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Published online: 17 Aug 2022.

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Natural controls on phosphorus concentrations in small Lakes in Central Alberta, Canada

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ABSTRACT

Small lakes can act as environmental sensors for understanding regional hydrogeological conditions and elemental cycles. Because of their small size, they react quickly to changes in nutrient runoff, groundwater exchange and climate. In the post-glacial landscape of Alberta, the Carvel Pitted Delta harbours a variety of small lakes, which, despite being close together, can have markedly different chemistries and nutrient characteristics. Here, we focused on nine lakes with surface areas <10 ha and maximal depths ranging from 5 to 18 m. We hypothesised that differences in their trophic states are caused by variations in Ca concentrations, controlled by groundwater inputs. All lakes tended toward permanent stratification due to small mixing depths (1.6–2.4 m). The deeper lakes were oligotrophic with high concentrations of Ca and a high fraction of phosphorus (Ca-bound P) in the sediments (HCl extractable fraction). A correlation was found between Ca-bound P and aqueous Ca concentrations at 0.5 m depth, suggesting that P stability could be estimated based on surface water chemistry. Calcium was shown to be concentrated in groundwater located above the bedrock, suggesting that groundwater inputs controlled Ca concentrations in the lakes. We conclude that the hydrogeological conditions and Ca inputs act as natural regulators for P availability and, by extension, water quality in these lakes.

RÉSUMÉ

Les petits lacs peuvent servir comme des capteurs environnementaux pour comprendre les conditions hydrogéologiques régionales et les cycles élémentaires. En raison de leur petite dimension, ils réagissent rapidement aux changements de ruissellement de nutriments, d'échange d'eau souterraine et de climat. Dans le paysage postglaciaire de l'Alberta, le Carvel Pitted Delta abrite une variété de petits lacs qui, malgré leur proximité, peuvent avoir des chimies et des budgets nutritifs très différents. Ici, nous nous sommes concentrés sur neuf lacs avec des superficies < 10 ha et des profondeurs maximales de 5–18 m. Nous avons fait l'hypothèse que les différences dans leurs états trophiques sont le résultat des variations de concentrations de Ca contrôlées par les apports d'eau souterraine. Tous les lacs tendaient vers une stratification permanente en raison des faibles profondeurs de mélange (1.6–2.4 m). Les lacs plus profonds étaient oligotrophes avec des concentrations élevées de Ca et une fraction élevée de P lié au Ca dans les sédiments (fraction extractible HCl). Une corrélation a été trouvée entre les concentrations de P lié au Ca et de Ca aqueux à une profondeur de 0,5 m, une indication que la stabilité du P pourrait être estimée sur la base de la chimie des eaux de surface. Il a été démontré que le calcium était concentré dans les eaux souterraines situées au-dessus du substrat rocheux, ce qui suggère que les apports d'eau souterraine contrôlaient les concentrations de Ca dans les lacs. Nous concluons que les conditions hydrogéologiques et les apports de Ca agissent comme des régulateurs naturels de la disponibilité du P et par extension de la qualité de l'eau dans ces lacs.

Introduction

The quality of inland waters is often described by trophic state, which is determined by the concentrations of nutrients, e.g. phosphorus (P), nitrogen (N), and primary production. While nutrient-poor and less productive lakes (i.e. oligotrophic) often provide the ideal niche for many plant and animal species, the opposite nutrient-rich state (i.e. eutrophic) favours the flourishing of highly competitive species, which can lead to an irreversible impairment of the water body for

human use (Carpenter et al. 1998). Certain lakes in Alberta, Canada suffer from high nutrient loads and eutrophication, often caused by nearby anthropogenic activities. Many lakes on the prairie landscape are eutrophic to hypereutrophic, due to nutrient-rich surface deposits (Orihel et al. 2017) and widespread agricultural land use. Many attempts have been made to mitigate lake eutrophication, including the use of chemicals to precipitate out P phases, which are then sequestered in sediments (Cooke et al. 2016). Specifically, elevated concentrations of Fe in solution can lead to the precipitation of P as Fe-phosphate phases. Artificial Fe additions in lakes have been performed since the 1960s as a means to reduce P availability, with successful experiments on certain lakes in Canada using the addition of $Fe(Cl)_3$ (Orihel et al. 2016). While Fe can effectively bind P under oxic conditions, mainly in the form of vivianite, anoxia and especially the presence of H_2S can lead to the resolubilization of Fe-bound P, making this chemical treatment temporary. In such cases, Ca becomes important as an alternative binding agent. Babin et al. (1989), Prepas et al. (2001) and Dittrich et al. (2011) demonstrated that treatment of stormwater ponds and small lakes in Alberta with $Ca(OH)_2$ and $CaCO_3$ can significantly increase the removal of dissolved P through binding to Ca, which can lead to a reduction of algal biomass. Phosphorus may not only form sparingly soluble Ca-phosphates (Bańkowska-Sobczak et al. 2020), but it can also co-precipitate with calcite (Otsuki and Wetzel 1972; Danen-Louwerse, Lijklema, and Coenraats 1995).

The Ca-bound phosphorus is often considered the most stable form (Ruban et al. 1999), given that only significant decreases in pH can lead to its release (Huang et al. 2005), while the Fe-bound form is affected by redox conditions and can be resolubilized during long-term anoxic states (Mortimer 1942).

While important as ecological bridging habitats, small lakes having a surface area less than $0.1 \, km^2$ are often neglected by regulators and researchers. There is a lack of current water quality and quantity information for small lakes, including basic morphometry, hydrology, ecosystem health and sportfish capacity. Over the past decades, some small lakes in Canada have exhibited declining lake levels and are increasingly impacted by eutrophication (Orihel et al. 2017). Compared to larger water bodies, small lakes are more strongly affected by anthropogenic and environmental factors and thus provide a more direct view on environmental conditions, giving them a sensory role on the landscape (Moiseenko et al. 2013; Slukovskii et al. 2020). Understanding geochemical

processes in small lakes, especially P cycling, can help in identifying their sensitivities to anthropogenic factors and may be vital for their preservation.

Much of the Canadian prairies is a post-glacial landscape having various deposits of glacial sediments that influence the chemistry of groundwater and lakes (e.g. Riera et al. 2000; Winter 2001). Within the central region of Alberta, Canada, numerous small lakes are found on the hummocky terrain of Parkland County (Figure 1), many of which are kettle lakes. There are approximately 26 named lakes and 70 unnamed lakes in this area. Decreasing water levels in many of these lakes (Regier and Trew 2016) creates partially or fully isolated basins, which makes the determination of the exact number of lakes challenging. Initial studies in this region focused on the evaluation of sport fishing capability (Miller and Macdonald 1949). Later studies looked at the trophic state and mixing patterns of selected lakes, such as Sauer, Hubbles and Gerharts lakes (Prepas and Trew 1983; Babin 1984; Babin and Prepas 1985; Murtaugh 1985) and recent reports were created to assess the state of lake watersheds (Logan, Trew, and Mussell 2016; Regier and Trew 2016; Gordy et al. 2018) as a step toward better management.

Smaller lakes on the hummocky terrain of Parkland County show large differences in terms of their trophic state, water clarity and faunal composition, while only being hundreds of meters apart. Thanks to the size and proximity of the lakes to each other, it is an ideal location to investigate the influence of hydrological and chemical interactions on surface water quality and consider potential for natural protection from eutrophication. Given the post-glacial landscape, it was hypothesized that differences in the availability of phosphate-binding cations, mainly Ca, are likely responsible for the high diversity observed among the small lakes. The water columns of nine lakes were then limnologically and geochemically characterized, and the P speciation in their sediments was assessed to determine its stability.

Materials and methods

Field sites

The lakes targeted by this investigation are located west of Edmonton, Alberta and situated entirely on the hummocky terrain known as the Carvel Pitted Delta (Figure 1). This lobate-shaped glacial deposit is primarily comprised of sand and gravel (Andriashek, Fenton, and Root 1979), varies from 25 to 95 meters thick in the study area (Hartman 2020) and contains potentially productive shallow aquifers that may be
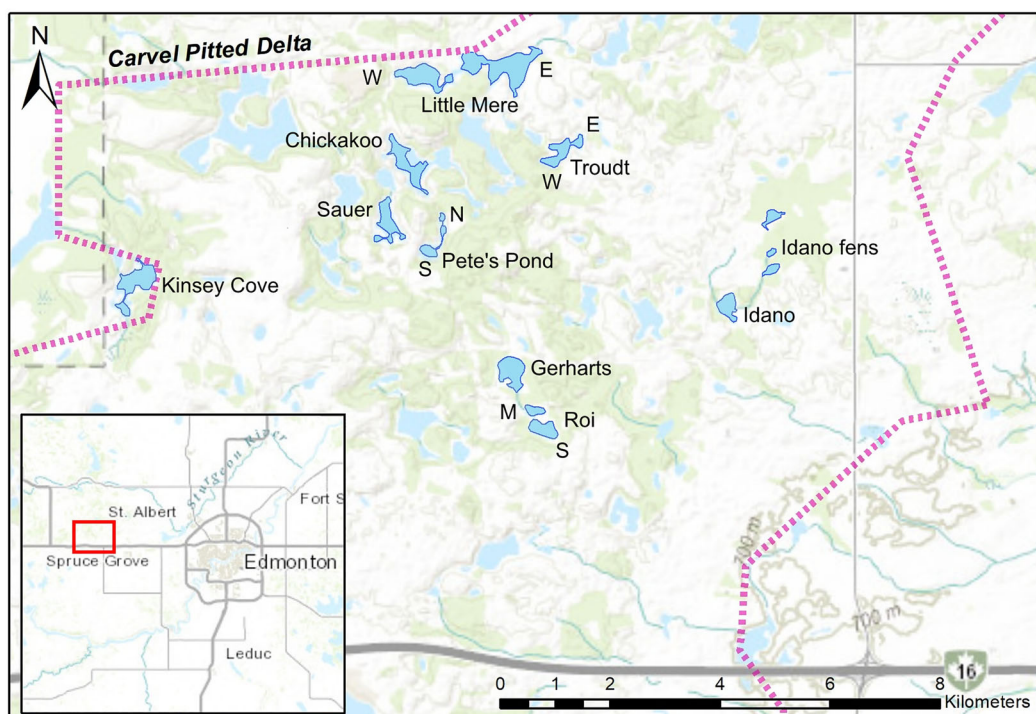
Figure 1. Overview of the sampled lakes. The approximate extent of the Carvel Pitted Delta (Andriashek, Fenton, and Root 1979) is depicted by a dashed line. Basemap by Esri (2020).

connected to small lakes in some locations (Oiffer 2019), but not in other places. The lakes investigated in this study are located in the north central parts of the Carvel Pitted Delta (Figure 1) within the depressions of the hummocky terrain. The bedrock underneath the surficial glacial deposits is the Late Cretaceous age Horseshoe Canyon Formation consisting of coal, shale, and sandstone (Prior et al. 2013). The bedrock is often targeted for domestic water supplies in this region (HCL (Hydrogeological Consultants Ltd.), 1998).

Within the study area, nine small lakes (less than 10 ha) and nearby water bodies were sampled between May and September 2020 and again for alkalinity between August and September 2021 (Table 1). Four of the 2020 lakes described here are formally named, and the remaining were assigned informal names as used by landowners. Five lakes were located in or near the Chickakoo Lake Recreational Area: Little Mere (W basin), Chickakoo Lake (W or main basin), Sauer Lake, Pete's Pond (S basin), and Troudt Lake (W basin). Chickakoo Lake is a eutrophic-hypereutrophic lake that is used recreationally and is accessible to the public. To reduce sportfish winterkill and summer algal blooms, the Municipality of Parkland County installed aeration devices in Chickakoo Lake in 2017 (PRC, 2016). Sauer Lake was previously described as a mesotrophic lake (Babin 1984). Other investigated lakes were Kinsey Cove, Idano, Gerharts,

and Roi lakes (S basin). Idano Lake is fed by a series of wetland (marl ponds) north of it through a creek. The lake has a permanent outflow in the south and an intermitted outflow in the west. Gerharts Lake has an outflow in the south going into Roi Lake, which has an outflow in the east. For comparison purposes, selected water and/or sediment samples were collected around the main lakes described above.

Water characterization

Full vertical water chemistry profiles were acquired for each lake once between May and September 2020 from a boat using a Van Dorn sampler after determining the deepest spot using a sounding line. Electrical conductivity and pH were measured in-situ in the collected samples from each depth using a PCTSTestr 50 multimeter (OAKTON), which was previously calibrated in the laboratory. Temperature and dissolved oxygen concentrations were measured at the same depths using a YSI ProSolo probe calibrated in the field. Secchi depths were determined using a 30 cm wide Secchi disk. Subsamples of each water sample were filtered through 0.45 μm nylon syringe filters and acidified to 2% nitric acid for analysis of major cations and trace elements by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) as described below. Additional unfiltered samples were collected from a depth of 0.5 m and analysed for

Table 1. Summary of sampling areas and lakes. Surface area (S.A.) refers to open water area determined by satellite images available in 2020. If the full profile or the shore was sampled is indicated by the month of collection in 2020. *Informal name used in this study.

Area	Water body	Coordinates N, W (°)	S.A.	Sampling	
				Date	Type
N	Little Mere East	53.6286, 114.0575	16.70	August 25	In-situ profile only
N	Little Mere West	53.6274, 114.0735	9.07	August 25	Full profile and deep sediments
N	Chickakoo	53.6201, 114.0494	7.25	July 27	Full profile and deep sediments
N	Sauer	53.6126, 114.0781	5.86	June 8	Full profile and deep sediments
N	Pete's Pond North*	53.6138, 114.0697	0.38	July 4	From shore only
N	Pete's Pond South*	53.6103, 114.0722	1.65	July 4	Full profile and deep sediments
N	Troudt Lake West*	53.6201, 114.0494	4.29	July 27	Full profile and deep sediments
W	Kinsey Cove*	53.6075, 114.1204	6.71	August 27	Full profile and deep sediments
SE	Idano*	53.6044, 114.0228	4.31	May 19	Full profile and deep sediments
SE	South fen*	53.6083, 114.0169	1.33	May 19	From shore only
SE	Middle fen*	53.6101, 114.0162	0.55	July 4	From shore only
SE	North fen*	53.6133, 114.0164	1.94	July 4	From shore only
SE	Gerharts	53.5990, 114.0574	7.29	August 25	Full profile and deep sediments
SE	Roi Middle*	53.5949, 114.0536	1.74	September 6	In-situ profile only
SE	Roi South*	53.5927, 114.0520	4.61	September 6	Full profile and deep sediments

bicarbonate by titration (method SM 23 2320 B m) by the Bureau Veritas laboratory. ^{222}Rn can be used as a tracer for groundwater, as ^{222}Rn activity increases with the residence time of interstitial water (Hoehn et al. 1992). Therefore, to characterize groundwater inflow, selected samples from were collected in 250 mL plastic bottles with no headspace for ^{222}Rn analysis and measured at the end of each day using a RAD7 radon detector (Durridge Company, Inc.). For lakes that had permanent outflow, creeks were gauged in the end of August using a Valeport model 801 electromagnetic flow meter.

To more closely examine the role of shallow groundwater as a source of Ca, water well chemistry reports were obtained from the Alberta Water Well Information Database (http://groundwater.alberta.ca/WaterWells/d/).

Sediment characterization and phosphorus fractions determination

Littoral sediments were collected by scooping them with a 50 mL polypropylene centrifuge tube after removing plant material from the sediment surface. Deep (profundal) sediments were obtained using an Ekman dredge, which collects the upper 10–20 cm of the lake sediments, thus averaging the seasonal compositional variations over several years. For the latter, after a successful grab sample was obtained, the sediments were mixed in the dredge before being collected into 50 mL tubes from the centre of the dredge body. In the laboratory, all sediment samples were centrifuged at 4000 g to liberate excess water. This was done to remove any trapped water because it could impact element mass fractions in the solid sample. Subsamples were air-dried, ground by mortar and pestle, sieved (1 mm) and analyzed for mineralogy using X-ray diffraction (XRD; Ultima IV, Rikagu with a Co X-ray tube at 38 kV, Kα_1 = 1.78900). Interpretation was done using the JADE 9.5 and the DIFFRAC.EVA software packages and the databases: 2020 ICDD PDF 4+ and PDF 4+/Organics. Another subsample was dried at 105 °C before grinding and sieving. Elements were extracted (6 mL 37% HCl and 2 mL 70% HNO$_3$, 3 h at 100 °C on a hotplate) from 0.2 g of sediment in triplicates (Ščančar, Milačič, and Horvat 2000). The resulting mixtures were diluted to 20 mL with 2% HNO$_3$ and 0.5% HCl, filtered through 0.45 µm syringe filters and further diluted to a final volume of 50 mL. Another 105 °C-dried sample was analyzed for total nitrogen (TN), total carbon (TC), and total organic carbon (TOC) using the dry combustion method on a Thermo Scientific Flash 2000 Organic Elemental Analyzer. Total inorganic carbon was calculated as TC-TOC.

Phosphorus speciation was determined in triplicates with 0.2 g of 105 °C-dried sediments according to the "SMT protocol" by Ruban et al. (1999) and Ruban et al. (2001). The 1st fraction, Fe-bound bioavailable P (also Al- and Mn-bound), was extracted using 20 mL 1 M NaOH (overnight on a rotary shaker). After centrifuging (2000 g, 15 min), 10 mL of the supernatant were removed and amended with 4 mL 3.5 M HCl. The solutions were left overnight, then centrifuged and the supernatant taken for elemental analysis. The residuals from the NaOH amendment were washed twice with 1 M NaCl and subsequently extracted with 20 mL 1 M HCl (2nd fraction, Ca-bound P, non-available) overnight. After centrifugation, the supernatant was recovered for analysis. The 3rd fraction (organic P, partially available) was estimated by subtracting the 1st and 2nd

fractions from the total P value, which was obtained by aqua regia digestion (see above). According to Ruttenberg (1992), for the total P determination, the aqua regia digestion is equivalent to ashing and acid extraction, as in Ruban et al. (2001), and usually leads to less loss of volatile compounds. In our case, the comparison of these two methods showed an average $P_{ash}/P_{aqua\ regia}$ factor of $100 \pm 18\%$ ($n = 12$) suggesting that the methods are comparable. Note that in the "SMT protocol," oxidation of sediment material may occur during sample drying, which could impact the P proportions bound to Fe phases (Xu et al. 2011).

ICP-MS

Water samples were analyzed directly on an Agilent 8800 Triple Quadrupole ICP-MS using the general matrix mode. Extracts and digestion solutions from sediment samples were diluted 2 times (digestions) and 5 times (extracts) and analysed in high matrix introduction mode using Ar gas for dilution. Internal standards (Sc, Ge, In, Bi) were added using an inline introduction system (Sakai 2015). Helium, hydrogen and oxygen were introduced into the reaction chamber to cope with polyatomic interferences (Sugiyama and Nakano 2014; Sakai 2015).

Lake morphometric features and thermodynamic modelling

Mixing depth E (in m) was estimated using lake fetch f (in km): $E = 4.4f^{0.5}$ (Davies-Colley 1988). Fetch was determined directly from the lake area A (in km²): $f = A^{0.5}$. The relative depth h_{rel} of the lakes was calculated based on the maximum depth h_{max} (in m) and the lake area A (in m²) according to Pieters and Lawrence (2014): $h_{rel} = h_{max}(4\pi^{-1}A)^{-0.5}$.

The chemical relationship between the water column chemistry and P stability in sediments is dependent on the solubility of phosphates (Syers, Harris, and Armstrong 1973). Using the software PHREEQC Interactive (version 3.4.0.12927; database Minteq.v4; Parkhurst and Appelo 2013) we calculated the saturation indices (SI, determined as $SI = \log(IAP/K_{sp})$), where IAP is the ion activity product and K_{sp} the solubility product of important P-containing phases, such as strengite ($FePO_4 \cdot 2H_2O$), vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$), hydroxylapatite ($Ca_5(PO_4)_3OH$), $CaHPO_4$, $Ca_4H(PO_4)_3 \cdot 3H_2O$, $MnHPO_4$ (Syers, Harris, and Armstrong 1973; Frevert 1980; Oxmann and Schwendenmann 2014) and other non-P phases that could be involved in P cycling, e.g. calcite and

ferrihydrite (Amirbahman et al. 2003). The calculations were made for the conditions at the surface (0.5 m depth below surface) as well as the bottom (deepest sampled layer, see Table S1) of each lake. Element concentrations, pH and temperature were entered based on collected data. No data were available for bottom inorganic carbon; therefore, the surface values for bicarbonate were used for the bottom calculations. For surface conditions, the E_H (electrical potential) value was calculated based on the oxygen concentration (Libes 2009), while for the bottom conditions it was estimated based on the dominant redox conditions according to Borch et al. (2010); e.g. for sulfate reducing conditions, -220 mV was used. Redox potential pe ($-\log[e^-]$) was then calculated based on: $pe = 2.3RT(FE_H)^{-1}$, where R is the universal gas constant, T is the temperature at the lake bottom and F is the Faraday constant.

Results

Characteristics of the water columns

The physical and chemical characteristics of the nine lakes were quite diverse. Maximum depths h_{max} varied from 5.3 to 18.1 m (Table 2). Calculations of the mixing depth based on Davies-Colley (1988) resulted in relatively shallow estimated mixing depths of 1.6–2.4 m for the lakes, suggesting limited seasonal mixing. Still, the larger and deeper lakes (Gerharts and Roi South) expressed well oxygenated epilimnia (4–5 m deep) (Figure 2). Limited mixing could be further confirmed by the relatively high relative depths of the lakes, a parameter that describes the relationship between the maximum depth and the surface area and can be used to describe the resistance of lakes to mixing. Calculated relative depths ranged from 1.8% to 6.9% (Table 2). Most natural lakes have relative depths of 2%, while for deep lakes, with higher resistance to mixing, relative depth is usually 4% or more (Pieters and Lawrence 2014).

All investigated lakes were fully stratified based on temperature and dissolved oxygen measurements (Figure 2). Chickakoo Lake was a special case due to its artificial aeration, which provided oxygen down to the lake bottom. The hypolimnia of the other lakes were anoxic and for the deeper lakes (Gerharts, Roi South, Idano, Sauer) a second conductivity increase at depth suggested the presence of an additional lower layer in the water column, which may not readily mix with the above layers (monimolimnion).

The lakes can be grouped by their average chemistries (averages of values in Table S1) based on the concentrations of Fe, S and Ca. Lakes Idano,

Table 2. Summary of relevant characteristics of lake water and sediments. Lakes ordered by depth. Trophic state based on surface P concentrations and following the Canadian classification (Galvez-Cloutier and Sanchez, 2007): 1 ultra-oligotrophic, 2 oligotrophic, 3 mesotrophic, 4 meso-eutrophic, 5 eutrophic, 6 hypereutrophic. Mineral abbreviations: Alb = albite, Ano = anorthite, Cal = calcite, Cli = clinochlore, Ill = illite, Kao = kaolinite, Lau = laubmannite, Mon = montmorillonite, Mus = muscovite, Nac = nacrite, Ort = orthoclase, Pyr = pyrite, Qua = quartz, Ser = sericite.

Parameter	Unit	Kinsey Cove	Troudt	Little Mere	Pete's South	Chickakoo	Sauer	Idano	Roi South	Gerharts
Depth parameters										
Max. depth h_{max}	m	5.3	6.5	7.2	8.0	9.7	12	12.3	16.2	18.1
Mix. depth h_{mix}	m	2.2	2.0	2.4	1.6	2.3*	2.2	2.0	2.0	2.3
Rel. depth h_{rel}	%	1.8	2.8	2.1	5.5	3.2	4.2	5.3	6.7	5.9
Secchi depth	m	1.2	2.8	1.4	1.7	1.9	4.0	5.0	4.9	6.3
Surface chemistry[1]										
HCO_3^-	mg/L	150	38.0	210	67	150	130	280	260	260
Na	mg/L	3.74	<0.855	7.59	10.2	4.50	5.29	19.8	16.5	15.1
Mg	mg/L	17.5	2.08	15.5	4.26	20.1	11.9	27.5	40.5	29.8
Al	µg/L	0.702	2.94	1.54	5.77	6.35	13.0	<1.44	0.844	<0.659
Si	mg/L	1.21	0.045	0.524	0.62	<0.0520	<0.0520	4.15	6.16	6.83
P	µg/L	24.7	18.2	30.3	16.2	173	26.2	6.99	3.58	3.57
S	mg/L	29.2	0.360	13.4	0.940	37.0	7.94	42.0	44.0	30.4
Ca	mg/L	49.9	5.42	38.3	12.2	47.8	25.8	76.6	64.2	56.5
Mn	µg/L	<1.47	<10.7	<1.47	2.70	25.9	42.9	16.7	<1.71	<1.47
Fe	µg/L	11.4	55.6	15.5	62.9	44.7	26.5	7.25	<1.48	<2.33
Sr	µg/L	391	22.1	233	63.6	300	170	631	748	625
Trophic state		4	3	4	3	6	4	2	1	1
Sediment composition (ICP-MS data given as averages of n = 3)[2]										
Minerals		Qua, Cal, Pyr, Ano, Mus, Ser	Qua, Alb, Mus, Kao	Qua, Cal, Pyr, Ser, Nac, Alb	Qua, Mus, Kao, Alb, Ort	Qua, Alb, Mon, Kao, Pyr	Qua, Pyr, Alb, Mus, Cli, Lau	Cal, Qua, Pyr	Cal, Qua, Pyr, Ano	Cal, Qua, Pyr, Ill
Mg	mg/g	3.84	1.76	3.76	1.87	3.04	3.11	3.09	4.36	3.28
S	mg/g	21.6	4.30	19.6	12.4	10.2	28.7	40.8	9.84	45.2
Ca	mg/g	46.7	3.05	48.6	4.75	5.63	6.31	166	230	171
Fe	mg/g	20.4	17.7	17.0	17.1	14.9	25.6	27.9	10.2	49.0
P	µg/g	1160	1400	1520	2030	851	1180	1150	422	606
Mn	µg/g	750	210	537	370	245	199	1480	701	977
Sr	µg/g	194	21.9	154	30.1	41.6	45.8	560	704	509
TN	w/w%	1.87	2.38	2.34	2.32	1.38	1.53	0.960	0.710	0.780
TIC	w/w%	1.13	0.640	2.29	1.36	12.6	0.620	5.78	3.60	2.92
TOC	w/w%	17.5	22.3	20.4	21.4	11.3	12.8	9.50	11.8	10.3
C:N:P	mol:mol:mol	414:36:1	423:38:1	385:34:1	289:25:1	724:36:1	293:29:1	343:18:1	941:37:1	563:28:1
P fractions (relative, averages of n = 3)[3]										
NaOH	µg/L	41 %	82 %	37 %	76 %	60 %	61 %	17 %	14 %	24 %
HCl	µg/L	32 %	9 %	28 %	8 %	28 %	21 %	61 %	27 %	51 %
Organic	µg/L	27 %	9 %	35 %	16 %	12 %	18 %	22 %	59 %	25 %

(continued)

Table 2. Continued.

Parameter	Unit	Kinsey Cove	Troudt	Little Mere	Pete's South	Chickakoo	Sauer	Idano	Roi South	Gerharts
Saturation indices (positive values shown in bold)										
Calcite at 0.5 m		**0.0**	−1.4	−0.3	−1.3	−0.4	−0.2	**0.3**	**0.3**	**0.6**
Calcite at h_{max}		−1.3	−3.9	−1.1	−2.7	−1.1	−1.6	−0.6	−0.4	−0.6
Hydroxylapatite at 0.5 m		**2.9**	−1.6	**1.3**	−1.7	**3.7**	**2.7**	**1.6**	**0.5**	**1.7**
Hydroxylapatite at h_{max}		**3.6**	−12.0	**2.9**	−0.2	**4.5**	**0.8**	**3.9**	**5.2**	**2.8**
CaHPO$_4$ at 0.5 m		−2.6	−3.5	−2.7	−3.3	−1.9	−2.7	−3.1	−3.5	−3.5
CaHPO$_4$ at h_{max}		−0.9	−4.4	−1.1	−1.2	−0.8	−1.5	−1.1	−0.8	−1.5
Ca$_4$H(PO$_4$)$_3$·3H$_2$O at 0.5 m		−6.7	−10.0	−7.6	−9.9	−5.1	−7.0	−8.0	−9.2	−8.5
Ca$_4$H(PO$_4$)$_3$·3H$_2$O at h_{max}		−4.0	−17.1	−4.8	−6.5	−3.3	−6.5	−4.2	−3.2	−5.4
Strengite at 0.5 m		−2.5	−1.6	−4.5	−1.4	−0.7	−2.2	−3.3	–	–
Strengite at h_{max}		**0.5**	−8.5	−9.4	−3.1	**0.4**	−9.2	−10.8	−11.8	−10.9
Vivianite at 0.5 m		−39.4	−37.6	−7.3	−37.2	−35.8	−38.2	−41.0	–	–
Vivianite at h_{max}		−17.5	−10.6	−7.3	**3.0**	−18.5	−6.1	−11.3	−14.5	−11.2
Ferrihydrite at 0.5 m		**2.0**	**2.7**	−0.7	**2.5**	**2.4**	**2.4**	**1.7**	–	–
Ferrihydrite at h_{max}		**1.2**	−6.9	−8.5	−3.6	**1.1**	−8.4	−9.6	−10.6	−9.3
Rhodochrosite at 0.5 m		–	–	–	−2.9	−1.7	−1.0	−1.4	–	–
Rhodochrosite at h_{max}		−0.9	–	−1.1	−1.9	−0.6	−1.2	−1.1	−0.8	−0.7
MnHPO$_4$ at 0.5 m		–	–	–	−1.1	**0.7**	**0.3**	−0.9	–	–
MnHPO$_4$ at h_{max}		**3.2**	–	**2.5**	**3.1**	**3.4**	**1.9**	**2.0**	**2.4**	**2.0**
Gibbsite at 0.5 m		−0.7	−0.1	−0.1	**0.6**	**0.5**	−0.6	–	−0.5	–
Gibbsite at h_{max}		**0.4**	−0.5	−0.1	**0.6**	**0.8**	**0.1**	–	–	–

*Much higher due to aeration.

[1]At 0.5 m. No CO_3^{2-} was detected in any of the lakes. See Table S2 for additional parameters.

[2]Deep (profundal) sediments. See Table S3 for more parameters and Figure S2 for XRD raw data.
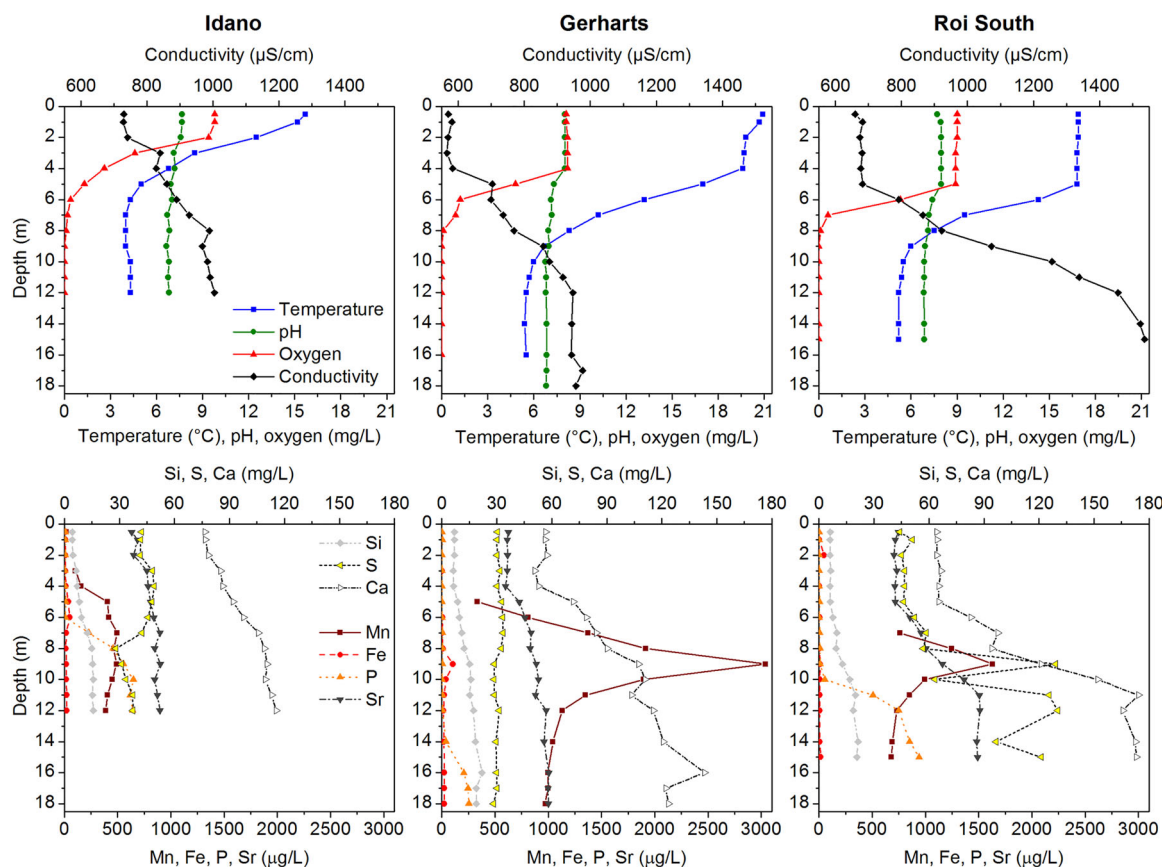
[3]See Table S4 for more details.

Figure 2. Physical (top) and selected chemical (bottom) parameters of the water columns of the lakes investigated in detail (see Table S1 for raw data). Note the different units on the top and bottom x-axes in each graph. For better visualization, the scales for each figure group were adjusted to match each other (e.g. same depths).

Gerharts, Roi South, and Kinsey Cove were low Fe ($<26\,\mu g/L$), high Ca (on average $>54\,mg/L$) and high S (on average $>30\,mg/L$) systems (characterized as Type I). Lakes Troudt and Pete's South were high Fe ($>4500\,\mu g/L$), low Ca ($<18\,mg/L$) and low S ($<1\,mg/L$) systems (Type II). Sauer, Chickakoo, and Little Mere were classified as Type III, having intermediate levels of Fe ($40-62\,\mu g/L$), Ca ($36-50\,mg/L$) and S ($8-42\,mg/L$).

Based on the surface P concentrations (0.5 m) and using the Canadian trophic state classification (Galvez-Cloutier and Sanchez, 2007), 3 lakes were ranked as oligotrophic (Type I, except Kinsey Cove), 2 lakes ranked as mesotrophic (Type II), and 4 lakes ranked as eutrophic (Type III and Kinsey Cove, Type I), which was consistent with their water clarities. The average Secchi depths of these three groups were 5.4 m, 2.3 m, and 2.1 m, respectively (Table 2).

The stratification in all lakes led to high differences between surface and bottom P, which varied from 25x (Sauer) to 262x (Roi South) (Figure 2). Surface concentrations varied from $3.57\,\mu g/L$ (Gerharts) to $173\,\mu g/L$ (Chickakoo), while bottom concentrations ranged from $254\,\mu g/L$ (Gerharts) to $4720\,\mu g/L$ (Pete's south). For larger and deeper lakes (e.g. Gerharts, Roi South), with small watershed typical of these hummocky landscapes a lower P input relative to their total size may have contributed to the overall lower P concentrations observed in these lakes.

In addition, surface Ca concentrations varied from $5.42\,mg/L$ (Troudt) to $76.6\,mg/L$ (Idano). The variation in Ca between surface and deep layers was less extreme than in the case of P. The smallest difference was 1.2x (Chickakoo, aerated), the largest 2.7x (Roi South) (Figure 2).

The increase of manganese (Mn) or the presence of a Mn spike at depth of most lakes suggested that Mn-reducing conditions may be present- (releasing Mn^{2+} into solution), while for Troudt and Pete's South lakes, reduction of Fe, the next electron acceptor in line, was driving Fe concentrations up to $15\,mg/L$ and $35\,mg/L$ at the bottom (Figure 2).

Composition and geochemistry of sediments

The chemical composition of lake sediments was diverse (Table 2). Large variations were seen in the Ca concentrations ($3-230\,mg/L$) with Roi South,
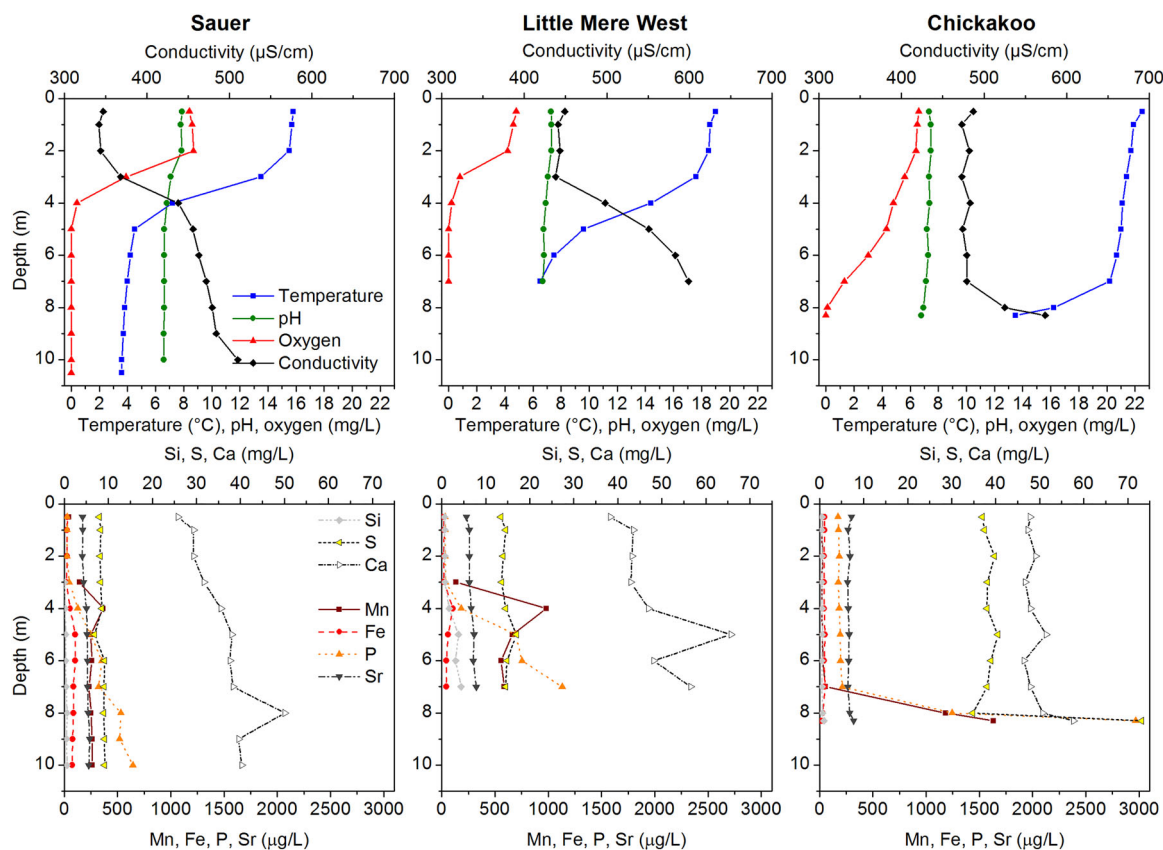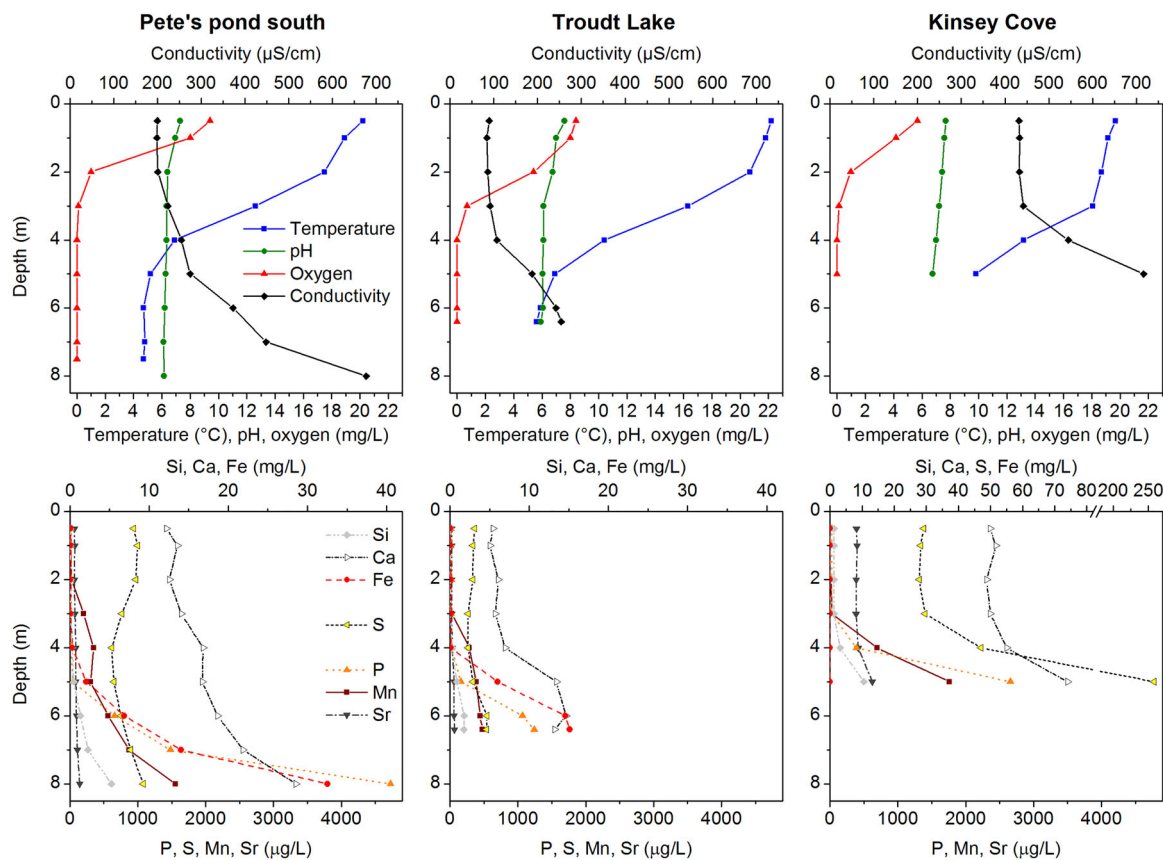
Figure 2. (Continued)

Figure 2. (Continued)

Gerharts, and Idano lakes having the highest. Calcite was dominant in the Type I systems but also present in Little Mere (Type III). In these lakes, Ca mass fractions in the sediments were >46 mg/g. Type I and III systems also showed traces of pyrite. Iron concentrations were similar in all sediments ranging from 10 to 49 mg/g. Sulfur was present at the same order of magnitude (4–45 mg/g) for all 9 lakes.

Total P in sediments ranged from 420 to 2000 µg/g with the lowest concentrations found in Roi South Lake (Type I), followed by the other Type I systems and ultimately Chickakoo Lake (Type III, aerated) (Table 2).

Considering that stability of P in the sediments can be expressed as the proportion of P in the most stable, HCl-fraction (Ca-bound; Ruban et al. 1999) the lakes can be ordered by the P stability as: Idano (61%, Type I) > Gerharts (51%, Type I) > Kinsey Cove (32%, Type I) > Little Mere = Chickakoo (28%, Type III) > Roi South (27%, Type I) > Sauer (21%, Type III) > Troudt (9%, Type II) > Pete's South (8%, Type II).

Hydrological and ecological observations

Groundwater inflow to lakes can be estimated from stable isotopes of water and also from the radioisotope radon (^{222}Rn), which has a half-life of 3.8 days. Measurements of samples for ^{222}Rn from Idano Lake indicated the highest ^{222}Rn concentrations between 4 and 6 m depth varying from 35 to 109 mBq/L. These concentrations were on the same order of magnitude as found in the fens feeding the lake (Table S5). Measurements done in Troudt Lake revealed 36–73 mBq/L between 4 and 6.4 m and in Pete's Pond South 163–244 mBq/L from 0.5 to 8 m. The elevated ^{222}Rn in the lakes suggested active groundwater discharge (Petermann et al. 2018) and confirmed the limited mixing of the water columns, even in the rather shallow lakes.

Gauging of the outflows of Idano, Gerharts and Roi South lakes once at the end of August also suggested groundwater inputs in these deep lakes. The total surface inflow into Idano Lake from the wetlands was 0.0019 m^3/s, while the total outflow (creeks south and west of the lake) was 0.00635 m^3/s, indicating a 3.3x larger outflow than inflow. Gerharts Lake had an outflow of 0.0049 m^3/s, while further south, Roi South Lake had an outflow of 0.0231 m^3/s, suggesting that another 0.0188 m^3/s were coming into the Roi South/Roi Middle system through groundwater inputs. However, these comparisons are based on single measurements and any further interpretation would require detailed water balance and hydrological work on these lakes.

The Ca-rich environments of the three deepest lakes (Idano, Gerharts and Roi South) as well as the fens north of Idano Lake were observed to host a variety of molluscs not seen in the other lakes. Following the key published by Bird and Duquette (1969) and the descriptions by Nordstrom (2003), the following mollusc species could be identified in the fens: the gastropods *Helisoma trivolvis*, *Lymnaea stagnalis*, *Stagnicola elodes*, all being found in shallow water on top of the sediments and the bivalve *Pisidium* spp. found within the sediments (Figure S1). All these molluscs likely benefit from the high Ca environments (Horsák and Hájek 2003). *Chara* spp., a charophyte, was also found in these 3 lakes. The Ca-rich environment in Idano lake led to the formation of a CaCO$_3$ crust on *Chara* spp. exposed in late summer at the surface (Figure S2).

Discussion

Phosphorus stability

Lakes can vary in their responses to phosphorus inputs based on their morphometric, hydrologic, and natural chemical attributes. In this study, the larger and deeper lakes had a lower trophic status, which is partially due to their larger volumes and the resultant dilution potential for incoming nutrients loads. The deeper lakes also have larger, stable hypolimnia, which are able to store nutrients, especially when the lake expresses meromixis. Furthermore, lakes with permanent outflows (Idano, Gerharts) have higher flushing rates by a natural cleaning mechanism that removes nutrients from the epilimnion. There is also chemical precipitation in which nutrients like P can be sequestered and stored in the sediments, as will be elaborated below.

Jensen et al. (1992) suggested that Fe:P weight ratios in sediments could be correlated to the internal loading potential of lake sediments and could be therefore used as an indicator for P stability. The small lakes in this study had Fe:P ratios ranging from 8 to 82; the deeper lakes, especially Gerharts (81.7), Roi South (25.5), Idano (23.3), and Sauer (21.3), had the highest ratios (Table S8). This suggests that these lakes are less prone to internal P loadings provided that their sediment surfaces remain oxidized. This, however, is rather unlikely given their depth and potential meromictic regime.

We observed that Ca (mg/L) was negatively correlated to P (µg/L) in the averaged water column (Pearson's correlation coefficient: −60%, n = 9), which could be approximated with the linear fit: $[P]_{average} = -3.8[Ca]_{average} + 580$, $R^2 = 0.36$. The correlation is more striking when comparing the P proportion in the HCl sediment fraction (P_{HCl}, in %) with the concentration of Ca in water (average column): $P_{HCl} = 0.59[Ca]_{average} + 0.15$, $R^2 = 0.98$. A similar fit can be found when only looking at the Ca concentrations at the surface: $P_{HCl} = 0.76[Ca]_{average} - 0.016$, $R^2 = 0.92$. These results suggest a natural P control mechanism for certain calcium-rich lakes. It also suggests that the P sediment distribution can be estimated if the surface Ca concentrations are measured, allowing for a rapid evaluation of the P stability.

The values for Roi South Lake were considered as outliers for these two linear fits. The relatively low HCl fraction in this lake may be caused by large proportions of P sorbed to calcite surfaces, which, to a certain extent, can be mobilised by NaOH extraction (Williams et al. 1971) making this fraction appear larger. It should be noted that while the average surface sediment composition is fairly similar throughout the year, the water column sampling of each lake constituted only a snapshot of the rather dynamic system. Seasonal variations due to temperatures, stratification and photosynthesis could lead to deviations from the proposed correlations. Based on the ^{222}Ra data and the similar temperature and conductivity curves of the lakes from different months we can, however, assume that only limited mixing was taking place during that time.

Similar correlations can be obtained for other lakes, where similar parameters were measured; however, the sparse data availability for small lakes worldwide makes this comparison challenging. Here, we attempted to combine data from 3 additional studies. Kotak and Trew (unpublished) provided data on various Alberta lakes, Ribeiro et al. (2008) investigated caldera lakes on the Azores, and Christophoridis and Fytianos (2006) analyzed P speciation in 2 lakes in Northern Greece (Table S6). The resulting linear fit can be expressed as: $P_{HCl} = 0.50[Ca] - 8.7$, $R^2 = 0.50$. There are of course several limitations to this approach. Not all the datasets were produced in the same way. For Kotak and Trew (unpublished) the average Ca concentration for the euphotic zone, and not the water surface Ca concentration, was collected (by composite water sampling using long tubing and a one-way foot valve), which potentially results in higher Ca concentrations than would be expected at the surface. Furthermore, all three additional datasets cover lakes that are much larger than those in this study, with an average surface area of 20 km^2 (range: 0.28–69 km^2). Therefore, it might be expected that the sediment conditions are less directly linked to the water column.

Despite the high correlations between Ca and P in the small lakes described here, the other parameters that influence the trophic state (depth, mixing, and outflow) can outcompete the influence of the water composition. This can be seen in the example of Kinsey Cove, which is a Type I lake with high Ca concentrations and a relatively large Ca-P fraction in the sediments. The lake even has an inflow from a small marl pond in the north (not yet characterized). Still, the lake is meso-eutrophic. This is likely because of its shallow depth, the lack of an outflow, and potentially because of considerable agricultural activity in the surrounding area.

Thermodynamic modelling suggested that several mineral phases could be saturated in water. Strengite, an Fe-phosphate, had a positive saturation index SI in lakes with sufficient oxygen supply at the bottom, i.e. the shallow lake Kinsey Cove and the aerated lake Chickakoo (Table 2). Vivianite only yielded a positive saturation index where extraordinarily high Fe concentrations were measured (Pete's South). Amorphous iron(III) oxyhydroxides (e.g. ferrihydrite) also play an important role by providing sorption sites for P (Amirbahman et al. 2003). Ferrihydrite oversaturation was predicted in nearly all lakes by the thermodynamic models, with the exceptions of Roi South, Gerharts and Little Mere. Therefore, precipitation of P with Fe phases is possible in several of the lakes.

In terms of Ca, calcite is one of the major phases that can interact and sequester P through co-precipitation (Danen-Louwerse, Lijklema, and Coenraats 1995). Calcite was the dominant mineral found by XRD in the sediments from Gerharts, Roi South, and Idano, and an important mineral in the sediments of Kinsey Cove and Little Mere. Thermodynamic modelling suggested oversaturation for calcite even in the surface water for Gerharts, Roi South, Idano and Kinsey Cove. In these lakes, some of the Ca-bound P can be expected to be in the form calcite.

We also expect certain Ca-phosphates to form, however, their concentration may be low and their presence primarily in the form of amorphous phases (no Ca-phosphates were detected by XRD). Octacalcium phosphate ($Ca_4H(PO_4)_3 \cdot 3H_2O$), a potential precursor of crystalline Ca-phosphates (Oxmann and Schwendenmann 2014), was not found to be

oversaturated in any of the lakes. Similarly, $CaHPO_4$, a phase that could form and co-precipitate with calcite (Frevert 1980), was never calculated to be oversaturated in any of the lakes. Instead, hydroxylapatite was oversaturated in all lakes except in the two Type II lakes. It is unlikely that hydroxylapatite would precipitate out of the water column; instead, hydroxylapatite can form in the sediments through transformation of calcite (Syers, Harris, and Armstrong 1973). Therefore, only lakes with sufficient calcite would favour the formation of this stable Ca-phosphate phase. The fully or partially developed anoxia in these lakes would additionally favour the formation of Ca-phosphates (Bańkowska-Sobczak et al. 2020), however, their presence and abundance would need to be evaluated. The understaturation of amorphous Ca-phosphate phases and the predicted formation of crystalline Ca-phosphate phases shows the complexity of the modelled systems and demonstrates the limitations of thermodynamic modelling to properly assess the precipitation of kinetically facile solid phases. It is important to point out that modelling inputs was made with water data, while the conditions in the interstitial water of the sediments might be different and vary depending on depth in the sediments, local chemistry and redox conditions. These conditions might benefit or suppress the formation of certain minerals.

Notable was the high concentration of Mn in the sediments of some of the lakes (Table 2). Manganese can play a role in the sequestration of P by the formation of minerals such as rhodochrosite and Mn-phosphates (Hongve 1997), such as the hypothetical mineral $MnHPO_4$. This alone would not lead to the discrepancies seen between the lakes, because the saturation index of $MnHPO_4$ at maximal depth was positive for most lakes (Table 2). Therefore, the co-precipitation of Mn with calcite (Walpersdorf, Neumann, and Stüben 2004) is more likely to lead to the accumulation of Mn in the Ca-rich lakes.

Aluminum is also a potential P-controlling factor as well. Aluminum is known to stabilize phosphates under anoxic conditions, particularly when Al is more abundant in the mobile sediment phases than Fe or P. According to Kopáček et al. (2005) this is the case if either (1) the ratio of the Al in a NaOH extract is >3x larger than the Fe in a bicarbonate-dithionite extract or (2) the ratio of the Al in a NaOH extract is >25x larger than the P in water and bicarbonate-dithionite extracts together. Differences in methodology make direct comparisons to the study of Kopáček et al. (2005) difficult. Still, we can cautiously

compare the Al:Fe and Al:P ratios from our NaOH phase (Table S8). Only the lakes Sauer and Chickakoo express high enough ratios (Al:P > 5) to argue that Al might play a stabilizing role in these lakes (mainly under anoxic conditions). The contribution of Al in Sauer is not clear. In the water column of Chickakoo, opposite to expectations based on the high Al:P ratio, a decrease of oxygen at depth co-exists with a spike in P, suggesting that Al does not play a major role in this lake for the binding/release of P.

In terms of Al, one important sediment phase to consider is gibbsite ($Al(OH)_3$), because the transformation of amorphous Al phases to gibbsite can reduce the P sorption capacity of sediments (Berkowitz, Anderson, and Amrhein 2006). This phase showed a positive saturation index in four of the lakes, including Sauer and Chickakoo (Table 2), however no gibbsite was found in any of the sediments by XRD.

Source of Ca

Calcium becomes an important player in the investigated lakes due to its ability to control the stability of P. A general trend emerges that deeper lakes show higher Ca concentrations (in mg/L) at the surface ($[Ca]_{0.5m} = 3.0\,h_{max} + 10.4$, $R^2 = 0.32$) or on average throughout the water column ($[Ca]_{average} = 6.0\,h_{max} - 7.0$, $R^2 = 0.58$). Combined with the presence of Ca, there is a negative correlation between depth and P concentrations (in μg/L) at the surface (Chickakoo Lake excluded, $[P]_{0.5m} = -1.5\,h_{max} + 33$, $R^2 = 0.52$) or for the average water column ($[P]_{average} = -35\,h_{max} + 740$, $R^2 = 0.49$). Across much of central and southern Alberta, Ca in the groundwater of glacial sediment deposits is greater than the underlying bedrock formations (Grasby et al. 2008). Considering the thickness of the glacial deposits associated with the Carvel Pitted Delta, it becomes apparent that groundwater inputs may play a major role in the Ca and P cycles of these lakes.

In groundwater, high concentrations of Ca (35–353 mg/L) were observed in water wells completed in the surficial sediments (24–76 m depth), while wells completed in bedrock underlying glacial sediments had low concentrations of Ca (1–4 mg/L) (Table S7). Using the water well drilling reports, geological profiles were created to show the position of the lakes in the study area in relation to the surface deposits and potential groundwater flow patterns (Figure 3). Lower elevation lakes and deeper lakes are likely to intercept groundwater sourced from glacial sediments and are therefore more likely to have
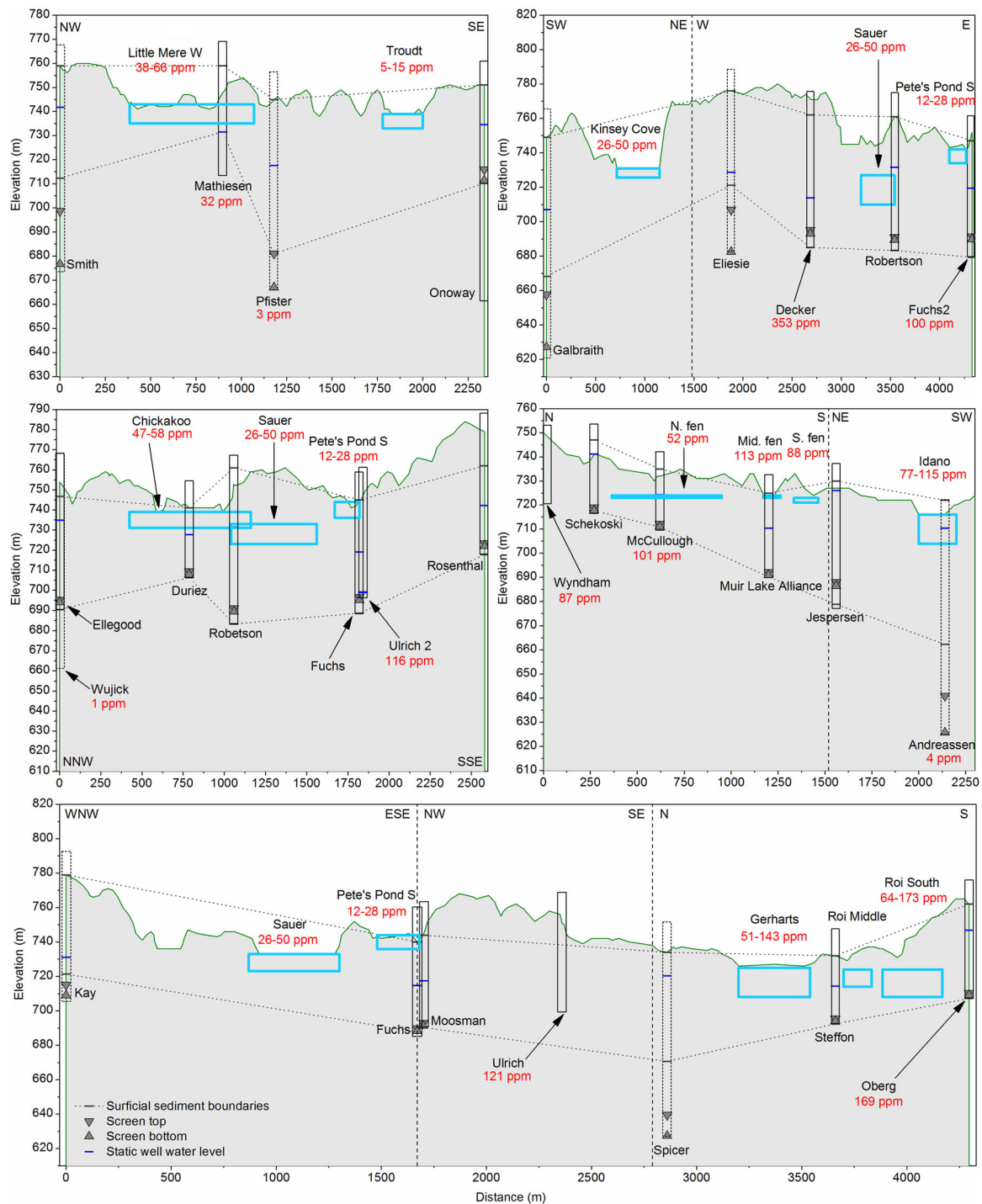
Figure 3. Vertical profiles of the lake systems. Calcium concentrations are indicated for lakes and wells (where available) with red numbers. Surficial sediment layers were summarized (includes till, gravel, sand, and clay fractions). Wells reaching into the bedrock are dashed. Surface elevation data based on Google Earth (2020).

connection to Ca-rich water source. The rate of groundwater inflow may be sufficient to supply enough water that permanent outflows are formed, as in the case of Idano, Gerharts, and Roi South lakes. The presence of ^{222}Rn within some of the lake water columns also corroborates groundwater inflow as a source of Ca. This interaction with groundwater in

the post-glacial landscape provides a crucial component for the natural control of P concentrations in lake water. The linkage between P and glacial landforms (e.g. Plach et al. 2016) may offer an approach for developing a regional framework that incorporates geological mapping, and knowledge of the differences in Ca that would originate from different continental

glaciations (e.g. Laurentide vs. Cordilleran glaciation; Grasby et al. 2010). Thus, a natural mitigation mechanism against eutrophication could exist in the terrain surrounding many small lakes of central Alberta.

Regional maps of Ca groundwater concentrations in the surficial sediments (Barker et al. 2013a) and in the upper 50 m of the bedrock (Barker et al. 2013b) indicate several Ca-rich zones within the mapped areas of Alberta. The Carvel Pitted Delta section studied here is situated within a zone of Ca-rich surficial sediment groundwater (50–100 mg/L) spanning north, northwest and northeast of Edmonton. Furthermore, it lies within a high Ca corridor of the upper bedrock groundwater (>65 mg/L) reaching approximately 75 km from west to east. In such areas, one could expect that deep lakes would show higher resilience to P-driven eutrophication due to the higher abundance of Ca. Significant amounts of Ca-phosphates can also be transported into lakes by overland flow (Penn and Auer 1997). These inputs would need to be considered when creating a complete P mass balance. Calcium-rich inflows were found for Idano and Roi lakes, which are all connected to Ca-rich lakes/ponds upstream (Figure 1 and Table S2).

Conclusions

Small lakes can be used as regional environmental indicators due to their small volumes and fast water exchange rates. In this study, we demonstrated how local hydrogeological conditions can control the water quality of small kettle lakes in Alberta. Calcium availability played an important role in providing a way of capturing and precipitating P from the water column. Calcite precipitation and P co-precipitation were likely the major mechanisms by which aqueous P species are transformed to the Ca-bound P in the lake sediments. By measuring a high surface water Ca concentration in a small lake, we were able to predict the abundance of P in the Ca-bound phase. However, while the P stability could be estimated based on P speciation, we do not know how resilient these systems are against continuous nutrient inputs. It can be assumed that the fragile balance between incoming and precipitation P could be disturbed if sufficient organic waste enters the lake. For example, local residents raised concerns about the Gerharts Lake after a nearby road was upgraded with new culverts, allowing developed land to drain onto the slopes of the lake. Beginning in 2018, the formation of small patches of filamentous algae was observed on the lake for the first time. Further research should aim to collect

limnological and geochemical data from a variety of small lakes (<0.1 km^2) across Alberta, which would help to identify unique hydrological systems and gain information on their importance as sensors for local and global changes element cycles. Collection and analysis of interstitial water and subsequent thermodynamic modelling may help to further understand mineral formation and P sequestration in the sediments of these small lakes. Potential remediation possibilities of highly eutrophic lakes by the addition of Ca-rich compounds could be further investigated and carefully assessed. The continuous monitoring and proper management of such systems can help to preserve valuable ecological habitats from the effects of development, eutrophication and climate change.

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Data availability statement

All data discussed in this work is provided in the figures and tables and the supplementary information.

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