fractions below that depth were permanently buried (Fig. 4b). We averaged the accumulation of labile fractions in sediments deposited from 1900-1959 and used that quantity to adjust all upcore burial of refractory P; the remaining P inventory we treat as an active pool of P (Fig. 4b) for some modeling purposes.

**Diatom-inferred total phosphorus (DI-TP)**

Among the seven cores analyzed for diatoms, most showed upcore increases in DI-TP (Fig. 2). All cores, except Buffalo Bay, showed pre-damming or pre-Euroamerican settlement TP concentrations in southern Lake of the Woods to be approximately 10 µg P/L. Cores from Muskeg, Big Narrows, and Big Traverse 4 showed increasing DI-TP upcore after 1900, whereas Big Traverse 3, Sabaskong, and Little Traverse had more marked increases in DI-TP after 1950. Buffalo Bay had higher DI-TP values than all other cores from Lake of the Woods with recent values exceeding 30 µg P/L. Values of DI-TP from the most recent sediments were typically between 20 and 30 µg P/L with several cores exceeding 30 µg P/L in the uppermost sections (Big Narrows, Muskeg, Buffalo Bay).

The DI-TP reconstructions of all cores were pooled and separated into time increments so that each time period had similar observations. This created approximately 5-year time frames back to 1990, decadal intervals to 1940, 20-year intervals to 1900, and pre-1900 samples grouped (Fig. 3a). Pre-damming whole-lake DI-TP trends suggest that pre-damming TP concentration were slightly less than 10 µg/L, which then steadily increased to a peak of 18.3 µg P/L in the 1970s. After the 1970s, DI-TP values stayed between 17 and 19 µg P/L until the most recent period (2005-2011) when whole-lake DI-TP jumps to over 24 µg P/L. Comparison of DI-TP with monitored TP values from within the cored basins suggest that average TP from 2005-2011 was 38.3 µg P/L and 31.3 µg/L in 1999
based on roughly monthly late spring-summer sampling during focused monitoring
efforts by US and Canadian agencies. It is also noted that in the southern basins there is
distinctly higher TP readings in the late summer months (>40 µg P/L) compared to spring
(20-32 µg P/L) values (Lake of the Woods Water Sustainability Foundation 2011).

To estimate historical outflow of P from the lake, whole lake DI-TP was estimated across
the same time intervals used from whole lake estimates of sedimentation and P burial.
DI-TP was multiplied by discharge at Big Narrows, which was estimated from 1900-
2011 based on scaling daily step outflows taken at both Kenora and Big Narrows from
2000-2010 (Fig. 5; Zhang et al. 2013).

**Biogenic silica (BSi)**
Biogenic silica composed 2-6% dry weight of Lake of the Woods sediment, with
markedly lower values in Buffalo Bay (Fig. 2). Upcore increases in BSi were noted in
near surface sediments of Big Traverse 3 and 4, and Muskeg bays, whereas Sabaskong,
Little Traverse, and Big Narrows had longer trends of increasing weight percent BSi,
mostly since the 1950s. When converted to accumulation rates, the flux of BSi increases
toward the top of all cores. Increased BSi flux since 1950 characterizes Big Narrows and
Little Traverse Bay, and Big Traverse 3. Big Traverse 4 and Sabaskong Bay have
continually increasing flux of BSi upcore, whereas Muskeg and Buffalo bays have little
long-term change in BSi flux except for their enriched surface sediments.

**Fossil pigments**
Downcore concentrations of fossil pigments and derivatives were grouped by algal types
or indicator value and plotted for each core (Fig. 6). There are two primary patterns
among pigment profiles from Lake of the Woods. Many sites including Big Traverse 3
and 4, Sabaskong, Muskeg, Little Traverse, and Big Narrows show a bimodal pattern of
increasing pigment concentration since damming that peaks around 1970, followed by
decreased concentrations in the 1980s, and then increased concentrations again in the last
15 years. This pattern is reflected in pigment profiles from most algal groups including
diatoms (e.g., diatosanthin), cyanobacteria (e.g. canthaxanthin, myxoxanthophyll), and
general algal indicators (e.g. lutein-zeaxanthin). Other sites have less defined patterns
including simple upcore increases (Buffalo Bay). Of note in all cores is the distribution
of the colonial cyanobacterial pigment myxoxanthophyll, an indicator of colonial and
filamentous cyanobacteria including *Microcystis*, whose distribution is mostly limited to
sediments deposited since the 1980s.

There is degradation of pigments and derivatives before permanent burial in Lake of the
Woods as evidenced by initial exponential declines at the core tops of most fossil
pigments. The degradation of pigments can be evaluated by comparing labile fractions
such as chlorophyll-a to its breakdown products (e.g. pheophorbide-a). Ratios of these
pigments explain the typical exponential decline in the near surface sediments of more
labile forms; however, more stable pigments such as B-carotene show similar near
surface profiles providing evidence that the recent increases in pigment concentrations
are reflecting productivity increases (Fig. 6).
Historical Phosphorus budget scenarios

Several whole basin, mass balance approaches and dynamic models were used to explore potential historical P loading scenarios to Lake of the Woods and historical in-lake nutrient dynamics (Engstrom and Rose 2013).

Model 1) Simple whole-lake mass balance
As outlined in the proposal, we first applied a simple one-box whole lake model that is commonly used to estimate historical P loading in lakes (Engstrom et al. 2009, Triplett et al. 2009),

\[ I = B + O, \]

where all inputs (I) of P to a lake have two inevitable fates, either permanent burial (B), or they are lost from the lake via outflow (O). The sum of burial and outflow is a first order estimate of historical P loading to the lake.

In this model outflow (O) is estimated using the whole-lake historical diatom-inferred concentrations of TP (DI-TP; Fig. 3a) multiplied by the outflow at Big Narrows (Fig. 5). Outflow or losses of P at Big Narrows increase after damming to initial peak levels in the 1970s of 286 t P/yr, decline slightly during the 1980s to 220 t P/yr, then increase upcore to outflow losses of 361 t P/yr from 2005-2011.

Burial (B) estimates of P for this model used focus-corrected flux rates of total sediment P for each lake basin that were summed across basins to generate a historical whole lake burial estimate of total sediment P (Fig. 4b).

Model Assumptions —
1. Simple model where P inputs (I) are estimated by sum of P lost through outflow (O) and P that is lost through permanent burial (B).
2. Assumes that burial of P is permanent with only minor internal loading.
3. Model works best in lakes with higher sedimentation rates with efficient burial of P.

Results —
Model 1 phosphorus loading estimates for Lake of the Woods are estimated to be approximately 646 t P/yr before damming. After damming, P loadings increase continuously to modern rates of 2009 t P/yr (Table 3). Based on monitored loading estimates (see Hargan et al. 2011, Anderson et al. 2013, Zhang et al. 2013), this model clearly overestimates modern loadings to the lake. Importantly we also do not see any modeled decreases in loadings to the lake since the 1980s that would reflect well-documented decreases in P loading from the Rainy River (Hargan et al. 2011).

Key Findings —
1. If we can assume that Lake of the Woods was a basin at long-term steady state before damming and Euroamerican settlement, this model can be used to generate pre-damming loading estimates to Lake of the Woods. We estimate annual loading of P to the lake was approximately 646 t P/yr before damming. Modern loading estimates are similar (2005-2011, 687 t P/yr partitioned between 529 t P/yr loadings from the Rainy River and 158 t P/yr from other sources; based primarily on Hargan et al. 2011).

2. Model estimates of modern loading to the lake are overestimated based on agency monitoring records and recent efforts to construct modern nutrient budgets for the lake (Hargan et al. 2011, Anderson et al. 2013, Zhang et al. 2013).

3. The high estimates of modern loads to the lake and no indication of decreased loading after 1980 in our burial estimates (Fig. 4) reflect the shortcomings of this model, which are driven by the assumption that Lake of the Woods rapidly and efficiently removes P from the lake via burial. Instead we know that there is large pool of readily exchangeable and mobile P fractions in Lake of the Woods sediments. Burial rates do not clearly reflect known declines in P loading to the lake because a large active pool of P has accumulated in the lake (Fig. 4).

Model 2) Whole-lake mass balance with active layer of sediment P

A second model that accounts for a large and active P layer in the sediments was constructed to overcome the deficiencies found in Model 1. Model 2 estimates historical phosphorus dynamics as:

\[ I = O + B + \Delta A + \Delta W, \]

where historical inputs or loadings of P (I) are the sum of P outflow (O), permanent burial (B), a flux to an active pool of P in the sediments (\( \Delta A \)), and a flux of P to the water column (\( \Delta W \)) based on DI-TP estimates.

For this model we use P loading estimates from Hargan et al. (2011) from the 1960s to present and solve for changes in the active layer such that:

\[ \Delta A = I - O - B - \Delta W \]

Model Assumptions—

1. We used Rainy River loading estimates for 1962-2010 and added 158 t P/yr from other sources (atmospheric, tributaries, minor sources, etc.) as outlined in Hargan et al. (2011). The 158 t P/yr from other sources was applied to all time periods in the core.

2. Burial (B) was estimated as "minimum burial" by subtracting the NaOH-P and Ex-P fractions from the total sediment P (Fig 4b).

3. Outflow (O) estimates were identical to Model 1 and based on whole basin historical DI-TP and outflow at Big Narrows (Figs 3a, 5).

4. The change in water column P (\( \Delta W \)) was estimated by change in P in the water column (whole lake DI-TP x lake volume) between time period 1 and time 2 (e.g. between adjacent decades, between the 1960s and 1970s).
5. The change in the active P layer ($\Delta A$) is defined as the amount of P that enters or leaves the actively exchanging pool of P in Lake of the Woods between time periods.

6. For pre-damming estimates of a P budget, it is assumed the lake was at a steady state defined as when $\Delta A$ and $\Delta W = 0$, i.e. for the pre-damming period, Model 2 results are identical to Model 1.

Results —

Model 2 phosphorus loading estimates for Lake of the Woods are estimated to be approximately 646 t P/yr prior to damming (Table 4). From the 1960s to present loading estimates from Hargan et al. (2011) record decreased loading reaching approximately 688 t P/yr in 2005-2011 for comparison to pre-damming levels. The active pool of P in Lake of the Woods builds in the 1960s and 1970s, but is shown to be readily releasing P to the lake through cycling and internal loading after the 1970s to achieve DI-TP water column concentrations and predicted outflows of P (Table 4). Moreover, changes in the active pool are increasingly negative.

Key Findings —

1. Model 2 estimates annual loading of P to the lake was approximately 646 t P/yr before damming. This compares to current loading estimates of 688 t P/yr and suggests that modern loading estimates may be underestimated. We must reconsider if current loading estimates have actively captured all sources of P to the lake.

2. Based on Hargan et al. (2011) loading estimates and effective burial of refractory P fractions, this model estimates that changes to the active pool of P were positive in the 1960s and 1970s, but have become increasingly negative to present as the active pool of P is being depleted at current P loading rates.

3. Changes in the active layer are large and negative in recent decades; there has been a net change of -13,000 T since 1960. The active layer today is estimated at ~20,000 T based on whole lake estimates of labile P fractions (Fig. 4b; summed by years per time interval), which means that active layer in c.1960 would have been at least 33,000 T, which is very large given possible P loads prior to 1960.

Model 3) Dynamic 2-box model, best guess scenario for 1950-2010

A two box dynamic model was constructed with Stella software and run from 1950 to 2010 to estimate pools of P in Lake of the Woods (Fig. 7). Loading inputs are estimated from Hargan et al. (2011; see also Model 2) and assume any input of P to the lake will quickly reach the sediment active pool of P through either particle-bound deposition or sedimentation of resulting algal productivity. The model gives this sediment pool two potential fates—permanent burial or movement in/out of the active layer to the water column at a fixed rate. The model sets several constraints, which are our "best guess" scenarios or conditions that we feel are well supported based on monitoring or sediment analysis: a fixed percent of active pool P being cycled to the water column, setting the model output to match the current active pool, and a conservative estimate of P burial. We also strive to match current water column estimates of DI-TP.
Model Assumptions—
1. We used Rainy River loading estimates for 1962-2010 and added 158 t P/yr from other sources (atmospheric, tributaries, minor sources, etc.) as outlined in Hargan et al. (2011). The 158 t P/yr from other sources was applied to all time periods in the the model, 1950 to 2010.
2. Potential burial rates were minimally estimated to be 950 t P/yr and set to be constant since 1960 based on estimated whole lake P accumulation rates (Fig. 4b). Burial in the 1950s was set at 917 t P/yr.
3. All inputs of P to the lake are expected to become part of the sediment pool quickly. Given the year-plus water residence estimates for Lake of the Woods (Anderson et al. 2013), the lake's polynictic nature, large depositional basin, and relatively high productivity, this seems reasonable.
4. For the best guess scenario, the amount of P that was released from the active pool to the water column was set at a fixed percentage of 1%.
5. The model was constrained so that modeled outflow P estimates matched whole lake DI-TP x outflow estimates (Fig. 5) in 2010.
6. The model was also constrained so that the modeled active sediment pool for 2010 matched the measured whole lake active P pool in 2010, approximately 25000 t P.

Results—
Model 3 results are presented from 1955 to 2010 and are best interpreted by looking at model estimates of water column TP and estimated changes in the active pool of P. Model 3 estimates of water column TP suggest that TP concentrations were higher than modern from 1955-1980 and ca. 33-37 µg/L (Fig. 8a). These values contrast with whole lake estimates of mean DI-TP which are approximately 17 µg/L from 1955-1980. After 1980, modeled water column TP declines to present levels of approximately 23 µg/L, as constrained by model parameters (Fig. 8a). The active pool of P is modeled at its highest level during the 1970s rising from a pool of slightly less than 40000 t P in 1955 to 41000 t P in the 1970s (Fig. 8b). The active pool is rapidly reduced after the 1970s to present, reaching modeled 2010 estimates of slightly more than 24000 t P (Fig. 8b).

Key Findings—
1. Model 3 estimates of water column TP do not closely match historical DI-TP estimates from 1955-2010. Model 3 consistently models a higher TP concentration for all years except 2010. Higher-than-modern TP levels from 1955-1980 may be a possibility given the monitored loading estimates from Hargan et al. (2011) that show two- to three-fold decreases in P loading from the Rainy River since 1980. Alternatively we might question the overall trend in DI-TP which shows a rise in TP from damming to the 1970s, a slight decline in the 1980s, then increases to modern TP concentrations of 24 µg/L, the highest TP values estimated by whole lake diatom-based reconstruction.
2. Model 3 was constrained to match the current active pool of P, but modeled trends from 1955 to 2010 are informative. The active pool of P peaks in the 1970s at 41000 t P before decreasing rapidly to modern levels. The modeled
decline supports that there is a substantial legacy source of P that is still fueling algal production in Lake of the Woods, and that the active pool was much greater in the past with peak accumulation in the 1970s. That the 1970s represented the peak active pool and also the period greatest P loading from the Rainy River (Hargan et al. 2011) lends support to several components of the "best guess" scenario.

**Model 4) Dynamic 2-box model, best fit scenario for 1950-2010**

A second modified two-box dynamic model was constructed in response to Model 3 results. Although based on many of the same input parameters and constraints as Model 3, Model 4 works to fit water the whole lake DI-TP concentrations that were reconstructed from 1950 to 2010 (Fig. 3a). This is done primarily by manipulating the percent of the active P pool that is available for exchange with the water column each year (Fig. 9; in contrast to a set percent exchangeable in Model 3; Fig. 7).

**Model Assumptions—**

1. We used Rainy River loading estimates for 1962-2010 and added 158 t P/yr from other sources (atmospheric, tributaries, minor sources, etc.) as outlined in Hargan et al. (2011). The 158 t P/yr from other sources was applied to all time periods in the the model, 1950 to 2010.
2. Potential burial rates were minimally estimated to be 950 t P/yr and set to be constant since 1960 based on estimated whole lake P accumulation rates (Fig. 4b). Burial in the 1950s was set at 917 t P/yr.
3. All inputs of P to the lake are expected to become part of the sediment pool quickly. Given the year-plus water residence estimates for Lake of the Woods (Anderson et al. 2013), the lake's polymictic nature, large depositional basin, and relatively high productivity, this seems reasonable.
4. For the best fit scenario, the amount of P that was released from the active pool to the water column was adjusted from 0.8 to 1.8%.
5. The model was constrained so that modeled 2010 outflow P estimates matched whole lake DI-TP x outflow estimates (Fig. 5). The model also attempted to match water column phosphorus concentrations predicted by DI-TP.
6. The model was also constrained so that the modeled active sediment pool for 2010 matched the measured whole lake active P pool in 2010, approximately 25000 t P.

**Results—**

Model 4 results are presented from 1955 to 2010 and similar to Model 3 are interpreted by looking at model estimates of water column TP and estimated changes in the active pool of P in the sediments. Model 4 estimates of water column TP track closely the whole-lake DI-TP estimates with modeled TP of 17-18 µg/L from 1955 until 1990 (Fig. 8c). After 1990, modeled and diatom-inferred TP increase to approximately 24 µg/L in 2010 (Fig. 8c). Behavior of the active pool in Model 4 follows a slightly different pattern compared to Model 3, notably not reaching similar elevated levels in the 1970s. The 1955 active pool in Model 4 is similar to modern levels of 25000 t P (Fig. 8d). The active pool increases rapidly to a peak
inventory in the 1970s of over 30000 t P before declining rapidly to modern pool of 24000 t P (Fig. 8d).

**Key Findings**

1. Model 4 estimates of water column TP closely match historical DI-TP estimates from 1955-2010.
2. The active pool of P increases to maximum levels in the 1970s, coincident with loading patterns from the Rainy River as estimated by Hargan et al. (2011). The current trajectory shows that the active pool of P is has been rapidly declining since the 1980.
3. The percent of the active pool of P that was available for cycling or internal loading was adjusted to match the whole-lake DI-TP in Model 4. The percent of the active pool began at 1.1% in 1955, reached its lowest value in 1980 of about 0.8%, then rose to its highest level in 2010 of approximately 1.8%. As a result the water column TP is increasing at the expense of the active pool, which is decreasing at a rate greater than Model 3.

**Discussion: Phase I Objectives and Research Questions**

Four questions were posed in the Phase I reconstruction of a historical phosphorus budget for Lake of the Woods. Below we discuss our findings in the context of addressing our specific research questions.

**1. How has P loading to LoW changed over the last 100 years?**

Based on existing monitoring data, we know that the primary source of phosphorus loading to Lake of the Woods, the Rainy River, has had declining loads of phosphorus since the 1980s (Hargan et al. 2011). Based on several efforts to model current P budgets for Lake of the Woods, we also know that modern loads of P to the southern lake are on the order of 359 to 688 t P/yr (Hargan et al. 2011, Zhang et al. 2013) including loads from the Rainy River and other sources. Pre-1960s loading data do not exist, although historical accounts suggest that nutrient levels would have increased in the Rainy River in the 20th century as logging, lumbering, pulp and paper, settlement, and agriculture commenced in the Rainy River basin and that degraded conditions likely would have been at their worst in the 1950s-1970s (Minnesota Department of Health 1964, Edlund et al. 2014).

The whole-lake historical P mass balance presented in Models 1 and 2 is the first line of evidence to suggest what pre-damming loading conditions may have been in Lake of the Woods. Results suggest annual P loads to the Lake of the Woods were around 646 t P/yr based on water column TP concentrations estimated at ca. 10 µg/L based on diatom-inferred reconstructions and steady state burial of P estimated at 518 t P/yr. The modeled loading estimate of 646 t P/yr compares to modern monitored loads estimated to be as high as 688 t P/yr (Hargan et al. 2011).
Model 1 suggests that loadings to Lake of the Woods have continued to rise since damming; it is the contrast in this trend with monitoring records (Hargan et al. 2011) that made it clear that other modeling efforts were needed to better understand the historical loading record, and more importantly the nature of the sediment pool of P in the lake.

2. How have biological communities (cyanobacteria and diatoms) changed over the last 100 years?

Many biogeochemical signals in the cores provide lines of evidence on how biological communities have changed in Lake of the Woods over the last 100 years. Community level changes in the diatoms will be discussed in detail elsewhere (Reavie et al. in prep.); however, biogenic silica and fossil pigments also record changes in historical diatom productivity. Historical changes in cyanobacteria communities and productivity are similarly recorded in the pigment records.

There are contrasting indicators of historical diatom productivity in Lake of the Woods sediments. Biogenic silica records suggest increased diatom productivity moving upcore to highest levels in the most recent decades. However, pigment records, particularly general algal indicators (e.g., lutein-zeoxanthin) and diatom specific pigments (e.g., diatoxanthin) suggest two periods of high productivity in the recent history of Lake of the Woods. The first period occurred from the 1950s through 1970s and was followed by a decline in productivity in the 1980s. Since the 1990s pigments indicate that there has been a second period of increased diatom productivity.

We also note that there are significant changes in diatom communities that drive the diatom-inferred increases in TP in the most recent decades. Increases in DI-TP reflect shifts in the diatom community to greater abundance of species with higher TP optima and include *Cyclostephanos dubius*, several small *Stephanodiscus* species, and *Aulacoseira granulata* (Reavie et al. in prep.); the most recent sediments preserve a diatom community that represents a species assemblage not previously seen in the lake. In spite of evidence from pigment proxies that suggest greater diatom productivity in the 1950s-1970s there is no indication that the most recent high-P indicator taxa were as common in the 1950s-1970s. Similarly, biogenic silica records, whether treated as concentration or flux to the sediment, do not suggest increased productivity during the periods of peak diatom pigment indicators deposited in the 1950s to 1970s.

The pigment records indicate two periods of elevated production of cyanobacteria in Lake of the Woods. The first period is from the 1950s-1970s and is characterized by high concentrations of cyanobacterial (e.g., echinone and canthaxanthin) and general algal indicators (e.g., lutein-zeoxanthin). The same pigment groups show a second increase since the 1990s in most cores. However, there is also an increase since the 1990s of an additional pigment, myxoxanthophyll, an indicator of filamentous and colonial cyanobacteria including several of the toxic forms.
(Microcystis), further suggesting that the biological communities present in the most recent decades are unique in the recent history of Lake of the Woods.

3. **Are trends in biological communities, nutrient dynamics, and sedimentation related to changes in external nutrient loading?**

At present there are two records of external nutrient loading that best describe historical loadings in Lake of the Woods. The reconstructed TP loadings from 1962-2010 that were compiled by Hargan et al. (2011) well accounts for monitored loads from the Rainy River as well as other tributary loads. It reports that loadings for the period of record were greatest in the 1960s at over 1500 t P/yr, only slightly lower in the 1970s, then declined rapidly to modern loadings of around 675 t P/yr. The other record of loadings are pre-damming estimates made in this study using whole lake mass balance of TP export and burial, which suggest pre-damming loading was approximately 646 t P/yr to the southern basins of the lake. Between damming and 1960, the whole basin reconstruction does not accurately report loadings because sediment burial of P does not reflect monitored loads. Instead we identified a mobile and active pool of sediment P that is most abundant in the upper sections of all sediment cores, and that required alternative modeling techniques to understand the nature of this pool and its ability to support internal loading to the lake.

The pigment record tracks monitoring records of mid-20th century external nutrient loading to the lake. A period of increased diatom, cyanobacteria, and general algal productivity is present in sediments deposited in the 1950s-1970s in most of the southern basins. Other biological records including biogenic silica and organic matter do not readily record this period of increased productivity in the 1950s-1970s, instead they suggest that productivity has continued to increase in recent decades.

4. **Do trends in biological communities, nutrient dynamics, and sedimentation reflect legacy nutrient effects?**

The abundance and distribution of phosphorus fractions in sediment cores indicate that there is a large pool of readily exchangeable P fractions in Lake of the Woods, and that the pool of P increases at the top of the core. The first observation was similarly identified by James (2012) from three sites in Big Traverse and Muskeg bays. However, it is the observation that this pool of exchangeable P increases at the core top that makes the spatial and temporal scale of the current study important. Our assessment of seven cores from throughout the southern lake basin indicates that none of the sites we studied is effectively burying P, but rather a large portion of the sediment P exists in an active legacy pool of P that is being readily cycled and supports internal loading to Lake of the Woods.

The same observation also prevents a more straightforward approach to a historical whole-lake mass balance of P and requires alternative approaches to understand the role
that the active pool of P. Using Model 1 we were able to estimate pre-damming P loading to the lake, but pre-damming levels are not much less than modern loading estimates (Hargan et al. 2011) suggesting that there may be modern loads that have not been fully accounted. Models 2-4 were developed to explore the behavior of the active pool of P. The three models each approached the active layer a bit differently, particularly how it exchanges with the water column and whether the historical DI-TP values had to be met with the model run. Regardless of the model, there are some very clear trends. First, burial rates of refractory P are increasing in Lake of the Woods compared to pre-damming levels. Second, there is a large pool of labile P that can only be accounted for if historical loading was larger (which was documented by Hargan et al. 2011). Third, most models indicate that the pool of active P was much larger in the past, and at its maximum size in the 1970s. Fourth, the active legacy pool is currently being depleted to support modern levels of productivity in Lake of the Woods (this could also be interpreted by invoking a large unaccounted P loading to the lake). Fifth, the rate at which the pool is being depleted varies among models, but generally shows the pool as being rapidly depleted since the 1970s.

Do the Phase I results have management implications? The first recommendation would be to revisit current P loading estimates for the lake to reconcile the small difference between pre-damming and modern loading estimates. The second management implication is that water quality in Lake of the Woods should start or be improving with depletion of the active legacy P. All models suggest that the active pool of P is being rapidly used. From a biological standpoint, we cannot say that the frequency and extent of cyanobacterial blooms is greater today than in the past in Lake of the Woods. Fossil pigment records indicate that cyanobacterial blooms were also a large part of the ecology of Lake of the Woods in the 1950s-1970s. The diatoms suggest a somewhat different scenario as communities have shifted toward more eutrophic indicators in recent decades and that diatom productivity based on biogenic silica is currently at its highest recorded levels (there is no evidence of selective dissolution in the cores). The shift in community makeup especially may indicate that the modern limnology of Lake of the Woods is different and may represent a combined response to climate drivers resulting in increased nutrient availability. Importantly, Phase II will explore in detail the modern limnological behavior of Lake of the Woods and use modeling of lake thermal structure to both forecast and hindcast limnological changes in the lake to better understand the past and predict future scenarios in Lake of the Woods.
References


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Minnesota Department of Health, Division of Environmental Sanitation, Section of Water Pollution Control. 1964. Census Data, Sewage Disposal Facilities, State of Minnesota.


## Tables

**Table 1.** Lake of the Woods core names, dates, coring locations, depth at core site, and core recovery.

<table>
<thead>
<tr>
<th>Core Name</th>
<th>Date</th>
<th>Lat (N)</th>
<th>Long (W)</th>
<th>State/Prov</th>
<th>Country</th>
<th>type</th>
<th>Depth (m)</th>
<th>Recovery (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LoW_BigNarrows A</td>
<td>20120228</td>
<td>49.39472°</td>
<td>94.79395°</td>
<td>Ontario</td>
<td>Canada</td>
<td>Piston</td>
<td>8.53</td>
<td>0.98</td>
</tr>
<tr>
<td>LoW_LittleTrav</td>
<td>20120228</td>
<td>49.24643°</td>
<td>94.67145°</td>
<td>Ontario</td>
<td>Canada</td>
<td>Piston</td>
<td>9.18</td>
<td>0.98</td>
</tr>
<tr>
<td>LoW_Sabaskong A</td>
<td>20120229</td>
<td>49.10064°</td>
<td>94.42108°</td>
<td>Ontario</td>
<td>Canada</td>
<td>Piston</td>
<td>6.85</td>
<td>0.98</td>
</tr>
<tr>
<td>LoW_BigTrav3</td>
<td>20120229</td>
<td>49.01931°</td>
<td>94.75391°</td>
<td>Minnesota</td>
<td>USA</td>
<td>Piston</td>
<td>9.18</td>
<td>0.98</td>
</tr>
<tr>
<td>LoW_BigTrav4</td>
<td>20120301</td>
<td>49.08941°</td>
<td>94.99497°</td>
<td>Minnesota</td>
<td>USA</td>
<td>Piston</td>
<td>10.13</td>
<td>0.96</td>
</tr>
<tr>
<td>LoW_Muskeg</td>
<td>20120301</td>
<td>48.97849°</td>
<td>95.17970°</td>
<td>Minnesota</td>
<td>USA</td>
<td>Piston</td>
<td>8.08</td>
<td>0.95</td>
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<tr>
<td>LoW_BB2H</td>
<td>20120818</td>
<td>49.10960°</td>
<td>95.22796°</td>
<td>Minnesota</td>
<td>USA</td>
<td>HTH</td>
<td>5.52</td>
<td>0.095</td>
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</table>

**Table 2.** Sediment focusing factors for each core site in Lake of the Woods. Focusing factors are estimated by the flux of unsupported $^{210}$Pb to the core site relative to known atmospheric depositional rates in the region (~0.5 pCi/cm² yr).

<table>
<thead>
<tr>
<th>Basin/core</th>
<th>Focusing factor</th>
<th>Modern sedimentation rate kg/m²/yr</th>
<th>focus corrected sedimentation rate kg/m²/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Big Narrows</td>
<td>1.51</td>
<td>0.750</td>
<td>0.495</td>
</tr>
<tr>
<td>Big Trav 3</td>
<td>1.09</td>
<td>0.650</td>
<td>0.596</td>
</tr>
<tr>
<td>Big Trav 4</td>
<td>1.30</td>
<td>0.600</td>
<td>0.462</td>
</tr>
<tr>
<td>Buff Bay</td>
<td>0.37</td>
<td>0.650</td>
<td>1.775</td>
</tr>
<tr>
<td>Little Trav A</td>
<td>1.24</td>
<td>0.700</td>
<td>0.566</td>
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<tr>
<td>Muskeg A</td>
<td>1.43</td>
<td>0.880</td>
<td>0.615</td>
</tr>
<tr>
<td>Sabaskong A</td>
<td>1.69</td>
<td>1.150</td>
<td>0.682</td>
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</table>
Table 3. Model 1 output where $I = B + O$, P Inputs (I), P Burial (B), and P Outflow (O) are in tonnes P/yr.

<table>
<thead>
<tr>
<th>Time Interval</th>
<th>P Input (t P/yr)</th>
<th>P Outflow (t P/yr)</th>
<th>P Burial (t P/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005-2011</td>
<td>2669</td>
<td>464.0</td>
<td>2205</td>
</tr>
<tr>
<td>2000-2004</td>
<td>2141</td>
<td>228.4</td>
<td>1913</td>
</tr>
<tr>
<td>1995-1999</td>
<td>2070</td>
<td>190.3</td>
<td>1880</td>
</tr>
<tr>
<td>1990-1994</td>
<td>1893</td>
<td>210.2</td>
<td>1683</td>
</tr>
<tr>
<td>1980-1989</td>
<td>1536</td>
<td>167.8</td>
<td>1368</td>
</tr>
<tr>
<td>1970-1979</td>
<td>1523</td>
<td>173.3</td>
<td>1350</td>
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<tr>
<td>1960-1969</td>
<td>1202</td>
<td>187.1</td>
<td>1015</td>
</tr>
<tr>
<td>1950-1959</td>
<td>1156</td>
<td>185.5</td>
<td>971</td>
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<tr>
<td>1940-1949</td>
<td>1100</td>
<td>159.5</td>
<td>941</td>
</tr>
<tr>
<td>1920-1939</td>
<td>883</td>
<td>134.1</td>
<td>749</td>
</tr>
<tr>
<td>1900-1919</td>
<td>868</td>
<td>147.1</td>
<td>721</td>
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<tr>
<td>pre-1900</td>
<td>646</td>
<td>128.3</td>
<td>518</td>
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Table 4. Model 2 output where \( I = O + B + \Delta A + \Delta W \), where \( P \) Inputs (I), \( P \) Burial (B), \( P \) Outflow (O), \( P \) flux to the water column (\( \Delta W \)), and \( P \) flux in the active sediment layer (\( \Delta A \)) are in \( t \) \( P/yr \).

<table>
<thead>
<tr>
<th>Time Interval</th>
<th>DI-TP (µg/L)</th>
<th>Sed rate (kg/m(^2)/yr)</th>
<th>Sed-TP rate (g/m(^2)/yr)</th>
<th>HCl-P + Org-P (gP/m(^2)/yr)</th>
<th>Ex-P + NaOH-P (gP/m(^2)/yr)</th>
<th>P Input (t P/yr)</th>
<th>P Outflow (t P/yr)</th>
<th>P Burial (t P/yr)</th>
<th>ΔP Lake (t P/yr)</th>
<th>ΔP Active (t P/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005-2011</td>
<td>24.61</td>
<td>0.687</td>
<td>0.718</td>
<td>0.439</td>
<td>0.284</td>
<td>688</td>
<td>361.0</td>
<td>1348</td>
<td>131</td>
<td>-1152</td>
</tr>
<tr>
<td>2000-2004</td>
<td>17.81</td>
<td>0.663</td>
<td>0.623</td>
<td>0.375</td>
<td>0.249</td>
<td>671</td>
<td>270.4</td>
<td>1151</td>
<td>-18</td>
<td>-732</td>
</tr>
<tr>
<td>1995-1999</td>
<td>18.77</td>
<td>0.756</td>
<td>0.612</td>
<td>0.402</td>
<td>0.210</td>
<td>732</td>
<td>278.5</td>
<td>1235</td>
<td>24</td>
<td>-805</td>
</tr>
<tr>
<td>1990-1994</td>
<td>17.52</td>
<td>0.681</td>
<td>0.548</td>
<td>0.343</td>
<td>0.205</td>
<td>815</td>
<td>243.7</td>
<td>1053</td>
<td>8</td>
<td>-490</td>
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<tr>
<td>1980-1989</td>
<td>17.09</td>
<td>0.589</td>
<td>0.446</td>
<td>0.282</td>
<td>0.163</td>
<td>735</td>
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Figures
Figure 1. Downcore profiles for seven Lake of the Woods cores for total $^{210}$Pb activity, date-depth relationship, sedimentation rate, and percent composition of organics, carbonates and inorganics as determined by loss-on-ignition analysis plotted against core depth (cm).
Figure 2. Geochemistry of seven Lake of the Woods cores including concentration (mg P/g sediment) and flux (mg P/cm$^2$ yr) of total sediment phosphorus and phosphorus fractions including HCl-P, NaOH-P, Organic-P, and Exchangeable-P, biogenic silica concentration (wt %; mg SiO$_2$/100 mg sediment) and flux (mg SiO$_2$/cm$^2$ yr), and water column diatom-inferred total phosphorus (DI-TP; µg/L) estimates plotted against core date.
Figure 3. Whole basin estimates of historical water column phosphorus and focus corrected sediment accumulation plotted against core date. Fig. 3a. Whole basin estimates of water column diatom-inferred total phosphorus (DI-TP; µg/L). Fig. 3b. Whole basin estimates of focus corrected sediment accumulation (kg/m² yr).
**Figure 4.** Whole basin estimates of historical accumulation of phosphorus (P) and P fractions in Lake of the Woods sediments by time period. Fig. 4a. Accumulation of P differentiated into refractory components (HCl-P and Organic-P; green bars) and labile components (NaOH-P and Exchangeable-P; yellow bars); minimum burial estimates of refractory fractions were used in Model 2. Fig. 4b. More conservative estimates of P burial were used in Models 3&4 where the buried fraction of P (brown bars) includes refractory components plus the labile fraction present before 1960. The red bars thus represent the current active pool of P in Lake of the Woods. Total P accumulation (sum of red and brown bars) was used in Model 1 to estimate total P burial (see Table 3).
Figure 5. Estimates of historical loss of phosphorus through outflow at Big Narrows by time period. These values represent the whole-lake historical diatom-inferred total phosphorus multiplied by historical flows at Big Narrows for each time period.
Figure 6. Concentration (nmol pigment/g organic) of fossil pigments and pigment derivatives preserved in seven cores from Lake of the Woods. Pigments and derivatives are grouped by algae type or indicator value.
Figure 7. Model 3 is a two-box dynamic model run from 1950-2010 with inputs estimated from Hargan et al. (2011), burial estimated at 950 t P/yr (Fig. 4b), and a set percentage of the active layer available for internal loading (1%).
**Figure 8.** Output of Models 3 and 4. Fig. 8a (upper left). Comparison of modeled water column total phosphorus (TP; µg/L) vs whole basin diatom-inferred TP (DI-TP; µg/L) for Model 3, 1955-2010. Fig. 8b (lower left). Modeled whole lake estimate of the active pool of P in southern Lake of the Woods (tonnes P) based on Model 3, 1955-2010. Fig. 8c (upper right). Comparison of modeled water column total phosphorus (TP; µg/L) vs whole basin diatom-inferred TP (DI-TP; µg/L) for Model 4, 1955-2010. Fig. 8b (lower right). Modeled whole lake estimate of the active pool of P in southern Lake of the Woods (tonnes P) based on Model 4, 1955-2010.
Figure 9. Model 4 is a two-box dynamic model run from 1950-2010 with inputs estimated from Hargan et al. (2011), burial estimated at 950 t P/yr (Fig. 4b), and a variable percentage of the active layer available for internal loading (1%) to most closely match diatom-inferred total phosphorus estimates (DI-TP).