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PALEOLIMNOLOGICAL STUDY OF PHOSPHORUS-IMPAIRED LAKES IN THE CANNON RIVER WATERSHED



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Daniel R. Engstrom

Adam J. Heathcote

David R. L. Burge

St. Croix Watershed Research Station Science Museum of Minnesota Marine on St. Croix, MN 55047

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Executive Summary

- 1. This study used paleolimnological analysis of dated sediment cores from 16 nutrient-impaired lakes in the Cannon River Watershed to constrain present-day lake phosphorus (P) budgets and reconstruct changes in ecological conditions over the last 150 years. Study lakes covered two environmental gradients likely important to lake response and recovery: lake depth and hydrological residence time.
- 2. Phosphorus burial was determined from P concentrations and sediment accumulation rates in the uppermost 10 cm of short cores collected from the central region of each lake. These burial rates were combined with estimates of watershed P loads and outflow P losses from recent TMDL studies to provide a closed P mass-balance for each lake in which all fluxes were independently determined.
- 3. Longer sediment cores (150-250 cm), collected from a single lake within each of four geomorphic groups deep/seepage, shallow/seepage, deep flow-thru, and shallow/flow-thru were dated by radioisotopic methods and analyzed stratigraphically for sediment P concentrations and fossil diatom remains to reconstruct past changes in algal communities and P burial.
- 4. Expressed on a whole-lake basis, the study lakes sequestered in their sediments between 0.17 and 13.7 Mg (10³ kg; metric tons) of P annually, and rates were systematically higher in the flow-thru lakes with larger watersheds (e.g. Byllesby, Gorman, Cannon). Based on historical reconstructions from the four long cores, present-day P burial rates were 1.5-3.5x higher than those prior to EuroAmerican settlement in the mid-19th century.
- 5. External P inputs compiled from TMDL reports ranged over two orders of magnitude, with lowest values in the shallow seepage lakes (0.08-2.3 Mg yr⁻¹) and highest in the flow-through lakes, both shallow (3.9-30.5 Mg yr⁻¹) and deep (1.8-228 Mg yr⁻¹). Outflow P losses, also compiled from TMDL calculations, range from 0.021 to 1.16 Mg yr⁻¹ in the seepage lakes and 0.37 to 157 Mg yr⁻¹ in the flow-thru lakes.
- 6. The net P flux from mass balance calculation ranged from a large excess (positive) load of 57 Mg yr⁻¹ in the Byllesby Reservoir (high-flow year) to a large loss (negative) load in Cannon and Gorman (-31 and -17 Mg yr⁻¹, respectively). Six of the study lakes (Cedar, Clear, Volney, Chub, Toner's, and Gorman) showed a consistent negative P net, while three (Byllesby, Fox, Upper Sakatah) show a positive P net. The seven remaining lakes (Frances, French, Shields, Loon, Roberds, Cannon, and Circle) exhibited a negative P net using a minimum estimate for external P load and a positive (or near zero) P net using a larger estimate of P load (external + 50% unaccounted).
- 7. As a group, the seepage lakes (both deep and shallow) tended toward a negative P mass balance while the flow-thru lakes, especially the deep group, tended toward a positive P mass balance. Some of the difference among lakes and groups can be explained by the higher external P loads to lakes with larger watersheds. Among all lakes, net P flux was positively correlated with watershed area, but when only seepage lakes were considered, the relationship was strongly negative. Lake-water TP was only strongly correlated with net P in seepage lakes.
- 8. Assuming steady-state future conditions under TMDL allowable loads, P burial rates calculated by difference (TMDL external inputs minus TMDL outflow losses) would decline by 40% to 90% from current conditions for all but three flow-thru lakes, Byllesby, Gorman, and Upper Sakatah.

- 9. Diatom communities from surface sediments in the study lakes were compared to a diatom/waterquality database of 89 representative Minnesota lakes. Most Cannon Watershed lakes clustered together with diatom communities from other lakes in the WCP and CHF ecoregions, but with variable cohesiveness by major lake groupings. The shallow/flow-thru lakes (Gorman, Cedar, Upper Sakatah, and Circle) formed a fairly tight cluster that represented moderate to high TP concentrations. Similarly, the deep/flow-thru lakes, Byllesby and Roberds, clustered closely to their shallower counterparts.
- 10. Diatom communities from dated sediment cores were analyzed for three of the study lakes (Loon, Roberds, and Upper Sakatah). Frances was originally included in this analysis, but had very poor diatom preservation throughout the sediment core. These diatom-based reconstructions clearly demonstrate the large ecological shifts that lakes in agricultural regions of Minnesota have undergone. The two cores that extend back to presettlement times, Loon and Upper Sakatah, show historic diatom communities characteristic of mesotrophic lakes today. These lakes were likely macrophyte-dominated, clear-water systems, unlike the turbid, algal-choked water-bodies seen today.
 - Loon (shallow/seepage) showed the most dramatic floristic change in the study with pre-1850 samples clustering most closely with the relatively pristine NLF lakes and then moving toward lakes of the WCP. These changes were mirrored by DI-TP (diatom-inferred TP) reconstructions, with a minimum of 23 μ g L⁻¹ around 1840, 75 μ g L⁻¹ in the early 1900s, and a maximum of 95 μ g L⁻¹ by the end of the 20th century.
 - Roberds (deep/flow-thru) had a truncated history due to its abnormally high rates of sedimentation, and its core represented only the last 100 years ecological change. During this time the diatom community circled in a tight cluster most similar to lakes from the Twin Cities metro region. Beginning around 1990 it moved progressively towards the more eutrophic lakes of the agricultural WCP and NGP ecoregions.
 - Upper Sahatah (shallow/flow-thru) diatom communities formed two major clusters in time, the first representing pre-European settlement and a second representing 20th century conditions. These two clusters were separated along a TP gradient, indicating that water quality was acutely impacted following initial land-clearance and has been gradually declining ever since. The DI-TP reconstruction closely follows this pattern with a gradual increase from 43 μg L⁻¹ to 117 μg L⁻¹, consistent with a historically mesotrophic system that has become hypereutorphic.
- 11. Phosphorus burial and diatom-inferred TP estimates from the Loon and Upper Sakatah long cores were combined to reconstruct external P loads in presettlement times, providing a baseline against which both current and TMDL-allowable loads were compared. These two contrasting lakes, one seepage and the other flow-thru, illustrate the likely range on conditions among the larger set of Cannon Watershed lakes. Their estimated presettlement P loads (58 and 5723 kg yr⁻¹) represent a fraction of total current P inputs, (0.16x and 0.13x, Loon and Upper Sakatah, respectively) and roughly half (0.5x and 0.6x) of TMDL allowable loads. Thus the magnitude of change in watershed P loads since presettlement times is upwards of 6-10x, while the target TMDL loads are roughly 2x higher than their presettlement baseline.

- 12. Despite uncertainty in estimated P fluxes from the TMDL modeling studies, the mass-balance framework provides a relative measure of recoverability from nutrient impairment. Most deep/seepage lakes (Cedar, Clear, Frances, French, Shields, and Volney) show a negative net-P flux (losses exceed inputs), suggesting that they are either at steady state or gradually depleting their inlake P burdens under present-day loading. This is especially so for those lakes with limited internal (unaccounted) loads including Cedar, Clear, Frances, and Volney, which are also among those in the study with the lowest water-column TP. The group of shallow/seepage lakes (Chub, Loon, and Toners) all show a negative or near-zero P mass balance, but also have a large unaccounted P load and high water-column TP, indicating a substantial internal P flux. Recoverability for this latter group will likely depend on the effectiveness of measures aimed at reducing internal P release.
- 13. The flow-thru lakes, both deep and shallow, with the exception of Fox, are high TP systems with large external P loads and outflow losses; P burial exceeds P outflow only in Fox and Roberds. Given the short residence time of these lakes, water column TP is largely a function of current-year loads (external and internal), and thus relatively insensitive to long-term sediment P burial. As a result, recovery of these lakes, especially those with large watersheds (Byllesby, Cannon, and Upper Sakatah) will be challenging.
- 14. Results from this study suggest that TMDL load reductions, if achievable, would substantially change P mass-balance in most Cannon Watershed lakes. Under reduced external loads, P burial, especially in seepage lakes, would sequester a larger fraction of P inputs, resulting in depletion of P stores in surface sediments and ultimately reduction of internal P loading. Considering the uncertainty in P budgets for most of the lakes, the timeframe for such responses is difficult to predict.
- 15. The results of this study, both the measurement of sediment P burial and the assessment of ecological condition, help constrain lake P budgets and place the nutrient-impaired lakes of the Cannon Watershed in a historical ecological context. What is needed at this point to improve the predictive power of nutrient reduction plans and their implementation is more systematic load monitoring and/or mechanistic watershed models to strengthen those parts of the nutrient budget.

Introduction

The Cannon River watershed in southeastern Minnesota contains 30 lakes that have phosphorus (P) levels exceeding state water-quality standards and are now on the EPA 303(d) list of impaired waters. A TMDL study completed by the MPCA (LimnoTech, 2016) identified P-load reductions needed to meet these standards, with the aim of developing restoration and protection strategies for subsequent implementation. Given the large number of lake-specific TMDLs in the watershed, uncertainties in modeled load reductions, and variability in lake characteristics, the question arises, what is the best allocation of implementation effort and what is the likelihood of success on a lake-by-lake basis? In some cases, small external load reductions could lead to rapid recovery, while in others, internal loading from legacy P in bottom sediments might overwhelm watershed restoration efforts for many years. Ideally, an accurate P mass balance would go a long way in addressing this question, but in reality internal loads are typically estimated by difference (model prediction vs. observed) and hence have substantial uncertainty. Another component of recovery that is seldom considered is the potential for internal loads to lag external load reductions. A decrease in internal loading ultimately depends on the gradual depletion or burial of P-rich surface sediments. Finally, there is natural variability among lakes in background trophic condition and the degree to which they have been altered by human perturbation. Some lakes may be naturally more productive than others or less sensitive to external P loads owing to differences in morphometry, hydrology, and watershed characteristics.

To help address these questions and better target restoration activities in the Cannon River watershed, we conducted a paleolimnological study of a selected set of the TMDL lakes with the dual aims of, (1) better constraining lake P budgets, and (2) determining the magnitude of ecological change experienced by a range of lake types.

To improve the accuracy and predictive power of lake P budgets, we measured whole-lake sediment Pburial and combined this flux with modeled estimates of watershed P loading and P losses in lake outflow from the TMDL study. Together these results quantify the degree to which external P inputs exceed losses (outflow + burial). The difference (inputs – losses) provides a direct estimate of load reductions needed to begin the recovery process and help confirm modeled load reductions derived from the TMDL study. This approach does not directly measure internal P loads, but it gives an assessment of those lakes in which inputs and losses are close to parity and hence more likely to respond to implementation of additional load-reduction strategies than lakes where external P loads far outstrip P losses. Ultimately, reductions in internal P loading depend on long-term burial of P-rich sediments – a function of overall sediment accumulation rates – as well as outflow losses.

Our second aim was to determine the magnitude and timing of ecological change in select TMDL lakes as measured by shifts in fossil algal (diatom) communities preserved in dated sediment cores. Lakes in which algal composition has changed little from pre-disturbance (pre-European settlement) conditions are likely better targets for remediation than lakes that have undergone wholesale shifts in biotic composition (Ramstack Hobbs et al., 2016). The rate and degree of ecological (diatom community) change are summarized for each lake by multivariate statistical methods and compared to a large database of diatom assemblages in Minnesota lakes to further place study lakes along a water-quality/ecological continuum.

Ultimately, the goal of restoration activities is the recovery of ecological health and beneficial uses of impaired water bodies. This study aids that process by gathering additional information from lake sediment records to better target restoration activities toward more "recoverable" lakes, thereby maximizing implementation resources and success.

Experimental Design

The primary aim of this project was to use paleolimnological analysis of dated sediment cores to constrain present-day lake phosphorus budgets and reconstruct changes in the lake condition over the last 150 years using multiple lines of evidence including geochemistry, sediment accumulation, and diatom remains as biological indicators. Because it would be cost-prohibitive to do detailed core analyses on all 30 TMDL lakes, a tiered approach was taken in which a subset of representative cores was examined in detail, augmented by a larger lake set in which only the more recent sediments were analyzed. Study lakes were chosen in consultation with MPCA staff and covered two environmental gradients likely important to lake response and recovery: lake depth and hydrological residence time. Depth is a strong determinant of lake stratification and P retention/release from bottom sediments, while residence time – itself a function of watershed area relative to lake volume – is directly related to external P loading and outflow losses. Thus we selected four lakes for detailed core study, one each representing shallow and deep flow-through lakes and shallow and deep "seepage" lakes (those with minimal inflows or outflows). The sediments from 12 additional lakes distributed among these four geomorphic categories were analyzed for present-day (the most recent ~ 10 years) P burial and diatom community composition. All told, 16 lakes were studied, 3 to 6 in each group. This strategy thus explores the P budgets of roughly half of the impaired lakes in the Cannon River Watershed and reconstructs ecological change over the last 150 years in a representative subset of four.

Phosphorus burial was determined from P concentrations and sediment accumulation rates in the uppermost 10 cm of short (~20 cm) cores collected from the central region of each lake. Using a lead-210 dilution technique recently developed by Hobbs et al. (2013) we were able to estimate whole-lake P burial from surface sediments collected from a single location in a lake basin. These burial rates were then combined with estimates of watershed P loads and Bathtub calculations of outflow P losses from the TMDL study (LimnoTech, 2016) to provide a closed P mass-balance for each lake in which all fluxes were independently determined.

Longer sediment cores (150-250 cm), collected from a single lake within each of the four geomorphic groups, were dated by radioisotopic methods and analyzed stratigraphically for sediment P concentrations and fossil diatom remains to reconstruct past changes in algal communities and P burial. Diatoms often make up the main type of algae in a lake, and therefore changes in diatom community structure are symptomatic of algal changes in response to water quality. Multivariate analyses, diatom-based transfer functions, and comparison of diatom assemblages with a data set of 89 Minnesota lake were used to relate changes in trophic conditions and diatom communities to human impacts in the local watershed. In the state of Minnesota, diatom analysis has been used as one line of evidence for developing nutrient criteria (Heiskary and Wilson, 2008), lake-specific nutrient standards (Edlund and Ramstack, 2007), and prioritizing management actions (Edlund et al., 2008).

Study Sites

The 30 nutrient-impaired lakes in the Cannon River watershed were classified as either deep (maximum depth, $Z_{max} > 5$ m) or shallow ($Z_{max} < 5$ m) and Seepage (watershed/lake area (W/L) < 10) or Flow-thru (W/L > 10). Of the 16 lakes ultimately chosen for study, six were in the Deep/Seepage (DS) group, three in the Shallow/Seepage (SS) group, three Deep/Flow-thru (DF), and four Shallow/Flow-thru (SF) (Table 1). The lakes were roughly similar in size (281 ± 162 ha; mean ± s.d.), ranging from ~50 ha for two small lakes (Loon and Toner's; ~ 50 ha) to ~600 ha for two large reservoirs (Byllesby and Cannon). Lake residence time varied predictably by group, longest in DS lakes (mean = 6.4 yr), intermediate in SS lakes (mean = 2.7 yr), and shortest in DF (1.0 yr) and SF (0.2 yr) lakes. Lakewater total-P concentrations followed a similar trend (mean DF = 121, DS, SS = 187, SF = 418 µg L⁻¹), reflecting the influence of watershed size on P loads and lake nutrient conditions. The four lakes selected for long-core paleolimnological study were Frances (DS), Loon (SS), Roberds (DF), and Upper Sakatah (SF).

Name	Lake #	Lake Type	Core Site Lat °N	Core Site Long °W	Water -shed (km ²)	Lake Area (km ²)	W/L	Res. time (yr)	Mean Depth (m)	Max Depth (m)	TP (ppb)
Cedar	66005200	DS	44.29607	93.42658	18.2	3.75	4.9	4.52	2.8	12.8	50
Clear	81001401	DS	44.09050	93.48321	7.9	2.62	3.0	7.70	3.0	7.6	80
Frances*	40005700	DS	44.21029	93.70417	16.6	3.52	4.7	9.90	5.0	18.3	85
French	66003800	DS	44.33416	93.39195	16.6	3.41	4.9	10.20	5.0	15.4	157
Shields	66005500	DS	44.37380	93.44315	27.8	3.55	7.8	2.63	3.1	9.4	293
Volney	40003300	DS	44.36972	93.36402	8.2	1.12	7.3	7.00	6.5	19.8	63
Chub	19002000	SS	44.55642	93.22002	6.0	1.22	4.9	1.50	1.0	2.9	173
Loon*	81001500	SS	44.08097	93.52036	1.9	0.48	3.9	3.80	1.0	2.4	210
Toner's	81005800	SS	44.16372	93.59686	1.2	0.51	2.3	2.90	1.0		178
Byllesby	19000600	DF	44.51740	92.96551	2968	5.58	531	0.10	3.2	15.2	236
Fox	66002900	DF	44.39208	93.32632	34	1.26	27	1.29	5.9	14.0	59
Roberds*	66001800	DF	44.32555	93.44400	37	2.65	14	1.58	3.1	11.6	266
Cannon	66000800	SF	44.26912	93.35083	766	5.97	128	0.10	2.5	4.6	310
Circle	66002700	SF	44.41837	93.34555	83	3.39	24	0.37	1.0	4.3	330
Gorman	40003200	SF	44.39650	93.66491	170	2.39	71	0.14	2.1	4.3	790
U Sakatah*	40000200	SF	44.22380	93.54954	534	3.57	150	0.10	1.0	3.0	242

Table 1. Physical characteristics of the study lakes

DS = deep/seepage, SS = shallow/seepage, DF = deep/flow-thru, SF = shallow/flow-thru * long-core lakes

Methods

Core Collection

Sediment cores (~150 cm in length) were collected from the four long-core study lakes on October 19-20, 2017 by means of a surface piston corer operated from the lake surface (boat) by rigid Mg-alloy drive rods. A second deeper but overlapping core of the roughly same length was collected at Roberds Lake where field observations suggested that the surface core would not be sufficiently long to encompass the historical period of interest (~200 years). Analyses from these two cores were subsequently integrated into a single continuous record. The cores were maintained in vertical position and sectioned in the field to a depth of ~24 cm, and then capped and returned to the lab to complete the sectioning. The cores were sectioned at 1-cm intervals to a depth of 15 cm and then at 2-cm intervals below that. Short sediment cores were collected from the frozen surface of the remaining 12 study lakes on March 8-9, 2018 using a HTH gravity corer (Pylonex, Sweden). The cores were immediately sectioned on site into two integrated intervals (0-5 and 5-10 cm). All samples were stored under refrigeration in polypropylene jars pending analysis.

Loss-on-Ignition

Dry-density (dry mass per volume of fresh sediment), water content, organic content, and carbonate content of the sediments were determined by standard loss-on-ignition techniques (Dean, 1974). Sediment samples of 1-2 g were dried overnight at 100° C and ignited at 550° and 1000° C for 1 hr each. Mass measurements were made of the wet samples and after each heating on an electronic analytical balance. Dry density was calculated from water content and fixed densities for organic, carbonate, and inorganic fractions.

Radiometric Dating

The four long cores were analyzed for 210 Pb activity to determine age and sediment accumulation rates for the past ~150 years. Lead-210 was measured at 13-21 depth intervals in each core through its grand-

daughter product ²¹⁰Po, with ²⁰⁹Po added as an internal yield tracer. The polonium isotopes were distilled from 0.5-1.0 g freeze-dried sediment at 550° C following pretreatment with concentrated HCl and plated directly onto silver planchets from a 0.5 M HCl solution (Eakins and Morrison, 1978). Activity was measured for 1-8 days on an Ortec alpha spectroscopy system. Unsupported ²¹⁰Pb was calculated by subtracting supported activity from the total activity measured at each level; supported ²¹⁰Pb 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 c.r.s. (constant rate of supply) model (Appleby, 2001) with errors calculated by first-order propagation of counting uncertainty. Core-specific sediment accumulation rates were corrected for sediment focusing (the redistribution of fine-grained sediments by wave and current action) to derive a whole-lake average flux using the method of (Engstrom and Rose, 2013). In this approach core-specific accumulation rates are multiplied by a "focusing factor" – the ratio of ²¹⁰Pb flux in a core to that in atmospheric deposition (0.49 pCi cm⁻² yr⁻¹ for southern Minnesota) (Lamborg et al., 2012).

For cores with problematic activity profiles (Roberds and Loon), gamma spectrometry was used to measure supported ²¹⁰Pb (as ²¹⁴Pb) and the fallout radionuclide, ¹³⁷Cs, to identify sediments deposited during the 1963-64 peak in atmospheric nuclear testing. Freeze-dried sediments (~ 5 cm³) were packed into 1-cm polycarbonate tubes, sealed with epoxy resin, and measured using an Ortec-EGG germanium well, photon detector coupled to a digital gamma-ray spectrometer (Dspec). The instruments were calibrated using a suite of analytical grade radioisotope standards encompassing a range of gamma emission energies from 46 kev to 1460 kev.

Sediment and total-P accumulation rates were calculated for the 12 short-core surface samples according to an atmospheric ²¹⁰Pb dilution model developed by Hobbs et al. (2013). This method uses the ratio of decay-corrected ²¹⁰Pb activity in the uppermost (last ~10 years) of sediment to the atmospheric flux of ²¹⁰Pb (0.49 pCi cm⁻² yr⁻¹) to calculate whole-lake accumulation rates for fine-grained sediments and constituents of similar density (e.g. organic matter) that deposit together in the basin. Thus for total-P,

$$F(P_b) = [P_s] / [^{210}Pb_s] \bullet F(^{210}Pb_{atm})$$
(Eq. 1)

The whole-lake burial flux $F(P_b)$ is equal to the concentration of total-P in the surface sediment $[P_s]$, divided by the ²¹⁰Pb activity in the surface sediments $[^{210}Pb_s]$, multiplied by the atmospheric flux of ²¹⁰Pb for the region $F(^{210}Pb_{atm})$. See Hobbs et al. (2013) for the derivation and assumptions of this model.

Sediment Phosphorus

Eight core increments from each of the four long cores and two increments from each of the 12 surface cores were analyzed for total sediment phosphorus following procedures in Engstrom (2005) and Engstrom and Wright (1984). Sediments were sequentially digested in 30% hydrogen peroxide (1 hr at 85° C), followed by 0.5 M HCl (0.5 hr 85° C) and the extract analyzed colorimetrically on a Unity Scientific SmartChem 170 Autoanalyzer. Sedimentation rates were then used to convert the measured sediment P concentrations in the core to P accumulation (burial).

Diatom Analysis

A total of eight increments from each of the long cores and a single surface increment from each of the 12 short cores were analyzed for diatom microfossils; six of the samples were concentrated in the upper part of the core representing about the last 120 years (ca. 20-year resolution). The remaining two samples were taken at core intervals representing pre-European settlement conditions (pre-1860). Samples were digested to remove carbonates and organic matter, dried onto microscope coverslips, and the coverslips mounted on micro slides using Naphrax. Diatoms were identified to species level using light microscopy with full immersion optics capable of 1200X magnification at an N.A. of 1.3. Initially diatoms were documented using a Q-Imaging 5.5 Megapixel camera to construct an in-house voucher flora. A

minimum of 400 valves were counted in each sample. Identifications were taxonomically verified with modern nomenclature using the Diatoms of North America website (<u>https://diatoms.org//</u>), Fallu et al. (2000) and Reavie and Kireta (2015). Chrysophyte microfossils were also enumerated and included in ecological interpretation.

Diatom assemblage data were condensed using canonical correspondence analysis (CCA) in order to track long-term reorganization of the assemblages and similarity in assemblages among lakes. CCA, as implemented in the R package "vegan" (Oksanen et al., 2013) compared sample assemblages based on chi-square distance along constrained environmental gradients (e.g., TP, pH). Analyses were performed on all cores and surface samples and contextualized via passive ordination by projecting these samples onto a previously published 89-lake training set (Ramstack et al., 2003) that spans all of Minnesota's ecoregions and lake-types.

Epilimnetic total phosphorus (TP) was reconstructed from fossil diatom assemblages using a diatomphosphorus calibration model, developed by Ramstack et al. (2003) and others from a suite of 89 Minnesota Lakes. We note that in hypereutrophic and shallow lakes, TP reconstructions can be problematic (Juggins, 2013), and are here considered only in relative terms, comparing trends over time and differences among lakes.

Phosphorus Mass-Balance

A simple mass balance was constructed for each of the study lakes in which watershed P loads (P_w) were compared with P losses in outflow (P_o) and sediment burial (P_b),

$$P_{w} = P_{o} + P_{b} + P_{net}$$
(Eq. 2)

where P_{net} is the difference between P inputs and losses on an annual or multi-year basis. Conditions under which inputs exceed losses increase the sediment P burden ($P_{net} > 0$) and those in which losses are greater than inputs ($P_{net} < 0$) decrease the sediment P burden. In this construction internal P loading is balanced by a return flux to the sediments plus any contribution to outflow or changes in P mass within the lake. On a annualized time-step, changes in lake P mass are assumed to be negligible, though in reality lake P concentrations can vary considerably between years. The primary outcome of this model construct is the determination of whether the P budget of the lake is at steady state or whether sediment P is being enriched or depleted under current loading. A large negative P_{net} would indicate a system in which water-quality might be expected to improve as sediment P concentrations – and associated internal loading – decrease over time, while declining water quality (or no improvement) would be expected if P_{net} was large and positive.

To complete this P mass balance for the Cannon area lakes, external (watershed) P loads and outflow losses were compiled from recently completed TMDL studies, including LimnoTech (2016, and associated internal files), Heiskary and Martin (2015), MSU Mankato (2016), and Pallardy et al. (2014). In these studies watershed P loads and outflows were largely modeled using runoff and P-export coefficients, with limited calibration to stream monitoring data, except in a few cases (Clear, Volney). The modeling software BATHUB was used to link external P loads with in-lake water quality (seasonal water-column TP) and estimate internal (unaccounted) P loads. By balancing outflow plus in-lake retention with total inputs (external + internal loads), BATHTUB calculations assume a long-term steady state with no net change in sediment P burial. But over the long-term sediments permanently bury a sizeable fraction of external P inputs, and changes in that burial are diagnostic of changing water quality over time.

Results & Discussion

Dating and Sediment Accumulation

The depth profiles of ²¹⁰Pb in the four long cores exhibit relatively uniform activity in the upper 3-4 measured intervals, followed by a roughly monotonic decline with depth to near constant (supported) values at depths ranging from 80 to 100 cm in Frances, Loon, and Upper Sakatah (Fig. 1). Despite the collection of an additional meter of sediment, the Roberds core did not reach supported background, even in the bottom sample at 240 cm, so that supported ²¹⁰Pb was instead determined by the gamma analysis of ²¹⁴Pb. In addition, because of the truncated profile, the chronology for Roberds could not be modeled directly, but rather had to be fitted to a known date (1963 at 160 cm) determined independently by ¹³⁷Cs dating (Fig. 1). Cesium dating was also completed for the Loon Lake core, where the 1963 peak was found at 50 cm. The ²¹⁰Pb date determined for this core interval (1971), although too young by 8 years, represents acceptable accuracy for sediment records from lakes with high and variable sedimentation rates such as Loon. Additional confirmation of the ²¹⁰Pb dating is provided by loss-on-ignition results, which show a sharp up-core increase in inorganic matter at depths dated to the onset of EuroAmerican settlement in the Cannon River watershed (1860-1880). This change in lithology is most obvious in Loon (97 cm) and Upper Sakatah (83 cm), but less so in Frances (63 cm) and absent in Roberds, which does not reach this far back in time (Fig. 2).



Figure 1. Radiometric dating results for the four long-core study sites. Error bars represent ± 1 s.d.

Lake	Unsup. ²¹⁰ Pb at Surface (pCi g ⁻¹)	Support. ²¹⁰ Pb (pCi g⁻¹)	No. of Support. Intervals	²¹⁰ Pb Flux (pCi cm ⁻² yr ⁻¹)	Focus Factor	Mass Sed. Rate since 2000 (kg m ⁻² yr ⁻¹)	Linear Rate since 2000 (mm yr ⁻¹)	Oldest Date	Depth of ¹³⁷ Cs Peak (cm)
Frances	10.52	0.74	4	1.07	2.18	0.81	5.7	1844	n/a
Loon	6.20	0.46	4	2.05	4.18	1.83	19.1	1853	49-51
Roberds	8.65	1.06	²¹⁴ Pb	3.80	7.76	3.36	35.8	1910	159-161
U Sakatah	4.78	0.58	3	0.86	1.76	1.58	6.4	1839	n/a

Table 2. Lead-210 dating parameters for long-core lakes

Sediment accumulation rates increased over time in all four lakes, beginning in the late 1800s and accelerated during the first half of the 20th century, then declined slightly around 1980 and rebounded in the last two decades (Fig. 1). The magnitude of change from background to peak rates is ~3x, though the absolute rates vary considerably among the four lakes, ranging from 0.8 to 3.4 kg m⁻² yr⁻¹ (2000 to present) between Frances and Roberds (Table 2). Much of the among-lake variation can be attributed to differences in sediment focusing, as is manifest in the ²¹⁰Pb fluxes measured in the cores. Because ²¹⁰Pb inputs to lakes are largely atmospheric and relatively constant over time, we can correct for sediment focusing using the ratio of ²¹⁰Pb flux in the core to that measured in atmospheric deposition (0.49 pCi cm⁻² yr⁻¹ for southern Minnesota) (Lamborg et al., 2012). These focusing corrections (focus factors) range

from ~2 in France and Upper Sakatah to nearly 8 in Roberds (Table 2) and when applied to the core-specific rates yield highly similar (whole-lake) accumulation rates of 0.37-0.44 kg m⁻² yr⁻¹ in Frances, Loon, and Roberds, but about twice that 0.90 kg m⁻² yr⁻¹) in Upper Sakatah. The extreme sediment focusing observed in Roberds is a consequence of basin morphometry; the lake is mostly quite shallow with a small deep hole (where the core was taken) that collects and traps sediments resuspended by wave and current action (and possibly carp) in littoral areas.

The short gravity cores from the 12 other lakes capture only the last 10-20 years of sediment accumulation, which is sufficient to determine recent rates of sediment P burial using a ²¹⁰Pb dilution model, as described in the methods section. This approach relies on the fact that ²¹⁰Pb inputs to lakes are largely atmospheric and regionally uniform, such that the concentration (activity) of ²¹⁰Pb in surface sediments is inversely proportional to rate of sediment accumulation. Most critical for this study is that the derived sediment (or P) accumulation rates are mean (whole-lake) values, numerically corrected for focusing.



Figure 2. Loss-on-ignition profiles for long-core sites

Lake	Total ²¹⁰ Pb (pCi g⁻ ¹)	²¹⁴ Pb (pCi g ⁻¹)	Decay Correct Excess ²¹⁰ Pb (pCi g ⁻¹)	DMAR (kg m ⁻² yr ⁻¹)	Total-P (mg/g)	Areal P Flux (g m ⁻² yr ⁻¹)	Lake Area (ha)	P Burial (Mg/lake)
Cedar	11.27	0.96	12.05	0.41	1.33	0.54	375	2.03
Clear	11.90	0.88	12.88	0.38	1.46	0.56	262	1.46
French	10.37	0.82	11.16	0.44	1.52	0.67	341	2.27
Shields	11.15	1.27	11.54	0.42	1.94	0.82	355	2.93
Volney	5.75	0.85	5.73	0.86	0.93	0.80	112	0.89
Chub	9.05	0.75	9.70	0.51	1.43	0.72	122	0.88
Toner's	8.76	0.66	9.46	0.52	1.35	0.70	51	0.36
Byllesby	3.65	1.36	2.67	1.83	1.34	2.45	558	13.70
Fox	6.13	0.88	6.13	0.80	1.16	0.92	126	1.16
Cannon	4.51	0.82	4.31	1.14	1.11	1.27	597	7.56
Circle	6.45	0.90	6.49	0.76	0.95	0.72	339	2.43
Gorman	5.39	1.05	5.07	0.97	1.97	1.90	239	4.54

Table 3. Lead-210 parameters and P burial calculations for surface-core sites

For the 12 lakes in this part of the study, total ²¹⁰Pb in the upper ~ 10 years of sediment ranges from 3.65 to 11.65 pCi/g. Subtracting supported $(background)^{210}Pb - measured as^{214}Pb$ by gamma spectrometry – and correcting for decay (10 years or approximately 0.5 half-life) yields excess (unsupported) ²¹⁰Pb ranging from 2.67 to 12.88 pCi/g (Table 3). The resulting dry mass accumulation rate (DMAR) ranges from 0.38 to 1.83 kg m⁻² yr⁻¹, inverse to the core-site 210 Pb activity. The highest DMAR are in the two large-river reservoirs, Byllesby and Cannon, and lowest in the seepage lakes (0.54 ± 0.16) kg m⁻² yr⁻¹), both deep (Cedar, Clear, French, Shields, Volney) and shallow (Chub, Toners) – a pattern reflecting the effect of watershed size on sediment delivery to lakes.

Phosphorus Burial

Total-P concentrations in the four long cores range from 0.7 to 3.4 mg g⁻¹ dry sediment, and are generally higher in the most recent sediments, but not in all cases (Fig. 3). In both Frances and Upper Sakatah P concentrations are equal to or higher at depth than at the surface and are lowest during the mid-1900s. The Roberds cores suggests a similar trend, but is truncated at ~1900



Figure 3. Total-P concentration and accumulation profiles for the four long-core sites.

and missing the older part of the record. This mid-core decline in P concentration is the result of dilution from an increased flux of sediment, principally inorganic matter from accelerated soil erosion following EuroAmerican settlement (Fig. 2). P inputs actually increase during this period in all lakes, as evident in the profiles for P flux (the product of P concentrations and DMAR) (Fig. 3). All four cores also show a sharp peak in both P concentration and flux in the top-most core interval (0-2 cm). This surface peak, a common feature of lake-sediment profiles, results from dissolution and up-core diffusion of P in sediment pore-waters as well as redox cycling of P into the water column (internal loading) and redeposition in algal biomass or inorganic precipitates. The result is a P-enriched surface layer that does not reflect longterm P burial, but rather moves upward as sediments accumulate over time. Excluding these surface peaks, the overall increase in P accumulation from presettlement times to the present ranges from 1.5x in Upper Sakatah to 3.5x in Loon (Fig 3).



Figure 4. Total-P concentrations in the upper two sediment intervals (0-5 and 5-10 cm) of the surface-core sites

P concentrations in the 12 gravity cores span a relatively narrow range (0.9-2.3 mg g^{-1}) in both the surface (0-5 cm) and subsurface (5-10 cm) intervals, and similar to the long cores, surface P concentrations are consistently higher than immediately below (Fig. 4). This surface enrichment is less obvious than in the long cores because the surface samples integrate deeper sediments (5 vs. 2 cm) with lower P content.

Long-term P burial rates were calculated for each lake using P concentration and DMAR in the subsurface intervals – 5-10 cm in the gravity cores and the penultimate interval (corresponding to ~1997) in the long cores. On a watershed areal basis these rates range from 2.9 to 24.3 kg ha⁻¹ yr⁻¹ and are systematically higher in the flow-thru lakes with larger watersheds (Byllesby, Gorman, Cannon) (Table 4). However, Upper Sakatah with the 3rd largest watershed but a modest burial flux of 5.8 kg ha⁻¹ yr⁻¹, is an outlier in this regard. The seepage lakes, shallow and deep together, show a fairly narrow range of P burial rates (6.1 ± 1.9 kg ha⁻¹ yr⁻¹). Expressed on a whole-lake basis, the study lakes sequestered in their sediments between 0.17 and 13.7 Mg (10^3 kg; metric tons) of P annually (Fig. 5, Table 4).

	Lake External		Unaccount (Internal)	Total	Out-		Net Flux (External	Net Flux (External +50%	Internal P Release
Name	Туре	Load	load	Load	flow	Burial	only)	Unaccount)	(mg m⁺ d⁺')
Fluxes in kg ha ⁻¹ yr ⁻¹									
Cedar	DS	3.00	-	3.00	0.29	5.42	-2.72	-2.72	-
Clear	DS	2.08	1.73	3.81	0.12	5.57	-3.62	-2.75	0.52
Frances*	DS	0.95	5.52	6.48	0.13	2.93	-2.10	0.66	1.51
French	DS	3.01	19.35	22.36	0.82	6.68	-4.48	5.19	5.00
Shields	DS	6.44	31.70	38.14	3.27	8.24	-5.07	10.78	8.00
Volney	DS	7.21	-	7.21	0.89	7.97	-1.65	-1.65	-
Chub	SS	0.96	5.31	6.27	0.93	7.22	-7.18	-4.53	1.45
Loon*	SS	2.87	4.69	7.56	0.81	3.47	-1.41	0.93	1.45
Toner's	SS	1.46	4.20	5.66	0.41	7.00	-5.95	-3.85	1.15
Byllesby (low flow) ¹	DF	255.52	-	255.52	179.81	24.53	51.18	51.18	-
Byllesby (high flow) ²	DF	408.14	_	408.14	281.57	24.53	102.04	102.04	_
Fox	DF	14.12	_	14.12	2.90	9.24	1.97	1.97	_
Roberds*	DF	7.08	28.93	36.00	4.79	10.90	-8.61	5.85	8.00
Cannon	SF	28.92	102.85	131.77	68.10	12.65	-51.84	-0.41	28.60
Circle	SF	11.58	32.87	44.46	13.56	7.17	-9.14	7.30	9.00
Gorman	SF	48.65	64.56	113.20	100.80	19.00	-71.15	-38.88	20.00
Upper Sakatah*	SF	85.50	73.91	159.42	32.87	5.78	46.85	83.80	20.25
									Unaccount
Codor	De	1 1 2		1 1 2	0.11	2.04	1.02	1 0 2	Luau (76)
Clear	03	0.55	-	1.12	0.11	2.04	-1.02	-1.02	
Ciedi Eronooo*	03	0.00	1.05	1.00	0.03	1.40	-0.95	-0.72	40
Frances	03	1.03	1.95	2.20	0.00	1.00	-0.74	0.23	83 87
Shiolds	03	2.00	11.25	13.54	0.20	2.20	-1.55	1.77	82
Volney	03	0.81	11.25	0.81	0.10	2.95	-1.00	0.10	00
Chub	50	0.01	0.65	0.01	0.10	0.09	-0.19	-0.19	85
Loon*	20	0.12	0.00	0.70	0.11	0.00	-0.00	-0.05	62
Toper's	20	0.14	0.23	0.00	0.04	0.17	-0.07	-0.20	74
Dyllooby (low flow) ¹		140.00	0.22	140.20	100.02	12 70	-0.01	-0.20	74
Byliesby (low llow)		142.70	-	142.70	100.42	13.70	20.00	20.00	-
Byllesby (high flow) ²	DF	227.93	-	227.93	157.25	13.70	56.98	56.98	-
Fox	DF	1.78	_	1.78	0.37	1.17	0.25	0.25	_
Roberds*	DF	1.87	7.66	9.53	1.27	2.89	-2.28	1.55	80
Cannon	SF	17.27	61.44	78.71	40.68	7.56	-30.96	-0.25	78
Circle	SF	3.93	11.14	15.07	4.60	2.43	-3.10	2.47	74
Gorman	SF	11.62	15.41	27.03	24.07	4.54	-16.99	-9.28	57
Upper Sakatah*	SF	30.48	26.35	56.84	11.72	2.06	16.70	29.88	46

Table 4. Total-P mass balances for the Cannon study lakes normalized to watershed area (yields) and on a whole-lake basis.

¹lower-flow conditions (2003 reference year) ²higher-flow conditions (2002 reference year)



Figure 5. Total-P mass balance for the study lakes on a whole-lake basis. Net flux (inputs - losses) based on two load estimates (external load only and external + 50% Unaccounted). Only the high-flow scenario (Table 4) is shown for Byllesby.

Phosphorus Mass-balance

External P inputs compiled from TMDL reports for the Cannon Watershed lakes vary by more than two orders of magnitude, with lowest values in the shallow seepage lakes (0.08-2.3 Mg yr⁻¹) and highest in the flow-through lakes, both shallow (3.9-30.5 Mg yr⁻¹) and deep (1.8-228 Mg yr⁻¹) (Fig. 5, Table 4). This pattern reflects, in part, watershed size (smaller in seepage, larger in flow-thru), but even when normalized for watershed area, external P yields are systematically higher in the flow-through systems (mean \pm s.d. = 3.1 \pm 1.3 kg ha yr⁻¹ in seepage vs. 107 \pm 146 kg ha yr⁻¹ in flow-thru).

In most cases, the TMDL BATHTUB models underestimated measured lake-water TP, and for a number of lakes, the resulting "unaccounted" load needed to fit the observed data was quite large, ranging from 46% to 87% of total P inputs (Table 4). Although the unaccounted loads were cautiously attributed to internal loading, the required loading rates for several of the lakes greatly exceeded experimentally measured rates of sediment P release: $> 20 \text{ mg m}^{-2} \text{ day}^{-1}$ in three of the shallow, flow-thru lakes (Cannon, Gorman, Upper Sakatah) and $> 8 \text{ mg m}^{-2} \text{ day}^{-1}$ in three others (Shields, Roberds, and Circle) (Table 4). Thus it seems likely that a portion of the unaccounted P loads represents an underestimate of external loads. Given this uncertainty, we used a second estimate of external P loading in our mass balance calculations, one that included 50% of the unaccounted (internal) P load. The two estimates of P loading (external only and external + 50% unaccounted) are assumed here to bracket the actual range of annual, external TP inputs. Four of the study lakes (Cedar, Volney, Byllesby, and Fox) had no unaccounted load, and thus have a single estimate of external TP inputs.

Total-P losses in lake outflow, also compiled from TMDL calculations, range from 0.021 to 1.16 Mg yr⁻¹ in the seepage lakes and 0.37 to 157 Mg yr⁻¹ in the flow-thru lakes (Table 4). As would be expected, outflow-P losses are dependent on lake hydrology and thus strongly correlated with watershed area (r = 0.99) (Table 5). However, for seepage lakes only (both shallow and deep) there is also a strong relationship of outflow P with lake-water TP (r = 0.69). Among seepage lakes, P burial consistently outweighs P outflow as the main loss vector, averaging 89% of total P removal, while among flow-through lakes where P-outflow averages 66% of total P loss, the reverse is largely true (Fig. 5).

		Watershed Area	Lake Area	W/L	Lake TP
All Lakes	External	0.98	0.51	0.98	0.08
	Burial	0.93	0.75	0.91	0.32
	Outflow	0.99	0.59	0.98	0.19
	Net (External only)	0.74	0.18	0.75	-0.23
	Net (Ext +50% Int)	0.89	0.49	0.91	-0.07
Seepage Lakes					_
	External	0.88	0.65	0.73	0.33
	Burial	0.91	0.84	0.54	0.18
	Outflow	0.76	0.43	0.68	0.69
	Net (External only)	-0.83	-0.80	-0.38	-0.31
	Net (Ext +50% Int)	0.68	0.39	0.58	0.73

Table 5. Correlation of mass-balance loads with lake and watershed areas and lake-water TP

The net P flux from our constructed mass balance ranges from a large excess (positive) load of 57 Mg yr⁻¹ in the Byllesby Reservoir (high-flow year) to a large loss (negative) load in Cannon and Gorman (-31 and -17 Mg yr⁻¹, respectively) (Fig. 5, Table 4). Six of the study lakes (Cedar, Clear, Volney, Chub, Toner's, and Gorman) show a consistent negative P net using either estimate of external load, while three (Byllesby, Fox, Upper Sakatah) show a consistently positive P net, though in some cases (Volney, Toner's, Fox) the difference from net-zero is small. The seven remaining lakes (Frances, French, Shields,

Loon, Roberds, Cannon, and Circle) exhibit a negative P net using the minimum estimate for external P load and a positive (or near zero) P net using the larger estimate of P load (external + 50% unaccounted).

As a group, the seepage lakes (both deep and shallow) tended toward a negative P mass balance while the flow-thru lakes, especially the deep group, tended toward a positive P mass balance. Some of the difference among lakes and groups can be explained by the higher external P loads to lakes with larger watersheds. Among all lakes, net P flux was positively correlated with watershed area, using either external P inputs alone (r = 0.74) or external + 50% unaccounted P (r = 0.89) (Table 5). However, these relationships are strongly influenced by the outsized watershed of the Byllesby Reservoir, the removal of which lowers the correlations (Pearson's r) to ~0.4. Moreover, when only seepage lakes are considered, the relationship between P net and watershed area becomes strongly negative (r = -0.83, assuming external P loads only) (Table 5). Lake-water TP, which might be expected to contribute to the P mass balance, is only strongly correlated with net P in seepage lakes (r = 0.73, assuming external + 50% unaccounted P loads).

To correct for the large range in P loads among lakes, net P flux can be expressed as a fraction of total P inputs, thereby normalizing P loss or gain to the overall P mass balance (Fig. 6). In this representation, five lakes stand out as having a consistently strong negative P flux (Cedar, Clear, Chub, Toner's, and Gorman), while Volney is only slightly negative. Of the lakes with consistently positive P net (Byllesby, Fox, and Upper Sakatah), the difference from net zero is relatively small (<50% of inputs) owing to





comparatively large losses (outflow + burial), especially in Byllesby and Upper Sakatah. The remaining seven lakes have either strongly negative P net or modestly positive P net, depending on assumed external load (external only or external + 50% unaccounted).

TMDL Mass Balance

The outcome of TMDL P-load reductions can be explored using the same mass-balance framework, substituting allowable TP loads and lake-water TP goals for those under current conditions. Allowable loads in this exercise were based on BATHUB modeled load reductions (LimnoTech, 2016) required to meet ecoregion or site-specific water quality standards and represent a decrease from current TP loads of 32%-96% (Fig. 7, Table 6). External loads were adjusted here by the same percentage, assuming a proportional change in both tributary and unaccounted inputs. Finally, outflow losses were adjusted based on the proportional reduction in lake-water TP from current conditions to those under TMDL goals, assuming no change in watershed hydrology or flows (Fig. 7). This is likely an over-simplification owing to differences in the seasonality of lake-water TP under modeled scenarios, but serves to illustrate the consequences of TMDL load reduction on sediment P burial.

The TMDL load reductions, if implemented, would initially result in a strongly negative P mass-balance (losses >> inputs) for all the study lakes, but the resulting decline in lake-water P would ultimately lower outflow losses and decrease P burial rates. Assuming steady-state future conditions under TMDL allowable loads, P burial rates calculated by difference (TMDL external inputs minus TMDL outflow losses) would decline by 40% to 90% from current conditions for all but three flow-thru lakes, Byllesby, Gorman, and Upper Sakatah (Fig. 7, Table 6). For Gorman, P-burial would be reduced to near zero (-67 kg yr⁻¹), while it would actually increase by 130% in Byllesby (high-flow conditions) and 190% in Upper Sakatah.

Name	Lake Type	Current Lake TP (ppb)	TMDL Goal Lake TP (ppb)	TMDL Allowable Load	% Load Reduction	TMDL External Load	TMDL Outflow	TMDL Burial	% ∆ Burial
Cedar	DS	50	40	0.70	38	0.70	0.09	0.62	-70
Clear	DS	80	65	0.68	32	0.37	0.03	0.66	-55
Frances*	DS	85	40	0.49	78	0.07	0.02	0.47	-54
French	DS	157	40	0.58	92	0.08	0.07	0.51	-78
Shields	DS	293	40	0.57	96	0.10	0.16	0.41	-86
Volney	DS	63	40	0.33	60	0.33	0.06	0.26	-71
Chub	SS	173	60	0.12	84	0.02	0.04	0.08	-90
Loon*	SS	210	90	0.11	69	0.04	0.02	0.10	-43
Toner's	SS	178	60	0.04	87	0.01	0.01	0.03	-91
Byllesby (low flow) ¹	DF	236	90	54.19	62	54.19	38.30	15.89	16
Byllesby (high flow) ²	DF	236	90	91.52	60	91.52	59.97	31.55	130
Fox	DF	59	40	0.74	58	0.74	0.25	0.49	-58
Roberds*	DF	266	40	0.50	95	0.10	0.19	0.31	-89
Cannon	SF	310	60	9.60	88	2.11	7.86	1.74	-77
Circle	SF	330	60	1.39	91	0.36	0.84	0.55	-77
Gorman	SF	790	60	1.76	93	0.76	1.83	-0.07	-101
Upper Sakatah*	SF	242	60	8.92	84	4.79	2.91	6.02	192

Table 6. Total-P mass balance under TMDL allowable loads and lake TP goals

Fluxes in Mg yr⁻¹



Figure 7. Total-P mass balance for the study lakes under TMDL load reductions on a whole-lake basis. Burial is the difference between the TMDL allowable load and outflow under TMDL lake-water TP goals; the change in burial is the percentage difference between current and TMDL burial estimates.

The question is, whether these scenarios represent reasonable future conditions or, alternatively, large errors in the underlying BATHTUB models and lake P budgets. Clearly, a complete cessation (Gorman) or a near-doubling (Upper Sakatah) of P burial points to problems with estimated fluxes in the P mass balance and/or TMDL projections. For Byllesby and Upper Sakatah the modeled increase in P burial under TMDL load reductions is a numerical consequence of the small fraction of external P load that is buried under current conditions (6-7%). That is, small errors in inflow or outflow estimates, under current or TMDL conditions, would produce large errors in burial estimates under TMDL projections. In the case of Gorman, the large change in lake-water TP (from 790 to 60 ppb) has a similar destabilizing effect on outflow and P-burial estimates under TMDL conditions.

But what about the remaining 13 lakes with reductions of 40% to 90% in P burial; are those numbers reasonable or even attainable by historical standards? The sediment records from the four long cores (Frances, Loon, Roberds, and Upper Sakatah) indicate an increase in P burial of 1.5-3.7x between presettlement and recent times (Fig. 3). A similar increase (~3.5x) was reported from an earlier paleolimnology study of Lake Volney (Umbanhowar Jr. et al., 2003). Working backwards, this change would represent a decrease in P burial of 35-73% from current conditions to pre-settlement background. Assuming these five lakes are representative of the region, it would seem that the TMDL scenarios are largely reasonable with respect to measured rates of P burial.

Model Uncertainty

This mass-balance analysis is based largely on modeled data with all the uncertainty attendant of such estimates. Except for two lakes (Clear and Volney), external P loads were estimated using P-export coefficients with only limited stream load-monitoring to calibrate model output, and many lakes required substantial internal loads to balance measured values of lake-water TP. The TMDL reports from which these data are derived clearly recognize the limitations of such estimates and recommend follow-up monitoring and more mechanistic modeling (HSPF, SWAT) to better constrain P budgets and identify priority pollutant sources going forward. There is also uncertainty in the measured P-burial rates from this study, although the approach and analytical tools have been well-validated by comparison to multi-core, whole-lake measures of sediment burial (Hobbs et al., 2013).

Although we cannot validate these mass-balance calculations with independent data, it is possible to look for internal consistency with observable characteristics of the study lakes. For example, seepage lakes with long residence times tend to be effective traps for influent P loads owing to minimal outflows and efficient sediment burial. In the case of Lake Volney, monitoring and sediment-core studies indicate that the lake retains in excess of 90% of the influent P load (Pallardy et al., 2014; Umbanhowar Jr. et al., 2003). And indeed Volney has a current P net of near zero, meaning that estimated P loads and measured sediment burial are effectively balanced (Fig. 5, Table 4). For the other eight seepage lakes in this study (residence time = 1.5-10.2 yr; Table 1), burial rates equal or exceed external P loads, with the difference amounting to an annual flux of 1.5-6.0 kg per watershed hectare (Fig. 5). Adding in 16-38% of the unaccounted P load would bring four of these lakes (Frances, French, Shields, and Loon) into balance (net P = 0). For the four remaining seepage lakes (Cedar, Clear, Chub, and Toner's), total P inputs (external + 100% unaccounted) balance burial with a net difference of -1.7 to -2.7 kg ha⁻¹ yr⁻¹). As such these results suggest that current load estimates from the TMDL studies are not far off the mark for seepage lakes. On the other hand, uncertainty is much greater for the flow-thru lakes, where outflow P losses greatly exceed burial (with the exception of Fox and Roberds), and measured P burial is a poor constraint on modeled watershed loads.

Another test of our mass-balance results is lake-water TP. In those few lakes with low mean summer phosphorus (Cedar, Clear, Volney, and Fox; Table 1), we might expect P losses to balance or exceed P inputs (lest the lake be far more eutrophic), and indeed that is largely the case, although Fox has a small

positive net of 14% of total P inputs (Fig. 6). The reverse cannot be said of the more productive lakes where internal loading likely contributes to high mid-summer TP, thereby masking any uncertainty in estimated external loads or outflow losses. By using two estimates of external P load in our calculations (external only; external + 50% unaccounted) we have endeavored to bracket the uncertainty inherent in most watershed P models. Nonetheless, it is important to recognize the limitations of the data and to interpret results more in relative rather than absolute terms.

Modern Diatom Communities

Diatom communities of lakes in the Cannon River Watershed were composed of 118 mesotrophic to eutrophic species. Cluster analysis of the modern diatom assemblages generated three prominent communities (Fig. 8). The first cluster of lakes (group 1) includes Cedar, Chub, Fox, and Toner's. These lakes are set apart by higher abundances of epiphytic and benthic diatoms *Achnanthidium minutissimum* (Kützing) Czarnecki, *Cocconeis pediculus* Ehrenberg, *Cymbella proxima* Reimer, *Epithemea turgida* (Ehrenberg) Kützing, and *Gomphonema truncatum* Ehrenberg. Chub and Toner's lakes were further separated within this group by prominent populations of *Staurosira venter* (Ehrenberg) Cleve & J.D.Möller and *Fragilaria mesolepta* Rabenhorst accounting for greater than 10%. The second major



Figure 8. Cluster analysis of diatom assemblages in surface (modern) sediments of the study lakes. Colors refer to major lake groups (deep/seepage DS, shallow seepage SS, deep/flow-thru DF, shallow/flow-thru SF); numbers following lake names indicate average lake TP concentrations (μg L⁻¹). break in diatom community structure separates Clear, French, Loon, Roberds, Shields, and Upper Sakatah from Volney, Cannon, Gorman, Byllesby, and Circle. The latter (group 2) are distinguished as a cluster by the dominance of *Aulacoseira ambigua* (Grunow) Simonsen and *Cyclostephanos dubius* (Fricke) Round as well as lower than average taxa richness when compared with the other cluster groups. The former (group 3) is characterized by abundant populations of *Aulacoseira granulata* (Ehrenberg) Simonsen, *Stephanodiscus niagare* Ehrenberg, and *Stephanodiscus minutulus* (Kützing) Round.

Diatom Paleorecords

Cluster analysis of modern diatom assemblages places Loon Lake into group 3 with most of the Cannon watershed lakes. Over the history of the lake, diatom assemblages have shifted across the modern cluster groups (Fig. 9). In the mid 19th century Loon Lake was dominated by mesotrophic, tychoplanktonic diatoms, *Staurosira venter* (Ehrenberg) Cleve and *Staurosira sp.* 1, and the assemblage was more representative of the modern cluster of group 1. During the first half of the 20th century a shift from tychoplanktonic to eutrophic planktonic diatoms occurred with an increase in *Stephanidscus minutulus* (Kützing) Round and *S. parvus* Stoermer & Håkansson. In the last half of the 20th century the diatom community shifted from a dominance of eutrophic planktonic diatoms to mesotrophic planktonic diatoms *Asterionella formosa* Hassall, *A. granulata*, and *F. mesolepta*. Also making a notable appearance during this time was *Epithemia turgida* (Ehrenberg) Kützing. This diatom is fairly unique, as it has an endosymbiotic relationship with the capabilities of fixing atmospheric nitrogen. Chrysophyte abundance relative to diatom abundance declined over the 200-year reconstruction of Loon Lake.



Figure 9. Stratigraphic profile of major diatom species in Loon Lake sediment core. Values are percentage of total diatom counts.



Figure 10. Stratigraphic profile of major diatom species in Roberds Lake sediment core. Values are percentage of total diatom counts.

Roberds Lake diatom assemblages of the early 20th century (Fig. 10) were composed of *Cyclostephanos invisitatus* (M.H.Hohn and Hellermann) E.C.Ther., Stoermer and Håk., *Fragilaria crotonensis* Kitton, *F. mesolepta, Staurosirella venter*, and *Stephanodiscus niagarae*. This assemblage is a mix of mostly mesotrophic planktonic diatoms. While present throughout the record, two eutrophic planktic species, *S. mintulus* and *S. parvus*, became more dominant in the late 20th century. These diatoms gave way to a mesotrophic assemblage of *Asterionella formosa, Aulacoseira ambigua, A. granulta, Cyclotella menenganiana*, and *Stephanodiscus niagarae*, mostly aligned to cluster group 3. The relative number of chrysophtes increased over the 20th century in Roberds Lake.

In the 19th century the diatom assemblage of Upper Sakatah Lake was dominated by the mesotrophic tychoplanktonic diatoms, *Staurosira construens*, *S. pinnata*, and *Stephanodsicus minutulus*, a very similar assemblage to the modern diatom cluster group 1 (Fig. 11). This assemblage transitioned in the early 20th century to a more planktonic, eutrophic community of *S. minutulus*, *Stephanodiscus niagarae* Ehrenberg, and *S. parvus*. At the end of the 20th century through to present-day, the Upper Sakatah diatoms have shifted to an assemblage dominated by *Asterionella formosa*, *Aulacoseira ambigua*, *A. granulata*, *Cyclotella meneghiniana*, and *Cyclostephanos dubius*. The 20th and 21st century diatom communities are most similar to both the modern cluster groups 2 and 3. Throughout the history of Upper Sakatah Lake a

small population of *E. turgida* has persisted in the diatom community. Chrysophytes peaked in abundance early in the Upper Sakatah Lake paleo-record, steadily declining since \sim 1890.



Figure 11. Stratigraphic profile of major diatom species in Upper Sakatah Lake sediment core. Values are percentage of total diatom counts.

Diatom Ordination and TP Reconstruction

Diatom communities from surface samples for 15 of the 16 lakes were compared to a representative sampling of Minnesota lakes via the 89-lake training set previously published by Ramstack et al. (2003). Frances was excluded from this analysis because of poor diatom preservation in the sediments. Passively plotting surface samples onto a larger ordination of Minnesota lakes allows us to better understand how the lakes within the Cannon River Watershed fit both within their ecoregions (Western Cornbelt Plain [WCP] or Central Hardwood Forest [CHF]), and, in comparison to other ecoregions across Minnesota. Lakes were ordinated along major environmental gradients based on water quality data collected for the training set, allowing us to partially disentangle drivers that may be organizing the diatom communities such as nutrient concentrations and lake color (dissolved organic carbon, DOC). The major gradients in the first two axes of the CCA (shown in Fig. 12) represent a eutrophication/conductivity signal (CCA1) and a lake color (DOC) signal (CCA2). Other intermediate drivers include pH, maximum depth, and chloride concentrations (Cl).

Figure 12 shows the spread of the 15 lakes from this study with the constraining environmental gradients superimposed in the top left. In general, the modern diatom assemblages from these lakes cluster where we would expect them, well within observed communities from other lakes within the WCP and CHF ecoregions. When looking at the four distinct lake types in this study, we found variable cohesiveness by these groupings. The shallow/flow-thru lakes (SF; Gorman, Cedar, Upper Sakatah, and Circle) formed a fairly tight cluster that represented moderate to high TP concentrations. Similarly, the deep/flow-thru (DF) lakes, Byllesby and Roberds, clustered closely to their shallower counterparts. The DF lake Fox, however, was an outlier among the flow-thru lakes perhaps due to its significantly lower modern TP concentrations (Fox = 59 μ g L⁻¹, other DF lakes average = 251 μ g L⁻¹). Four of the five deep/seepage





Figure 12. CCA ordination of modern diatom communities in Cannon watershed lakes together with diatom communities in 89 lakes from different ecoregions of Minnesota. Inset shows the major environmental gradients associated with the 89-lake training set. Study lakes colored according to morphometric/hydrologic groups (DS, SS, DF, SF).

(DS) lakes also clustered closely together, with the exception of Volney which was most closely related to the outlying DF lake, Fox. The shallow seepage (SS) lakes showed the most intragroup variability, though they still fell well within the larger grouping of the Cannon Watershed lakes, with the exception of Chub. Chub fell outside of both the Cannon Watershed lakes and the ecoregion lakes from the larger Minnesota training set. It principally diverged along the 2nd CCA axis, which corresponds most closely to lake color (Fig. 12, inset). Although we do not have color or DOC data for Chub, the diatom community seems to align more closely to the tannin-stained lakes of the Northern Lakes and Forest (NLF) ecoregion.

Diatom communities from dated sediment cores were counted for three of the study lakes (Loon, Roberds, and Upper Sakatah). Frances was originally included in this analysis, but had very poor diatom preservation throughout the sediment core. Similar to the surface samples, fossil diatom assemblages from each core were passively plotted along the 89-lake training set to track changes in water quality as



CCA, 89 MN Lakes, Loon Lake fossil data

Figure 13. Changes in fossil diatom communities in Loon Lake sediment core relative to modern diatom assemblages in 89 Minnesota lakes; Inset shows the major environmental gradients associated with the 89-lake training set.

indicated by turnover in diatom species through time. Core sections were then connected chronologically to illustrate the trajectory of the diatom community and lake over the last 100+ years. In addition to this qualitative interpretation of floristic change in diatoms, we used Ramstack et al.'s (2003) weighted-averaging TP transfer function to produce quantitative estimates of diatom-inferred TP (DI-TP). This produced a predicted value of water-column TP based on the preference and tolerance ranges of the diatoms present in each sample. These results were then plotted through time to show the trajectory of nutrient pollution in each of the three lakes.

Loon (SS) showed the most dramatic floristic change in this study with pre-1855 samples clustering most closely to the relatively pristine NLF lakes and then departing to a region of the CCA most similar to lakes of the WCP and Minnehaha Creek Watershed District (MCWD) (Fig 13). Because this change occurs across both CCA1 and CCA2, it likely encompasses major change in the nutrient concentrations as well as color and pH over this time period. The initial shifts are likely closely tied to the founding of the



Figure 14. Lake TP concentrations reconstructed from fossil diatom assemblages and training set of modern diatom communities and associated water-quality parameters from 89 Minnesota lakes. The shaded regions represent the RMSEP (root-mean-square error of prediction).

city of Waseca, which surrounds the lake and was incorporated in 1868. From 1882 to present, the community moves gradually along the CCA1 axis, indicating increasing nutrient concentrations, before settling into a tight cluster from 1997 to present. These changes are mirrored by the DI-TP reconstructions (Fig. 14), showing a minimum TP of 23 μ g L⁻¹ (RMSEP: 15-36 μ g L⁻¹) around 1839, which tripled to 75 μ g L⁻¹ (46-122 μ g L⁻¹) by ~1922, and then gradually rose to its maximum of 95 μ g L⁻¹ (59-152 μ g L⁻¹) in ~1997. Interestingly, Loon shows a decrease in DI-TP to 43 μ g L⁻¹ (27-69 μ g L⁻¹) around 1975, which coincides with a similar decrease noted in Upper Sakatah, below.

Roberds (DF) has a somewhat truncated history due to the abnormally high sedimentation rate discussed above, but still represents more than 100 years of diatom community change (Fig. 15). In general, the diatom community in Roberds circled in a small cluster in the lower-central region of the CCA, most similar to lakes from the Twin Cities metro region. Starting with a jump in ~1991 the diatom community



CCA, 89 MN Lakes, Roberds Lake fossil data

Figure 15. Changes in fossil diatom communities in Roberds Lake sediment core relative to modern diatom assemblages in 89 Minnesota lakes; Inset shows the major environmental gradients associated with the 89-lake training set.

moved progressively towards the more eutrophic lakes in the training set from the primarily agricultural WCP and NGP ecoregions. The DI-TP reconstruction for Roberds (Fig. 14) also reflects this change with a gradual increase from a baseline of 41 μ g L⁻¹ (25-66 μ g L⁻¹) to a maximum of 109 μ g L⁻¹ (68-174 μ g L⁻¹). This result is consistent with contemporary monitoring at Roberds Lake which classifies it as a hypereutrophic lake (TP > 100 μ g L⁻¹). These results indicate that, although Roberds was a relatively productive system in the past, it has become more similar to the most impacted lakes in the state in the last ~30 years. Finally, it should be noted that had we been able to capture even older sediments from Roberds, the change in DI-TP would likely have been even more pronounced. Based on results from the other two lakes above, it appears that lakes in the Cannon River watershed began changing near the end of the 19th Century, well before the earliest diatom samples from the Roberds core (~1912).



CCA, 89 MN Lakes, Upper Sakatah fossil data

Figure 16. Changes in fossil diatom communities in Upper Sakatah Lake sediment core relative to modern diatom assemblages in 89 Minnesota lakes; Inset shows the major environmental gradients associated with the 89-lake training set.

Upper Sakatah (SF) shows two major clusters in time (Fig. 16). The first represents pre-European settlement (1820-1894) and the second represents 20^{th} century conditions (1917 to present). These two clusters are separated along CCA1, which represents the primary eutrophication axis. This indicates that water quality of Upper Sakatah due to eutrophication was acutely impacted following land-clearance and has been gradually declining since that time. Although the more recent sections still plot within the CHF ecoregion, they have been gradually becoming more similar to the impacted lakes of the WCP and Northern Glaciated Plains (NGP) ecoregion. The DI-TP reconstruction (Fig 14) closely follows this pattern with a gradual increase from 43 μ g L⁻¹ (27-70 μ g L⁻¹) to 117 μ g L⁻¹ (73-188 μ g L⁻¹). There is a small divergence from this pattern around 1970 where DI-TP is predicted to have decreased and which may be tied to some local watershed improvements made at that time, but have since been overwhelmed. These reconstructions are consistent with a historically mesotrophic system that has become hypereutorphic.

Synthesis and Conclusions

Presettlement P Mass-balance

Phosphorus burial and diatom-inferred TP estimates from the long sediment cores can be combined to reconstruct external P loads in presettlement times, thereby providing a baseline against which both current and TMDL-allowable loads may be compared. External P loads can be calculated as the sum of outflow and burial losses, as expressed in Eq-2 and assuming steady-state conditions (net P flux = 0). This approach has been used to estimate historical P loading to Lake Pepin and Lake St. Croix (Engstrom et al., 2009; Triplett et al., 2009) and, in turn, to inform TMDL goals for both of these large riverine lakes.

In this study we have only two lakes, Loon and Upper Sakatah, for which diatom reconstructions extend into presettlement times. The Roberds core was too short (relative to the lake's high sedimentation rate) to reach back to the 19th century, and poor diatom preservation in Frances precluded reconstruction of that record. In this exercise, we used the ratio of presettlement DI-TP to that in current times to scale current P outflow (LimnoTech, 2016) to the P outflow under presettlement conditions – following the same approach used in the TMDL mass-balance, above. These outflow losses were summed with presettlement P-burial rates to arrive at an estimate of external TP loads prior to land-used disturbance from EuroAmerican settlement (Table 7).

	DI-TP (µg L ⁻¹)	DI-TP Pre/Cur	Outflow P (Cur)	Outflow P (Pre)	Burial P (Pre)	External P Load (Pre)	TMDL Allow P Load	Total P Load (Cur)	P Load (Pre/ TMDL)	P Load (Pre/Cur)
Loon										
Modern	95	0.24	39	9	49	58	112	364	0.5	0.16
Presettlement	23									
Upper Sakatah										
Modern	117	0.37	11,719	4,307	1,416	5,723	8,924	56,836	0.6	0.13
Presettlement	43									
	1									

Fluxes in kg P yr⁻¹

Pre = presettlement; Cur = current

These two contrasting lakes, one seepage and the other flow-thru, illustrate the likely range on conditions among the larger set of Cannon Watershed lakes. Their estimated presettlement loads (58 and 5723 kg yr^{-1}) range over two orders of magnitude. More importantly they represent a fraction of total current P inputs, (0.16x and 0.13x, Loon and Upper Sakatah, respectively) and roughly half (0.5x and 0.6x) of TMDL allowable loads. Thus the magnitude of change in watershed P loads since presettlement times is upwards of 6-10x, while the target TMDL loads are roughly 2x higher than their presettlement baseline.

Recoverability

Returning to the question initially posed by this study, can we better predict which lakes are most likely to respond to implementation efforts aimed at reducing watershed (and internal) P loads? The measured rates of whole-basin P burial along with the diatom-based assessment of ecological condition from this study add considerable information to modeled load estimates from TMDL reports. The original objective of our mass-balance approach was to determine which lakes had current P losses (burial plus outflow) equal to or exceeding P inputs, and were thus heading toward possible recovery from nutrient enrichment. However, and as noted previously, there is a high degree of uncertainty in the estimated P fluxes from the TMDL modeling studies, making quantitative assessment difficult.

Despite these limitations, our mass-balance calculations provide a relative measure of recoverability. Thus the deep/seepage lakes (Cedar, Clear, Frances, French, Shields, and Volney) show, for the most part, a negative net-P flux (losses exceed inputs), suggesting that they are either at steady state or gradually depleting their in-lake (surface sediment and water column) P burdens under present-day loading. This is especially so for those lakes with limited internal (unaccounted) loads including Cedar, Clear, Frances, and Volney, which are also among those in the study with the lowest water-column TP. The other two lakes in the deep/seepage group, French and Shields, have substantial unaccounted (internal) loads and high lake-water TP, and are thus are more uncertain with respect to recoverability. The group of shallow/seepage lakes (Chub, Loon, and Toners) all show a negative or near-zero P mass balance. These three lakes also have a large unaccounted P load and high water-column TP, indicating a substantial internal P flux. Recoverability for this latter group will likely depend on the effectiveness of measures aimed at reducing internal P release.

The flow-thru lakes, both deep and shallow, are, with the exception of Fox, high TP systems with large external P loads and outflow losses; P burial exceeds P outflow only in Fox and Roberds. Given the short residence time of these lakes, water column TP is largely a function of current-year loads (external and internal), and thus relatively insensitive to long-term sediment P burial. As a result, recovery of these lakes, especially those with large watersheds (Byllesby, Cannon, and Upper Sakatah) will be challenging.

At the same time, results from this study suggest that TMDL load reductions, if achievable, would substantially change P mass-balance in most Cannon Watershed lakes. Under reduced external loads, P burial, especially in seepage lakes, would sequester a larger fraction of P inputs, resulting in depletion of P stores in surface sediments and ultimately reduction of internal P loading. Considering the uncertainty in P budgets for most of the lakes, the timeframe for such responses is difficult to predict.

Ecological Condition

The diatom communities in surface (recent) sediment of the study lakes demonstrate ecological groupings similar those expressed by their P budgets. Those lakes in which P losses are predominantly through sediment burial tend to cluster together (diatom groups 1 and 3), separate from those with large outflow P losses (principally shallow/flow-thru lakes; group 2). This ecological division is not entirely clear cut (e.g. Volney clustering with group 2 lakes or Upper Sakatah with group 3), and further appears to be related more to hydrology than to depth or lake-water TP (Fig. 17). Regarding the weak fidelity with depth, the ecological overlap is not surprising, as all of the study lakes are relatively shallow, and even the deepest ones (Volney , Frances) have extensive littoral areas. This morphometric influence is reflected in the dominance of tycoplanktonic species (benthic taxa also found in the plankton) among all lake types, indicting the importance of benthic production and resuspension on the composition of diatom communities. Nonetheless, there is ecological coherence, especially in a constrained ordination with other Minnesota lakes, where the high-P, flow-thru lakes diverge from lower TP seepage lakes along the TP gradient of CCA axis-1 (Fig. 12).

The study lakes, by their selection, are all eutrophic or hypereutrophic and thus cluster with other culturally-impacted lakes in the WCP and NGP ecoregions (Fig. 12). However, diatom-based reconstructions from the long cores in this study clearly demonstrate the large ecological shifts that lakes in agricultural regions of Minnesota have undergone. The two cores that extend back to presettlement times, Loon and Upper Sakatah, show historic diatom communities characteristic of mesotrophic lakes today. These lakes were likely macrophyte-dominated, clear-water systems, unlike the turbid, algalchoked water-bodies seen today. This interpretation is well supported by other paleolimnological studies of similar lakes in southern and western Minnesota, which show the same ecological shift from clearwater to turbid with the onset of EuroAmerican settlement (Ramstack Hobbs et al., 2016). Moreover, these related studies clearly demonstrate the stability of the turbid-algal state and the difficulty of shifting such lakes back to a clear-water state, even with top-down manipulations (fish kills) (Hobbs et al., 2012). These studies also suggest that top-down impacts to lake food-webs from fish introductions are a more important cause of regime shifts than increased nutrient availability. Such results suggest that management efforts aimed at restoring macrophyte communities and stabilizing sediment P retention (reducing internal loading) are equally important to reductions in external P loading as envisioned in TMDL goals.

Future Studies

The results of this study, both the measurement of sediment P burial and the assessment of ecological condition, help constrain lake P budgets and place the nutrient-impaired lakes of the Cannon Watershed in a historical ecological context. However, because of large uncertainties in P loads and outflow losses, the resulting P mass-balances remain largely qualitative. Indeed, our conclusions regarding restoration targets and recoverability could largely be made based on existing knowledge of lake trophic status, morphometry, and hydrology as documented in recent TMDL studies. What is needed at this point to improve the predictive power of nutrient reduction plans and their implementation is more systematic load monitoring and/or mechanistic watershed models to strengthen those parts of the nutrient budget.

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