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Evidence for internal phosphorus loading in a large prairie reservoir (Lake Diefenbaker, Saskatchewan)

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A R T I C L E I N F O

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A B S T R A C T

Increasingly, our global water storage is contained in large reservoirs that retain nutrients. Given the value of reservoirs to ecosystem services, it is important to know the risks associated with the mobilization of legacy phosphorus (P) from sediments. From 2011 to 2013, Lake Diefenbaker was a significant sink for P retaining 91% of the external total phosphorus (TP) and 41% of the dissolved reactive phosphorus (DRP) loaded from the tributaries. We investigated if this retained P has the potential to re-enter the water column through internal P loading from sediments. In 2013, we estimated the rates of internal P loading with a specific focus on measuring TP, DRP, and total dissolved iron release from sediments. We estimated that over the whole reservoir, the internal load (based on TP increases) was 169 mg TP m^{-2} $summer^{-1}$ and 229 mg TP m^{-2} $winter^{-1}$. Year-round, the mean daily internal P loading rate was 1.8 mg TP m^{-2} day^{-1}, representing ~24% of the annual external TP load. Although our internal load estimates are dependent upon sedimentation rates, they do suggest winter internal P loading is important, resulting in a continuous release of P from the sediments into the overlying water year-round. Internal loading from sediments is an unaccounted-for source of P to Lake Diefenbaker and should be considered in future management of this critically important reservoir. Our recommendations for other reservoirs in obtaining realistic estimates of internal P loading include year-round estimates considering both the stratification and flow regimes.

Introduction

Globally, lakes and reservoirs are becoming greener, mostly due to anthropogenic eutrophication (Bennett et al., 2001). Enrichment with nutrients can cause excessive algal biomass production with a resulting deterioration in water quality. Efforts to manage eutrophication include reduction of external nutrient loading with a primary focus on phosphorus (P) due to its ultimate control on primary producers (Schindler, 2012; Schindler, 1977; Schindler et al., 2012). However, the history of nutrient loading to waterbodies is retained in bottom sediments and mobilization of this legacy P often causes significant delays in the recovery of lakes and reservoirs (Jeppesen et al., 2005; Marsden, 1989). The cumulative impact of multiple anthropogenic stressors such as eutrophication and climate change (which can alter the thermal regime in lakes) can result in increased P loading from sediments causing declines in water quality manifested as increases in undesirable algal populations (North, R.P. et al., 2014). Given that sedimentary P mobilization can also lead to the production of algal toxins (Orihel et al., 2013), there is a need to better understand sedimentary P cycling. This holds particularly true in the Canadian prairies where, although understudied, reported internal P loads into prairie lakes are often higher than in other locations in North America (Loh et al., 2013; Orihel et al., 2015; Shaw and Prepas, 1990), which has been attributed to their hardwater characteristics (i.e., high sulphur and low iron content; Nürnberg, 1994).

Lake Diefenbaker is a large, multi-purpose reservoir located on the Canadian prairies that serves as the most valuable source of freshwater in Saskatchewan (Saskatchewan Water Security Agency (SWSA), 2012). Consequently, water quality and the legacy effects of P loading from its major tributary, the South Saskatchewan River, are of concern. It has long been suggested that internal P loading must be a significant (Saskatchewan Environment and Public Safety, Water Quality Branch and Environment Canada, Inland Waters Directorate, Water Quality

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Branch, 1988) and increasing (Hall et al., 1999) source of P to Lake Diefenbaker. Based on Lake Diefenbaker sediment core analyses, Lucas et al. (2015) observed high concentrations of redox-sensitive P fractions in the upper portions of the sediment profiles in down-reservoir locations.

Our understanding of the mechanisms that facilitate both the short- and long-term P release from sediments is still in its infancy, but we do know that it is controlled by a combination of factors related to the source of P and conditions within the sediment (i.e., diagenetic reactions occurring prior to permanent burial) as well as at the sediment–water interface (SWI). The relative influence of the mechanisms controlling P release from sediments is dependent upon the P speciation in the sediments with the acknowledgement that there are many different phosphate-containing minerals and a variety of surface complexes. Conditions at the SWI directly influencing short- term P release include 1) the concentration of dissolved oxygen (DO), which affects the redox potential and thus the reductive dissolution of orthophosphate adsorbed on Fe oxides and subsequent release from anoxic sediment surfaces (Mortimer, 1941; Nürnberg, 2009); 2) sulfide concentrations, as sulfide binds Fe in sediments, thus liberating P from the previously described Fe complexes (Gächter and Müller, 2003; Katsev et al., 2006; Molot et al., 2014); 3) temperature, pH, and the concentration of nitrate (Jensen and Andersen, 1992); 4) release from polyphosphates (Hupfer and Lewandowski, 2008); 5) liberation from the organic pool via diagenetic processes (i.e., metabolism causing mineralization of organic matter and enzymatic liberation of phosphate; Reitzel et al., 2007); and 6) bioturbation related to the activities of burrowing invertebrates (Edwards et al., 2009; Holdren and Armstrong, 1980). The factors controlling long-term P flux are mostly related to sedimentation versus deep burial rates of both organic and mineral matter.

Reservoirs function as large sediment traps, retaining nutrients and improving the overall water quality of downstream lakes. In the South Saskatchewan River Basin, this is a service that Lake Diefenbaker and other reservoirs on the Saskatchewan River system provide for downstream Lake Winnipeg (Manitoba, Canada; Donald et al., 2015). As the number of reservoirs increase worldwide, it is important to know if this ecosystem service is associated with any long-term negative feedbacks such as nutrient release from bottom sediments. Phosphorus released from sediments is in a biologically available form (e.g., dissolved reactive phosphorus [DRP]), which makes it more accessible to primary producers than external P loads. For example, in 2012, the external tributary TP loads to Lake Diefenbaker were 78.1–94.2% particulate P (Johansson et al., 2013) from which DRP must be released prior to algal utilization.

This paper represents the first published estimate of internal P loading to a Canadian reservoir, illustrating the gap in our understanding of reservoir nutrient dynamics. Thus, our objective was to determine rates of internal P loading on a year-round and spatially resolved basis in a large Canadian reservoir and assess these rates in the context of external P loading. We achieved these objectives through an observational approach based on seasonal and spatial patterns in water chemistry profiles and *in situ* estimates of internal load. We anticipate that this comprehensive assessment of internal P loading to Lake Diefenbaker will assist in the management of this important prairie reservoir to maintain its water quality well into the future. This work also contributes to our understanding of the relative importance of P loading from sediments in highly retentive systems subjected to high external loads. Finally, we address the importance of spatially and seasonally resolved characterization of internal P loading in lakes and reservoirs and assess the value of year-round data, including the possibility of underestimating year-round rates if under-ice processes are not accounted for.

Materials and methods

Study site description

The South Saskatchewan River sub-basin has an effective drainage area of 82 300 km^2 (representing 54% of the gross drainage area, 152 700 km^2; Saskatchewan Watershed Authority, 2012), illustrating the non-contributing nature of prairie hydrology (Shaw et al., 2013). The Lake Diefenbaker reservoir (51°01′53″N, 106°50′09″W) was created as a result of damming of the South Saskatchewan River by the Gardiner and Qu'Appelle Dams in 1967. Its watershed originates in the Rocky Mountains and extends across the prairie ecozone fed primarily by the Old Man, Bow, and Red Deer rivers in southern Alberta. In fact, 98% of the water that flows into Lake Diefenbaker originates in Alberta (Saskatchewan Water Security Agency, SWSA, 2012), as local inflows from surface runoff or ephemeral creeks are considered to be negligible (Pomeroy and Shook, 2012). Limnological characteristics of Lake Diefenbaker are described for 2011–2012 in Abirhire et al. (2015) and Hudson and Vandergucht (2015), and for 2013 in Dubourg et al. (2015). Briefly, the reservoir is approximately 182 km long with 458 km of shoreline, covering an area of 394 km^2 with a volume at full capacity (556.9 m a.s.l.) of approximately 9 km^3 (Sadeghian et al., 2015). Drawdown of the water levels usually occurs during the winter months and can be as much as 9 m (Saskatchewan Water Security Agency, SWSA, 2012). Lake Diefenbaker has a mean depth of 22 m, a maximum depth of 59 m near the Gardiner Dam (Sadeghian et al., 2015), and a water residence time of 1.1 years (Donald et al., 2015). It is a classic river valley reservoir that deepens gradually from the shallow and polymictic region at the inflow, to the deep stratified region near the Gardner Dam. For the purposes of this study, we divided the reservoir into 4 regions (Fig. 1) representing the polymictic up-reservoir region, dimictic down-reservoir region, dimictic lacustrine Gardiner arm, and polymictic lacustrine Qu'Appelle arm (Fig. 2; Dubourg et al., 2015). According to Wetzel's (2001) trophic index for TP concentrations, the 4 regions of Lake Diefenbaker (Fig. 1) can be categorized as meso- to eutrophic in the up-reservoir and down-reservoir regions, and oligo- to mesotrophic in the Gardiner and Qu'Appelle arms during the open-water season (Dubourg et al., 2015).

Internal loading rate estimates

We estimated internal P loading rates to Lake Diefenbaker from *in situ* TP increases, which represent somewhere between net and gross estimates dependent upon sedimentation rates. In addition, *in situ* DRP and total dissolved iron (TDFe) rates were calculated in order to investigate the mechanisms regulating internal P loading in this prairie reservoir.

The *in situ* internal loading approach as described for both stratified and polymictic lakes in Nürnberg (2009; Method 1) was determined from *in situ* chemical increases. For heterogeneous Lake Diefenbaker, we differentiated between polymictic and stratified regions of the reservoir (Fig. 1) and time periods related to flow conditions. The thermocline was defined by a change in water temperature gradient > 0.5 °C m^{-1}, as determined from sonde-based (Yellow Springs Instrument [YSI], model 6600 V2) temperature-depth profiles in the field. This temperature-depth stratification criterion was the basis for the distinction between the epilimnetic, metalimnetic, and hypolimnetic water layers in the reservoir. Spatial reservoir mixing classification was determined by calculating the Schmidt stability index (S), which is a quantification of the mechanical work hypothetically necessary to transform the observed density distribution into a vertically homogeneous distribution through mixing (Schmidt, 1928). We calculated S using Lake Analyzer (Read et al., 2011) on each sampling day and station from temperature-depth sonde profiles. The establishment of Schmidt criteria (S_{crit}), defined as the critical value between periods of stratification ($S > S_{crit}$) and homothermy indicating polymixis ($S < S_{crit}$), allowed the classification of 4 regions within the reservoir. Informed by our temperature-depth stratification criteria, we defined different S_{crit} for the 4 regions of the Diefenbaker reservoir as follows: up-reservoir, 60 J m^{-2}; down-reservoir, 60 J m^{-2}; Gardiner arm, 350 J m^{-2}; Qu'Appelle arm,

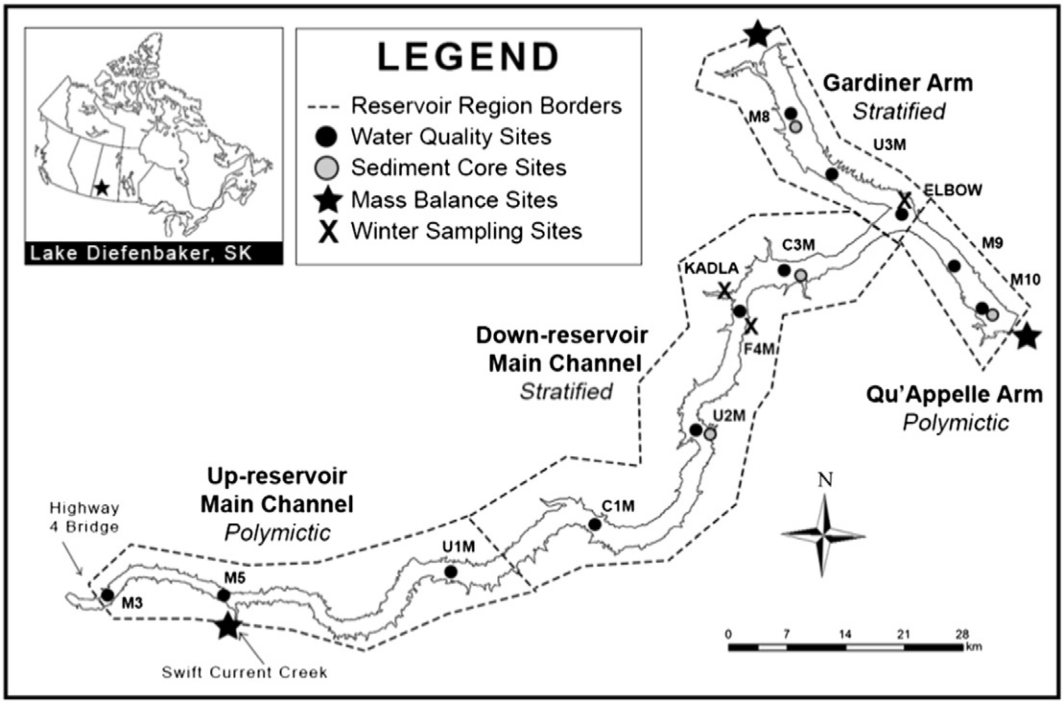

Fig. 1. A map of sampling stations in Lake Diefenbaker, Saskatchewan, Canada. The reservoir was separated into 4 regions based on the stratification regime during the 2013 open-water season. The map depicts the 12 open-water water quality sites, 4 sediment core sites (Lorne Doig, University of Saskatchewan, 2015, personal communication), 3 winter water quality sites, and 3 mass balance sites. The 4th mass balance site located upstream on South Saskatchewan River at the Lemsford Ferry (51°01′26.81″N, 109°8′0.18″W) was not depicted due to scaling issues.

100 J m^{-2}. Upon the application of S_{crit} to S, we were able to distinguish spatial and temporal differences in stratification.

Under stratified conditions (down-reservoir and Gardiner arm; Fig. 1), *in situ* internal load (mg m^{-2} $summer^{-1}$) was calculated from increases in volume-weighted hypolimnetic chemical concentrations over the stratified summer season per unit surface area following Nürnberg (2009):

$$\textit{In situ}\ \text{stratified internal load} = ((\text{[hypochemical\_t}_2] \times \text{V\_t}_2)/\text{A}_\text{o}\text{\_t}_2) - ((\text{[hypochemical\_t}_1] \times \text{V\_t}_1) / \text{A}_\text{o}\text{\_t}_1) \quad (1)$$

where t_1 is the initial sampling date during stratified conditions and t_2 is the date at the end of the stratification period. We defined [hypochemical] as the volume-weighted hypolimnetic chemical concentration, and the volume (V) and surface area (A_o) were adjusted to daily water level changes in the reservoir.

Under polymictic conditions (up-reservoir and Qu'Appelle arm; Fig. 1), *in situ* internal load (mg m^{-2} $summer^{-1}$) was calculated based on Nürnberg (2009), with the exception that instead of the maximum summer TP concentration, monthly summer internal loads were calculated and summed to reflect the multiple internal loading events occurring under a polymictic mixing regime:

$$\textit{In situ}\ \text{polymictic internal load} = \sum_{i=t2}^{t5} {}^{[epichemical\_ti]\times V\_ti}\Big/_{Ao\_ti} - ((\text{[epichemical\_t}_1] \times \text{V\_t}_1) / \text{A}_\text{o}\text{\_t}_1) \quad (2)$$

where t_1 is the initial summer (June) sampling date and [epichemical] is the 2 m (epilimnetic) TP, DRP, or TDFe concentration. In 2013, heavy rainfall in southern Alberta caused a large increase in flow to Lake Diefenbaker, which peaked in late June/mid-July (Hudson and Vandergucht, 2015). This high flow event caused significant nutrient influx into the reservoir resulting in very high nutrient concentrations at up- and down-reservoir sites (Dubourg et al., 2015). Since these high concentrations were unrelated to release from sediments, we excluded them from our assessment of the chemical concentrations during the course of the summer. As before, V and A_o were adjusted to daily water level changes in the reservoir.

Winter estimates of *in situ* internal TP and DRP load (mg m^{-2} $winter^{-1}$) were only calculated for sites F4-M and Elbow due to the lack of bathymetry in the Kadla embayment (Fig. 1). Winter internal P loads were based on the *in situ* polymictic Eq. (2) above, with the exception that mid-water column P concentrations were used instead of the 2 m (epilimnetic) concentrations. In Lake Diefenbaker, maximum annual phytoplankton biomass occurred under-ice during the winter. In 2013, our two winter stations had mean phytoplankton biomass

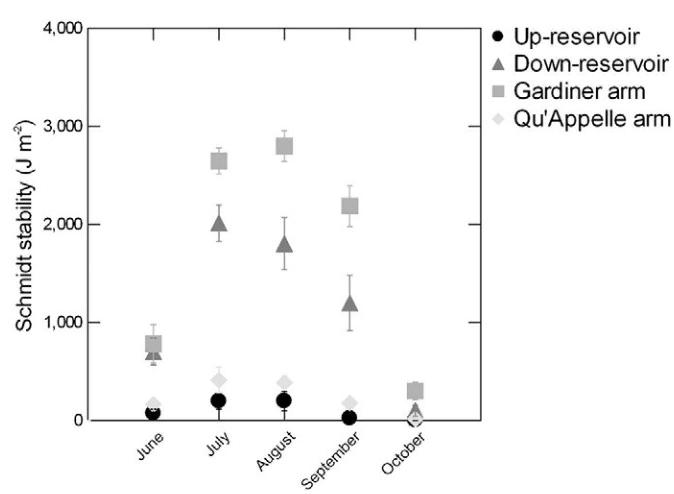

Fig. 2. Lake Diefenbaker Schmidt stability index values. Stability was calculated for the open-water season of 2013 and differentiated by reservoir region (Fig. 1). The error bars represent the standard error of the monthly mean from multiple stations within each region ($n = 2$–4).

(2 m depth) of 645 ± 398 mg m^{-3} (North et al., unpublished data). This under-ice biomass was ~3 times higher than that reported for the 2013 open-water down-reservoir (226 ± 203 mg m^{-3}) and Gardner arm (141 ± 46 mg m^{-3}) regions (Dubourg et al., 2015). Given that this high phytoplankton biomass was included in our TP measurements, we chose to exclude the epilimnetic (2 m) samples from our winter internal P load estimates. Instead, we chose to use our mid-water column P samples in the calculations, as these sample depths were below the chlorophyll *a* (a proxy for phytoplankton biomass) peaks as determined from our sonde profiles.

In situ winter internal load

$$= \sum_{i=t2}^{t3} {}^{[P\_ti]\times V\_ti}\Big/_{Ao\_ti} - (([P\_t_1] \times V\_t_1) / A_o\_t_1) \tag{3}$$

where t_1 is the initial winter (February) sampling date and [P] is the mid-water column (7–28 m) TP or DRP concentration. As above, V and A_o were adjusted to daily water level changes in the reservoir.

Whole-reservoir phosphorus mass balance

We calculated the P (TP and DRP) mass balance of the reservoir in order to put our internal rates in perspective with gross external P loading. Given the managed nature of the reservoir, we accounted for the effect of water level changes on the mass retained on a seasonal basis, wherein P retention was expressed as a percentage:

$$\text{Retention} = ((\text{Pload}_{\text{in}} - \text{Pload}_{\text{out}}) - (\Delta \text{ water level} \times [\text{P}])) / \text{Pload}_{\text{in}} \tag{4}$$

where Pload_{in} is the sum of the monthly P loads (P concentration × flow) from the South Saskatchewan River and Swift Current Creek, $\text{Pload}_{\text{out}}$ is the sum of the monthly P loads from below the Gardner and Qu'Appelle Dams, change (Δ) in water level is the difference in reservoir water levels within each season, and [P] is the mean water column P concentration for the entire reservoir. For details on the P loading calculations refer to Johansson et al. (2013).

Water sample collection

Surface water samples for mass balance calculations were collected from the South Saskatchewan River at Lemsford Ferry (representing 98% of the inflow; Saskatchewan Water Security Agency, SWSA, 2012) and Swift Current Creek at Regional Road 738 (representing <1% of the inflow; Saskatchewan Water Security Agency, SWSA, 2012), the only two tributaries to the reservoir (Fig. 1). The two outflows from Lake Diefenbaker were the Qu'Appelle River below the Qu'Appelle Dam (representing 1% of the outflow; Saskatchewan Water Security Agency, SWSA, 2012) and the South Saskatchewan River below the Gardiner Dam (representing 99% of the outflow; Saskatchewan Water Security Agency, SWSA, 2012; Fig. 1), which were sampled from May 2011 to October 2013 inclusive. From late May to early November, field samples were obtained on a bi-weekly basis with sampling frequency reduced to monthly collections from late November to March. Surface water samples were obtained via a Van Dorn (Qu'Appelle River below Qu'Appelle Dam), wading (Swift Current Creek at Regional Road 738, South Saskatchewan River below Gardiner Dam), or off the side of transport ferries (South Saskatchewan River at Lemsford). All field samples were immediately placed into coolers and stored overnight in an incubation chamber set to ambient lake temperatures in the Limnology Lab at the University of Saskatchewan (Johansson et al., 2013).

Water chemistry samples were collected during monthly sampling of 12 stations along the length of Lake Diefenbaker during the open-water season (June–October) of 2013 and at 3 stations during the ice-covered 2013 winter (February–April; Fig. 1). For P chemistry, discrete water samples were collected with a Van Dorn sampler from 4 depths representing the epilimnion, metalimnion, hypolimnion, and 1 m off bottom during conditions of stratification. During isothermal conditions, samples were collected from a 2 m depth and 1 m off of the bottom. Trace metal clean techniques were applied for the collection of TDFe samples through the use of a peristaltic pump from aforementioned depths. Within 12 hours of collection, the samples were stored at ambient temperatures in an environmental chamber at the University of Saskatchewan until processing the following day.

Physical parameters

Daily inflows from the South Saskatchewan River and Swift Current Creek (Fig. 1), outflows through both dams, and daily reservoir water level data were reported as in North, R.L. et al. (2014). Bathymetry, derived from Saskatchewan Property Management Corporation (SPMC), S.D. ca. (1986), combined with daily water levels was used to calculate volumes, surface areas, mean, and maximum depths.

A sonde was used to obtain vertical depth profiles of temperature, chlorophyll *a*, and DO concentrations at each station. Sonde DO concentrations were measured with a 6150 ROX Optical DO sensor, which underwent a 2-point calibration on a weekly basis. Calibration of DO concentrations from the sonde DO sensor were conducted previously using the Winkler method. Titrations were performed within 4 hours after fixation but otherwise followed the procedures described in Carignan et al. (1998) using an automated titrator (Mettler Toledo DL 50; Mettler Toledo, Mississauga, ON, CAN). The coefficient of variation of replicate DO measurements averaged 0.05% based on DO measurements from air-equilibrated Lake Simcoe (Ontario, Canada) water. The difference between sensor-derived DO concentrations and replicate Winkler titrations was 0.41 mg DO L^{-1}. In Lake Diefenbaker, we used the vertically resolved sonde DO profiles for a given date to determine the minimum DO concentration at each station that could potentially interact with bottom sediment based on the stratification regime and S. For example, if the station was isothermal on a particular date, the lowest DO concentration occurring in the water column on that date was reported, assuming that as the water mass circulates, the low DO water would interact with the sediments. Conversely, if the water column was stratified, the lowest DO concentration in the hypolimnion was reported.

Water chemistry

Total P and DRP were measured according to Parsons et al. (1984) with persulfate digestion for TP samples. Samples for DRP and TDFe were obtained through syringe filtration (0.2 μm polycarbonate filters) followed immediately by acidification with nitric acid (0.2%) for the TDFe filtrate. Analyses of TDFe samples were conducted on a graphite furnace atomic absorption spectrometer (AAnalyst 800, Perkin Elmer, USA). The quality control and assurance of the Fe analyses was maintained using a certified multi-element standard (GFAAS Mixed-standard, Perkin Elmer, USA), appropriate method blank, and standard spiking and recovery procedure. In addition, a certified river water reference material (SLRS-5; National Research Council of Canada) was also analyzed to ensure that the recovery of Fe was within the acceptable range (96%) with a detection limit of 0.05 μg L^{-1}.

Statistics and data analysis

One-way analyses of variance (ANOVAs) were used to test for regional differences in P internal loading rates within the reservoir, followed by a Tukey-Kramer *post hoc* test with a significance value of $p < 0.05$. Prior to analysis, the TP internal loads were transformed (Log_{10} [x + 100]) to meet the conditions of normality; the DRP internal loads did not require transformation. The 12 stations were grouped into the 4 identified regions of the reservoir, thus each region was represented by 2–4 stations (Fig. 1).

Results

Physical regime

Lake Diefenbaker has both stratified (down-reservoir and Gardiner arm) and polymictic (up-reservoir and Qu'Appelle arm) regions (Fig. 1) as defined by the difference between S (Fig. 2) and S_{crit}. During the open-water season from June to October, our sampling captured both summer stratification (June–September) and fall overturn (October) in the regions of the reservoir that stratify (Fig. 2).

Year-round, the minimum DO concentration occurred up-reservoir in August in response to organic loads from the South Saskatchewan River where the conditions were characterized as polymictic riverine, high flow, and shallow. Low DO conditions were also present in August in the quiescent, lacustrine, polymictic Qu'Appelle arm of the reservoir. However, minimum DO concentrations never fell below 2.24 mg L^{-1} (Fig. 3). Under-ice DO concentrations were high with an average minimum DO of 11.77 $\pm$ 1.26 mg L^{-1} relative to the average open-water minimum DO concentration of 6.95 $\pm$ 2.53 mg L^{-1} (Fig. 3). With the exception of August, there were no obvious spatial differences in minimum DO concentrations along the length of the reservoir (Fig. 3).

Chemical regime

In 2013, Lake Diefenbaker TP and DRP vertical profiles show year-round increasing concentrations with depth toward the sediments, with the highest concentrations (exclusive of those associated with 2013 high flow event) occurring in the fall (Fig. 4A,B). During the open-water season (June–October) DRP formed 53% of the bottom-water TP concentrations, while in the ice-covered season, DRP represented 68% of the bottom-water TP.

Correlational analyses revealed no relationships between P and TDFe concentrations, nor were there any vertical trends in TDFe concentrations (Fig. 4C). A uni-modal seasonal distribution was seen with maximum TDFe concentrations occurring in July and August (Fig. 4C). Estimates of *in situ* TDFe summer internal loading were 143 mg m^{-2} $summer^{-1}$ and displayed no regional differences.

Estimate of internal phosphorus load

The *in situ* summer internal load estimates based on seasonal increases in TP and DRP concentrations were significantly different between the 4 regions of the reservoir ($F_{3,8} = 26.679$, $p < 0.0005$, Fig. 5A; $F_{3,8} = 4.752$, $p = 0.035$, Fig. 5B; respectively). TP internal loading rates in the polymictic up-reservoir and Qu'Appelle arm regions were significantly higher than in the stratified down-reservoir and Gardiner arm (Fig. 5A). On a whole-reservoir basis, the mean summer *in situ* TP internal loading estimate was 169 mg m^{-2} $summer^{-1}$ (Fig. 5A, Table 2). The DRP internal loading rate was 51 mg m^{-2} $summer^{-1}$ with significantly higher rates in the Gardner arm relative to the up-reservoir region (Fig. 5B). The two winter stations had *in situ* internal TP load estimates that were ~40 times higher than the summer rates for the same two stations. Rates were 175 mg TP m^{-2} $winter^{-1}$ (implying a P source) and −36 mg DRP m^{-2} $winter^{-1}$ (implying a P sink) for the Gardiner arm, and 283 mg TP m^{-2} $winter^{-1}$ and 53 mg DRP m^{-2} $winter^{-1}$ for the down-reservoir region. On a daily basis, the mean year-round internal P loading rate was 1.8 mg TP m^{-2} day^{-1}, representing ~24% of the external TP load.

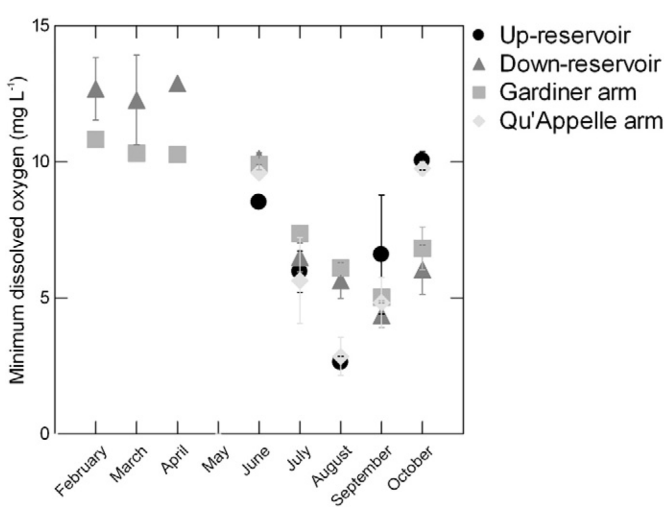

Fig. 3. The 2013 year-round minimum dissolved oxygen concentrations in Lake Diefenbaker. The error bars represent the standard error of the monthly mean from multiple stations within each region ($n = 2$–4). Winter sampling did not include stations located in the up-reservoir or Qu'Appelle arm regions of the reservoir.

Mass balance of Lake Diefenbaker

Lake Diefenbaker is a highly depositional environment with retention rates representing 89 and 84% of the external TP loadings, and 38 and 44% of the DRP load from the South Saskatchewan River and Swift Current Creek during the 2011 and 2012 hydrologic years (the 2013 hydrologic year was incomplete; Table 1). Apparent increases (i.e., negative retention) in biologically available DRP were observed under ice in the winter (Table 1), indicating Lake Diefenbaker may be a source of DRP to downstream systems during the winter as more DRP was leaving the system than entering. The average TP external load (2011 and 2012 hydrologic years) was 1074 tonnes yr^{-1} (2727 mg m^2 yr^{-1}; 7.57 mg m^2 day^{-1}).

Discussion

Lake Diefenbaker is highly effective in retaining P. In a recent study of the 28 largest lakes and reservoirs in the Lake Winnipeg basin, Lake Diefenbaker had the highest TP retention rates (Donald et al., 2015). While effectively retaining P, Lake Diefenbaker also displays year-round P release from sediments. While overall not a significant source of P to the reservoir, internal P loading does supply the limiting nutrient P (Dubourg et al., 2015) to phytoplankton populations within and downstream of Lake Diefenbaker on a year-round basis. Lake Diefenbaker appears to be unique in its departure from classically defined indicators of internal P loading (Nürnberg, 1984) due to its complicated mixing regime and sediment redox processes, wherein the down-reservoir and Gardiner arm are seasonally stratified systems, yet up-reservoir and Qu'Appelle arm regions exhibit polymixis. The largest contributing factor to internal P loading rates appeared to be the mixing regime because the polymictic regions of the reservoir experienced significantly higher rates than the stratified regions. We believe this is due to the multiple internal loading events occurring over the summer, relative to one event in the fall in the stratified regions. Recent literature also provides evidence that polymictic lakes have particularly high internal P loading rates (Orihel et al., 2015). Overall, the annual reservoir mass balance does not indicate a large influence of internal P loading as 91% of the TP is retained (positive retention, P sink). However, *in situ* P loading rates were measurable on a year-round basis in 2013.

The importance of winter

Previous work has demonstrated the temperature-dependence of P release rates (Jensen and Andersen, 1992; Liikanen et al., 2002) and shown that winter internal P loads often represent a small (0 and 35%, respectively; Nürnberg et al., 2013; Nürnberg et al., 1986) portion of the summer load. In Lake Diefenbaker, our winter internal P load was 40 times higher than our estimated summer internal load. We suggest that while winter internal P loading is not a large component of the

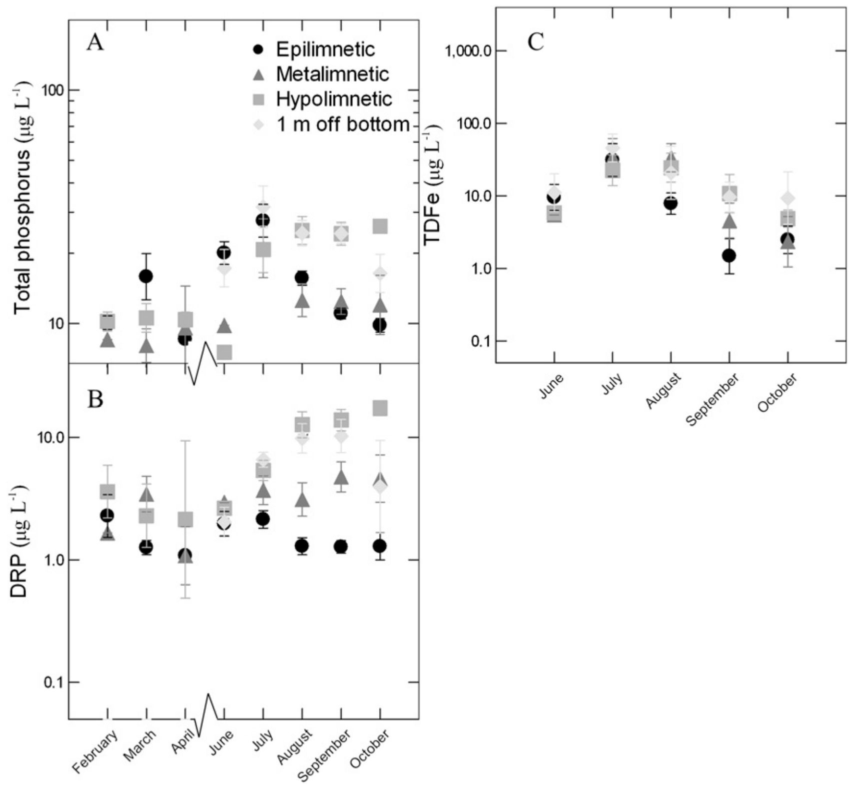

Fig. 4. The vertical distribution of (A) total phosphorus, (B) dissolved reactive phosphorus, and (C) total dissolved iron in Lake Diefenbaker in 2013. The error bars represent the standard error of the monthly mean from multiple stations within each region ($n = 2$–4).

overall P budget of Lake Diefenbaker, it may be important in more productive lakes susceptible to low DO conditions in the bottom waters under ice cover. The relationship between DO concentrations and experimental sediment core release rates (RRs) in Lake Diefenbaker (Lorne Doig, University of Saskatchewan, 2015, personal communication) demonstrate that on a reservoir-wide basis, RR_{TP}s were 35% higher under anoxic (<1 mg L^{-1}) relative to suboxic (~2 mg L^{-1}) conditions, and anoxic release rates were 91% higher than under high DO (~9 mg L^{-1}) conditions. Although recent studies report relatively high DO concentrations throughout the reservoir (Hudson and Vandergucht, 2015), there is historical evidence of low DO concentrations (0.2 and 0.8 mg L^{-1}) in two up-reservoir locations in August 1984, and under-ice in the winter (1.8 mg L^{-1}; March 1985) in the Qu'Appelle arm (Saskatchewan Environment and Public Safety, Water Quality Branch and Environment Canada, Inland Waters Directorate, Water Quality Branch, 1988).

When the major external nutrient input (South Saskatchewan River inflow) decreased, the relative influence of its high nutrient load diminished. Winter DRP loads leaving the reservoir were higher than the incoming loads, indicating that Lake Diefenbaker may be a source of DRP in the winter months. Many processes and factors can interact to produce DRP in the reservoir water column during winter including P distribution processes, suspended particle dissolution, and reduced assimilation by phytoplankton communities. Dissolution of sedimenting particles (i.e., the particulate portion of TP) as they settle into the bottom waters would appear as increases in DRP concentrations. Perceived increases in DRP could also be attributed to reduced P assimilation by under-ice phytoplankton communities. There is support for reduced winter P uptake in Lake Diefenbaker, as the winter season was a time of maximum year-round light limitation and minimal year-round P deficiency, even though phytoplankton biomass was also high (North et al., unpublished data). While it cannot be inferred from the winter negative P retention rates alone that internal DRP loading occurred, *in situ* winter internal load estimates (229 mg TP m^{-2} winter^{-1}) indicate that this may be a possibility. However, caution should be exercised when extrapolating these winter internal loading rates to the whole reservoir as they were only assessed at 2 sites representing the down-reservoir and Gardiner arm regions.

Limitations to our approach for calculating internal loading

This initial attempt at quantifying internal P loading rates in Lake Diefenbaker revealed the complicated nature of making such estimates, and we encourage more detailed studies on the reservoir. We agree with comments by Nürnberg (2009) regarding spatial and temporal considerations in estimating internal P loading, specifically related to morphometry and the stratification regime. Our results demonstrate the difficult nature of calculating internal P loading rates for complex managed reservoirs such as Lake Diefenbaker, with highly variable water levels and flow. This contributes to considerable uncertainty regarding the most defensible approach for estimating internal loading. Estimates of internal P load are approximate and their representation of *in situ* net rates is dependent upon sedimentation rates. For example, we acknowledge the fact that our estimate of the *in situ* stratified internal load is compromised by the settling of nutrients and particulate matter into the hypolimnion and our rates could be closer to net or gross, depending on the timing of sedimentation relative to our sampling. With our *in situ* approach, our monthly sampling frequency would not have captured the probable daily polymixis in large areas of the reservoir. In the case of the winter rates, sampling was dependent on safe ice conditions, thus we cannot ensure all P release from sediments were quantified in our February–April winter sampling.

Given the high variability in internal P loading between years in other systems (Nürnberg et al., 2012, 2013), estimates of both external and internal loads would ideally be conducted in a year representative of long-term averages. Our 3-year P mass balance agrees well with a study conducted during the previous 3 years (2008–2011) where they report 94% TP and 64% DRP retention within the Diefenbaker reservoir

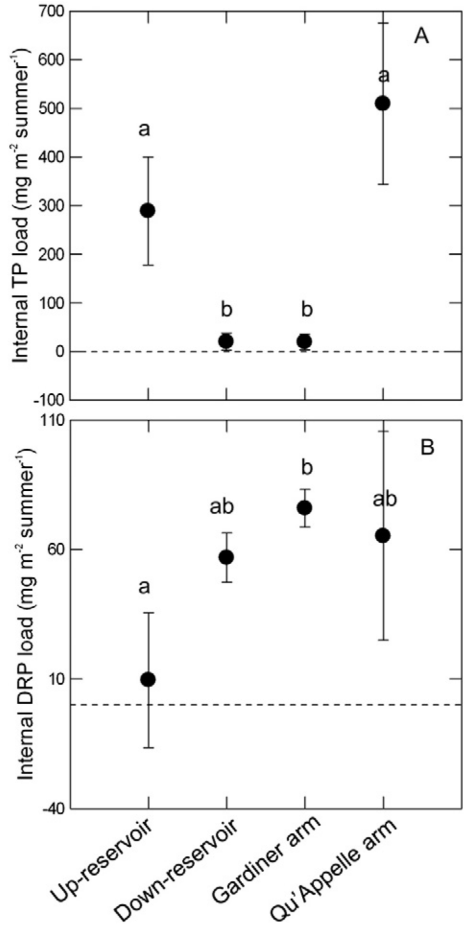

Fig. 5. *In situ* phosphorus internal loading estimates for the open-water season of 2013 from summer increases in (A) total phosphorus and (B) dissolved reactive phosphorus. Internal load estimates are differentiated by reservoir region (Fig. 1) and the error bars represent the standard error of the mean from multiple stations within each region ($n = 2$–4). Lower case letters report the results of ANOVAs with Tukey-Kramer *post hoc* comparisons between *in situ* internal loading estimates and regions of the Lake Diefenbaker reservoir. *Post hoc* tests were conducted if ANOVA factors were identified as significant ($p < 0.05$). The letters for the post hoc comparison indicate statistical differences between regions. Regional differences were not statistically significant ($p < 0.05$) if the letters are identical.

(Donald et al., 2015). In 2013, Lake Diefenbaker experienced higher than average flows (Hudson and Vandergucht, 2015) with external TP loading rates during peak flow approximately five times higher than the mean of the previous 2 years. Nürnberg et al. (2012) reported a negative relationship between external and internal P loading; thus, the high 2013 external loads to Lake Diefenbaker may indicate that our 1-year internal P loading rates may underestimate the "typical" internal load. Lake Diefenbaker internal P loading rates may be higher in years with lower flow and external P loading.

The disconnect between P and TDFe in our water chemistry results could be explained by sediment geochemical processes. We hypothesize that sediment Fe may be tightly bound in sulphur–Fe complexes (Stumm and Morgan, 1970) resulting in the release of orthophosphate from sediments. Historical mean sulphate concentrations in Lake Diefenbaker (Pam Minifie, Environmental and Municipal Management Services Division, Water Security Agency, unpublished data 2014) from 1983 to 2012 were 65.3 ± 12.0 mg L^{-1}, ranging from 30 to 110 mg L^{-1}. Given these high sulphate concentrations, it's likely that under reducing conditions, sulphide is being produced, immobilizing Fe, leading to P release, and decreasing the P retention capacity of the sediments (Molot et al., 2014). Although Lake Diefenbaker serves as a case example of a prairie waterbody with high sulphate concentrations, these sediment geochemical processes are likely overwhelmed by the large external P load from the South Saskatchewan River. This large riverine influence highlights the importance of spatially discrete sampling in variable systems such as Lake Diefenbaker, and the importance of defining the best means to extrapolate point measurements to understanding whole systems. Given the importance of internal loading to lake modeling (e.g., Arhonditsis and Brett, 2005), we suggest that nutrient modeling applications should consider uncertainty in estimates of internal loading both in space and in time, and ideally that this uncertainty should integrate methodological uncertainty via use of data derived from multiple methods for estimating internal P loading.

Lake Diefenbaker in perspective

Compared to other mesotrophic lakes and reservoirs, Lake Diefenbaker has higher summer rates of internal P loading from sediments (Table 2). Lake Winnipeg, a eutrophic, polymictic lake, has 1.5-fold higher *in situ* estimates of internal P loading than Lake Diefenbaker (Table 2; Nürnberg, unpublished data). When Lake Diefenbaker internal P loading rates are compared to other lakes experiencing both stratified and polymictic conditions, such as Lake Pyhäjärvi, Finland (Nürnberg et al., 2012), and Mona Lake, Michigan (Steinman et al., 2009; Table 2), we see that both the anoxic RR_{TP}s (Mona) and the *in situ* internal P loading (Pyhäjärvi) are much higher in Lake Diefenbaker (Table 2). Although Lake Diefenbaker's internal P loading rates may be high, they appear to have less of an impact on its water quality, due to the high external loading combined with the

Table 1
Mass balance of gross external P loading to Lake Diefenbaker. Input loads are from the South Saskatchewan River and Swift Current Creek and output loads are from below both the Gardiner and Qu'Appelle Dams (Fig. 1). Quantities in table are TP (total phosphorus), DRP (dissolved reactive phosphorus), tonne (metric tonne), year (hydrologic year), mass retained (diff) (mass of P retained by the reservoir), mass retained (Δ level)(mass of P attributable to water level changes retained by reservoir), R (P retention attributable to water level changes, expressed as a percentage of input load) (see Eq. (4)). Seasons were defined based on flow: peak flow (May–August), low flow (September–December), winter (January–April).

Year	Season	Flow ($m^3 s^{-1}$)		ΔWater level (m)	TP (tonne)					DRP (tonne)				
		In	Out		Input	Output	Mass Retained (diff)	Mass retained (Δ level)	R(%)	Input	Output	Mass Retained (diff)	Mass retained (Δ level)	R(%)
2011	Peak flow	786	800	0.56	1388	142	1246	7	89	59	44	15	3	20
	Low flow	133	254	−2.93	31	40	−9	−23	45	3	8	−5	−9	138
	Winter flow	113	229	−1.81	114	27	87			5	8	−3		
	Annual	**344**	**428**	**−4.18**	**1533**	**209**	**1324**	**−42**	**89**	**67**	**60**	**7**	**−19**	**38**
2012	Peak flow	527	355	4.62	489	39	450	29	86	46	11	35	13	47
	Low flow	133	227	−2.68	26	28	−2	−19	65	4	6	−2	−9	187
	Winter flow	158	261	−1.54	101	28	73	−8	80	5	13	−8	−2	−122
	Annual	**273**	**281**	**0.4**	**616**	**95**	**521**	**2**	**84**	**55**	**30**	**25**	**1**	**44**
2013	Peak flow	645	476	4.44	4814	24	4790	47	98	40	3	37	11	64
	Low flow[a]	192	231	−2.04	20	10	10	−14	122	2	2	0	−7	365

[a] Only data up until October 2013 were available at time of publication. Winter P concentrations were not collected in hydrological year 2011.

Table 2
Rates of internal total phosphorus loading in Lake Diefenbaker compared to other waterbodies. Indicators of internal TP loading in Lake Diefenbaker from all stations sampled across the study period relative to values reported in the literature for lakes and reservoirs. Mean ± standard deviations and ranges in brackets, for two indicators of internal TP loading are reported. NR = Not Reported.

Study System	Trophic status	RR_{TP} (mg m^{-2} day^{-1})	*In situ* internal load (mg m^{-2} $summer^{-1}$)
Chub[1]	Oligotrophic	1.53[a]	32.11 ± 9.40 (20–47)
Diefenbaker[2,3]	Mesotrophic	17.33 ± 2.72[a] (14.96–21.24) 1.75 ± 1.29[b] (0.17–3.27)	168.66 ± 211.53 (−15.36–599.65)
Simcoe[4,5]	Mesotrophic	6.3[a] (3.30–9.90)	85
Pyhäjärvi[6]	Mesotrophic	NR	62.5 ± 31.14 (44–109)
Kinneret[7]	Mesotrophic	3.3 ± 0.55[a] (1.5–5.1)	NR
Winnipeg[4,8]	Eutrophic	11.4[a] (1.70–22.80)	260
Mona[9]	Eutrophic	6.31 ± 4.31[a] (0.80–15.56)	NR
Mitchell[10,11]	Hyper-eutrophic	NR	814.72 ± 704.89 (0–2279)
Nakamun[12]	Hyper-eutrophic	6.80 ± 0.60[a]	NR
Krishnagiri[13]	Hyper-eutrophic	40.97[c] (10.19–77.83)	NR

[1] Nürnberg et al., 1986.
[2] This study.
[3] Doig, 2015, personal communication.
[4] Loh et al., 2013.
[5] Nürnberg et al., 2013.
[6] Nürnberg et al., 2012.
[7] Orihel et al., 2013.
[8] Nürnberg, 2015, personal communication.
[9] Steinman et al., 2009.
[10] Nürnberg, 2009.
[11] Nürnberg, 2005.
[12] Orihel et al., 2015.
[13] Arunbabu et al., 2014.
[a] Derived from anoxic incubations.
[b] Derived from oxic incubations.
[c] Derived from sediment P concentrations.

low light environment. This is in contrast to a system such as Lake Simcoe, where internal and external TP loading rates are lower, but internal rates appear to have a larger impact on this P limited system (Nürnberg et al., 2013).

Is there evidence that the internal P loading is controlling algal productivity in the reservoir?

Cyanobacterial blooms are infrequent in Lake Diefenbaker (Abirhire et al., 2015; Tse et al., 2015; Vogt et al., 2015), likely related to the high flow (Abirhire et al., 2015; Yip et al., 2015), and low light and P-deficient (Dubourg et al., 2015) environment. Surface processes related to the inflow of the South Saskatchewan River and its high particulate loads create an unsuitable light environment for large populations of cyanobacteria. This is not unlike Lake Winnipeg, where light availability is low in the South basin but improved light conditions are associated with cyanobacterial bloom development in the North basin of the lake (Schindler et al., 2012).

The ultimate impact of P mobilized from sediments to primary producers is dependent on many factors, including dilution, chemical conditions, and the proximity and nutrient status of the phytoplankton communities. At times, Lake Diefenbaker phytoplankton exhibit symptoms of P deficiency and were most responsive to additional P sources when they had sufficient light available (Dubourg et al., 2015). Although Lake Diefenbaker was light limited 59% of the time during the 2013 open-water season, the best light environment occurred in the Gardiner and Qu'Appelle arms during the stratified summer. This also happens to be when and where they were most P limited, in addition to being the most productive (Dubourg et al., 2015). As such, it would appear that Lake Diefenbaker is most sensitive to an additional source of bioavailable P in the deep lacustrine arms of the reservoir. In the stratified Gardner arm, hypolimnetic sources of P typically remain in the bottom waters and only become available to photosynthetic phytoplankton during thermocline erosion and subsequent fall overturn. However, overturn also causes deeper mixing depths, resulting in phytoplankton light limitation which would prevent the phytoplankton communities from taking full advantage of the new P source. This is supported by Dubourg et al. (2015) who show no change in phytoplankton biomass or primary productivity during the isothermal fall period. Internal P loading rates were highest in the polymictic Qu'Appelle arm and may be a possible contributor to the infrequent occurrence of cyanobacterial blooms in this region (Vogt et al., 2015; Yip et al., 2015). In the Qu'Appelle arm, we hypothesize that internal P loading, warmer water temperatures, and calm conditions may facilitate bloom development (Paerl and Huisman, 2008) when light conditions are optimal.

In the future, changes in flow (i.e., nutrient loading), water clarity, and water temperatures will have the largest and most direct effect on water quality in the reservoir. Given that the TP concentrations directly upstream of the reservoir have not changed significantly from 1985 to 2000 (Saskatchewan Watershed Authority SWA, 2007), and there is no evidence of a long-term change in water quality within Lake Diefenbaker (Vogt et al., 2015; Yip et al., 2015), no imminent threat to the water quality of the reservoir is evident. However, highly variable flow regimes affect the reservoir in many ways, via impacts on stratification, turbidity, and P load, and potentially affecting rates of internal P loading. This suggests a more complete understanding of climate and reservoir management impacts on biogeochemistry is merited.

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