Internal phosphorus loading in Canadian freshwaters: A critical review and data analysis

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Internal phosphorus loading in Canadian freshwaters:
A critical review and data analysis

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Many physical, chemical, and biological processes in freshwater ecosystems mobilize the nutrient phosphorus (P) from sediments, which in turn, may contribute to the formation of harmful algal blooms. Here, we critically reviewed internal P loading in Canadian freshwaters to understand the geographic patterns and environmental drivers of this important process. From 43 publications, we consolidated 618 estimates of internal P loading from Canadian freshwater ponds, lakes, reservoirs, and coastal wetlands ($n = 70$). Expressed in terms of total phosphorus, short-term gross rates in sediment samples (L_{gross}) ranged from -27 to 54 mg m⁻² d⁻¹ ($n = 461$) while long-term net rates in whole-ecosystems (L_{net}) ranged from -1694 to 10,640 mg m⁻² y⁻¹ ($n = 157$). The main environmental drivers of this variation were oxygen, pH, geology, and trophic state. Internal P loading tended to be higher during the open-water season, and most prominent in small prairie lakes. Priorities for future research on internal P loading should include resolving methodological problems, assessing the relative importance of different mechanisms, examining the influence of anthropogenic activities, and quantifying rates in under-studied ecosystems.

Introduction

Globally, eutrophication is one of the key drivers of change in aquatic ecosystems (Millenium Ecosystem Assessment 2005). Eutrophication causes poor water clarity, oxygen depletion, fish kills, and biodiversity loss, among others problems, which in turn lead to the impairment of ecosystem services to human society (Carpenter et al. 1998; Smith 2003). Nutrient enrichment can also amplify infection and disease in wildlife (Johnson et al. 2010) and many cyanobacteria favored by eutrophication produce brain and liver toxins. As well, eutrophication decreases the economic value of fisheries, tourism, and property, and increases the costs of water treatment and health care (e.g., Dodds et al. 2009). These substantial ramifications have prompted scientists and policy makers to seek strategies for improving water quality in nutrient-polluted ecosystems. Efforts to combat eutrophication by diverting sewage effluent or implementing advanced wastewater treatment have been successful in many water bodies around the world (Cooke et al. 2005; Schindler 2012). However, such measures have not led to the desired changes in water quality in many cases, and any improvements have often been delayed by several years or decades (Cullen and Forsberg 1988; Marsden 1989; Jeppesen et al. 2005).

The partial and delayed recovery of water bodies in response to reductions in external nutrient loading is often caused by the internal cycling of an important algal nutrient: phosphorus (P). In aquatic ecosystems with a long history of nutrient pollution, sediments harbour a large reservoir of legacy P, which under certain conditions, can be recycled to surface waters and stimulate algal blooms (Welch and Cooke 1995; Søndergaard et al. 2012). The release of nutrients from sediments, commonly referred to as “internal loading”, is a complex process that can result from a number of physical and biogeochemical mechanisms (Boström et al. 1988; Søndergaard et al. 2003; Smolders et al. 2006). These mechanisms operate on different temporal and spatial scales and are influenced by a multitude of factors (Katsev et al. 2006). Consequently, the importance of internal P loading varies widely among water bodies, ranging from an almost negligible contribution in some systems to adding as much, if not more, than external P

inputs to whole-ecosystem P budgets on an annual basis. This complexity makes controlling eutrophication in freshwaters a tremendous challenge for resource managers.

In this paper, we synthesized and analyzed the available knowledge on internal P loading in Canadian freshwaters. Canada is the second largest country in the world by area, spans over 40 degrees of latitude, and contains an impressive diversity of freshwater ecoregions (Abell et al. 2008). As such, the findings of our comprehensive review and data analysis are useful not only to scientists and decision makers in this country, but also advances our understanding of the processes and drivers of internal P loading in freshwater ecosystems worldwide. Our specific objectives are to: i) determine the importance of internal P loading in Canada; ii) map the geographical patterns of internal P loading across the country; iii) examine the environmental drivers of internal P loading across a broad range of aquatic ecosystems; and iv) identify key knowledge gaps and generate new hypotheses about internal P loading to guide future research on this subject. We restricted the scope of our study to freshwater ponds, lakes, reservoirs, and coastal wetlands within Canada, but included transboundary waters. Remediation strategies for internal P loading have been previously reviewed (e.g., Cooke et al. 2005; Zamparas and Zacharias 2014) and are beyond the scope of this paper. The primary impetus for our study is to understand where, when, and why this process occurs in Canadian freshwaters—knowledge that is critical for effectively managing eutrophication of nutrient-polluted water bodies in this country and developing realistic goals for eutrophication recovery. While a few reviews on internal P loading have been written (e.g., Boström et al. 1988; Søndergaard et al. 2003; Smolders et al. 2006; Hupfer and Lewandowski 2008), none of them attempted to quantitatively synthesize data from across numerous studies to identify the main drivers of internal P loading as we have done here.

This paper is organized into five sections. To begin, we define internal P loading (Section 1) and review the mechanisms responsible for this process (Section 2), emphasizing recent advances in this field and including conceptual schematics to facilitate understanding by non-specialists. We then present the

results from our analyses of the available published data on internal P loading from Canadian freshwater sediments (Section 3). Rates of internal P loading across the country are illustrated, as well as statistical tests of the environmental factors associated with variation in this process. Next, we examine several case studies of internal P loading in well-studied water bodies in Canada, selected to represent different types of ecosystems (namely, large lakes, nearshore environments, coastal wetlands, reservoirs, small prairie lakes, and Precambrian Shield lakes) (Section 4). Finally, we describe the key knowledge gaps identified from our study and provide recommendations for new research on this important problem impacting the health of freshwaters (Section 5). A glossary of key terms used in this paper is provided in Box 1.

1 Definitions

Although limnologists have referred to the “internal loading” of P from lake sediments in the primary literature for over 40 years (e.g., Vollenweider 1975), operational definitions of this process can be vague and often inconsistent across studies. This has led to confusion about exactly what constitutes internal P loading. There are three main issues that complicate the concept of internal P loading. First, the delineation of the boundary of the sediment “box” from which nutrients are released to overlying lake water is debatable. For example, should sediment-associated organisms be included or excluded in the sediment “box”? Further, if P-rich groundwater from the watershed flows through sediment to a lake, should this be included in the estimate of internal loading? Second, the time scale over which P release from sediment is measured is critically important. Should internal loading be measured on the scale of hours or years, and how should these different estimates be interpreted? Furthermore, how do we deal with the iterative recycling of an individual P molecule between sediment and water within a given time step? Finally, internal P loading can be estimated as a gross or net flux from sediment to overlying lake water, but the meaning and ecological implications of these two types of estimates differ considerably.

We would like to propose some standard terminology to describe internal P loading that we hope will be embraced by the limnological community. We suggest “internal phosphorus loading” be used as a

generic term to refer to all physical, chemical, and biological processes by which P is mobilized and translocated from the benthic environment to the overlying water of aquatic ecosystems. We explicitly define the “benthic environment” as the bottom sediments of a water body, plus all organisms living in or on the sediments (including periphyton, macrophytes, and benthic invertebrates). Our rationale for defining internal P loading in this manner is that, in most cases, concerns about internal P loading in freshwater ecosystems are intimately linked with concerns about excessive growth of nuisance phytoplankton in surface waters. Hence, we define internal P loading in terms of what phytoplankton could potentially access. For example, if P originating from sediments is directly taken up by a thick growth of periphyton growing on the sediment surface, this P is not directly available to phytoplankton while retained by these organisms, and therefore should not be included in estimates of internal P loading. Finally, we consider the inflow of P to an aquatic ecosystem through groundwater as “external loading”, with the caveat that many methods to estimate internal P loading (e.g., benthic flux chambers and mass balances) are not able to distinguish this input from true sources of internal P loading.

Next, we propose two operational definitions for internal P loading (Figure 1), as well as briefly describe common methods for their quantification:

Gross benthic phosphorus flux (L_{gross}) is the gross rate of P release per unit area of sediment measured in a sediment sample over hours to days, and is typically expressed in units of $\text{mg m}^{-2} \text{d}^{-1}$. The most common method for quantifying L_{gross} is a sediment incubation experiment, in which an intact core of sediment is incubated in the laboratory (or a lander in the field, as described by Orihel and Rooney 2012) and the concentration of P in overlying water is measured at designated intervals, from which the rate of change is used to calculate L_{gross} . One can also estimate L_{gross} directly in the field by deploying benthic flux chambers (e.g., Hendzel et al. 1994) or measuring pore water P concentrations across the sediment-water interface (SWI; Box 1) and applying a diffusion coefficient to calculate L_{gross} based on Fick’s first law of diffusion (e.g., Carignan and Lean 1991; Monbet et al. 2008). L_{gross} can be interpreted as a near-

133 instantaneous input of “new” P to overlying water which, under P-limiting conditions and sufficient light
134 conditions, could stimulate an algal bloom.

135 **Net internal phosphorus loading rate** (L_{net}) is the net rate of P release per unit area of sediment
136 estimated for a whole ecosystem over one year, and is typically expressed in units of $\text{mg m}^{-2} \text{y}^{-1}$. This
137 term represents the balance, on an annual basis, between the upward flux of P released from the benthic
138 environment and the downward flux of P from the water column. L_{net} can be estimated through modelling,
139 usually by constructing a whole-lake mass balance of P (e.g., Mitchell 1984). In general, these empirical
140 models calculate inputs (e.g., inflowing streams, overland runoff, and atmospheric deposition) and
141 outputs of P (e.g., outflowing streams) from lake basins, and assume that any missing input of P comes
142 from internal P loading. In aquatic ecosystems with a legacy of P in sediments from many years of
143 anthropogenic P loading, L_{net} may be positive in a given year. In such cases, L_{net} can be interpreted as the
144 contribution of internal P loading to long-term changes in P concentrations in a water body, and is
145 particularly important for understanding trajectories of recovery after reductions in external P loading.

146 We emphasize that these two operational definitions are not synonymous, and should not be used
147 interchangeably. Theoretically, L_{gross} and L_{net} are related to another through a sedimentation term (i.e., L_{net}
148 $= L_{\text{gross}} - S$, where S is the rate of sedimentation of P from the water column), if L_{gross} is scaled-up
149 appropriately in space and time. However, this is challenging in practice because extrapolating L_{gross} from
150 a short-term estimate of a small sediment sample to a whole ecosystem over a long time scale is fraught
151 with uncertainty, as L_{gross} varies spatially and temporally within a water body and we lack a complete
152 mechanistic understanding of the factors driving this variation (as we explain in detail in Section 2).

153 Finally, it is important to recognize that P released from the benthic environment during the process
154 of internal P loading does not represent a “new” source of P to the water body. Rather, internal P loading
155 represents the re-mobilization of P previously deposited to the water body from external sources in the

watershed (e.g., sewage discharge, agricultural runoff, or fertilizers). Thus, the rate of internal P loading in a given ecosystem is ultimately a function of the rate of external P loading.

2 Theory

Phosphorus occurs in lake sediments in solid and aqueous phases under a variety of organic and inorganic molecular forms or species. To understand the mechanisms of P release from sediments, it is necessary to understand how P speciation in sediment changes over time and with depth. This section includes a detailed overview of the molecular level mechanisms by which P may be released from the solid to the aqueous phase (2.1), and a discussion of how these mobilisation mechanisms are affected by changing conditions to enhance or inhibit internal P loading (2.2). A simplified conceptual model of internal P cycling at the SWI, including all the processes discussed within this section, is provided in Figure 2. The key ways in which P may be immobilised within sediment and how this P may be released to the aqueous phase are listed in Table 1. Forms of P typically measured in pore water or overlying water of sediments are: total phosphorus (TP), total dissolved phosphorus (TDP), and soluble reactive phosphorus (SRP) (see definitions in Box 1).

2.1 Mechanisms of internal phosphorus loading

The interactions between iron cycling and P mobility have dominated discussion of internal P loading in the literature for decades. This is largely due to the early identification of the mechanistic link between reduction of iron oxides and P release, which is a dominant process in many environments (Einsele 1936; Mortimer 1941). Internal loading of P can occur in a variety of ways depending on the P species present in sediment and many examples of internal loading in the literature, particularly in recent years, are not dominated by iron cycling (Katsev et al. 2006; Joshi et al. 2015; Li et al. 2015). Phosphorus can enter the water column from sediment by diffusion or advection through pore water following: i) desorption of organic or inorganic P bound to mineral surfaces (Figure 2: 7); ii) dissolution of minerals including phosphate within their crystal structure, as a coprecipitate or within occlusions (Figure 2: 9); iii)

hydrolysis or mineralisation of organic matter (Figure 2: 13); iv) excretion of exudates by macrophyte roots or bacteria (Figure 2: 12) and; v) dissociation of ternary P complexes with humics (Figure 2: 14). Solid phase P may also enter the water column by resuspension of sediment particles; this process is discussed in more detail in section 2.2.8 (Jones and Welch 1990; Ekholm et al. 1997). In addition, cyanobacteria may also contribute to internal P loading (Xie et al. 2003), as they migrate seasonally between shallow sediment and surface water (Istvánovics et al. 1993; Verspagen et al. 2004). It should be recognised that each of these P release mechanisms may be balanced by an opposing retention mechanism (i.e., sorption, precipitation, assimilation, complexation, sedimentation and burial of cyanobacteria) which can prevent internal loading by removing P from pore water. Internal P loading is a net process that requires P release to be greater than P retention. If P retention is greater than P release, burial of P within sediments occurs and the internal loading flux is negative.

2.1.1 Desorption

Phosphate occurs almost entirely as singly or doubly protonated anions (H_2PO_4^- and HPO_4^{2-}) within the common pH range of natural waters (i.e., 5–9). Phosphate anions adsorb to hydroxylated surfaces on oxide minerals and to aluminol edge sites on clay minerals by ligand exchange/inner sphere surface complexation (Goldberg and Sposito 1985). Ferric oxyhydroxides and hydrous ferric oxides are excellent sorbents of phosphate in oxic environments due to their high surface area, but many other minerals also have significant sorptive capacity towards phosphate including aluminum hydroxides (e.g., gibbsite), clay minerals (mostly edge sites), and calcite.

Desorption of P from mineral surfaces may be caused by changes in pH, ionic strength, aqueous phosphate concentration or an increase in concentration of other anions competing for surface sorption sites. Increases in pH may result in desorption of surface sorbed phosphate due to decreased electrostatic attraction and increased electrostatic repulsion towards deprotonated phosphate species. However, pH changes may also result in the dissolution or precipitation of sorbed phases causing a net change to the number of surface sites available. Sediments with multiple mineral phases may exhibit complex P

mobility – pH relationships (Wang et al. 2005). Sorption increases slightly at high ionic strengths at high pH but this effect is weaker than changes to pH. In the acidic conditions occurring in soft water sediments, changes to ionic strength do not result in distinguishable changes to surface sorption (Antelo et al. 2005).

In addition to hydroxyl ions, several other common anions compete with phosphate for sorption sites on mineral surfaces including arsenate (Hongshao and Stanforth 2001) and sulfate (Geelhoed et al. 1997) on goethite and bicarbonate, oxalate, and citrate on kaolinite and montmorillonite (Kafkafi et al. 1988). Increased concentration of these competing anions, or phosphate in solution may result in desorption of phosphate (Froelich 1988). Increases to aqueous silica concentrations have also been shown to result in desorption of P from sediment (Tuominen et al. 1998) with competition for surface sorption sites proposed as the mechanism. The equilibration time for competing anions at the goethite surface influences competitive effects and surface precipitation reactions may be required to explain the competition between arsenate and phosphate (Hongshao and Stanforth 2001). Slow sorption processes into micropores may also be an important kinetic control on P mobility (Torrent et al. 1992).

Although few studies report full sorption isotherms for organic P species on sediment minerals (Ruttenberg and Sulak 2011), organic P sorption on mineral surfaces has been demonstrated. Sorption complexes studied include glucose-1-phosphate (G1P) to α -FeOOH (Olsson et al. 2010), myo-inositol hexaphosphate (IHP) to α -FeOOH, illite and kaolinite (Celi et al. 1999, 2001), and multiple organic-P species to aluminum (oxyhydr)oxides (Yan et al. 2014). The adsorption mechanism in all cases is via the phosphate group with the organic moiety only causing conformational hindrance (Celi et al. 1999). Highest sorption densities occur with the lowest molecular weight organic P species (Yan et al. 2014). Organic-P mineral surface complexes occur over a range of pH conditions, even above the minerals' point of zero charge, indicating a strong surface interaction (Ruttenberg and Sulak 2011).

2.1.2 Dissolution

Minerals with phosphate in their structure have been directly detected or predicted to occur within lake sediments. Dissolution of these minerals, or other mineral phases with sorbed P, increases aqueous P concentrations. The most commonly occurring phosphate minerals in lake sediments are calcium, iron, manganese, and aluminum phosphates. These may occur either as distinct mineral grains or as impurities within oxide and carbonate minerals. Metal phosphates may be formed during diagenetic processes within sediment, or deposited following erosion and transport. Mineral structure, thermodynamic stability, precipitation, and dissolution kinetics vary over several orders of magnitude (Brantley et al. 2008). Therefore, specific mineralogical information about phosphate-bearing phases in sediment is important in order to predict changes in P concentrations under different environmental conditions. As iron/manganese oxides and phosphates are redox-sensitive, they are subject to dissimilatory reduction by facultative and obligate anaerobic bacteria in anaerobic sediments, which often results in mobilisation of P to pore water with depth. Other key factors affecting precipitation and dissolution include pH conditions (e.g., precipitation of carbonates at high pH and dissolution at low pH), temperature (e.g., increasing solubility of CaCO_3 at low temperature), and solution composition.

Pore water in sediments of hard water lakes are often supersaturated with respect to various calcium phosphates (Figure 3). Despite this, pure authigenic calcium P minerals are uncommon in their pure crystalline form and usually occur as minor impurities within authigenic calcium carbonate minerals. Calcium phosphate minerals that may occur within lake sediments include amorphous calcium phosphate ($\text{Ca}(\text{H}_2\text{PO}_4) \cdot \text{H}_2\text{O}$), brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), monetite (CaHPO_4), hydroxyapatite ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$), carbonate-fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), $\text{Ca}_5(\text{CO}_3 \cdot \text{PO}_4)_3\text{F}$, and fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$). Some sequential extraction schemes are able to differentiate between allogenic (transported from another location) and authigenic (produced *in situ*) calcium phosphates based on this variation in reactivity (Ruttenberg 1992; Ruttenberg et al. 2009). Allogenic calcium phosphates, particularly fluoroapatite, have been shown to occur as mineral grains in lake sediments but show very different chemical reactivity when

253 compared to authigenic calcium phosphates. Calcium phosphates are not directly susceptible to redox
254 driven precipitation and dissolution processes but are extremely sensitive to changes in pH, temperature,
255 and alkalinity, which may occur simultaneously.

256 Although P is often associated with ferric oxyhydroxides by adsorption processes, a variety of ferric
257 and ferrous phosphate minerals have also been thermodynamically predicted or demonstrated to occur in
258 lake sediments, such as anapaite ($\text{Ca}_2\text{Fe(II)(PO}_4)_2 \cdot 4\text{H}_2\text{O}$), vivianite ($\text{Fe}_3(\text{II})(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$), strengite
259 ($\text{Fe(III)PO}_4 \cdot 2\text{H}_2\text{O}$), and santabarbarite ($\text{Fe}_3(\text{III})(\text{PO}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$). Additionally, poorly characterised
260 ferric phosphate phases have been shown to occur in estuary environments (Hyacinthe and Van Cappellen
261 2004) and presumably may also occur in lake sediments under similar conditions. Vivianite is thought to
262 occur at less than 1% concentration which has made its direct identification challenging; despite this,
263 several studies show convincing spectroscopic evidence of vivianite in lake sediments (e.g., Manning et
264 al. 1991; Fagel et al. 2005; Sapota et al. 2006; Rothe et al. 2014). Additionally, its presence has been
265 inferred from thermodynamic calculations (e.g., Nriagu and Dell 1974; Matisoff 1980). Santabarbarite,
266 altered vivianite (Pratesi et al. 2003), has been shown to occur as an amorphous rim around Lake Baikal
267 vivianite concretions (Fagel et al. 2005). Ferric phosphates are sensitive to reductive dissolution both
268 chemically and by microbial metabolism (Jones et al. 1983). Their use as an electron acceptor in
269 anaerobic microbial metabolism is more thermodynamically favourable than ferric oxides (Hyacinthe and
270 Van Cappellen 2004). Conversely, ferrous phosphates have been shown to be sensitive to rapid oxidative
271 dissolution and precipitation as ferric phases in the presence of oxygen (e.g., Roldán et al. 2002) and by
272 nitrate-reducing, iron-oxidising bacteria (Miot et al. 2009; Carlson et al. 2013).

273 Supersaturation of pore water with respect to reddingite ($\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$) has been shown in
274 several locations (Nriagu and Dell 1974; Jaquet et al. 1982) indicating that manganese phosphates may
275 also control P mobility; however, there is little conclusive spectroscopic or mineralogical evidence for
276 this in freshwater ecosystems.

2.1.3 *Hydrolysis and mineralisation of organic matter*

Since phosphorus is an essential element for life, it is incorporated into numerous biomolecules, primarily as phosphate bound to organic groups via either one (e.g., mononucleotides and phospho-sugars) or two ester bonds (e.g., phospholipids and deoxyribonucleic acid [DNA]). Less abundant P species present within the organic P fraction include phosphonates (with a direct C-P bond) and organic-polyphosphates (e.g., adenosine triphosphate [ATP] and adenosine diphosphate [ADP]). A thorough review of organic P species in the environment can be found in Turner et al. (2005).

Organic P species in sediments may also be produced by biota in the sediment via direct assimilation of orthophosphate in pore water (Figure 2: 11). Alternatively organic P can be incorporated into the sediment with necromass (dead and decaying matter) originating from primary production or higher organisms. The sedimentation of necromass has been shown to constitute a major P input to lake sediments, particularly in eutrophic systems (Joshi et al. 2015). Mobilisation of P from solid organic matter to the aqueous phase may occur due to enzymatic, photolytic, and surface catalysed hydrolytic processes (Figure 2: 13).

Phosphatase enzymes are exuded from micro-organisms within periphyton and sediment as well as from macrophyte roots as a strategy to increase the bioavailability of organic-P for assimilation and growth (Romaní and Marxsen 2002; Egamberdieva et al. 2010; Jansa et al. 2011). These extracellular hydrolytic enzymes act upon both particulate and aqueous organic-P species resulting in production of orthophosphate, which is more easily accessible to biota. Phosphorus concentrations can increase due to the action of other hydrolytic enzymes acting on different types of bonds, resulting in mobilisation of aqueous organics containing one or more phosphate groups.

Enzymatic hydrolytic processes contribute to orthophosphate concentrations on both seasonal and decadal timescales due to variations in the lability of organic P species. Rapid hydrolysis of labile species such as poly- and pyrophosphate occurs close to the SWI leading to strong differences between organic-P

speciation in surface water and sediments and to significant release of orthophosphate (Reitzel et al. 2007, Shinohara et al. 2012). More recalcitrant organic P species may persist for many years due to slow degradation rates. The half-life of organic-P species in lake sediments below the SWI has been estimated between 13 and 23 years (Ahlgren et al. 2005).

Surface catalysed hydrolysis of organic-P species is considered to be minor in comparison to enzymatic hydrolysis (Olsson et al. 2010). However, differences in sediment mineralogy can result in order of magnitude differences to the rate of surface catalyzed hydrolysis. Baldwin et al. (1995) have shown that monoester P degradation rates are $\text{MnO}_2 \gg \text{Fe}(\text{OH})_3 > \text{TiO}_2 > \text{Fe}_2\text{O}_3 > \alpha\text{-FeOOH} \gg$ kaolinite, bentonite, and quartz. Olsson et al. (2010) have also demonstrated that surface catalyzed hydrolysis of monoester P increases with pH but remains minimal.

2.1.4 Excretion of exudates

Bacteria, fungi, and vascular plants have all been shown to release various organic exudates including extracellular enzymes (Wetzel 1991), electron shuttles (Konhauser 2006), and chelating agents (Neilands 1995) into pore water (Figure 2: 12). The structure of these exudates is highly variable depending on their purpose but most contain some P within their structure. The flux of P from the solid to aqueous phase through this mechanism is not well constrained but is likely negligible compared to P assimilation by biota in sediments. The degradation of such exudates is poorly understood but it is likely that part of this organic P will subsequently be mineralised to orthophosphate.

2.1.5 Dissociation of ternary P complexes with humics

Humic substances, chemically complex recalcitrant organic matter, generally account for 40 to 80% of total organic matter in lakes (Wetzel 2001). Since the 1970s, it has been clear that an important proportion of aqueous-P may be associated with high molecular weight organic matter in lake waters and sediments (Minear 1972; Lean 1973; Jackson and Schindler 1975; Ansems 2012; O'Connell et al. 2014). Direct binding of phosphate to humic substances is not thought to occur (Hens and Merckx 2001), but

there is strong indirect evidence for the existence of binding via bridging trivalent cations such as iron (III) or aluminum (III) (Jones et al. 1988, 1993; Gerke and Hermann 1992). Several recent studies have characterised synthetically produced organic matter-metal-phosphate complexes (Kizewski et al. 2010; Erro et al. 2012) and structurally similar arsenate complexes (Mikutta and Kretzschmar 2011). Interest in such ternary complexes, dubbed “super-phosphates” has been shown from agricultural chemists (e.g., Erro et al. 2012; Urrutia et al. 2014). The conditions under which humic-metal-phosphate complexes dissociate to orthophosphate are not well defined, but include ultraviolet radiation and pH decreases (Gerke and Hermann 1992; Jones et al. 1993; Hens and Merckx 2001) (Figure 2: 14).

2.2 Drivers of internal phosphorus loading

As demonstrated in Section 2.1, a multitude of molecular level mechanisms exist that transfer P from the solid phase to pore water, thereby increasing the concentration gradient at the SWI, ultimately resulting in internal P loading. These mechanisms are often interdependent and counterbalanced by P retention mechanisms occurring simultaneously, or sequentially at depth within a sediment profile. The relative importance of different P release mechanisms may also vary temporally due to changing conditions at the SWI and spatially depending on environmental variables such as geological setting or climatic zone. Some of the key drivers of internal loading and the mechanisms behind them are discussed below; however, we have avoided speculation over the relative importance of different mechanisms generally due to the large variability present between different environments. The importance of different mechanisms driving internal phosphorus loading depends on the timescale evaluated. In any particular environment, a process resulting in important short-term (e.g., daily, weekly) P fluxes from sediment may not be important when determining net retention or release of P by sediment over annual to decadal timescales (Figure 3), as discussed in Section 1.

2.2.1 *Oxygen concentration*

Oxygen plays an important role in the redox state of elements associated with P in sediments, as well as accelerating decomposition of P containing organic matter. Iron, and to a lesser extent, manganese oxides, which often immobilise P in surface sediments, are protected from reductive dissolution by the presence of oxygen in the overlying water column. If the SWI is anoxic or aerobic respiration consumes oxygen at a greater rate than provided by the diffusive flux from surface water, the microbial community transitions to using alternative electron acceptors. The strong association between iron and P in oxic sediments at circumneutral pH, with release of P due to dissolution of iron oxyhydroxides under anoxic conditions, is commonly observed and has been documented since Einsele (1936) and Mortimer (1941). The dissolution of iron oxyhydroxides may occur either due to burial of surficial sediments or changing oxygen at the SWI. This coupled cycling of iron and P under anoxia is commonly referred to as the “classical model” of internal P loading.

In addition, microbes at the SWI have been shown to uptake and release P in response to oxygen concentration (Gächter et al. 1988). This is reflected as changes in P speciation with polyphosphates increasing in benthic biomass during oxic conditions, and decreasing during anoxic conditions (Khoshmanesh et al. 2002; Ahlgren et al. 2011). Microbial polyphosphate accumulation through this process has been adopted extensively in the treatment of wastewater and a comprehensive review of this process in relation to aquatic sediments is also provided by Hupfer et al. (2007).

Despite protecting iron and manganese oxides from reductive dissolution and allowing for polyphosphate accumulation in bacterial biomass, the presence of oxygen at the SWI accelerates organic matter degradation due to the thermodynamic efficiency of oxygen as a terminal electron acceptor in heterotrophic metabolism. Carbon in organic matter may be partially mineralised to dissolved inorganic carbon or carbon dioxide during this process, but P within biomass remains in sediment pore water, primarily as phosphate. Although P assimilation within microbial biomass may partially offset the release

of soluble P, the net effect of organic matter degradation and mineralisation is often an increase in P concentration in pore water.

2.2.2 Iron speciation and ratios in sediments

The relationship between iron and P in oxic sediments has received considerable attention in the literature with several authors identifying the influence of iron-to-phosphorus ratios (hereafter, Fe:P) on internal loading. The maximum stoichiometric Fe:P due to the incorporation of orthophosphate with pure ferric hydroxides is 2:1 (Gunnars et al. 2002; Thibault et al. 2009). However, iron speciation in sediment may vary considerably and iron can occur within other minerals such as phyllosilicates, which have a lower capacity for P sorption than iron oxyhydroxides. In lake sediments, some variation of the solid Fe:P necessary to control internal loading in oxic sediments has been reported. Jensen et al. (1992) showed that sedimentary Fe:P ratios in excess of 15 (by weight, 8.32 by mole) may be necessary to control P mobility in shallow lakes. Others demonstrate that high rates of internal P loading may occur even under high Fe:P (>20 by weight, 11.1 by mole) (Phillips et al. 1994). Thus, although total depositional fluxes of P to sediment impose maximum limits on re-mobilisation fluxes of P from sediment, changes to Fe:P or changes to iron speciation in deposited sediment may modulate P flux from sediments below this limit. This can apply even with permanently oxidising conditions at the SWI if iron oxide surfaces reach a saturation threshold with respect to phosphate sorption. Ultimately, the fraction of P within deposited sediment which is subsequently re-mobilised is dependent not only on Fe:P ratio but on the ratio between the concentration and speciation of P complexing components (e.g., calcium, iron, and manganese) and P concentration in deposited sediment.

2.2.3 pH

As discussed in Section 2.1, both pH and alkalinity play a role in sediment P binding. At higher pH values, P binding to oxidised iron decreases as P is replaced by hydroxyl ions on iron particle surfaces (Andersen 1975; Jensen and Andersen 1992). As photosynthesis results in elevated pH, increased P release during high productivity events has been observed (e.g., Koski-Vähälä and Hartikainen 2001).

Increases in sediment pH due to photosynthesis may also affect P binding efficiency (e.g., Søndergaard 1988; Welch and Cooke 1995). Apatite, calcite, siderite, and rhodocrosite ($\text{MnCO}_{3(s)}$) solubility is also affected by pH and in lakes with seasonal calcite precipitation, seasonal dissolution of authigenic calcite and subsequent P release has been observed (e.g., Ashley 1983; Murphy et al. 1983; Boström et al. 1988; Brooks and Edgington 1994; Burley et al. 2001; Whitehouse 2010; McCulloch et al. 2013).

2.2.4 Water hardness

In hard water systems, where bicarbonate is abundant throughout the depth profile in equilibrium with calcium carbonate, ferrous iron may be permanently removed from solution by the formation of siderite ($\text{FeCO}_{3(s)}$). This may also prevent the formation of vivianite in a similar way to the presence of sulfate and the formation of iron sulfide as discussed in Section 2.2.7. The amount of vivianite, siderite, or mackinawite as the final product of iron diagenesis is largely determined by the combination of pH, the relative concentrations of phosphate, bicarbonate, and sulfide at depth, and time. However, decreases to the permanent burial of P within vivianite in hard water systems may be offset by increases to permanent burial of P within calcium phosphate minerals as discussed in Section 2.2.2. The net effect is a change to the speciation of P, subject to permanent burial with changes to water hardness.

2.2.5 External loading of organic matter and P

Organic matter inputs in freshly deposited sediment typically reflect stoichiometry associated with primary production and therefore contain significant P. Phosphorus associated with organic matter usually decreases with sediment depth as organic matter breaks down to dissolved inorganic carbon from microbial respiration. Heterotrophic microbial activity within surficial sediments is typically limited by the availability of electron donors that fresh organic matter inputs provide. Electron acceptors in sediment are consumed by the microbial community in order of energetic efficiency, most often coupled to the oxidation of organic matter: typically, oxygen (aerobic respiration), nitrate (denitrification), manganese(IV), iron(III), sulfate, carbon dioxide (hydrogenotrophic methanogenesis), and acetic acid (acetoclastic methanogenesis). In P-limited systems, phosphate groups are also preferentially cleaved

from organic P compounds through the action of extracellular phosphatase enzymes. However, some more recalcitrant organic P species have been shown to persist in lake sediments for several decades (Ahlgren et al. 2005). As labile organics become mineralised over time (and depth) the organic matter fraction within sediments becomes increasingly recalcitrant and humified leading to an increased likelihood of the formation of recalcitrant ternary phosphate-metal-humic complexes.

As electron acceptors are reduced and organic matter mineralised, P is released, both directly from organic matter and due to the dissolution of P hosting iron and manganese oxides. Released P may be immobilised by mineralogical mechanisms (precipitation or adsorption), assimilated into biomass, or result in upward diffusion and internal loading. As such, increased organic matter deposition, containing significant P, and mineralisation in the absence of increased mineral deposition will typically result in higher internal P loading (Katsev et al. 2006) such as in hypereutrophic, low-iron systems (see Section 3.2.2).

2.2.6 Nitrate concentrations in surface water

The presence of high nitrate in surface water acts against internal P loading (Matthews et al. 2013; Parsons et al. 2017). The reasons for this appear to be three-fold. First, nitrate availability at the SWI reduces the likelihood of reductive dissolution of iron (oxyhydr)oxides during short periods of bottom water anoxia. This is due to nitrate's higher energetic efficiency as an electron acceptor than iron (e.g., Hansen et al. 2003; Parsons et al. 2017); as nitrate must be consumed prior to the onset of iron reduction (Reed et al. 2011), longer periods of anoxia are required to cause release of iron bound P. Second, heterotrophic nitrate reduction (denitrification) coupled to the oxidation of organic matter may deplete the sediment of labile organic matter, decreasing the probability, or rate, of reductive dissolution of iron oxyhydroxides at greater sediment depth due to electron donor limitation. Thirdly, nitrate reduction can be coupled directly to the oxidation of upward diffusing iron(II) from more reduced sediments (e.g., Straub et al. 1996; Hauck et al. 2001; Melton et al. 2012). This can result in the precipitation of iron(III)-

oxyhydroxides below the oxic zone in sediments, providing a greater barrier to upward diffusing P, which can decrease or prevent internal P loading.

2.2.7 Sulfate concentrations in surface water

In comparison to iron, the role of sulfate has received relatively little attention in the literature pertaining to internal P loading, particularly in freshwater systems. However, sulfate concentrations, and microbial sulfate reduction within a sediment depth profile, play a key role in determining internal P loading, particularly over longer timescales (Caraco et al. 1989; Roden and Edmonds 1997). In addition to a large body of empirical evidence (Caraco et al. 1989; Roden and Edmonds 1997), the detailed conceptual model presented by Gachter and Muller (2003), based on observations of Gachter and Wehrli (1998), has led to a fundamental change in our understanding of coupled Fe, C and P cycling to include sulfur. Sulfate in surface water, in addition to competing with P for sorption sites at mineral surfaces, influences sediment iron-mineralogy at depth causing a decrease in the abundance of minerals that permanently retain P in the solid phase. Without S, pore water iron and phosphate concentrations can be expected to increase, in a maximum stoichiometric ratio of 2:1, due to the reductive dissolution of iron (oxyhydr)oxides. This may result in supersaturation with respect to vivianite, which can represent a permanent sink for P and has the stoichiometric potential to immobilise all phosphate associated with iron (oxyhydr)oxides (e.g., Manning et al. 1991; Fagel et al. 2005). In lakes with high sulfate concentrations, following reduction of iron oxyhydroxides, sulfate will also be reduced during the oxidation of organic carbon, resulting in aqueous bisulfide. Although mackinawite (FeS , $\log K_{\text{sp}} = -4.6$) is more soluble than vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\log K_{\text{sp}} = -36.0$), iron(II) is removed from solution as iron sulfide before the formation of vivianite is possible. This is due to the faster precipitation kinetics of FeS and the often much higher concentration of aqueous sulfide compared to phosphate. Assuming re-oxidation by oxygen does not occur, iron sulfide represents a permanent sink for iron as further diagenesis can result in the formation of pyrite (FeS_2 , $\log K_{\text{sp}} = -18.479$) (Berner 1970; Peiffer 1994). Removing iron(II) from solution in this way results in the persistence of P in pore water allowing for its upward (and downward) diffusion.

2.2.8 *Benthic bioturbation, bioirrigation, and vertical migration*

Benthic biota may also substantially influence internal P loading through various mechanisms, which are often collectively referred to as bioturbation. Specific mechanisms include bioirrigation (solute transport), bioconveying (particulate transport), and sediment mixing (Andersson et al. 1988). Bottom feeding fish such as carp have been shown to contribute significantly to internal loading processes in some environments by physically disturbing fine surface sediment rich in P into the water column and thus increasing TP concentrations (Prescott and Tsanis 1997; Chow-Fraser 1998). Invertebrate tube dwelling organisms can also disturb sediments during burrow construction. Population densities for such bioturbating organisms may reach 50,000 individuals per m² (Pelegri and Blackburn 1995; Parsons et al. 2017), potentially resulting in significant sediment mobilisation. Tube dwelling invertebrates have also been shown to enhance solute transport between pore water and surface water via bioirrigation, increasing fluxes of SRP (Matisoff and Wang 1998; Chaffin and Kane 2010). Additionally, burrow construction and bioirrigation increases the complexity of oxic–anoxic surfaces in sediments, which may radically alter the flux of nutrients from sediments (Hölker et al. 2015). There is some evidence for a linear relationship between sediment P fluxes and bioturbation including a tipping point where oxygen concentrations become too low to support adequate bioturbation (Diaz and Rosenberg 1995). However, Lewandowski and Hupfer (2005) demonstrated that bioirrigation may actually decrease P release rates from sediment due to oxidative precipitation of iron oxyhydroxides along burrow walls which effectively retain P. In addition, cyanobacteria may also contribute to P regeneration from the sediments (Xie et al. 2003), as they migrate seasonally between shallow sediment and surface water (Istvánovics et al. 1993; Verspagen et al. 2004).

2.2.9 *Sediment deposition versus diffusion*

The interplay between downward sedimentation, burial fluxes and upward diffusion of aqueous P towards the SWI varies significantly between environments. Consumption of oxygen, nitrate, and sulfate by biological (e.g., heterotrophic respiration coupled to the oxidation of organic matter) and chemical

diagenetic processes (e.g., chemical oxidation of aqueous sulfide and ferrous iron) in sediments results in concentration gradients of aqueous species, pH, and redox (e.g., Wang and Van Cappellen 1996; Canavan et al. 2006). These gradients drive precipitation, dissolution, sorption, desorption, complexation, and dissociation reactions, which may mobilise or retain P as illustrated in Figure 3. Important factors controlling P speciation with depth in sediments include oxygen concentration at the SWI, sediment texture and particle size distribution (Selig 2003), organic matter concentrations (Katsev et al. 2006) and water hardness (House et al. 1986a, 1986b). As discussed earlier, P speciation in surficial sediments is often dominated by association with iron oxides and hydroxides (e.g., FeOOH, Fe(OH)₃) and by freshly deposited particulate organic matter (Figure 3). Both of these pools typically diminish with depth due to the microbially mediated reductive dissolution of iron oxides (Couture et al. 2010) and the mineralisation and enzymatic hydrolysis of fresh particulate organic matter, respectively (Canavan et al. 2006; Reitzel et al. 2007). A change to sedimentation rate does not therefore drive internal loading or increased retention of P. The deposition rate of P within sediments, compared to the P retaining capacity of the deposited sediment after early diagenetic processes does however control the rate of permanent P burial, and hence internal P loading.

3 Data analyses of Canadian freshwaters

In addition to the work performed to develop a theoretical understanding of internal P loading, there has also been considerable interest from scientists and resource managers in quantifying this process in aquatic ecosystems. Over the last three decades, there have been dozens of studies that have estimated internal P loading in Canadian water bodies, generally in response to concerns about water quality in a specific water body or region. Here, we consolidate and analyze all the published data on internal P loading in Canadian ponds, lakes, reservoirs, and coastal wetlands. A national-scale synthesis provides an opportunity to broaden out from individual study sites and assess the significance of internal P loading across Canada. Specifically, our goals were to map geographical patterns of internal P loading across the

country, and then to examine environmental drivers of this process across aquatic ecosystems in a broad range of environmental settings.

3.1 Methods

3.1.1 Literature search

We sought studies that produced quantitative measures of internal P loading in freshwater ecosystems in Canada (including transboundary waters). Between February to December 2016, we conducted our literature search using Web of Science and the ProQuest thesis and dissertation database, as well as contacted Canadian researchers via email list-serves. We limited our search to journal articles, student theses, and technical reports. In total, 43 studies were found from which we extracted quantitative measures of internal P loading. Data were extracted from text, tables, and figures of publications. Where data were presented in figures, Graph Click (Bovet 2008) was used to capture values. Some researchers provided their published data to us in spreadsheets (Azevedo 2007; Taranu et al. 2010; Ballard 2011; Loh et al. 2013; Orihel et al. 2015).

We created a database to archive the data we extracted from our literature review. The database is publicly available (DOI: 10.5281/zenodo.810047). A list of the water bodies found in the database is provided in Table A1 of Supplement A. Supplement A also contains descriptions of all database tables, along with definitions of each table field. References for the studies from which data were extracted are found in the “REF” database table (Table A2). First, we created a unique code (LAKE_ID) for the physical location of each lake, reservoir, or wetland. For large lakes (namely Lakes Simcoe, Erie, Huron, and Ontario), bays were considered a separate location if they were distinct from the main basin. We also specified the surficial geology of each location (in the database table “GEOL”; Table A4) obtained from Natural Resources Canada’s GeoGratis repository (Wheeler et al. 1996). Second, we identified specific sites (each with a unique SITE_ID) within each lake, reservoir, or wetland. For each SITE_ID, we specified the LAKE_ID associated with the site, along with its water depth, sediment characteristics (loss

on ignition, sediment P, and iron concentrations) (in the database table “SITES”; Table A5). Finally, we entered values of sediment P flux in the database table “PFLUX” (Table A5), along with method of estimation, season and date of measurement, duration of experiment, experimental conditions (temperature, pH, oxygen, and light), and number of experimental replicates. The sediment P flux value of SRP, TDP, or TP was entered in the table, along with the units in the paper (in a subsequent query, all L_{gross} flux values were converted to $\text{mg m}^{-2} \text{d}^{-1}$ and all L_{net} flux values were converted to $\text{mg m}^{-2} \text{y}^{-1}$). If flux values for multiple replicates of an experimental treatment were reported over the same period of time in a study, the average of each treatment was entered in the database.

3.1.2 Data analyses

The studies included in our analyses quantified internal P loading in a variety of ways, including core incubations and pore water profiles (both of which typically measure L_{gross}), mass balances (which typically measure L_{net}), or other types of models (which either measure L_{gross} or L_{net} depending on the formulation). These methods were described in Section 1. In order to compare studies where L_{gross} or L_{net} was reported in different forms of P (SRP, TDP or TP; Box 1), we first needed to express all values in terms of a single form (TP). We used data from two studies (Nürnberg 1988; Orihel et al. 2015) to develop linear regression models (Supplement B), which were used to convert the TDP and SRP values in our database to TP.

First, to visually examine the geographic patterns of internal P loading, we created maps of L_{gross} and L_{net} from ponds, lakes, reservoirs, and coastal wetlands across the country. The values on each map represent averages of all estimates from that water body for each of the 70 water bodies in our database. Next, we evaluated relationships between environmental variables and L_{gross} . For these analyses, only L_{gross} values derived from core incubations were considered, since this is a standard method of estimating fluxes in the literature and the most common method in our database ($n = 153$). Where there was more than one estimate of L_{gross} at a single sampling site within a lake, the data were averaged to give one estimate per site (resulting in $n = 145$ sites where L_{gross} was estimated by core incubation). The data did

not meet the assumptions of parametric tests, even following transformations, so non-parametric tests were used. Relationships with categorical variables (lake pH category, trophic state, and oxygen treatment) were evaluated using one-way Kruskal–Wallis tests with Dunn’s tests used for pairwise comparisons and relationships with continuous variables (sediment pH, site depth, lake maximum depth and lake area) were evaluated using Spearman rank correlation tests. All statistical analyses were performed in R (R Core Team 2015; Version 3.2.2).

3.2 Results and Discussion

3.2.1 Geographic patterns

From 43 publications, we compiled 618 measurements of L_{gross} and L_{net} from 70 water bodies across Canada, with values from 8 of the 10 provinces. Expressed in terms of TP, values of L_{gross} ($n = 461$) ranged from -27 to $54 \text{ mg m}^{-2} \text{ d}^{-1}$, while L_{net} ($n = 157$) ranged from -1694 to $10,640 \text{ mg m}^{-2} \text{ y}^{-1}$, where the negative fluxes represent a loss of P from the water column into the sediment (Figure 4). The upper end of the range of L_{gross} we report here is comparable to other studies that compiled rates of internal P loading from sediments of lakes and reservoirs worldwide: 0 to $52 \text{ mg P m}^{-2} \text{ d}^{-1}$, $n = 64$ (Nürnberg 1988); 0 to $80 \text{ mg P m}^{-2} \text{ d}^{-1}$, $n = 6$ (Christophoridis and Fytianos 2006); and 6 to $26 \text{ mg P m}^{-2} \text{ d}^{-1}$, $n = 17$ (Carter and Dzialowski 2012). These previous studies report L_{gross} of 0 or greater, whereas in our database, 5% of values were negative.

There are distinct regional differences in internal P loading, with the highest values concentrated in the prairies and the lowest from the Canadian Shield in Ontario and Nova Scotia (Figure 5). There is also substantial variability within regions, particularly in central Alberta, where the range of P flux rates spans the range observed across all of Canada. The highest density of sample sites were found in central Alberta, southern Ontario, and the Maritimes (although all of the sites in New Brunswick and Nova Scotia came from one PhD thesis; Beauchamp 1990). There were no data from Newfoundland and Labrador, Prince Edward Island, nor any of the territories.

3.2.2 Relationships between phosphorus flux and lake characteristics

To understand the observed geographic patterns, we statistically tested relationships between environmental drivers and internal P loading. We were limited in our ability to statistically assess all relationships because data was unavailable for several drivers. For instance, there were relatively few cases where adequate estimates of external P loading were available, so this was not considered in our analyses. Case studies where this contextual data were available are discussed in Section 4. Finally, we caution that a number of interactions and co-linearities exist among environmental drivers, and thus care must be taken when interpreting these relationships. As we describe below, our data analyses revealed that dissolved oxygen, geology, pH, and trophic state were the main factors significantly associated with L_{gross} . Results of other statistical analyses, including relationships with site depth, lake maximum depth and lake area, are provided in Supplement C.

3.2.2.1 Oxygen concentration. Core incubations performed under anoxic (oxygen concentration less than 0.5 mg L^{-1}) or hypoxic (oxygen concentration between 0.5 and 2 mg L^{-1}) conditions (medians = 8.90 and $7.13 \text{ mg TP m}^2 \text{ d}^{-1}$, respectively) had significantly higher L_{gross} compared with those performed under oxic conditions (median = $0.62 \text{ mg TP m}^2 \text{ d}^{-1}$) (Kruskal–Wallis, $H = 54.0$, $p < 0.001$; Figure 6A). While this result is consistent with the classical model of retention of P bound to redox-sensitive iron oxyhydroxides under aerobic conditions (Mortimer 1941), anoxia may also stimulate P release by other mechanisms. For example, lysis of aerobic bacteria caused by the onset of anoxia can also be responsible for P release from sediments (Ricciardi-Rigault et al. 2000). Further, benthic bacteria that store P in their cells in the form of polyphosphate may affect P fluxes by redox-dependent changes of their physiology (Hupfer et al. 2007).

3.2.2.2 Iron speciation and ratios in sediment. High L_{gross} values were observed at sites where the sediment Fe:P ratio was above the critical thresholds outlined in Section 2.2.2. As discussed in that section, this ratio is highly pH dependent, and our data bore this out, with a significant correlation between pore water pH and sediment Fe:P ($r = 0.87$; $p < 0.001$). At sites where Fe:P was between 8.32 and 11.1 (by mole), oxic fluxes ranged from 0.04 to $3.50 \text{ mg m}^{-2} \text{ d}^{-1}$ and anoxic fluxes ranged from 47.8

to 54.3 mg m⁻² d⁻¹. Where sediment Fe:P was greater than 11.1, oxic fluxes ranged from 0.04 to 25.7 mg m⁻² d⁻¹ and anoxic fluxes ranged from 8.3 to 28.5 mg m⁻² d⁻¹. These patterns are consistent with Phillips et al. (1994), where high fluxes persist even at high Fe:P, and offer further evidence that bulk Fe:P is not necessarily a good indicator of L_{gross} . Despite a clear mechanistic link between P retention and Fe:P ratios in iron (oxyhydr)oxides (Section 2.2.2), the link between Fe:P and potential for internal P loading is not universal.

3.2.2.3 pH. Surficial geology exerts a strong control on pH of aquatic ecosystems, both in the water column and in sediment pore water, and thus exerts an indirect control on L_{gross} . We observed that L_{gross} was higher in water bodies where the bedrock geology was sedimentary (median = 2.21 mg TP m² d⁻¹) compared with metamorphic (median = 0.26 mg TP m² d⁻¹) ($H = 8.44$, $p = 0.01$). This flux was also higher in alkaline lakes (pH > 7.8; median = 3.11 mg TP m² d⁻¹) compared with acidic (pH < 6.5; medians = 0.18 mg TP m² d⁻¹) or neutral lakes (6.5–7.8; median = 0.21 mg TP m² d⁻¹) ($H = 42.5$, $p < 0.001$) (Figure 6B). Importantly, all of the lakes on sedimentary bedrock are alkaline, while all of the lakes on metamorphic bedrock are acidic or neutral. When looking specifically at the pore water pH, the highest P fluxes were observed at moderately alkaline (7.8–9.0) pH values, with low P fluxes at pore water pH values less than 7 and greater than 9 (Figure 7).

To explain the high L_{gross} rates at moderately alkaline pH values, it is important to think about the control pH exerts on P solubility (as described in Section 2.2). While the relationship between pH and P solubility can be described for any individual mineral–phosphate combination, the heterogeneity of minerals in natural sediments mean that there may be variety of processes at any given pH value. At low pH values, ortho-phosphate generally occurs in the deprotonated form and sorptive processes exert a stronger control on P solubility because mineral surfaces are positively charged. At high pH values where mineral surfaces are negatively charged and ortho-phosphate is doubly deprotonated, sorption is less effective and precipitation processes are the main control on P solubility. Therefore, the high L_{gross}

observed at moderately alkaline pH values (Figure 7) may exist in a transition zone where neither mechanism is particularly effective at mitigating P flux from sediments to the overlying water column.

3.2.2.4 Trophic Status. Finally, we observed significantly higher rate of L_{gross} in hypereutrophic and eutrophic lakes (medians = 8.8 and 6.9 mg TP m² d⁻¹, respectively) compared with mesotrophic lakes (median = 1.77 mg TP m² d⁻¹), while oligotrophic lakes had significantly lower L_{gross} flux rates than all other trophic classes (median = 0.21 mg TP m² d⁻¹) ($H = 31.1$, $p < 0.001$; Figure 6C) (trophic classes defined based on Wetzel (2001)). The hypereutrophic lakes typically occur on sedimentary rock in the Canadian prairies, a landscape that is nutrient-rich (Barica 1993) with low iron concentrations in sediment pore water (Orihel 2013) and therefore has ideal conditions for promoting sediment P flux. Other studies have also reported high sediment P fluxes in eutrophic and hypereutrophic lakes and reservoirs (Nürnberg 1997; Andersen and Ring 1999; Penn et al. 2000; Carter and Dzialowski 2012).

3.2.3 Seasonal differences in internal phosphorus loading

During the winter (under ice-covered conditions), estimates of L_{gross} and L_{net} in Canadian water bodies were consistently lower than those reported for the open-water season (Table 2). Two exceptions were Lake Diefenbaker, Saskatchewan (North et al. 2015) and North Halfmoon Lake, Alberta (Reedyk et al. 2001). Winter L_{gross} and L_{net} ranged from 5–300% of the associated open-water rates with an average of 66%. Winter internal P loading may be due to dissolution of iron oxyhydroxides due to persistent anoxia at the bottom of the lake or dissolution of calcium-bound P due to low pH under ice. In general, winter L_{gross} and L_{net} are a small contribution to year-round internal P loading estimates, probably due to low temperatures, though there are some exceptions (e.g., Lake Diefenbaker) that illustrate the fact that reporting rates representative of a small proportion of the year in temperate systems may be underestimating year-round rates of loading and their relative importance. Significant differences in seasonality have also been noted in hypereutrophic US lakes (Penn et al. 2000) and even in lakes that do not experience ice cover, such as eutrophic Danish lakes (Jensen and Andersen 1992; Søndergaard et al. 1999); in both of these cases, P fluxes from sediments were lower during the winter.

4 Case studies of Canadian freshwaters

The previous section clearly demonstrated that rates of internal P loading vary widely across the country. In this section, we use a case study approach, gathering information from different water bodies and regions to explore the importance of internal P loading in lake P budgets and to the formation of cyanobacterial blooms in Canadian water bodies. We explore five categories of water bodies. We begin with an overview of internal P loading in large lakes (Section 4.1), where we differentiate between offshore and nearshore environments and associated coastal wetlands (Section 4.2). We then summarize a case study of internal P loading in a Canadian reservoir (Section 4.3), and put it in perspective with smaller prairie lakes (Section 4.4). Finally, we discuss Precambrian Shield lakes (Section 4.5).

4.1 Large lakes

Canada is known for its abundance of large lakes, but internal P loading has only been quantitatively addressed in the offshore regions of five of them, including: Lake Simcoe (Ontario), Lake Winnipeg (Manitoba), Lake of the Woods (Ontario/Manitoba), Lake Erie (Ontario), and Lake Champlain (Quebec).

4.1.1 Lake Simcoe

Located ~100 km north of the City of Toronto, in Ontario, Canada, Lake Simcoe is a large (722 km²) lake that serves as a municipal drinking water source to several communities, and is an important site for recreational activity (North et al. 2013). Increased P inputs to the lake led to issues of eutrophication and the collapse of the cold-water fishery in the 1960-70s, driving extensive management efforts to reduce P loadings (Winter et al. 2011). Internal P loading appears to be a significant source of P to Lake Simcoe. Measurements of L_{gross} in sediment cores under anoxic conditions averaged 6.3 mg TDP m⁻² d⁻¹ (Loh et al. 2013). On an annual basis, internal P loading was estimated to range from 63–97 mg TP m⁻² y⁻¹, depending on estimation methods (Nürnberg et al. 2013a). This represents 64–97% of the external TP loading rate from all known sources (100 mg TP m⁻² y⁻¹; Palmer et al. 2013).

The majority of internal P loading likely occurs during summer months based on changing redox conditions at the SWI. Due to the generally dimictic nature of Lake Simcoe's stratification patterns, erosion of the thermocline in the autumn will introduce this sediment-derived source of biologically available P into the photic zone where it is available for primary producers. This mesotrophic, P-limited (Guildford et al. 2013) lake displays no long-term changes in TP concentrations nor bottom-water oxygen concentrations, despite significant efforts to reduce external TP loading from the watershed (North et al. 2013). There have, however, been significant decreases in the hypoxic factor (i.e., the number of days that an area equivalent to the bay's surface area is overlain by water with $\leq 2 \text{ mg L}^{-1}$ of dissolved oxygen; Nürnberg et al. 2013a). Internal P loading is an important regulator of pelagic productivity in this large lake, as its timing during the autumn months corresponds to the year-round peak in primary production (Kim et al. 2015), total algal biomass (Baranowska et al. 2013), and cyanobacteria biomass (Nürnberg et al. 2013b).

4.1.2 Lake Winnipeg

Lake Winnipeg (Manitoba, Canada) is one of the world's largest lakes in surface area, with an area of $23,750 \text{ km}^2$, and a watershed more than forty times that size. Agricultural development combined with recent increases in precipitation, runoff, and flooding have led to major increases in P and primary productivity in the lake (McCullough et al. 2012). Internal P loading may also be important in this shallow lake where eutrophication has been linked to declines in water quality (McCullough et al. 2012) and increasing nuisance blooms of cyanobacteria (Schindler et al. 2012). High rates of L_{gross} (mean: $11.4 \text{ mg TDP m}^{-2} \text{ d}^{-1}$; range: $1.7\text{--}22.8 \text{ mg TDP m}^{-2} \text{ d}^{-1}$; Loh et al. 2013) were observed in anoxic core incubations, and there is clear evidence that P fluxes from sediment are important in the P balance of the lake. L_{net} and L_{gross} ranged from $259\text{--}468 \text{ mg TP m}^{-2} \text{ y}^{-1}$ depending on estimation method (Nürnberg and LaZerte 2016). These long-term (1999–2012), year-round (based on the assumption that winter internal P loads are negligible), TP inputs represented 75–135% of the external TP loads ($347 \text{ mg TP m}^{-2} \text{ y}^{-1}$) during these years (Nürnberg and LaZerte 2016). Historically, Lake Winnipeg displayed a well-mixed thermal

regime, but stratification and anoxia in the bottom waters were recorded for the first time in 2003 (Environment Canada and Manitoba Water Stewardship 2011). Significant positive correlations between L_{net} and phytoplankton and cyanobacterial biomass (Nürnberg and LaZerte 2016) indicate that internal P loading plays an important role in this large, spatially diverse lake.

4.1.3 Lake of the Woods

Lake of the Woods is a large (3,850 km²) multi-basin lake that crosses provincial and international borders, spanning parts of Ontario, Manitoba, and Minnesota. The lake has experienced cyanobacterial blooms since the 1800s, but there is growing concern regarding the effects of eutrophication and climate change in exacerbating these blooms in recent decades (Hargan et al. 2011). The Winnipeg River catchment, in which Lake Winnipeg is located, is an important nutrient source to Lake Winnipeg, and like Lake Winnipeg, sediments are a significant source of P to the water column of Lake of the Woods. L_{gross} from both anaerobic (8.3–12.5 mg SRP m⁻² d⁻¹) and aerobic (0.2–0.6 mg SRP m⁻² d⁻¹) sediments have been quantified (James 2017), and a variety of approaches have been used to calculate L_{gross} and L_{net} including the determination of aerobic fluxes and two independent modelling approaches (James 2012, 2017). These three approaches generally agreed, resulting in L_{gross} and L_{net} to Lake of the Woods of 144–156 mg TP m⁻² y⁻¹ (James 2012), representing 31–51% of the annual external P loading rate (307–462 mg TP m⁻² y⁻¹) which is dominated by tributary inputs from the Rainy River (Clark and Sellers 2014). This lake has been managed as a P-limited system; however, the response of the algal community to P derived from internal loading remains unresolved. Recent studies (Pla et al. 2005; Zhang et al. 2013) suggest that other factors (e.g., hydrodynamics, water temperature, light, or nitrogen) may play a large role in the algal communities response to P, with large temporal (Pla et al. 2005) and spatial (Zhang et al. 2013) variability in trophic status present across this multi-basin lake.

4.1.4 Lake Erie

Lake Erie is the shallowest of the Laurentian Great Lakes, and the Great Lake most impacted by eutrophication. It is also complicated by the fact that it has three distinct basins, varying in their internal

and external P load (Zhang et al. 2016); stratification regime, sediment properties, and redox conditions (Small et al. 2014); as well as water column P concentrations and nutrient status of the phytoplankton communities (Guildford et al. 2005). Also relevant to P dynamics and sediment redox conditions (see Section 4.1.6), is the distinct differences in dreissenid population densities between the three basins (Patterson et al. 2005).

In the western basin of Lake Erie, it has been suggested that internal P loading is an important source of P (Elsbury et al. 2009), with implications for the increase in cyanobacterial blooms (Michalak et al. 2013). Matisoff et al. (2016) utilized 8 different approaches to estimate internal P loading and reported mean year-round aerobic internal P loads (L_{net} and L_{gross}) ranging from 157–332 mg SRP m⁻² y⁻¹ (depending on estimation method). They also measured significantly higher summertime L_{gross} under anaerobic conditions (6.01 mg SRP m⁻² d⁻¹; range: 1.84–8.18) relative to aerobic conditions (1.35 mg SRP m⁻² d⁻¹; range: 0.95–1.79) more reflective of the oxygen concentrations in the western basin (Matisoff et al. 2016). Their year-round aerobic L_{gross} estimates represented 3–7% of the target external P load (11,000 mg P y⁻¹) with the spatial distribution of TP in surficial sediments indicating that the external loads from the tributaries, and in particular, the Maumee River, are the source of P. Recent work in the central basin of Lake Erie reports L_{gross} based on aerobic and anaerobic sediment core incubation experiments and pore-water P concentration profiles ranging from 0.05 mg TDP to 0.58 mg SRP m⁻² d⁻¹ (Paytan et al. 2017). These internal P fluxes represent 8–20% of the total external input to the western basin of Lake Erie (Paytan et al. 2017). A unique and novel approach using the isotopic signature of phosphate in the extractable fraction of the sediments was used to illustrate that the sediments are an important internal source of P to the central basin of Lake Erie (Paytan et al. 2017). Mass balance modelling efforts for the entirety of Lake Erie indicate it is a net sink of P (Katsev 2017) as was reported for the western basin (Matisoff et al. 2016). Across all three basins, the P internal-to-external loading ratio was estimated to be 0.99 (Katsev 2017).

Previous studies have focused on the biological (i.e., bioturbation and bioirrigation) and physical (i.e., resuspension) mechanisms of P release from sediments. For example, actions of burrowing mayflies resulted in an increase in L_{gross} from sediments of $1 \text{ mg SRP m}^{-2} \text{ d}^{-1}$ relative to an experimental control (Chaffin and Kane 2010). Estimates of TP flux attributed to resuspension of sediments were $500 \text{ mg TP m}^{-2} \text{ y}^{-1}$, rates that are equivalent to that of externally loaded TP from the tributaries (Matisoff and Carson 2014). While this resuspended P is likely not as biologically available as that derived from tributary loads, it could be a significant source of P (Matisoff and Carson 2014). The response of Lake Erie to P load reductions is evidence of the control P has on the phytoplankton communities. Proximate indicators of nutrient deficiency have also provided evidence of P deficiency (Guildford et al. 2005; Majarreis et al. 2014), as well as nitrogen deficiency (Guildford et al. 2005; Chaffin et al. 2011; Majarreis et al. 2014), and co-limitation of P, nitrogen, and iron (North et al. 2007; Havens et al. 2012), which differ both seasonally and spatially across this trophically disparate Great Lake.

4.1.5 Lake Champlain

Lake Champlain, Quebec, is an example of a dreissenid-impacted, large shallow ($\sim 22 \text{ m}$) lake, with a history of eutrophication issues (Smeltzer et al. 2012). Annual lake-wide L_{gross} expressed on an areal basis were $2.1 \text{ mg SRP m}^{-2} \text{ d}^{-1}$, which was 28% of the terrestrial and atmospheric sources (Cornwell and Owens 1999), indicating internal P loading may not be a large contributor to the overall lake P budget. The highest SRP L_{gross} were found in Missisquoi Bay, St. Albans Bay, and in the southern lake (Cornwell and Owens 1999). The results of mass balance studies in Missisquoi Bay from 2001–2010 indicated that L_{gross} was $400 \text{ mg TP m}^{-2} \text{ y}^{-1}$, representing 20% of the TP inputs during the whole year and 43% during the summer period (LimnoTech 2012). In Missisquoi Bay, iron is thought to play a strong role in P cycling at the SWI, and fluctuations in redox state have been correlated with P flux (Smith et al. 2011). In St. Albans Bay, SRP and TP L_{net} were estimated at $17,928$ and $63,191 \text{ mg m}^{-2} \text{ y}^{-1}$, respectively, ~ 110 times higher than the external TP load ($566 \text{ mg TP m}^{-2} \text{ y}^{-1}$; Druschel et al. 2005), indicating that internal P

loading is critically important source of P in this seasonally anoxic bay of Lake Champlain (Druschel et al. 2005).

4.1.6 Nearshore environments

The nearshore zone is a unique area of a lake where there can be strong impacts of the geology and land use of a watershed and is an area of critical habitat in terms of human uses – as it is the area of a lake most people spend time in and around (Makarewicz and Howell 2012). In the nearshore, high light penetration can support benthic productivity, and the nearshore can have a uniquely important role as habitat and food web support. Biogeochemical cycling in the nearshore likely differs from other areas, with deltaic regions showing terrestrial fingerprints including the potential for higher carbon content (McKee et al. 2004), warmer summer temperatures, and higher rates of sedimentation. The nearshore is linked to the offshore via hydrodynamics, as well as mobile organisms, which can move carbon and nutrients between these habitats.

Major changes in nearshore habitats have been caused by the invasion of dreissenids (zebra and quagga mussels) in central Canada. Dreissenids are mostly found in the shallow nearshore regions and their filter-feeding behaviour has fundamentally changed the functioning of the nearshore relative to the offshore (Hecky et al. 2004; Higgins and Vander Zanden 2010). Nearshore biota can intercept, detain, and assimilate P, thus challenging our estimations of internal P loading from sediments in nearshore regions and complicating its use as a source of P to pelagic phytoplankton. Dreissenid presence results in deeper light penetration (Higgins et al. 2005; Depew et al. 2011; North et al. 2012), which drives the flow of energy to the lake bottom, encouraging benthic algal growth (Zhu et al. 2006). Exudates released by benthic macroalgae have been shown to promote bacterial degradation (Wyatt et al. 2014), contributing to oxygen-depletion in the bottom waters, which could promote P release from sediments.

The presence of dreissenids and benthic algae may have contrasting effects on sediment P release. In Lake Simcoe, dreissenids serve as a significant source of P with excretion rates as high as $776 \text{ mg SRP m}^{-2} \text{ y}^{-1}$ (Ozersky et al. 2013), which is approximately 7 times higher than either the external or internal P

loading rates (86 and $100 \text{ mg TP m}^{-2} \text{ y}^{-1}$, respectively; Nürnberg et al. 2013a). In addition to serving as a source of P, dreissenids also have the ability to change the sediment redox conditions with implications for P release. Ozersky et al. (2013) found higher respiration rates on dreissenid-colonized substrates, which could potentially lead to reduced oxygen conditions at the SWI, thereby increasing the P flux from the sediments. Phosphorus uptake by benthic algae may also intercept P released from sediments, masking the impact of internal P loading (Depew et al. 2011). Rooted macrophytes derive 28–36% of their P directly from sediments (Carignan 1982), a situation not present in the deeper offshore regions. For example, in Lake Erie, sediment P and organic matter content increased from nearshore to offshore (Pennuto et al. 2014). In the Laurentian Great Lakes, model simulations suggest that the presence of dreissenids could result in a 25% increase in the rates of P removal from water column resulting from a 20% decrease in the P recycling efficiency of the sediments (Katsev 2017).

Evidence for the importance of nearshore processes to internal P loading can be found in Lakes Simcoe and Erie. In Lake Simcoe, recent modelling studies reported much lower L_{net} ($13 \text{ mg TP m}^{-2} \text{ y}^{-1}$; Gudimov et al. 2015) than previous studies ($63\text{--}97 \text{ mg TP m}^{-2} \text{ y}^{-1}$; Nürnberg et al. 2013a) that did not account for dreissenids and associated nearshore processes. These lower rates were attributed to the high P retention (Dittrich et al. 2013) and presence of dreissenids and macrophytes resulting in L_{net} representative of 30–35% of the external TP load (1999–2007; Gudimov et al. 2015). However, in the western basin of Lake Erie, both aerobic and anaerobic SRP fluxes were higher at sites with dreissenids, than those without (Matisoff et al. 2016). Sequestration into the growing dreissenid biomass has been demonstrated to have a significant impact on internal P loading rates in Lake Michigan (Katsev 2017).

A consequence of the nearshore P shunt (Hecky et al. 2004) is that nearshore regions tend to have more P, and the pelagic phytoplankton communities are typically P sufficient while their offshore counterparts tend to be P deficient (North et al. 2012; Guildford et al. 2013). Thus, it is important to recognize that P flux from sediments may directly supply the nearshore food web with no overall impact

on the offshore environment. The effects of nearshore processes, particularly in dreissenid-invaded systems should be considered when estimating the extent and impact of internal P loading from sediments in large lakes.

4.2 Coastal wetlands

More than 2000 coastal wetlands remain in the Laurentian Great Lakes region (Cvetkovic and Chow-Fraser 2011). These wetlands provide important ecosystem services, and despite the extensive loss of wetland habitat and degradation of these wetlands, they are still estimated to retain 4000 tonnes of total P across the Laurentian Great Lakes, which is approximately equal to the mass flowing out of the St. Lawrence River (Sierszen et al. 2012). While nutrient retention is considered the norm in these wetlands, rates of internal loading can be high, and in some cases, may lead to net release of P from the wetland (Sierszen et al. 2012), suggesting there is spatial variation in the role of coastal wetlands as sinks, sources, and transformers of P (sensu Reddy and Gale 1994).

Cootes Paradise is a 250 ha drowned river mouth marsh in Hamilton Harbour (located at the western end of Lake Ontario). Delisting of the harbour and marsh as an Area of Concern under the Great Lakes Water Quality Agreement is anticipated in the next few years (Hall et al. 2006; Theysmeijer 2011); however, internal P loading remains a concern (Chow-Fraser 1998; Gudimov et al. 2011) that may impede achievement of restoration goals. Specifically, high internal P loading and abundant phytoplankton may prevent reestablishment of macrophytes (Chow-Fraser 1998) which have a key role in nutrient retention capacity (Reddy and De Busk 1985; Engelhardt and Ritchie 2001).

Internal regeneration of P is extremely important to the P balance in the marsh – with estimates suggesting internal P loading varies between 50 and 70% of total annual P load (Chow-Fraser 1998). Wind-induced resuspension in this shallow marsh (<1m mean depth) and activity of large carp (now excluded, but once estimated at 23% of summer loads) have both been important terms in the P budget (Kelton and Chow-Fraser 2005). L_{gross} is extremely variable ($0.27\text{--}5.25 \text{ mg SRP m}^{-2} \text{ d}^{-1}$) with maximal

860 rates in areas affected by a wastewater effluent (Mayer et al. 2006). Mean rates of summer L_{gross} in the
861 marsh are estimated to be $2.02 \text{ mg SRP m}^{-2} \text{ d}^{-1}$. Over summer and assuming a 1-m water column,
862 estimates suggest that L_{gross} alone contributes $57\text{--}503 \text{ } \mu\text{g SRP L}^{-1}$ (Mayer et al. 2006). Efforts to estimate
863 system-wide P fluxes suggest diffusion from sediments is responsible for 23% of inputs (Kelton and
864 Chow-Fraser 2005).

865 4.3 Reservoirs

866 To our knowledge, there is only one reservoir in Canada for which internal P loading from sediments
867 has been extensively studied: Lake Diefenbaker, Saskatchewan. Located in the Lake Winnipeg watershed
868 and the Qu'Appelle sub-watershed, Lake Diefenbaker is a prairie river valley reservoir fed primarily by
869 flows from the South Saskatchewan River, the major source of external P loads (Hewlett et al. 2015;
870 North et al. 2015). Considered “old” (Juracek 2015), this 49 year-old reservoir serves as a sink for P, with
871 the highest TP retention rates of the 28 largest lakes and reservoirs in the basin (Donald et al. 2015). In
872 Lake Diefenbaker, L_{gross} from both anoxic ($17 \text{ mg TP m}^{-2} \text{ d}^{-1}$) and oxic ($2 \text{ mg TP m}^{-2} \text{ d}^{-1}$) sediment core
873 incubations (Doig et al. 2016) illustrate the importance of bottom water oxygen conditions on P release
874 from sediments. On an annual basis, L_{net} was estimated at approximately $400 \text{ mg TP m}^2 \text{ y}^{-1}$, representing
875 ~24% of the annual external TP load ($2727 \text{ mg TP m}^2 \text{ y}^{-1}$; North et al. 2015). Phytoplankton communities
876 in Lake Diefenbaker are likely P-limited (Dubourg et al. 2015). However, unlike in Lake Simcoe, peaks
877 in primary production and algal biomass do not correspond with occurrences of internal P loading, and
878 instead, appear to be driven by changes in the light environment experienced by the phytoplankton
879 communities (Dubourg et al. 2015).

880 4.4 Small prairie lakes

881 The prairies are a naturally nutrient-rich landscape typified by lakes of high productivity (Barica
882 1993). Anoxic conditions are common during summer and winter (Barica 1993) and, as demonstrated in
883 Section 3, internal P loading is an important process in prairie lakes. Estimates across 36 polymictic lakes

in Alberta (Trew personal communication in Taranu et al. 2010) suggest L_{net} can be 13 fold more important than external loads in the short-term, though newer studies suggest that internal and external loads in urban Alberta lakes can be equivalent (Nürnberg 2017). These differences reflect the importance of varied hydrology, as wet-dry cycles may lead to vast interannual differences in the importance of internal and external loads, but clearly demonstrate sediment phosphorus regeneration can be important. Recent work has shown that internal P loading in polymictic lakes is directly related to maximum depths, which may be due to the greater likelihood that deeper systems will undergo transient anoxia under calm conditions (Taranu et al. 2010). Increases in TP concentrations with depth has been clearly shown in western Canadian lakes, implying that during periods of mixing internal P loading is a significant source of P, particularly in shallow lakes (Prepas and Vickery 1984). While winter L_{gross} tend to be lower than other seasons (Table 2), within three of the Qu'Appelle lakes in Saskatchewan, winter L_{net} is thought to exceed 4–12 mg SRP m⁻² d⁻¹ (Allan and Williams 1978), and high winter L_{net} has been shown in Lake Diefenbaker (North et al. 2015).

Within two Alberta Lakes (Nakamun and Halfmoon Lakes), mixing events after stratified periods led to increases in TP concentrations of 3 to 52%, and these increases in TP were associated with increased chlorophyll a. Not surprisingly, L_{net} was estimated at 30-40 times more important to P budgets than external loads during these periods (Riley and Prepas 1984). More recent work confirms the high rates of internal loading in Nakamun Lake have persisted (L_{gross} : 6.8 mg TDP m⁻² y⁻¹; Orihel et al. 2015), and identifies low pore water iron as a critical factor allowing these high rates of internal P loading, with experimental work demonstrating that iron amendment can decrease P fluxes (Orihel et al. 2016). Low iron availability across many prairie lakes (Allan and Williams 1978) is associated with low N:P and cyanobacterial dominance (Orihel et al. 2015). A suite of factors compound to maintain prairie lakes in a eutrophic state: a naturally P rich landscape, widespread agriculture, limited wastewater treatment, sediments with low iron and often high sulfate, high rates of internal loading, shallow morphometry, and

frequent summer and winter anoxia. Despite efforts to reduce P loading to priority water bodies, such as Lake Winnipeg and the Qu'Appelle lakes, recovery is likely to be slow.

4.5 Precambrian shield lakes

Lakes of the Precambrian Shield tend to have relatively low rates of internal P loading (Section 3.2.2). In experimentally eutrophied Lake 227 at the Experimental Lakes Area in northwestern Ontario, additions of radiotracers indicated that P tends to be retained by sediments, even under anoxic conditions. Less than 5% of newly sedimented P was remobilized over a 10 week period (Levine et al. 1986). Over the longer-term, high retention of P in the lake has continued, again indicative of low rates of internal P loading (Schindler et al. 1987). Experimentally eutrophied Lake 303 also has a low rate of internal P loading demonstrated by a return of P concentrations to pre-impact levels within months of the cessation of P addition (Levine and Schindler 1989). This rapid recovery was also shown in Lake 304 (Campbell 1994; Schindler 2012).

Chub Lake, located on the Precambrian Shield in the Muskoka region of Ontario, is an oligotrophic softwater lake where very low rates of internal P loading have been reported under anoxic conditions (L_{gross} : 2.2 mg TP m⁻² y⁻¹; Nürnberg et al. 1986). Despite these low rates, they are thought to be ecologically important because the P is highly bioavailable, and because many Precambrian shield lakes are highly P-limited (Healey and Hendzel 1980; Lean and Pick 1981). The work of Nürnberg et al. (1986) reports L_{gross} equal to 38% of the external load from runoff and atmospheric deposition, with winter L_{gross} contributing approximately one quarter of the annual L_{gross} .

Although rates of internal P loading in Chub Lake are low (1.43 mg TP m⁻² d⁻¹; Nürnberg 1988) relative to a full spectrum of lakes, they may be high relative to other lakes on the Precambrian Shield. Among seven lakes in this region, Chub Lake was reported to have the highest rates of internal P loading, with the majority of lakes having internal loading rates approximately one-quarter of the estimated rate for Chub (Dillon and Molot 1996). Indeed, model-based work within the Muskoka region suggests that

932 internal P loading is responsible for contributing $2 \mu\text{g L}^{-1}$ P or less to water column P in 90% of lakes in
933 the area, while in the other lakes, it may contribute up to 50% of lake P (Nürnberg and LaZerte 2004).

934 **5 Knowledge gaps**

935 In this section, we discuss the limitations of current methods to estimate internal P loading (5.1) and
936 provide recommendations for future research to improve our understanding of the mechanisms (5.2) and
937 drivers (5.3) of internal P loading. Finally, we identify specific ecosystems in Canada for which data on
938 internal P loading is lacking and deserve more study (5.4).

939 **5.1 Methodological issues**

940 As described in Section 1, internal P loading is a generic term for a number of different physical,
941 chemical, and biological processes that operate on a continuum of spatial and temporal scales; this
942 complexity makes it difficult to obtain accurate measurements of sediment P flux, and even more
943 problematic to model internal P loading at an ecosystem scale.

944 Phosphorus concentrations across the SWI obtained from pore water peepers (or emerging tools such
945 as DGT [diffusive gradients in thin films] and DET [diffusive equilibration in thin films]; e.g., Monbet et
946 al. 2008; Matisoff et al. 2016) are used to estimate sediment P flux based on the thin film boundary layer
947 model. This approach assumes diffusion is the primary process responsible for internal P loading. Yet, we
948 know that sediment P can also be translocated by resuspension of sediment particles by water movements
949 or through vertical migration of cyanobacteria and other organisms, and is also affected by bioturbation of
950 benthic invertebrates and fish (Section 2.2.8). Estimates from pore water profiles also do not take into
951 account changing conditions at the SWI. Core incubations and also benthic chambers may capture several
952 simultaneous processes responsible for P release from sediments; however, these methods inevitably
953 change the redox potential and supply of fresh organic matter at the SWI, as well as other artifacts
954 associated with containers. Pore water peepers, core incubations, and benthic chambers all provide

955 instantaneous gross estimates of benthic P flux under specific environmental conditions from a small
956 sediment surface area. Extrapolating these rates to relevant spatial and temporal scales is fraught with
957 uncertain assumptions, and usually ignores important long-term processes controlling internal P loading
958 (e.g., sediment diagenesis; Katsev and Dittrich 2013).

959 Empirical models, including mass balances, have been widely used to estimate internal P loading in
960 Canadian lakes (e.g., Nürnberg 1984). These methods, while providing a basis for understanding
961 ecosystem scale P fluxes, are hindered by issues of error. Specifically, there is the need to estimate the
962 potential magnitude of error in internal loading estimates derived from these methods. For example, if
963 groundwater inputs are not accounted for, this can overestimate rates of internal loading. Another concern
964 is that sedimentation and resuspension are often omitted from empirical models, hence they yield net rates
965 of internal P loading, missing episodic releases of P that are important for stimulating algal blooms.
966 Furthermore, most empirical models lack external validation beyond the suite of lakes for which they
967 were developed. The assumption of many of these models, that P is only released from anoxic sediments,
968 was specifically challenged by Hupfer and Lewandowski (2008). It is now clear that hypolimnetic anoxia
969 does not necessarily lead to P release and P release can indeed occur in lakes with oxic water columns
970 (Caraco et al. 1991; Prairie et al. 2001). The results of our analyses further corroborate that P release
971 occurs under oxic conditions, although at a lower rate than under anoxic conditions (Figure 6A).

972 We recommend more comparative studies be performed that simultaneously apply multiple
973 techniques for measuring internal P loading, such as the recent study by Matisoff et al. (2016). As each
974 method has its own assumptions and limitations, we emphasize that great care must be taken when
975 selecting the appropriate method for a particular study, as well as comparing output from different
976 methods. We also suggest that the limnological community invest more effort in understanding how
977 internal P loading changes spatially and temporally within a given water body in order to improve
978 strategies for scaling up estimates of L_{gross} to provide relevant information for ecosystem management. A
979 specific challenge to address is improving models of internal P loading for large, heterogeneous

ecosystems and also those with irregular stratification patterns. Finally, annual estimates of internal P loading are usually based on summer conditions. Given that over half of the internal P loading that occurs in summer may also occur under ice cover (Table 2), we encourage researchers to consider winter measurements to achieve realistic year-round estimates of P contribution from sediments.

5.2 Poorly understood drivers

A critical area of research we strongly encourage the scientific community to pursue is understanding the influence of anthropogenic activities on internal P loading in freshwater ecosystems. Here, we provide three important examples: aquaculture, sulfur pollution, and climate change.

5.2.1 Aquaculture

In Canada, aquaculture is a rapidly expanding commercial industry that currently produces approximately 155,000 tonnes of fish per year at a value of about \$900 million (Gardner-Pinfold Consulting Economists Ltd 2013). Freshwater aquaculture in Canada currently occurs in the provinces of Ontario (Lake Huron), Saskatchewan (Lake Diefenbaker) and British Columbia (Lois Lake and Lake Georgie) (Department of Fisheries and Oceans Canada 2015). Intensive aquaculture can lead to water quality impairment, particularly in small lakes and closed embayments of larger lakes (Yan 2005). The impact of aquaculture on internal P loading in Canadian freshwaters has received little attention to date, but one study suggests that aquaculture wastes are a source of internal P loading. An experimental aquaculture cage rearing rainbow trout was operated in a small oligotrophic lake in the Experimental Lakes Area, Ontario (Azevedo et al. 2011). The aquaculture operation quickly changed the lake's sediment and pore water chemistry (Rooney and Podemski 2010), resulting in depletion of oxygen and accumulation of P in bottom waters (Bristow et al. 2008). According to an unpublished report (Azevedo 2007), L_{gross} values of up to 1054 mg TDP $\text{m}^{-2} \text{d}^{-1}$ were measured in sediment under the aquaculture cage, which are orders of magnitude higher than those measured 250 m away from the cage ($< 0.5 \text{ mg TDP m}^{-2} \text{d}^{-1}$). Even so, less than 1% of the P added to this lake via the aquaculture operation was released from

sediments (Department of Fisheries and Oceans Canada 2015). Note, however, that this boreal lake is located in a geological region of Canada where high P retention in sediment is expected (Figure 5), and thus likely underestimates the impact of aquaculture on internal P loading in other types of ecosystems.

Studies from other parts of the world support the hypothesis that aquaculture increases internal P loading. For example, bottom sediments from three Scottish lakes collected under aquaculture cages of juvenile Atlantic salmon (*Salmo salar*) had higher L_{gross} (2–58 mg TP m⁻² d⁻¹) than control sediments collected 200 m away from these cages (<1 mg TP m⁻² d⁻¹) (Kelly 1993). Likewise, cage farming of tilapia in the Lake Kariba, Zimbabwe, increased L_{gross} by 4-fold relative to control sediments (Troell and Berg 1997). In addition, a study concerning rainbow trout farming in a deep oligotrophic lake in Patagonia, Argentina, reported exceedingly high rates of L_{gross} : 815 mg m⁻² d⁻¹ under oxic conditions and 2331 mg m⁻² d⁻¹ under anoxic conditions (Temporetti and Pedrozo 2000). However, such high rates of internal P loading may not necessarily translate into immediate harm on an ecosystem, as impacts of aquaculture operations may be reduced by physical and biological processes such as water currents and consumption of wastes by native fish (Gondwe et al. 2011).

Internal P loading has rarely been parameterized in lakes with aquaculture operations (Yan 2005). Clearly, the paucity of internal P loading from freshwater sediments enriched by aquaculture wastes in Canada is a knowledge gap, and studies on how aquaculture affects this process in Canadian freshwaters are needed. Further, we recommend that the susceptibility of ecosystems to internal P loading (Figure 5) should be considered when situating aquaculture facilities and mitigating their impacts.

5.2.2 Sulfur pollution

Anthropogenic sulfur emissions began increasing on a global scale in the late 1800s and rose to over 70 million metric tons per year until the 1980s, after which stringent emission regulations were enacted in North America and Europe (Stern 2006). Today, the nature of sulfur pollution has changed quite dramatically. The world's coal, petroleum, metallurgy, and mining industries currently mobilize an

estimated 190 million tons of sulfur compounds per year (Rappold and Lackner 2010). Less than 30% of this sulfur is released to the atmosphere, and the remainder is reclaimed for use mainly as a chemical leaching or catalytic reagent in industrial processes or an active ingredient in agricultural fertilizers. The flux of sulfur to the environment from discharges of industrial wastes and runoff of fertilizers from agricultural fields (approximately 80 million tons y^{-1}) now exceeds atmospheric sulfur emissions on a global scale (Rappold and Lackner 2010). Notably, as a result of the reduction in atmospheric sulfur emissions during the 1990s, sulfur deficiencies in crops are more common and the use of sulfur fertilizers is increasing (Till 2010). Furthermore, the supply of sulfur reclaimed from industrial processes exceeds the demand for sulfur products, so excess sulfur is stockpiled as element sulfur on land or injected as hydrogen sulfide underground. In other words, efforts to reduce acid rain by capturing an ever increasing proportion of the sulfur in fossil fuels has resulted in a global surplus of sulfur compounds whose environmental fate and ecological consequences are poorly understood.

Unfortunately, little is known about the impact of sulfur pollution on internal P loading (Kopáček et al. 2015). However, three lines of evidence suggest increasing sulfate concentrations can affect P cycling in aquatic environments. First, enhanced P release has been observed in sulfate-amended sediments in the laboratory (Roden and Edmonds 1997; Zak et al. 2006), and in sulfate-amended enclosures in the hypolimnion of a boreal lake (Curtis 1989) and a mesotrophic anaerobic ditch (Van Der Welle et al. 2007). Second, positive correlations have been reported between surface water sulfate concentrations and P release rates across aquatic ecosystems (Caraco et al. 1989, 1993), between the concentration of acid volatile sulfur in sediments and the accumulation of TP in the water column within a softwater lake (Murray 1995), and between sulfide concentrations and orthophosphate concentrations in sediment pore waters across a large mire complex (Smolders and Roelofs 1993). Third, reactive-transport model simulations have demonstrated that dissolved sulfate increases long-term P efflux from sediments (Katsev et al. 2006). Clearly, sulfate can play an important role in P cycling in sediments (see also Section 2.2.7) but whether sulfur pollution has altered sulfate concentration in aquatic ecosystems enough to alter P

cycling is debatable. As argued by Orihel et al. (2016), sulfur pollution holds the potential to push some ecosystems over a tipping point to a more eutrophic state but more research is needed to corroborate this hypothesis.

5.2.3 *Climate change*

Climate change is a potent catalyst for the proliferation of cyanobacterial blooms (Paerl and Huisman 2008). Increases in temperature, thermal stratification, and water column stability predicted by climate change modelling are expected to directly promote the growth of cyanobacteria (Brookes and Carey 2011). Indeed, warmer climates have been shown to boost cyanobacterial dominance in a study of 143 shallow lakes along a latitudinal transect (Kosten et al. 2012). However, climate change may also benefit cyanobacteria and other algae indirectly by stimulating P release from sediments. This hypothesis has not been explicitly tested, but several lines of evidence point to the possibility that a warming climate may exacerbate internal P loading in freshwater ecosystems, which in turn, may amplify harmful algae blooms.

Experiments, modeling studies, and monitoring data suggest P release from sediments is stimulated by warmer temperatures. When Chen et al. (2014) incubated sediments from Lake Taihu, China at 4, 15, 25, or 32°C, greater phosphate concentrations in sediment pore waters were observed at higher incubation temperatures. Likewise, 2 m aquatic mesocosms that were heated (+4°C) had significantly higher concentrations of SRP than those of mesocosms at ambient temperatures (Feuchtmayr et al. 2009). A modeling exercise to examine the effect of weather on eutrophication of a shallow, eutrophic lake in Finland indicated that warm summer periods stimulate algal growth due to high internal P loading (Kallio 1994). Malmaeus and Rydin (2006), based on a model of P dynamics in sediments of Lake Erken, Sweden, suggest that climate warming will change the sediment-water equilibrium of P in sediments and result in higher P concentrations in the water column. Similarly, a model developed by Genkai-Kato and Carpenter (2005) predicts that warmer temperatures are likely to intensify eutrophication and make restoration less successful due to increased internal P loading from sediments. Analysis of long-term

monitoring data has shown that summer water temperature is a positive driver of internal P loading in Loch Leven, Scotland (Spears et al. 2011). Finally, North et al. (2014) concluded that an increase in deep-water SRP concentrations in the (Lower) Lake of Zurich, Switzerland, was most likely the result of enhanced internal P loading associated with a climate-induced increase in extent and duration of hypoxia.

Climate change may also influence internal P loading by changing thermal stratification patterns and ice cover. Stratification events in polymictic lakes may become more frequent under climate change. For example, in Lake Müggelsee, Germany, the number of stratification events increased significantly between 1982–2007 (Wagner and Adrian 2011). Given the importance of stratification events as catalysts of P release from sediments, more intense periods of stratification in polymictic lakes in a warming climate is predicted to intensify harmful algal blooms by increasing internal P loading (Orihel et al. 2015).

5.3 Under-studied ecosystems

Reservoirs represent approximately 6% of all surface water bodies globally (Downing et al. 2006) and are increasing in number rapidly, with an additional 3,700 large hydro dams coming online in the next two decades (Zarfl et al. 2015). Impounding water upstream of dams is known to change the nutrient balance of a river system as reservoir sediments can act as efficient sink for P (Friedl and Wüest 2002). Globally, the mass of TP trapped in reservoirs nearly doubled (42 Gmol y^{-1}) between 1970 and 2000 and about 17% of the total TP load of rivers is expected to be retained in sediments of reservoirs by 2030 (Maavara et al. 2015). While Canadian reservoirs have been shown to have a high capacity to retain P (e.g., Donald et al. 2015), sediments of these reservoirs are potentially poised to be a significant source of P given the right environmental conditions. This legacy of P in reservoirs could be particularly problematic to downstream ecosystems following the decommissioning of hydro dams. Unfortunately, there is only one peer-reviewed estimate of internal P loading in a reservoir created by flooding uplands (i.e., Lake Diefenbaker; North et al. 2015), despite the presence of nearly 10,000 dams across the country (Canadian Dam Association) and the fact that water levels of many Canadian lakes are regulated. Clearly, more estimates of internal P loading from Canadian reservoirs are needed.

In addition to reservoirs, we recommend studies on internal P loading be conducted in northern Canada. No data on internal P loading was available from ecosystems above a latitude of 55 degrees (Figure 5). Although the territories of northern Canada are sparsely populated in comparison to the provinces to the south, northern lakes are not immune to nutrient pollution. For example, Meretta Lake, located in Resolute Bay on Cornwallis Island, Nunavut experienced eutrophication as a consequence of receiving untreated sewage between 1949 to 1998 (Douglas and Smol 2000). Further, as climate change proceeds, anticipated changes in permafrost thaw, length of seasonal ice cover, and water temperatures will likely increase the productivity of northern ecosystems (Antoniades et al. 2011). In fact, increases in internal P loading in boreal lakes in northern Alberta due to climate change have resulted in long-term increases in lake productivity (Hazewinkel et al. 2008; Kurek et al. 2013; Summers et al. 2016).

Conclusion

Arguably, internal P loading is a “wicked problem” in aquatic science and management. A wicked problem is one which is ill-defined, complex, and constantly changing (Rittel and Webber 1973). Internal P loading has often been poorly and inconsistently defined in the literature (Section 1) and its measurement is plagued by methodological issues (Section 5.1), generating confusion about this concept in the scientific community. This process is also complicated owing to the numerous physical, chemical, and biological mechanisms that cause the release of P from sediments (Section 2). There are a multitude of environmental drivers, from the redox chemistry of sediment pore water to bioturbation by benthic organisms, that influence the rate of internal P loading, which means that this process changes in space and time within and among ecosystems (Sections 2-4). Furthermore, anthropogenic activities are potentially changing internal P loading in freshwater ecosystems, but more research is needed to understand where, when, and how (Section 5). The variability in internal P loading in space and time, and in its importance to P budgets among different ecosystems, make this a vexing issue for resource

managers working to control eutrophication. Our systematic analysis of internal P loading in Canadian ponds, lakes, reservoirs, and coastal wetlands has helped to glean insights into this important process:

1. Internal P loading is a common phenomenon in Canadian freshwaters. By compiling a comprehensive database on internal P loading, as well as an in-depth examination of case studies, we found that P is released from sediments in all types of aquatic ecosystems, but that the rate of this process varies widely among water bodies, from being negligible in some to contributing as much, and sometimes more, than external P loading to whole-lake P budgets over annual time scales.
2. By mapping the geographical patterns of internal P loading in Canadian freshwaters, we determined that this process is detectable in water bodies in provinces from coast to coast, with the highest rates ($L_{\text{gross}} > 6 \text{ mg m}^{-2} \text{ d}^{-2}$; $L_{\text{net}} > 2190 \text{ mg m}^{-2} \text{ y}^{-1}$) occurring in Alberta, Saskatchewan, and Manitoba. No data were available for northern Canada.
3. The three most important environmental drivers of internal P loading across the broad range of aquatic ecosystems in Canada were oxygen, pH, and trophic state. Specifically, rates of L_{gross} were highest under anoxic or hypoxic conditions, in systems with moderately alkaline water, and in hypereutrophic water bodies. Notably, geology exerted an indirect effect on L_{gross} , presumably because the pH of aquatic systems was largely a function of their surficial geology.
4. Our analyses suggest that internal P loading is very important in small prairie lakes and Lake Winnipeg. In contrast, very low rates of internal P loading occur in Precambrian Shield lakes.
5. We recommend improvements in techniques to quantify internal P loading, especially with respect to extrapolating measurements of L_{gross} up to meaningful scales for lake management. More research is needed to understand how anthropogenic activities, such as aquaculture, sulfur pollution, and climate change, affect rates of internal P loading. More work is required to obtain a true national assessment of internal P loading, including reservoirs and northern lakes.

This critical review suggests we need to reframe our view of internal P loading, in both the Canadian and global contexts. Firstly, the notion of internal P loading as solely due to the redox-sensitive

dissolution of iron oxides is an erroneous over-simplification. Unfortunately, many models of internal P loading still rely on this presumption. As reviewed in Section 2, there now exists an impressive body of evidence that internal P loading can occur through a variety of physical, chemical, and biological mechanisms (although our understanding of which ones dominate under various conditions is still in its infancy), and thus, we should strive toward more sophisticated, mechanistic models of internal P loading. Second, we need to better recognize that the importance of internal P loading to eutrophication is highly variable across ecosystems. Our findings reinforce that sediments in aquatic ecosystems can function along a continuum of P source to P sink. This means not only that more care needs to be taken when extrapolating study findings across different ecosystem types, but also that we need to appropriately temper our expectations of how different ecosystems respond to external P reductions. The contrast between boreal and prairie lakes is a clear example. Third, the results of our data analyses (Section 3) will guide resource managers in screening water bodies for their vulnerability to internal P loading. This information will, in turn, inform management decisions on environmental impact assessments of industrial projects, future watershed management planning, and of course, suitable strategies for controlling eutrophication.

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2787 **Boxes**2788 **Box 1.** Definitions of key terms.

Benthic environment is the bottom sediments of a water body, plus all organisms living in or on the sediments (including periphyton, macrophytes, and benthic invertebrates).

Gross benthic phosphorus flux (L_{gross}) is the gross rate of P release per unit area of sediment measured in a sediment sample over hours to days, and is typically expressed in units of $\text{mg m}^{-2} \text{d}^{-1}$.

Internal phosphorus loading refers to all physical, chemical, and biological processes by which phosphorus is mobilized and translocated from the benthic environment to overlying water of aquatic ecosystems.

Net internal phosphorus loading rate (L_{net}) is the net rate of P release per unit area of sediment estimated for a whole ecosystem over one year, and is typically expressed in units of $\text{mg m}^{-2} \text{y}^{-1}$.

Overlying water is the water located directly above the sediment surface.

Pore water is the interstitial water in the spaces between sediment particles.

Sediment-water interface (SWI) is the boundary between the sediment surface and the overlying water of an aquatic ecosystem.

Soluble reactive phosphorus (SRP) is the molybdate-reactive fraction of phosphorus in a filtered (typically, $0.45 \mu\text{m}$) water sample.

Total dissolved phosphorus (TDP) is the total mass of all forms of phosphorus measured in a filtered (typically, $0.45 \mu\text{m}$) water sample.

Total phosphorus (TP) is the total mass of all forms of phosphorus in an unfiltered water sample.

2789 **Tables**

2790 **Table 1.** Chemical and biological processes affecting phosphorus release rates from sediments.

P immobilisation mechanisms in lake sediments	Possible release mechanisms (diagram process number ^a)	Causal factors for release	Analytical/Spectroscopic determination method ^b	Examples in literature
Surface sorbed P species	Dissolution of host phase (9) or desorption (7)	Desorption: pH increases, competing ligand concentration (e.g., arsenate), ionic strength decreases	Chemical extraction, XPS, XAS	Martin and Smart 1987, Mallet et al. 2013
Phosphate minerals	Dissolution (9)	Redox changes, pH changes, concentration changes of aqueous species	Chemical extraction, XRD, XANES, ⁵⁷ Fe Mossbauer	Manning et al. 1991, Fagel et al. 2005, Güngör et al. 2007
Co-precipitated/occluded phosphate	Dissolution (9)	Eh, pH changes, concentration changes of aqueous species	Chemical extraction, XANES	House and Donaldson 1986, Ruttenberg 1992, Gunnars et al. 2002, Ruttenberg et al. 2009
Organic P species in bio- and necromass	Surface promoted hydrolysis Enzymatic hydrolysis Photolysis (SWI) (13)	Presence or absence of mineral surfaces, microbial activity and nutrient ratios	³¹ P NMR, XANES	Ahlgren et al. 2005, Cade-Menun 2005, Reitzel et al. 2007
Ternary complexes	Dissociation (15)	UV irradiation, pH decrease	Ultrafiltration or size exclusion chromatography combined with chemical determination	Jones et al. 1993, Hens and Merckx 2001, Gerke 2010

2791 ^a Release mechanisms are numbered according to Figure 2; ^b XPS: X-ray photoelectron spectroscopy; XAS: X-ray absorption spectroscopy; XRD: X-ray diffraction; XANES: X-ray absorption near edge structure; NMR: Nuclear magnetic resonance.

2793

2794 **Table 2.** Comparison of ice-covered and ice-free rates of gross benthic phosphorus flux (L_{gross}) and net internal phosphorus loading rate (L_{net}).

2795 Reported are the mean values derived from the literature and our calculated ratio of ice-free to ice-covered and associated rock types.

Lake name	Province	Rock type	L_{gross} (mg TP m ⁻² d ⁻¹)		Ratio	Reference
			Ice-covered	Ice-free		
Crooked	AB	Sedimentary	0.20	4.28	21.0	Reedyk et al. 2001
Nakamun	AB	Sedimentary	1.20	19.0	16.0	Orihel et al. 2016
Baptise	AB	Sedimentary	0.73	5.60	7.70	Reedyk et al. 2001
Jenkins	AB	Sedimentary	0.57	3.48	6.10	Reedyk et al. 2001
Simcoe	ON	Sedimentary	0.11	0.87	8.00	Dittrich et al. 2013
Halfmoon	AB	Sedimentary	2.62	5.23	2.00	Prepas et al. 2001
Lofty	AB	Sedimentary	1.55	1.20	0.77	Reedyk et al. 2001
North Halfmoon	AB	Sedimentary	21.5	2.40	1.10	Reedyk et al. 2001
			L_{net} (mg TP m ⁻² d ⁻¹)			
Halfmoon	AB	Sedimentary	1.72	4.33	2.5	Babin et al. 1994
Diefenbaker	SK	Sedimentary	4.50	1.50	0.33	North et al. 2015

Figure Captions

Figure 1. Schematic of two operational definitions of internal phosphorus (P) loading. Gross benthic phosphorus flux (L_{gross}) is the gross rate of P release per unit area of sediment measured in a sediment sample over hours to days, and is typically expressed in units of $\text{mg m}^{-2} \text{d}^{-1}$ (A). Net internal phosphorus loading rate (L_{net}) is the net rate of P release per unit area of sediment estimated for a whole ecosystem over one year and is typically expressed in units of $\text{mg m}^{-2} \text{y}^{-1}$ (B).

Figure 2. A conceptual diagram of the key solid and aqueous P pools that occur in lake sediments and the water column and the processes that cause changes between these pools. Physical processes affecting solid particles are shown as red arrows, physical processes affecting aqueous species are shown as blue arrows and chemical or biological processes are shown with black arrows. Physical processes: advection/diffusion = 1; external transport = 2; sedimentation = 3; resuspension = 4; burial = 5. Chemical and biological processes: adsorption = 6; desorption = 7; precipitation = 8; dissolution = 9; recrystallization = 10; assimilation = 11; exudates = 12; hydrolysis/mineralisation = 13; complexation = 14; dissociation = 15; death = 16; migration = 17; intracellular processes = 18.

Figure 3. Schematic drawing of soft water and hard water lake sediment profiles showing key P forms based on release mechanism and general likelihood of presence with depth. Soft water lakes are more acidic and have less calcium than hard water lakes. Fe-OOH-P are redox-sensitive iron oxyhydroxides with adsorbed P (such as ferrihydrite and goethite; e.g., Lavoie and Auclair 2012); POC-P are particulate organic carbon with P and include necromass (recently sedimented material); Humic-P are humic-metal-phosphate complexes (e.g., Jackson and Schindler 1975; Tipping 1981a, 1981b; Ansems 2012; Jilbert and Slomp 2013; Dijkstra et al. 2014; O'Connell et al. 2014); Ca-P are calcium phosphate minerals (along the gradient from calcite with phosphate to apatite (Murphy et al. 1983, 1988; Murphy and Prepas 1990; Dittrich et al. 1997; Hamilton et al. 2009); and Fe-P are iron phosphate minerals (e.g., vivianite; Nriagu and Dell 1974; Fagel et al. 2005). Lake nutrient loading and catchment history play a role in the relative

2820 importance of each P form for net P release from sediments (e.g., McCulloch et al. 2013). Sediment depth
2821 ranges for short-term and long-term phases are drawn from previously cited literature plus modelling by
2822 Katsev et al. (2007) and Katsev and Dittrich (2013).

2823 **Figure 4.** Frequency histograms of A) gross benthic phosphorus flux (L_{gross} ; $n = 461$) and B) net internal
2824 phosphorus loading rate (L_{net} ; $n = 157$) in ponds, lakes, reservoirs, and coastal wetlands across Canada.

2825 **Figure 5.** Geographical distribution of A) gross benthic phosphorus flux (L_{gross} ; $n = 48$) and B) net
2826 internal phosphorus loading rate (L_{net} ; $n = 22$) in ponds, lakes, reservoirs, and coastal wetlands across
2827 Canada. In cases where there was more than one study or site in a given water body, the rate shown was
2828 the average of all measurements (Supplement A). Rates are expressed in terms of total phosphorus
2829 (Supplement B). Background colors indicate surficial geology (Wheeler et al. 1996). Inset maps provide
2830 more detail for areas indicated by the red boxes.

2831 **Figure 6.** Differences in gross benthic phosphorus flux (L_{gross}) from core incubations ($n = 145$) based on
2832 A) oxygen treatments (anoxic, $< 0.5 \text{ mg L}^{-1}$; hypoxic $0.5 - 2 \text{ mg L}^{-1}$; oxic $> 2 \text{ mg L}^{-1}$); B) pH classes
2833 based on epilimnetic pH (alkaline, > 7.8 ; neutral, $6.5 - 7.8$; acidic < 6.5); and C) trophic states based on
2834 Wetzel (2001)(Supplement A). The boxes represent the 75th, 50th and 25th percentiles, the whiskers
2835 represent the 90th and 10th percentiles, and the dots represent outliers greater than the 90th or less than the
2836 10th percentiles. Different letters indicate significant ($p = 0.05$) differences among categories based on a
2837 Kruskal-Wallis test.

2838 **Figure 7.** Relationship between gross benthic phosphorus flux (L_{gross}) from core incubations and sediment
2839 pore water pH ($n = 42$). Different shapes indicate different surficial geology classes. The dashed line
2840 indicates the acid dissociation constant (pKa) of protonation for phosphate.

A. Gross Benthic Phosphorus Flux (L_{gross})

Time Scale:

- Hours to days

Spatial Scale:

- Sediment sample

Units:

- $mg\ P\ m^{-2}\ d^{-1}$

Common Methods:

- Core incubation
- Flux chamber
- Pore water profile

B. Net Internal Phosphorus Loading Rate (L_{net})

$$\Delta W_{t \rightarrow (t+1)} = (I + L_{net}) - O$$

Time Scale:

- One year

Spatial Scale:

- Whole-ecosystem

Units:

- $mg\ P\ m^{-2}\ y^{-1}$

Common Methods:

- Mass balance
- Other models

Short-term:
redox- & POC
necromass-induced
P release
 NO_3^- & SO_4^{2-} reduction
(1–10 cm range)

Long-term:
stable P phases
(>20 cm range)

Depth/Redox

A

B

A

Gross Benthic Phosphorus Flux
(L_{gross}) ($\text{mg m}^{-2} \text{d}^{-1}$)

- < 0
- 0 - 1.5
- 1.5 - 3.0
- 3.0 - 6.0
- > 6.0

B

Net Internal Phosphorus Loading Rate
(L_{net}) ($\text{mg m}^{-2} \text{y}^{-1}$)

- < 0
- 0 - 547
- 547 - 1095
- 1095 - 2190
- > 2190

Geology

- Igneous rocks
- Sedimentary rocks
- Metamorphic rocks
- Lakes

0 650 1,300 km