



## A total phosphorus budget for the Lake of the Woods and the Rainy River catchment

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### ABSTRACT

The overall goal of this study was to quantify the major and minor sources and losses of total phosphorus (TP) to the Lake of the Woods (LOW), summarized as a nutrient budget. This research was initiated in response to degradation in lake water quality, including elevated TP concentrations and increased cyanobacterial blooms, which has resulted in LOW's classification as an "Impaired Waterbody" in Minnesota. The whole-lake LOW TP budget shows that tributary inflow is largely dominated by a single source, the Rainy River, draining 79% of the LOW catchment by area. Currently, there is only a small TP contribution from shoreline residential developments (6 t; ~1%) at a whole-lake scale, relative to the large TP loads from atmospheric deposition ( $95 \pm 55$  t; 13%) and the Rainy River ( $568 \pm 186$  t; 75%). Overall, the annual TP load to LOW was ~754 t with ~54% TP retained within the lake. The nutrient budget for the Rainy River catchment revealed that contributions from point sources along the river constitute the largest anthropogenic TP source to the Rainy River and eventually to LOW. Historical load calculations along the Rainy River show that this load has been significantly reduced since the 1970s, and presently just over 100 t of P enters LOW from anthropogenic point sources. These TP budgets provide insights into the major sources of TP influencing the overall LOW water quality and with future refinement may provide a greater understanding of linkages between TP loading and spatial and temporal water quality changes in the LOW.

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### Introduction

The Lake of the Woods (LOW) (48°50'16" to 49°45'37"N, 93°49'56" to 95°19'26"W) is an international water body straddling the borders of the Canadian provinces Ontario and Manitoba and the state of Minnesota, USA (Fig. 1). The LOW has a surface area of approximately 3850 km<sup>2</sup> and, together with its drainage basin (69,750 km<sup>2</sup>), comprises 47% of the Winnipeg River drainage basin (DeSellas et al., 2009). The lake experiences vast, toxic cyanobacterial blooms that occur annually, which is a concern shared with many other lakes in North America (e.g., Lake Winnipeg and other Ontario lakes; Chen et al., 2009; Winter et al., 2011). Due to elevated total phosphorus (TP) and chlorophyll concentrations in the lake, LOW has recently been listed as an "Impaired Waterbody" in the state of Minnesota, and an International Joint Commission Task Force has been created to recommend management and governance options for this international lake. Since LOW provides drinking water to many towns and

cities, including the cities of Winnipeg, MB and Kenora, ON, its water quality is of great concern. With increasing political attention, there is a need for basic water quality research on LOW (DeSellas et al., 2009). Nutrient work, including the development of the first TP budget presented here, has been identified as a significant data gap.

Although historical accounts dating back to the 1800s suggest that cyanobacterial blooms were a component of past aquatic conditions on the LOW (McElroy and Riggs, 1943), there is a growing perception that the magnitude and duration of these blooms has increased in the northern regions of the LOW. An increase in the magnitude of these blooms may be exacerbated by eutrophication and/or conditions associated with global climate change (e.g., higher air temperature and an increased period and strength of stratification; Chen et al., 2009; Rühland et al., 2010). As a first step, knowledge of the major sources of P to the LOW is needed to address the potential causes contributing to this reported degradation in water quality.

In addition to providing a significant source of drinking water, the LOW water quality has wider significance downstream to Lake Winnipeg. Nutrient loading to Lake Winnipeg via the Winnipeg River catchment is the second largest source of nutrients to Lake Winnipeg (13% of the TP load; Salki et al., 2006), with more than half of the Winnipeg River flow originating from the LOW. Given that stricter P regulations are likely to form part of a management strategy for LOW, it is important that we fully understand the relative sources of TP to the lake, and explore possible relationships between nutrient levels and recent algal

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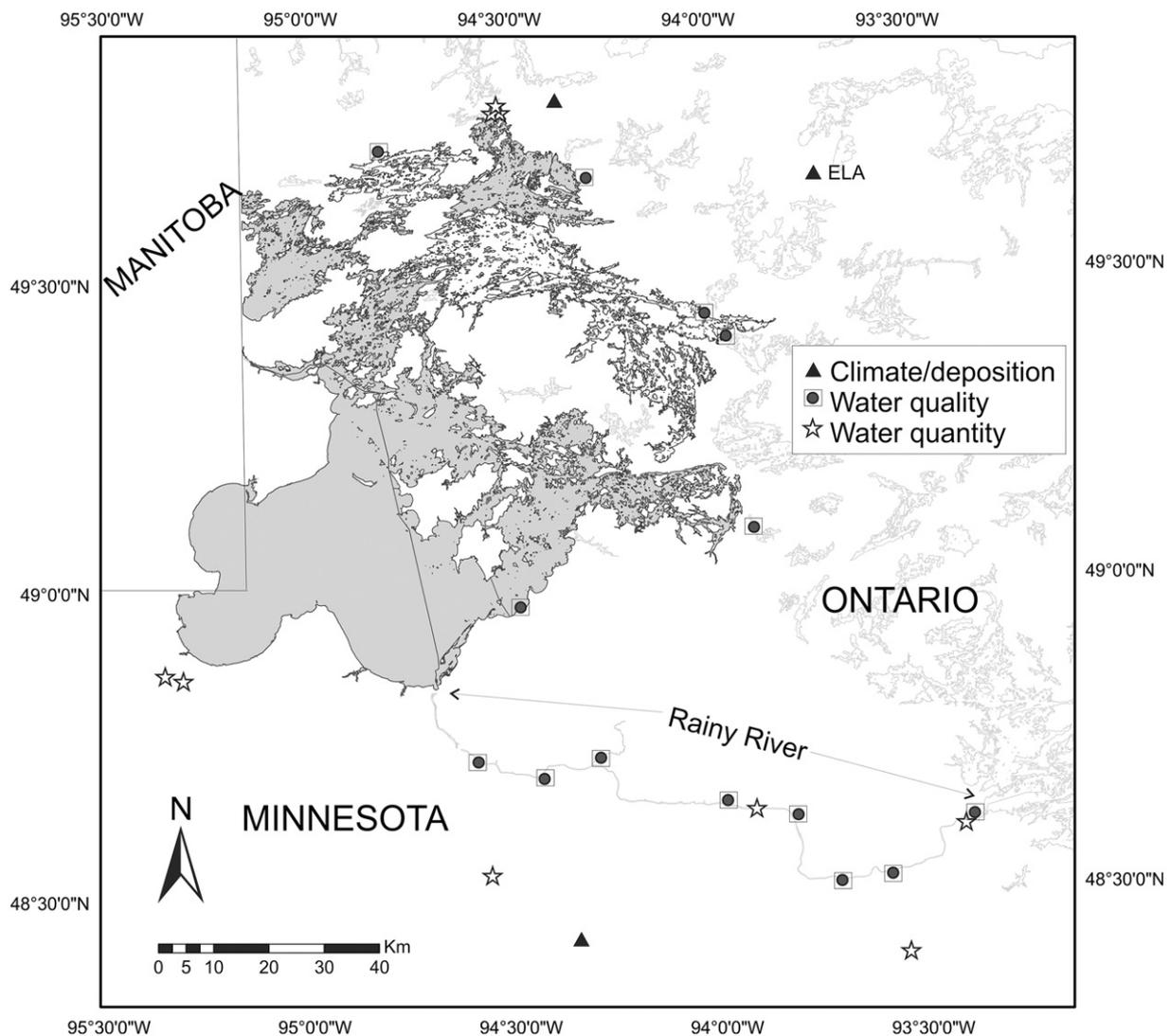


Fig. 1. Location of the Lake of the Woods and the Rainy River, showing locations of climate and tributary monitoring stations.

blooms to further our knowledge on both LOW and Lake Winnipeg water quality.

Phosphorus loading (i.e., the amount of P added to the lake per unit area per unit time), has been commonly used to measure the nutrient status of a lake (Dillon and Molot, 1996; Dillon et al., 1993; Hutchinson et al. 1991; Winter et al., 2007). A lake P budget by definition is a quantification of the sources and sinks of P into and out of a lake (Reckhow and Chapra, 1983). Once a lake nutrient budget is established, models can utilize these data to make predictions about current and future lake P concentrations under different management regimes, and other water quality indicators such as chlorophyll and dissolved oxygen concentrations (e.g., Molot et al., 1992; Nicholls and Dillon, 1978).

External components of lake P budgets that are commonly considered include atmospheric deposition, tributary inflow, non-tributary runoff, shoreline residential development, and anthropogenic point sources including wastewater treatment plants and industry discharge. In the LOW, most of the tributary inflow is captured by a single source, the Rainy River, which drains 79% of the LOW catchment. Of particular interest is the drainage area southwest of Fort Frances-International Falls, where the Rainy River discharges into the LOW. This area captures the 130 km long stretch of the Rainy River and represents 31% of the total area of the Rainy River basin. Within this region, herein referred to as the Lower Rainy River basin, there are ten point sources discharging directly into the Rainy River, a

population of over 40,000 residents, and 13.9% of the land use is agriculture (DeSellas et al. 2009). Anthropogenic contributions likely play a dominant role in this region of the LOW drainage basin. Therefore, important insights into the different components of the Rainy River P entering LOW would be gained from a P budget for the Rainy River.

Although P is found in several forms, and orthophosphate is the form of P that can be most easily assimilated by bacteria, algae and plants (Correll, 1998; Currie and Kalff, 1984), TP is the fraction of P most commonly measured in lakes for several reasons. It is relatively easily measured with good precision, it is a chemical measurement of a fraction that can be readily defined, and it is the P measure best related to the trophic status of a lake. All TP at some point is likely to be converted to orthophosphate or other bioavailable forms (Brett and Benjamin, 2008; Dillon and Reid 1981). Moreover, historical data collected in the LOW and the Rainy River is based on TP concentrations.

To gain a better understanding of the TP sources to and losses from the LOW, three tasks were carried out: (1) identification and quantification of the major and minor TP fluxes to the LOW which also included the creation of a water budget for the lake, (2) development of a basic TP budget for the Rainy River catchment, and (3) evaluation of historical TP loading to the LOW (from 1960) and the Rainy River.

## Study site

The Upper, Central, and Lower Rainy River catchments comprise the Rainy River basin and have drainage areas of 18,813 km<sup>2</sup>, 19,314 km<sup>2</sup>, and 16,760 km<sup>2</sup>, respectively (Gartner Lee Limited, 2007). The remainder of the LOW catchment (draining into the LOW rather than the Rainy River) covers an area of approximately 14,860 km<sup>2</sup>, and for simplicity is referred to as the 'Local LOW basin'. Together, all four catchments are predominantly forested (59%) consisting of a mixture of coniferous and deciduous trees (Gartner Lee Limited, 2007). However, there is some variability in land use among these catchments, including more extensive agriculture immediately south of the LOW, with 7.2% cropland in the southern Local LOW basin and 13.9% cropland in the Lower Rainy River basin.

The LOW region experiences a continental climate with variation in temperature among four distinct seasons. Mean summer and winter temperatures are 17.8 °C and –15.0 °C, respectively. Snow is typically on the ground from November through April, with the warmest month being July. The region receives an average of 625–742 mm (1916–2004) of precipitation per year, most of which falls between the months of May and September (DeSellas et al., 2009).

The geology of the LOW catchment is fairly complex, but generally can be separated from north to south into two geologically distinct portions. The northern portion is underlain by Precambrian Shield bedrock (dominance of granitic and metavolcanic rocks), characterized by a thin discontinuous till veneer that creates large areas of exposed bedrock. The northern region consists of numerous distinct depositional basins, hundreds of inlets and bays and over 14,000 islands (Chen et al., 2007). The southern portion of the LOW catchment (Lower and Upper Rainy River) and the southern basin of the LOW (Big Traverse Bay) is underlain by old lake sediment deposited by glacial Lake Agassiz. Additionally, a large band of late Archean metasedimentary rocks transects the basin in the northern portions of the Upper and Lower Rainy River catchments. There is also a change in soil type across the LOW basin with histosols in the northern Local LOW basin and Lower Rainy River basin and orthic podzols throughout the eastern Local LOW basin and Upper and Central Rainy River basins.

The LOW water levels are primarily influenced and controlled by five dams: two on the Namakan lakes, one at Rainy Lake outlet, and two at the LOW outlets. Both of the LOW outlets discharge into the Winnipeg River. The estimated mean flushing rate of the LOW is seven years (established from lake discharge records between 1893 and 2006 and lake volume estimates) (DeSellas et al., 2009). Lake outflow also includes losses to the City of Winnipeg through Shoal Lake.

## Methods

### Water balance

Daily flow data from the Rainy River were downloaded from the United States Geological Survey (USGS) for two stations (Manitou Rapids and Fort Frances) from 1960 to 2009. The remaining inflow to the LOW occurs from tributaries within the Local LOW basin that are currently ungauged. Discharge for these tributaries was calculated using monthly-weighted flow calculations based on average discharge per unit area from gauged catchments within the LOW and Winnipeg River drainage basins that were similar to the un-gauged tributaries in geology and land-use (Water Survey of Canada (WSC) and USGS).

Daily lake outflow to the Winnipeg River was available from the WSC and the Lake of the Woods Control Board (LWCB) for two stations: LOW western outlet at Norman Dam and Powerhouse and LOW outlet at Mink Creek. Smaller losses of water to Shoal Lake and

the Kenora waste-water treatment plant (WWTP) were not estimated.

The sources and losses of water for LOW were quantified for each year (Jan 1–Dec 31) from 1995 to 2005. Sources included precipitation on the lake surface and tributary runoff and water losses included lake evaporation and outflow to Winnipeg River. Evaporation was calculated using precipitation minus catchment runoff (Parker et al., 2009) measured at Lake 239. Groundwater movement in this region is unknown, but elsewhere on the Canadian Shield it has been reported to be a minimal component of the water budget (Parker et al., 2009). However, surficial geology varies significantly through the catchment and thus groundwater inputs may be more important in some areas of the catchment (e.g., southern LOW basin). Changes in lake water storage were accounted for and the accuracy of the measured water balance was calculated as per Winter et al. (2007):

$$\text{Balance (\%)} = \frac{[(\text{sum of loss terms} - \text{sum of supply terms}) / \text{sum of loss terms}] \times 100}{(1)}$$

Areal water discharge ( $q_s$ ; m/yr) was calculated using daily measurements of lake outflow:

$$q_s = \text{outflow volume} / \text{lake area} \quad (2)$$

When all measured water supply and loss sources were accounted for, the primary unknown source of water to the LOW (i.e., runoff from the Local LOW basin) was estimated from the difference.

### The LOW TP budget

#### Atmospheric deposition

To quantify TP loading to the LOW from the atmosphere, bulk precipitation chemistry (wet and dry fallout) from the Lake 239 meteorological station in the Experimental Lakes Area (ELA) was used. The ELA station is located just outside of the Local LOW basin, but represents the best historical dataset of atmospheric deposition chemistry available near the LOW basin. Atmospheric P deposition in northern Minnesota is not monitored. From October 2008 to September 2009, Environment Canada measured atmospheric TP deposition at three sites across the LOW drainage basin, which include Buffalo Point (the southern Manitoba portion of LOW), Sioux Narrows (Whitefish Bay), and Kenora, Ontario.

Precipitation (ppt) volume on the lake surface was calculated using two long-term climate records located at opposite ends of the lake: Kenora, ON, climate station (Station A at the northern end of LOW) and Baudette, MN, climate station (southern end of LOW) (Fig. 1). Since both of these stations are located in very close proximity to the LOW, precipitation from each was weighted equally. Depositional data received from Lake 239 at the ELA include volume-weighted mean annual dissolved and particulate P concentrations. Environment Canada (at ELA) removed outlier monthly P concentrations from contamination prior to providing their temporal data set. Annual TP loads to LOW from atmospheric deposition were calculated using the equation:

$$\text{Annual loading} = (\text{particulate} + \text{dissolved P concentrations } (\mu\text{g/L})) \times \text{annual ppt(m)} * \text{lake surface area (m}^2) \quad (3)$$

Eq. (3) was used to calculate TP deposition using the ELA data where annual measurements of two types of P were provided. From the TP concentrations for wet deposition only and precipitation measured at three sites across the LOW basin, Environment Canada calculated annual TP loads using the equation:

$$\text{Annual loading} = \text{monthly VWM(mg/L)} * 12 \text{ months} * \text{total volume ppt} / \text{bucket opening (m}^2) * \text{lake surface area (m}^2) \quad (4)$$

Where TP concentration was averaged across all months into a monthly volume weighted mean (VWM). Monthly TP measurements were excluded if the sample had leaves or insects present, was dirty, or the sampler failed to open for a significant period of time during the month. For these months, the mean annual depositional TP concentration for that site was used to calculate the monthly VWM. Annual load deposition to the LOW was calculated for the three LOW sites to examine spatial variability in depositional loading across the lake; these sites were averaged to yield an annual TP deposition load to the LOW for 2008–2009.

#### Tributaries and terrestrial input

The two TP monitoring stations (Minnesota Pollution Control Agency (MPCA)) used on the Rainy River were located at International Bridge at Baudette (closest site to the LOW) and Rainy River at International Bridge at International Falls (capturing the Rainy Lake outflow).

Estimates of the TP load from the Rainy River were made using two approaches that relied on the number of seasonal TP samples collected:

$$L = \sum_{i=1}^n (C_i * \bar{Q}_{pi}) \quad (5)$$

$$L = Q_a * C_a \quad (6)$$

where  $C_i$  is the instantaneous concentration associated with individual samples, and  $\bar{Q}_{pi}$  is the discharge for the interval between samples. Eq. (5) was applied for years with five or more TP samples, and Eq. (6), with  $Q_a$  the mean annual flow and  $C_a$  the average concentration of all TP samples collected in a year, was used for years with less than five TP samples. Eq. (6) was also used to calculate loads for years with five or more TP samples to compare the two load calculation methods.

Due to the distance between the flow gauge and the TP sampling station, and the TP sampling station and the mouth of the Rainy River, a correction had to be made to account for a small, ungauged area of the Rainy River drainage basin. The flow station at Manitou Rapids, Rainy River drains an area of 50,244 km<sup>2</sup>, but the Rainy River drainage basin is approximately 54,479 km<sup>2</sup>. The overall discharge from the Rainy River into LOW was calculated as follows:

$$\text{Discharge at LOW} = \left( \frac{\text{Area of Rainy River drainage basin}}{\text{Area of the drainage basin at Manitou Rapids}} \right) \times \text{flow at Manitou Rapids} \quad (7)$$

The TP load correction was made from the flow gauge station as it is likely that the additional runoff from the ungauged ~4200 km<sup>2</sup> is more influential on the TP load than the potential change in TP concentration. This method may overestimate the load from this ungauged area due to the large number of point sources included in the load calculation at Manitou Rapids. An alternative method to calculate the load for this ungauged area would be to use a P export coefficient for forested land cover, since the different percentages of land cover for this area are unknown. One disadvantage of this method is it results in a single load estimate that is the same each year.

Although water chemistry was collected from six tributaries to the LOW from April to October 2009 the remaining Local LOW catchment is ungauged. Estimates of TP export from the Local LOW basin were made using two approaches due to the lack of runoff data corresponding to TP measurements at the monitored tributaries. To estimate runoff, the closest gauge (WSC or USGS) to each tributary with a similar catchment size and no human manipulation (e.g., hydro dam) was selected. Monthly loads from April to October were calculated using measured TP concentrations, and the TP load during the remaining months was calculated using the mean TP concentration in each tributary during the months with monitoring. Eq. (6)

was applied to the Warroad River flow and TP concentration data (Table 1) to estimate the load from this tributary. The amount of ungauged area within the Local LOW basin was determined by subtracting the drainage area of the seven monitored tributaries (six Canadian tributaries and Warroad River) from the total area of the Local LOW drainage basin. The TP load from the rest of the unmonitored Local LOW basin was prorated using the loads calculated for these seven monitored tributaries. For comparison, the load from the unmonitored area was also estimated using an empirical relationship refined by Paterson et al. (2006) that estimates TP export when wetlands are a common feature in a catchment:

$$TP(\text{kg/yr}) = \text{catchment area}(\text{km}^2) * (0.47 * \% \text{ wetland area} + 3.82) \quad (8)$$

The TP load from Eq. (8), used to calculate the remaining unmonitored catchment TP load, was added to the tributary loads to get a second estimate of TP export from the Local LOW basin.

#### Loss via outflow

Water chemistry monitoring at the outflow is coordinated by the Ontario Ministry of Natural Resources (OMNR) and the Ontario Ministry of the Environment (OMOE). However, since the outflow sector

**Table 1**

Data sources and monitoring years used in the Lake of the Woods and Rainy River total phosphorus (TP) budgets. The years used to analyze historical TP loading are shown in italics.

Data type	Agency	Years
<i>Lake of the Woods TP budget data</i>		
Rainy River [TP] at International Bridge, Baudette	MPCA	1990–2009; 1962–2009
Rainy River flow at Manitou Rapids	USGS	1990–2009; 1962–2009
Local LOW basin tributary and LOW outflow [TP]	OMOE	Apr.–Oct 2009
Local LOW tributary flow—closest gauge	WSC; USGS	2009
LOW outflow, Winnipeg River, Kenora	WSC, LWCB	1990–2009
Warroad River flow, MN	USGS	1945–1980
Warroad River [TP]	MPCA	2003–2009
Atmospheric deposition chemistry, L239, ELA, Dryden, ON	EC	1990–2005; 1970–2005
Kenora A, ON climate station precipitation	EC	1990–2005; 1970–2005
Baudette, MN climate station precipitation	NOAA	1990–2005; 1970–2005
Atmospheric deposition chemistry, Sioux Narrows, Buffalo Point, and Kenora, ON	EC	Oct. 2008–Sept. 2009
Warroad Sewage Treatment Facility, MN	MPCA	1998–2007
<i>Rainy River TP budget data</i>		
Rainy Lake outflow, Fort Frances, ON	WSC	1996–2008
Rainy River [TP], International Bridge at International Falls	MPCA	1996–2008
US tributaries flow and [TP]: Little Fork, Big Fork, Rapid, Winter Rd. River	USGS; MPCA	1996–2008
Canadian tributaries [TP]: Lavallee, Sturgeon and Pinewood River	OMOE	Apr.–Oct 2009
Pulp and Paper Mill, International Falls, MN	MPCA	1999–2007
Pulp and Paper Mill, Fort Frances, ON	EC	Flow: 1996–2008; [TP]: 2005–2008
Emo Lagoon, ON	OMOE	2007–2008
Barwick Lagoon, ON	EC; IJC	Flow: 1998–2007
Rainy River Lagoon, ON	EC; IJC	2007–2008
Manitou Rapids Lagoon, ON	n/a	2007–2008
Fort Frances Waste Water Treatment Plant, ON	OMOE	Flow: 1996–2008; [TP]: 2005–2008
N. Koochiching Waste Water Treatment Plant, International Falls, MN	MPCA	1996–2008
Baudette Lagoon, MN	MPCA	Flow: 1998–2007
ISD 363 Public School, MN	MPCA	2005–2008

is only monitored every six years by these agencies, it was additionally monitored once every two weeks in the 2009 open water season to better quantify TP loss from the LOW. TP losses through the lake outflow were calculated using Eq. (5) for 2009 and Eq. (6) for all previous years using the mean TP concentration from 2009 since there is no constant P sampling station near the lake outflows.

#### Input from anthropogenic sources

For the LOW, anthropogenic point sources of TP to the lake are from shoreline development (i.e., septic systems), WWTPs, and industry (e.g., pulp and paper mills (PPMs)). Numbers of shoreline residences and their usage rates were estimated from Lake of the Woods District Property Owners Association (LOWDPOA) reports and data received through the Municipal Property Assessment Corporation (MPAC) assessments for Ontario. These data provided the type of development, the shoreline linear footage, number of bathrooms, and the year built for properties within 300 m of the lake's shoreline. TP contribution from areas not assessed (e.g., First Nations land) were estimated from population numbers (Ontario Ministry of Natural Resources, 2004), where an average of 3.07 people per day (Paterson et al., 2006) for 365 days was equal to the load from one permanent development.

There are 14 effluent point sources in the LOW drainage basin where TP concentration and effluent flow monitoring data are available, but none of these discharge directly into LOW and are accounted for in other loading calculations (e.g., the Rainy River TP budget) (Table 1). Additionally, the Kenora Area Water Pollution Control Centre discharges to the Winnipeg River approximately 1.2 km downstream of the Kenora dam, and so was not included in the LOW TP budget.

A method for estimating the contribution of P from shoreline development, including the numbers for mean number of people per development and the concentration of effluent from septic tanks have been published in Paterson et al. (2006). Phosphorus supply from septic systems takes into account the mean TP concentration in the effluent of septic tanks (9 mg/L) and daily per capita water usage (200 L/capita/day), which estimates a per capita P contribution of 0.66 kg TP/capita/yr Paterson et al. (2006). Generally there is an average of 3.07 people per development and the usage of a seasonal development is approximately 140 days per year, which is the number of days from the May long weekend until the Canadian Thanksgiving weekend in early October, but varies for development type, as described in Paterson et al. 2006. Additionally vacant properties or shoreline cleared for buildings (with holding tanks or on municipal sewage) contributed a TP export of 0.04 kg TP/lot/yr (Paterson et al., 2006).

#### Minor sources and losses

The minor components of a P budget that were considered include fish angling and restocking, input of P from shoreline leaf litter, dry pollen deposition, and nesting bird colonies. Generally all estimates of minor TP fluxes in LOW were made using equations and relationships established by or published as part the Ontario government's Lakeshore Capacity Assessment—Trophic Status Model (Dillon et al., 1986).

The removal of TP from the LOW through fish angling was estimated from personal communication with, and publications from, the Fisheries Assessment Unit OMNR (Ontario Ministry of Natural Resources, 2004). The wet to dry ratio of fish was estimated at 4:1, with the TP concentration of whole fish approximately 4% of the dry weight. A more recent study by Sereda et al. (2008) also found that the mean dry-weight elemental composition of P to be 4% across a range of fish species.

Aside from fish anglers, there are other natural avenues of fish removal from the LOW which can be considered. The LOW has a very large bird population, including white pelicans which consume an average of 1.4 kg of fish per day and cormorants which consume ~0.5 kg of fish each day (DeSellas et al., 2009). Although the total population of birds on the LOW is unknown, as of 2004 the LOW

supported one of the largest white pelican nesting sites in Canada with an estimated 8264 breeding pairs. Thus, the removal of TP through pelican feeding from June through September can be estimated. Additionally, the amount of P recycled back to the lake water by birds through their feces was estimated. An annual P load of 0.59 mg/m<sup>2</sup>/yr from bird colonies was determined from a study performed on a lake with a large waterfowl nesting colony (Manny et al., 1994).

The TP contribution from allocthonous shoreline and neighboring forests was previously determined by Hanlon (1981) using leaf litter traps. An average input of 260 kg dry weight of litter/km/yr from wooded lake shoreline was determined, with the average TP concentration of leaves 0.16% dry weight (Hanlon 1981). The Ontario portion of the LOW perimeter, including island shorelines, has been previously estimated at 10,000 km (Schupp and Macins, 1977).

Additionally, it has been hypothesized that wet deposition of pine pollen (likely captured in the atmospheric load) is probably an insignificant fraction of the total pine pollen flux because the residence time of pine pollen in the atmosphere is short due to its large deposition velocity (Doskey and Ugoagwu, 1989). In the ELA, conifer pollen deposition was estimated at 7 kg/km<sup>2</sup> during May and June with conifer pollen containing 0.5% P by weight (Graham et al., 2006).

#### Phosphorus re-suspension

Internal P loading in the southern Big Traverse Bay may also be a potential source of P to the lake due to its shallow depth and large fetch. Although internal loading was not quantified or modeled as part of this study, these analyses are currently being undertaken by researchers at St. Cloud State University, in partnership with the MPCA.

#### Retention

From the TP budget, the overall TP retained within the LOW was calculated using estimated P loads and losses:

$$R = \text{net gain}/\text{total load} \quad (10)$$

where the net gain is the sum of the TP sources to the lake minus the TP losses. Additionally, an areal loading rate was calculated for the entire LOW catchment.

#### The Rainy River TP budget

Total phosphorus loads were calculated for Rainy Lake, seven tributaries and ten anthropogenic point sources to the Rainy River. Eqs. (5) and (6) were used to calculate the TP loads from Rainy Lake and the American tributaries (Little Fork River, Big Fork River, Rapid River, and Winter Road River). The three Canadian tributaries were monitored for TP from April to October 2009. Flow was prorated to the catchments of these tributaries using the closest gauged tributaries: Sturgeon River, Chisholm, MN (USGS 05130500), Rapid River, MN and Big Fork River, MN. Generally, there was only a single monthly TP and flow measurement for the point sources, so annual load estimates were made using Eq. (6). Point source pollution data from WWTPs and PPMs was available through reports by the International Rainy River Water Pollution Board, (2007, 2008) (Table 1).

## Results

#### Water balance

Mean annual Kenora, ON precipitation (1990 to 2005) was 840 mm and mean annual precipitation (1990 to 2005) at the Baudette, MN climate station was 590 mm. For this time period, the Kenora, ON precipitation ranged between 585 and 1069 mm, whereas the minimum and maximum Baudette, MN precipitation were 419 and 759 mm, respectively. Based on these two stations, the average precipitation on the

LOW from 1990 to 2005 was 715 mm. The LOW areal water load ( $q_s$ ), from 2000 to 2007 and 1980 to 2007 was  $3.8 \pm 3$  and  $3.6 \pm 2.5$  m/yr respectively. From 1995 to 2005, the mean water balance applying Eq. (1) was  $-1.2\%$ , and estimated mean runoff from the Local LOW basin was 0.18 m/yr.

#### The LOW TP budget

##### Atmospheric deposition

The mean total dissolved P concentration and particulate P concentration from the ELA for the period of 1990–2005 was  $17.6 \text{ mg/m}^3$  and  $16.7 \text{ mg/m}^3$ , respectively. Average annual TP deposition on the LOW from 1990 to 2005 and from 2000 to 2005 was 95 t/yr (std dev 55 t) and 129 t/yr (std dev 71 t) respectively. Of the three sites monitored by Environment Canada, the highest mean TP deposition values (calculated using Eq. (4)) were measured in northern LOW near Kenora ( $123.8 \text{ mg/m}^2/\text{yr}$ ). Atmospheric deposition in Kenora was twice the TP deposition at Buffalo Point ( $54.6 \text{ mg/m}^2/\text{yr}$ ) and four to five times more than deposition at Sioux Narrows ( $26.1 \text{ mg/m}^2/\text{yr}$ ). Averaging the deposition at all three sites, the Environmental Canada data estimated a TP deposition on the LOW from October 2008 to September 2009 of 263 t.

##### Tributaries and terrestrial input

Mean TP load from the Rainy River (corrected for the distance between flow station and the mouth of the Rainy River) from 1990 to 2009 based on Eqs. (5) and (6) was 568 t/yr and 521 t/yr from 2000 to 2009, with standard deviations of 186 t and 155 t, respectively. In 2009, the most frequent TP sampling to date occurred on the Rainy River and yielded a volume-weighted TP load estimate of 438 t (404 t at the flow gauge). The ungauged contributions from the flow gauge to the mouth of the Rainy River at LOW accounted for a TP load to the Rainy River of  $\sim 45$  t/yr. By comparison, calculating the load from this ungauged area using an export coefficient of  $5.5 \text{ mg/m}^2/\text{yr}$  (the export coefficient used in the LCM for areas with wetland land cover less than 3.6%) yields a load of 23 t annually. The latter method, however, does not account for annual variations in flow (e.g., as a result of inter-annual variations in climate).

A comparison of this Eq. (5) to the crude load estimate using annual mean TP concentration and mean flow (Eq. (6)) showed a slight bias for Eq. (6) to predict higher TP load estimates, whereas from 1990 to 2009 ( $n=9$ ), Eq. (6) estimated a TP load on average 28 t more than Eq. (5). However, there was no significant difference between the two methods of estimating TP load ( $p>0.05$ ).

The average TP concentration of tributaries within the Local LOW basin from April to October 2009 was  $21.3 \text{ }\mu\text{g/L}$ , ranging between  $10.2 \text{ }\mu\text{g/L}$  and  $43.0 \text{ }\mu\text{g/L}$ . Tributaries located in northwestern LOW had mean TP concentrations in the mesotrophic range (13.9–19.6), whereas tributaries located in the eastern Local LOW drainage basin, Atikwa River and Berry Creek, had lower mean TP concentrations of  $11.7 \text{ }\mu\text{g/L}$  and  $10.2 \text{ }\mu\text{g/L}$ , respectively. From 2003 to 2008, Warroad River located in the southwestern Local LOW basin had a mean TP concentration of  $40 \text{ }\mu\text{g/L}$ . Overall, loads from these seven tributaries ranged between 0.255 t/yr (Deception Creek) and 8.3 t/yr (Atikwa River). Prorating the tributary loads from these seven monitored tributaries in the Local LOW basin to the rest of the ungauged catchment gave a load from this basin of  $\sim 46$  t/yr. The annual TP load using these tributary loads but applying Eq. (8) to the unmonitored area was considerably higher at  $\sim 81$  t/yr.

##### Loss via outflow

Prior to monitoring in 2009, mean annual lake TP loss via the outflow from 1999 to 2008 was estimated at 245 t/yr, with a range from 91 to 384 t/yr (Eq. (6)). This was estimated using a mean outflow TP concentration of  $16.1 \text{ }\mu\text{g/L}$  (measured concentrations from Coney Island). The increased monitoring from April to October 2009 resulted

in a total of 15 duplicate TP samples and yielded a mean TP concentration at the outflow of  $20.3 \text{ }\mu\text{g/L}$  and a lake TP loss from the LOW of 464 t/yr (Eq. (5)). Using this concentration and average annual flow, the mean TP loss to the Winnipeg River from 1990 to 2009 was estimated at  $306 \pm 103$  t/yr (Fig. 2).

##### Input from development

Presently on the LOW (including the American side), there are  $\sim 3180$  developments with septic systems that are used both seasonally and permanently (Table 2). Additionally, there are nine Native Reserves where the type and number of sanitation systems were not known for this study. Overall, the TP contribution from shoreline development and populations residing on the LOW shoreline is estimated at 6 t annually, assuming that 100% of the TP from septic tanks reaches the lake.

##### Minor sources and losses

A TP removal of 8.1 t/yr was estimated to occur through fish angling, and white pelican breeding pairs on the LOW were estimated to remove  $\sim 28$  t of TP annually through fish consumption. Overall the total P lost from the LOW by fish removal was 36 t/yr. Based on population numbers for pelicans and cormorants on the LOW, the TP contribution from bird feces was  $\sim 2.3$  t annually. The contribution of TP to the LOW from shoreline leaf litter was estimated to be 4 t annually. Conifer pollen was estimated to annually contribute  $\sim 0.14$  t of TP to the LOW.

##### Retention

The total TP load to the LOW, considering all sources, is approximately 754 t, with a net TP load of 412 t annually (Fig. 2). Overall this equates to an areal TP loading of  $0.195 \text{ g/m}^2/\text{yr}$ . The TP retention in the LOW calculated using Eq. (9) is 0.54 (i.e., 54% of the TP load to the LOW is being retained within the lake).

##### Rainy River TP budget

Three Canadian tributaries to the Rainy River, two downstream of the Rainy River TP monitoring point and one upstream, were sampled in 2009. The mean TP concentration of these tributaries measured from April to October 2009 was  $77.1 \text{ }\mu\text{g/L}$ . The Lavallee River had both the highest mean monthly TP concentrations and maximum TP fluctuations over the sampling period (a maximum difference of  $196 \text{ }\mu\text{g/L}$  between measured TP concentrations). Little Fork River contributes the largest TP load to the Rainy River, aside from Rainy Lake (Table 3). Together the PPMs are the largest anthropogenic sources to both the LOW and the Rainy River comprising approximately 12% and 16% of the total TP budgets, respectively (Fig. 2). Overall, more than 100 t of TP entering the LOW from the Rainy River were not accounted for in the Rainy River TP budget.

##### Historical fluxes

Historical atmospheric TP deposition on the LOW steadily declined from the 1970s to the 1990s reflecting a period of drought (Parker et al., 2009). In the late 1990s, with an increase in precipitation, TP deposition on the LOW more than doubled (Fig. 3). Historical TP loads to the LOW from the Rainy River suggest a large decline after 1975 (Fig. 4). Prior to 1975, annual TP loads from the Rainy River range from 500 t/yr to over 2500 t/yr in 1971. There is no significant, directional change in historical mean annual flow at Manitou Rapids, Rainy River. Shoreline development on the Ontario LOW shoreline began in the late 1800s and peaked in the 1960s (Fig. 5).

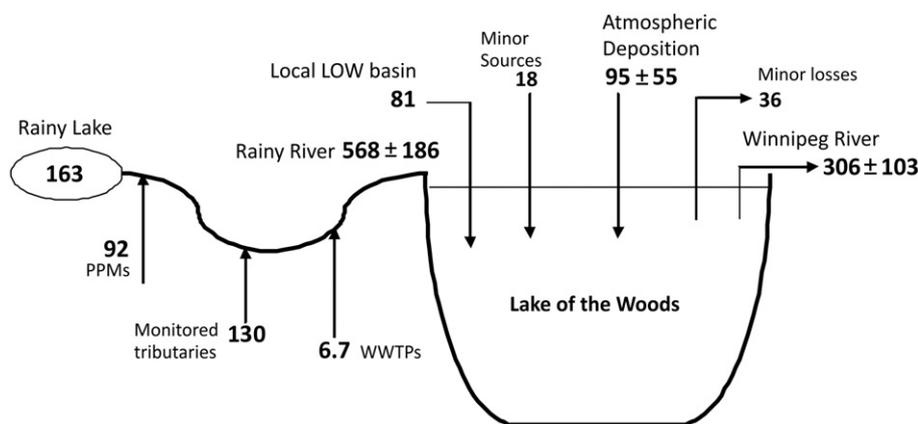


Fig. 2. Schematic of summarized of annual total phosphorus fluxes to the Rainy River and the Lake of the Woods (LOW) in metric tons. (PPMs = pulp and paper mills, WWTPs = waste-water treatment plants).

## Discussion

Previous studies have determined that nutrient concentrations within different regions of the LOW are largely influenced by proximity to the Rainy River inflow (Chen et al., 2009; Pla et al., 2005). The TP budget demonstrates that, on average, the Rainy River provided ~75% of the TP entering the LOW and thus was the greatest external source of TP to the lake. The estimates for Rainy River TP loads were made using two calculation methods to minimize the uncertainty associated with the spatial and temporal lumping of model parameters. In a study by Johnes (2007), uncertainties in annual riverine P load estimation were examined for different catchment types and sampling frequencies using several load calculation methods. In their study, rivers with moderate baseflow index, population density, and both weekly and monthly sampling intervals, Eq. (5) returned the least imprecise and uncertain load estimates (Johnes, 2007). Additionally, in past nutrient budget studies in Ontario, Eq. (5) has been the most commonly used method to estimate P loads (Dillon and Rigler, 1974).

Atmospheric deposition was the 2nd largest source of TP to the LOW TP budget. Generally, for lakes with small catchment area: lake area ratios and minimal shoreline development, atmospheric deposition may be a significant source of P and in some cases may contribute more than half of the total load (Dillon et al., 1993). However, due to the LOW's large catchment to lake ratio and extensive shoreline development, the large atmospheric P input likely reflects both the large surface area of the LOW, as well as the close proximity of the LOW (and ELA) to prairie dust sources in Manitoba and possibly the Great Plains, which are known to be important contributors to mineralogy of lake sediments at the ELA (east of the LOW) (Parker et al., 2009). Despite these high depositional TP concentrations, overall bulk deposition was within the range of load values measured for southern Ontario. For example, the LOW's areal TP load of  $25 \text{ kg/km}^2$  was less than Lake Simcoe's atmospheric TP

load of  $32 \text{ kg/km}^2$  (Winter et al., 2007) but greater than several other lakes in south-central Ontario with a precipitation load ranging between 16.7 and  $21.7 \text{ kg/km}^2$  (Dillon et al., 1993; Paterson et al., 2006).

From one year of measured atmospheric TP deposition at three sites across the LOW basin, there appears to be great spatial variability in atmospheric TP deposition to the lake. The highest mean TP deposition values were measured in the northern LOW near Kenora ( $123.8 \text{ mg/m}^2/\text{yr}$ ), which was more than twice the TP deposition at Buffalo Point ( $54.6 \text{ mg/m}^2/\text{yr}$ ) and four to five times greater than the deposition at Sioux Narrows ( $26.1 \text{ mg/m}^2/\text{yr}$ ). In contrast to the ELA, these deposition rates are very high, as in the ELA's 35 years of monitoring atmospheric P deposition; the mean deposition was  $21.4 \text{ mg/m}^2/\text{yr}$  with a maximum deposition in 2002 of  $58 \text{ mg/m}^2/\text{yr}$ . Mineral aerosols (or dust) are the dominant form of atmospheric TP, followed by anthropogenic TP introduced from fossil fuel and bio-fuel combustion (Mahowald et al., 2008). It is possible that the high TP deposition in the urban area of Kenora, compared to other areas of the LOW and the ELA, is caused by greater dust sources (e.g., from construction or road dust) and emissions of TP from local industrial and fossil fuel combustion sources.

The tributary TP concentrations measured across the Local LOW basin during the 2009 open water season ranged between 8 and  $64 \mu\text{g/L}$ . Of the several physical changes across the LOW basin (e.g., geological, land-use) that may explain this variation, differences in soil type may be most important. Although the northern bays of the LOW are recognized for their pristine water quality and lake trout habitat, Deception Creek (draining Deception Lake), draining into Clearwater Bay had mesotrophic to eutrophic TP concentrations (OMOE classification). This northwestern portion of the Local LOW

Table 2

Summarized number and type of shoreline developments on the Lake of the Woods. Phosphorus retention in catchment soils was assumed to be zero.

Residencies	Current number	Usage (capita yrs/yr) <sup>a</sup>
Permanent	816	2.56
Seasonal	2365	0.69
Resorts and condominiums (20 units each)	1060	1.27
Trailer parks (30 units each)	210	1.18
Campground (50 units each)	500	0.37
Vacant cleared lots or lots with holding tanks	2446	0.04 kg TP/lot/yr

<sup>a</sup> An explanation for the calculation of development usage (capita yrs/yr) can be found in Paterson et al. (2006).

Table 3

Total phosphorus (TP) fluxes to the Rainy River from monitored tributaries and anthropogenic point sources (PPM = pulp and paper mill, WWTP = waste-water treatment plant).

Source	TP (t/yr)	Point source	TP (t/yr)
Rainy River at Fort Frances (Rainy Lake)	163	IDS Indus Public School	0.95
Big Fork River	33.3	Baudette WWTP	0.72
Little Fork River	64.5	N. Koochinling WWTP	4.1
Winter Rd. River	1.8	Boise Cascade Corp. PPM	44.3
Rapid River	14.1	Fort Frances WWTP	0.73
Pinewood River	7.5	Emo lagoon	0.13
Sturgeon River	3.3	Rainy River lagoon	0.1
Lavallee River	5.4	Barwick lagoon	0.003
		Manitou Rapids lagoon	N/A
		Abitibi Fort Frances	47.2
Total	292.7	Total	98.2

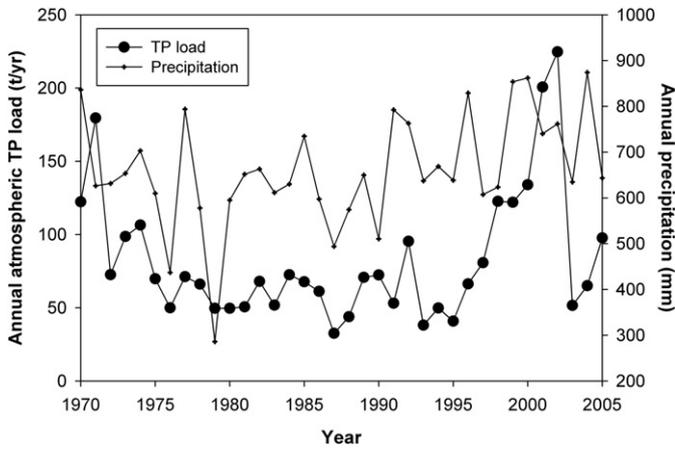


Fig. 3. Historical annual precipitation and atmospheric total phosphorus (TP) deposition on the Lake of the Woods.

basin, including the Deception Creek catchment, is covered by dystic histosols (i.e., peat soils) which are characteristic of wetlands and are known to export greater TP than forested areas located on the Precambrian Shield (Dillon and Molot, 1997; Prepas et al., 2001). The eastern area of the Local LOW basin, and the Central and Upper Rainy River drainage basins are covered with orthic podzols which are more typical of coniferous regions, and are nutrient-poor, leached, sandy soils (DeSellas et al., 2009). A combination of this soil type, Precambrian Shield geology, and forested land-cover likely yield the oligotrophic TP concentrations measured for the Atikwa River and Berry Creek. The Little Grassy drainage basin is covered by albic luvisols, which are

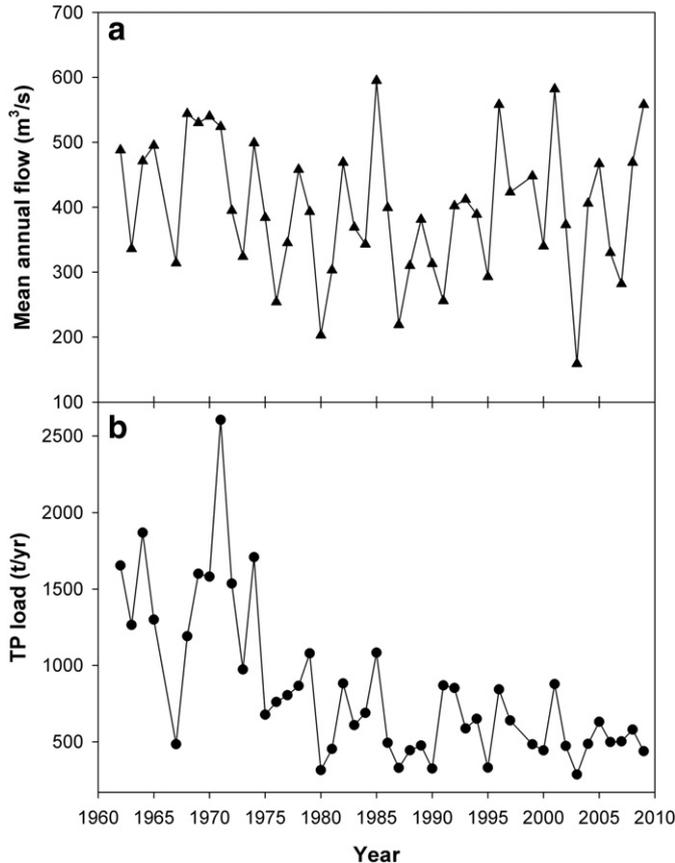


Fig. 4. a) Historical flow at Manitou Rapids, Rainy River and b) total phosphorus (TP) loads from the Rainy River to the Lake of the Woods.

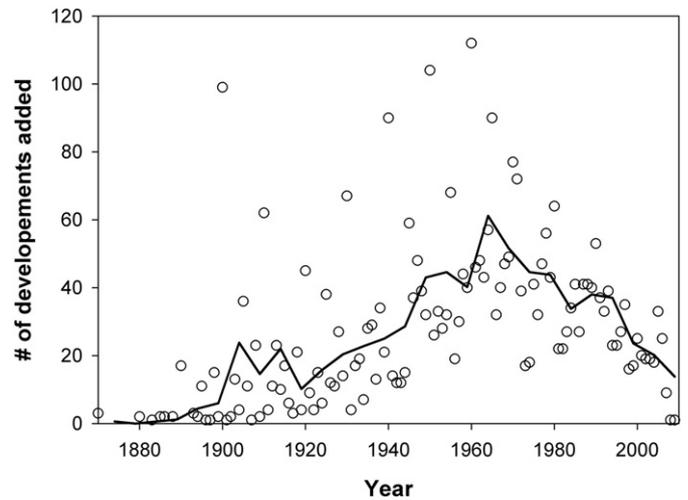


Fig. 5. Historical shoreline development on the Lake of the Woods with a 5-yr running mean (solid line).

characterized by sandy/silty particles (DeSellas et al., 2009). Albic luvisols are widely distributed around the world and an important soil type for grain production (Han et al., 2005). Overall, the 2009 tributary monitoring confirms that there is wide spatial variability in tributary TP concentration across the Local LOW basin.

Using both the tributary TP monitoring data and the TP export equation incorporating the % wetland in a catchment (Eq. (8)), there was a wide range in the overall estimate of TP export from the Local LOW basin (46–81 t/yr). When the load from the monitored tributaries was estimated using the closest USGS and WSC gauges for flow and then prorated to the ungauged portion of the Local LOW basin, a load of ~46 t/yr was estimated. The use of Eq. (8) to estimate the remaining unmonitored catchment of the Local LoW basin plus the loads from the seven monitored tributaries yielded a annual TP load from this basin of 81 t/yr. Using this method, the tributary monitoring likely only captured ~22% of the TP load from the Local LoW basin, and the total basin runoff was the 3rd largest TP source to the LOW. Since the tributaries monitored in 2009 drained more than half of the Local LOW basin, their load might be underestimated, or the load from the ungauged area may be over estimated. However, without more spatial tributary monitoring with flow data, we cannot say for certain which estimate is most accurate for this basin.

Shoreline development contributed a small portion of the TP to the overall LOW P budget (~1%). Although there is extensive development on the shoreline of the LOW, with somewhere between 5000 and 7500 buildings, in proportion to the Rainy River and atmospheric deposition these appear to be a minor source of TP in the overall budget. However, it is important to note that TP budgets for isolated embayments show that shoreline developments can contribute greater than a third of the of P loading to these specific areas (Hargan, 2010). Thus, from a lake management prospective it may be important to consider the impact of shoreline development to distinct regions of this highly complex lake.

The attenuation of septic system P in catchment soils across the LOW was unknown. As a precautionary approach, a soil retention factor of zero was used to estimate shoreline development load to the lake. Management agencies have traditionally assumed that all P from septic systems is mobile over the long term, but there are some environmental factors that can reduce the mobility of P to surface waters (Paterson et al., 2006). P attenuation is controlled by both adsorption to charged surfaces and precipitation as insoluble minerals. Reviews on the transport of P through soils have shown that, in general, various types of soil particles have strong interactions with P and can reduce P transport to waters (Jones and Lee, 1979). Although studies of mature septic systems show that P migration is

attenuated compared to surrounding ground water, migration rates still remain sufficiently fast to be of concern considering the long-term operation and minimal setback of septic systems from adjacent water bodies (Robertson et al., 1998). Due to the heterogeneous geology and soil type along the LOW shoreline, it is likely that the retention of P from septic systems varies greatly. Lastly, although P has been found to be mobile in all soils draining septic systems, P concentrations at all sites in the Robertson et al. (1998) study were found to be attenuated compared to the effluent values ranging from 23 to 99%.

The loss of TP through the LOW's outflow, the Winnipeg River, was estimated at  $\sim 306 \pm 103$  t annually. This estimate was based on the TP monitoring in the 2009 open water season. Prior to 2009, there was no nutrient monitoring at the outlet of the LOW and the closest monitoring station was downstream in the Winnipeg River. However, diatom-inferred TP from sediment cores in the north end of the LOW show little change in inferred TP concentration over the last 100 years (Rühland et al., 2010) suggesting that the 2009 water chemistry should reflect similar outflow TP concentrations as the past decade. Since close to half of the Winnipeg River discharge at Lake Winnipeg originates from the LOW, it would be expected that close to half of the TP load to the Winnipeg River originates from the LOW. This assumption would be true if there was similar TP export across the remaining Winnipeg River drainage basin. Presently, there is no published TP budget for the Winnipeg River, but rough TP budgets for Lake Winnipeg show that the final Winnipeg River load to Lake Winnipeg averages around 1000 t/yr (Environment Canada, Department of Fisheries and Oceans unpublished). This indicates that either (a) the outflow TP loss from the LOW to Winnipeg River is underestimated, and/or (b) there is greater TP export to the Winnipeg River downstream of the LOW outlet. Since the most western area of the Winnipeg River drainage basin is off the Precambrian Shield and agricultural land use is more prominent, it is possible that TP export is higher, similar to the TP export of tributaries located in the southern Local LOW drainage basin.

Several minor sources and losses of TP to the LOW were considered in the TP budget, including leaf litter, pollen, fish angling and bird guano. Generally, these minor sources are more significant to smaller lakes without anthropogenic TP sources. The contribution of P from shoreline leaf litter and debris to the LOW was estimated at 4 t/yr. The LOW has the largest measured shoreline of any inland lake in Ontario and perhaps Canada (including the US portion of the LOW), and thus leaf litter P contributions to LOW are larger than many other lakes. Although only the leaf litter input from the Ontario side was estimated, there are few islands on the US side, thus reducing shoreline perimeter compared to Ontario, and not significantly increasing the TP contribution from leaf litter.

Both atmospheric deposition and allochthonous inputs from leaf and wood litter have been estimated, but conifer pollen may additionally subsidize the LOW's productivity. It has been hypothesized that wet deposition of pine pollen (likely captured in the atmospheric load) is probably an insignificant fraction of the total pine pollen flux because the residence time of pine pollen in the atmosphere is short due to its large deposition velocity (Doskey and Ugoagwu, 1989). Several studies suggest that the rapid decomposition and enzymatic release of nutrients from conifer pollen grains contribute substantial amounts of nutrients to whole boreal catchments (Graham et al., 2006; Lee and Booth, 2003), and that the productive capacity of lakes is enhanced from conifer pollen releasing  $\sim 60\%$  of its TP in a soluble reactive form (Doskey and Ugoagwu, 1989). In the ELA, conifer pollen deposition was estimated at  $7 \text{ kg/km}^2$  during May and June (Graham et al., 2006). With conifer pollen containing only 0.5% P by dry weight, this equaled a TP contribution to the LOW of  $\sim 135 \text{ kg/yr}$ . Therefore, P contributions to lakes from pollen is likely important only to relatively small, oligotrophic lakes.

The amount of P removed through fish angling was  $\sim 8$  t annually, which is equivalent to or more than the TP load from shoreline

development for the LOW as a whole. Sereda et al. (2008) concluded that, given the high P content of fish and their slow turnover rates ( $\sim 103$  days), fish appear to be important P sinks in lakes and minor contributors to the nutrient supply of both of the lakes in their study, relative to the plankton community. In the LOW it is possible that a large portion of the P removed by fish angling would have eventually been lost through sedimentation, thus not contributing P to lake water. Additionally, two other avenues of fish removal were considered. The LOW has a very large bird population, including white pelicans which consume an average of 1.4 kg of fish per day and cormorants which consume  $\sim 0.5$  kg of fish each day (DeSellas et al., 2009). Only the TP removal by white pelicans was estimated, as the cormorant population on the LOW is not known. White Pelicans removed 28 t of TP annually from the LOW. Therefore, the several factors that constitute fish P removal and addition that make this calculation very difficult.

Bird colonies were estimated to contribute 2.6 t annually to the LOW. There are several examples where the TP contribution from birds, generally from large nesting colonies, comprises a large portion of a lake's P budget. For example, in Wintergreen Lake, Michigan, the waterfowl P load was 70% of the P budget (Manny et al., 1994) and in Cape Cod Kettle pond gulls contributed over 40% (or  $118 \text{ mg/mg}^2/\text{yr}$ ) of the annual P load (Portnoy, 1990). Generally both of these water systems are small (15 ha and 44 ha, respectively), and thus this load is large proportional to other natural P loads. A large variety of birds occupy the waters and shorelines of LOW and there are two regions on the LOW that have been designated as Important Bird Areas in Canada, housing habitat to 256 bird species (DeSellas et al., 2009). Since many of these birds are migratory, the majority of bird P contribution to the LOW likely occurs during the spring and summer seasons, as reported in other studies where more than half the annual load of P from aquatic birds occurs during this time (Manny et al., 1994; Portnoy, 1990). Although 2.7 t annually is a substantial load from birds, relative to the other TP loads to the LOW, the contribution of P from birds is minor.

#### Rainy River TP budget

The largest single load of P to the Rainy River is from its main source, Rainy Lake. The two largest tributary loads to the Rainy River are Minnesota's Big Fork and Little Fork rivers. Despite its smaller catchment, Little Fork River has a higher discharge and greater load than the Big Fork River. Big Fork River has a large area of peatland in its catchment, many lakes, and softer, fluvial sediments, which moderate runoff and flow. Little Fork River has a high portion of pastureland and hard igneous bedrock, which generate more runoff (Anderson et al., 2006). Additionally, these two tributaries have experienced erosion, undercutting, and straightening of their streambanks in recent years that may be contributing to high sediment loads and P to the Rainy River (Anderson et al., 2006). The Little Fork, Big Fork and the remaining American portion of the LOW and the US side of the Rainy River are covered by histosols, which are characteristic of wetland conditions with a thick, organic layer at the surface (DeSellas et al., 2009). Thus, the soil characteristics of this area of the LOW basin also contribute to a higher TP export to the Rainy River.

The three monitored Canadian tributaries to the Lower Rainy River had relatively minor loads ranging from 3.3 to 7.5 t/yr. However, it is likely that the increased agriculture in this area of the LOW basin contributes a large percentage of TP to these tributaries and the Rainy River. Data from the Agriculture and Agri-Food Canada show that approximately  $360 \text{ km}^2$  of cropland is located in the central Rainy River drainage basin (mostly the Canadian side of the Rainy River drainage basin) and the majority of this can be found within the drainage basins of these three tributaries. The large range in measured TP concentration from 10 to  $206 \mu\text{g/L}$  is likely linked to fertilizer and

manure runoff during storm events as the P accumulated in soils or freshly applied in fertilizer may be lost from soil through leaching and surface runoff (Hart et al., 2004).

There are several anthropogenic point sources to the Rainy River, including both WWTPs and PPMs. The contribution of TP from the WWTPs was only ~7% of that of the PPMs, and overall the two PPMs on the Rainy River constitute the largest anthropogenic source of TP to the LOW (assuming zero riverine TP retention). The manufacture of paper has historically generated significant amounts of wastewater and ranks third in the world, after the primary metals and the chemical industries in terms of freshwater withdrawal (Thompson et al., 2001). The raw waste waters from paper mills can potentially be very polluting; when untreated or poorly treated effluents are discharged to receiving waters, they may be characterized by high biochemical oxygen demand, chemical oxygen demand, suspended solids, nutrients, toxicity, and color (Pokhrel and Viraraghavan, 2004; Thompson et al., 2001). Depending on the type of paper mill, the effluent can be greater and more contaminated. For example, printing and writing paper produced by the Fort Frances PPM, as opposed to newsprint, uses more water and historically used phosphoric acid in its production (Thompson et al., 2001).

The Rainy River is likely retaining little to none of its external P loading because the TP load at Manitou Rapids is larger than the cumulative TP loading from Rainy Lake to Manitou Rapids (loads presented in Table 3). However, the dynamics of P in the aquatic environment are complex and include many processes. P can be sorbed and released from suspended and bed sediment or precipitated with calcite. P may be removed from the interstitial pore water in the bed sediment by macrophytes or from the water column by epiphytic algae (Wade et al., 2002). Additionally, some of these processes may contribute internal sources of P to the Rainy River that are not considered in the Rainy River TP budget.

#### *Trends in historical TP loads*

Historical changes in TP loading to the Rainy River and eventually the LOW are difficult to establish, as there was little historical nutrient monitoring prior to the 1990s. Calculations of the historical P loads from the Rainy River to the LOW depict a large decline in P loads after the 1970s, which prior to the 1980s were annually above 1000 t/yr. Many inferences for changes in historical TP loading can only be based on qualitative observations and general knowledge of when advances in basic P management technology occurred (e.g., development of secondary and tertiary wastewater treatment). Today, mills on the Rainy River use a secondary treatment process as well as primary treatment, which involves aerating the effluent and microorganisms to remove oxygen-consuming materials and significantly decreasing the toxicity of the effluent (Environment Canada, 2003). Significant changes in PPM effluent to the Rainy River would have occurred around 1992 when the Federal Government passed the Pulp and Paper Regulatory Framework consisting of the Pulp and Paper Effluent Regulations (PPER) under the Fisheries Act and two regulations under the Canadian Environmental Protection Act. The PPER revoked and replaced an earlier set of regulations passed in 1971 (Environment Canada, 2003). Monitoring of PPM effluent on the Rainy River became more extensive from 1996 onwards to ensure that effluent quality met compliance levels.

Furthermore, the Fort Frances WWTP was rebuilt and upgraded in January 1998 to include secondary treatment and P removal. For the past decade, point source discharges to the Rainy River from municipal and industrial sources have remained relatively constant from a loadings perspective and it is foreseen that these discharges will remain at current levels into the foreseeable future (IRLBC/IRRWPB, 2002).

The atmospheric TP loads on the LOW calculated from the ELA depositional data mirror the results published in Parker et al. (2009).

The TP depositional trends can thus be summarized by a long period of slow decline in TP deposition during the 1970s through early 1990s corresponding to a period of declining precipitation. Following this there was a rapid increase in the late 1990s and then a decline in the past few years. No significant trends in either the volume-weighted concentration or deposition of TP were found (Parker et al., 2009).

Although there was no seasonal study of atmospheric deposition to the LOW, results from a study on the global distribution of atmospheric P suggest a strong seasonal cycle in TP concentrations at many locations, having a maximum in the summer and fall in the European mid-latitudes (Mahowald et al., 2008). Seasonal patterns have also been documented in south-central Ontario where TP deposition is highest in the spring and summer and substantially lower in the fall and winter (Eimers et al., 2009). Since TP deposition from ELA was provided as annual means of monthly concentrations, it was not possible to account for potentially higher TP deposition in the summer along with greater precipitation.

#### **Conclusions**

The three main TP sources to the lake can be grouped into three loads: atmospheric deposition, the Rainy River, and the runoff from Local LOW catchment, accounting for ~744 t of TP entering the LOW annually. Attempts were made to determine the key contributors of P to these three main sources. This revealed that the Rainy River has significant TP loading from the PPMs which likely constitute the greatest anthropogenic TP source to the LOW. Preliminary atmospheric TP monitoring data collected by Environment Canada suggest that TP deposition across the LOW is highly variable and greater than at the ELA, located ~50 km to the northeast of the LOW. There was a wide range in tributary TP concentrations across the Local LOW basin linked to varying geology, soil type and land use. The estimates of P loading from this basin were uncertain as nutrient monitoring only began in 2009.

Regarding the management of P in the Rainy River catchment, it may be difficult to reduce P loading from the atmosphere and the Local LOW catchment. Historical load calculations along the Rainy River show that this load has been significantly reduced since the 1970s, and presently just over 100 t of P enters the LOW from anthropogenic point sources (including shoreline development). These load reductions likely indicate that the water quality of the LOW, with respect to nutrient loading only, has improved over the last few decades. If further water quality indicators (e.g., phytoplankton taxa, chlorophyll *a* concentration) suggest that the water quality of the lake is deteriorating, then it may be linked to other environmental factors or a combination of stressors. For example, the synergistic effect of both nutrients and climate change may promote a degradation of the LOW water quality (Michelutti et al., 2009; Rühland et al., 2010). This first TP budget for the LOW identifies the major and minor TP sources to the lake and Rainy River, significant changes in historical TP loading, and major data gaps in our knowledge on the lake. Continuing to refine the TP budget will provide insights into factors influencing the overall LOW water quality, but also triggers of spatial and temporal change in water quality across the lake. For example, as new data becomes available the possibility of nutrient resuspension in southern LOW and internal loading in northern LOW may be addressed.

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