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Phosphorus forms by depth in sediments from the Qu'Appelle lakes, Saskatchewan, Canada

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Understanding sediment phosphorus (P) compounds is essential to managing P in lake sediments because P speciation will determine bioavailability and reactivity. Little is known about organic P (P_o) in hardwater eutrophic lakes in the North American Great Plains, or the role of metals in P_o cycling. Sediment cores (0–12 cm deep) collected from four lakes from the Qu'Appelle chain in Saskatchewan, Canada, were sectioned by depth and analyzed by solution P nuclear magnetic resonance spectroscopy to characterize P forms. Concentrations and pools of calcium (Ca), magnesium (Mg), iron (Fe), manganese (Mn), and aluminum (Al) were also determined. A range of P compounds was detected with significant interactions between lakes and depth for orthophosphate, phytate and DNA, and significant differences among lakes or with depth for polyphosphates and phosphonates. The main class of P_o compounds identified in all lakes was orthophosphate diesters, including phospholipids and DNA, typical of living biota, suggesting that P immobilized by microbes and algae is an important pool in the sediments of these lakes. There were significant differences in metal concentrations among the lakes. In three lakes, Ca concentrations were high, and P was tightly bound with Ca compounds of low solubility. In the fourth lake with lower Ca concentrations, P appeared to be loosely bound to Al and Fe compounds. Our study indicates that there were significant differences in P compounds and the factors controlling their cycling among these four lakes in the same chain, which has implications for P management and water quality control.

KEYWORDS

P-NMR, metals, calcium, hardwater lakes, organic P, P biogeochemistry

Introduction

Phosphorus (P) is an essential nutrient to organisms for energy and growth. As a widely used fertilizer, P plays a crucial role in global food security (Jarvie et al., 2015). In freshwater ecosystems, P enrichment from external loads can degrade water quality by causing cultural eutrophication and triggering harmful algal blooms (Schindler, 2012). Anthropogenic activities can enhance external loads; this can contribute to a build-up of

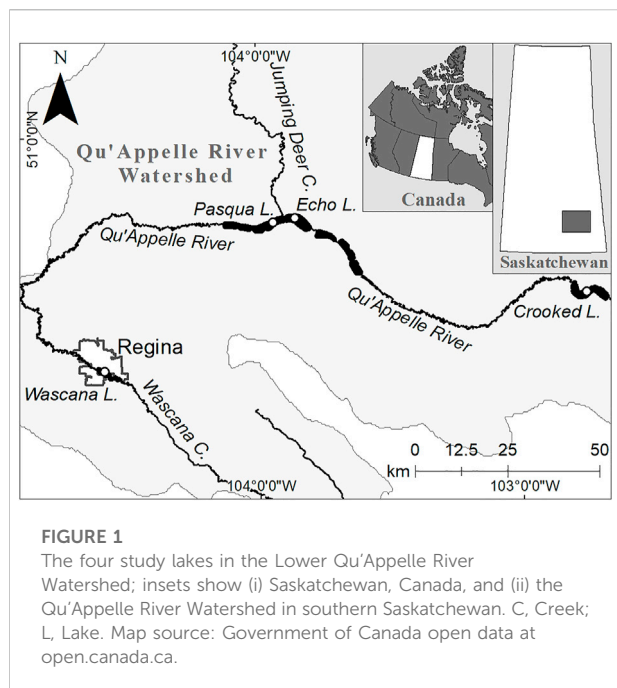
legacy P in lakes (Carey and Migliaccio, 2009), which in turn can be biogeochemically recycled *via* internal sediment P loading. Phosphorus in lakes can be operationally characterized into particulate and dissolved pools based on retention on filters, and chemically defined as inorganic and organic P. Inorganic P (P_i) forms include phosphates ($H_2PO_4^-$ or HPO_4^{2-} , at environmentally relevant pH), pyrophosphate (two phosphates linked by anhydride bonds) and polyphosphates (three or more linked phosphates). Organic P (P_o) compounds contain P groups linked to C groups, and are grouped by bonding type into orthophosphate monoesters ($ROPO_3^{2-}$; e.g., phytate, a storage compound in terrestrial plants), orthophosphate diesters [$R_1O(RO)PO_2^-$, which are components of living cells, e.g., deoxyribonucleic acid (DNA), phospholipids], and phosphonates [$RP(O)(OH)_2$, with a direct C-P bond, e.g., ciliatine in cilia of protozoa or the herbicide glyphosate; Condrón et al., 2005].

Lake sediments are deposited from allochthonous, autochthonous, and decaying organic matter (OM) particulates in the overlying water, and undergo diagenetic changes that control P distribution and cycling, creating a complex matrix of organic and inorganic materials with varied P compounds reflective of point and non-point sources and sediment chemistry (Carpenter et al., 1998; Correll, 1998). Phosphorus forms vary in chemical characterization, which affects their retention or release within sediments and their bioavailability. Phosphorus retention processes for both P_i and P_o compounds include sedimentation, direct uptake and biological assimilation, sorption, and precipitation (Boström et al., 1988; Reddy and Delaune, 2008a), which are important sediment P control mechanisms. However, there is considerable scientific interest in sediment P mobilization processes due to their essential roles in sediment nutrient budgets and influence on lake trophic status and recovery from eutrophication. The P-control mechanism of the sediment iron (Fe III)-P complex is a significant factor in many lakes (Mortimer, 1941), but Fe is not the only metal cation controlling phosphate release at the sediment-water interface (SWI) in lakes. Phosphorus compounds can react with dissolved compounds in sediments, including (hydr)oxides of iron, manganese (Mn) and aluminum (Al), and carbonates of calcium (Ca) and magnesium (Mg; Mortimer, 1941; Hupfer and Lewandowski, 2008; Reddy and Delaune, 2008a) and can be incorporated into OM or bridged to OM by metals (Williams et al., 1976; Søndergaard et al., 2001). The precipitation or adsorption of P forms to Al, Fe or Mn tends to form unstable amorphous compounds, which can stabilize to crystalline or organically-complexed compounds (Reddy and Delaune, 2008a). In calcareous sediments, P compounds adsorb and precipitate with Ca carbonates ($CaCO_3$) and Mg-calcite, which are affected by changes in temperature and pH (Boström et al., 1988). In lakes with high Fe and Mn concentrations, sediment P cycling tends to be controlled by oxidation-reduction reactions (Nürnberg, 1988). In all lakes, P

cycling is strongly influenced by microbial activities, temperature, and pH (Otsuki and Wetzel, 1972; Reddy and Delaune, 2008b; Hamilton et al., 2009; Read et al., 2014).

Most studies measuring P in lakes have used simple colorimetric analyses of total P (TP) and soluble reactive P_i or operationally-defined P pools, but have not examined the distribution and cycling of chemically-defined P_i and P_o species in sediments (Condrón and Newman, 2011). Detailed information on sediment P composition can be gained from advanced analytical spectroscopic techniques, such as solution ^{31}P nuclear magnetic resonance (P-NMR) spectroscopy, which has been used to characterize P in lake sediments in Europe (Hupfer et al., 2004; Ahlgren et al., 2005; Paraskova et al., 2015), Asia (Bai et al., 2009; Dong et al., 2012; Shinohara et al., 2012), Australia (Baldwin, 1996), the United States (Amirbahman et al., 2013; Giles et al., 2015), and Eastern Canada (Audette et al., 2018; O'Connell et al., 2020). However, there have been no P-NMR studies of lake sediments in the Northern Great Plains to date. The Northern Great Plains region in the United States and Canadian Prairie Ecozone has relatively flat grasslands with a large agricultural land base, important for global food security (Tollerud et al., 2018; Baulch et al., 2019). In the Canadian Prairies, lakes are alkaline (Hammer, 1986), and several lakes show historical evidence of eutrophication through nutrient loading (Barica, 1993; Quinlan, 2000; Patoine and Leavitt, 2006). High internal sediment P loading can occur in sediments of reservoirs (North et al., 2015; D'Silva, 2017; Doig et al., 2017) and lakes (Allan and Roy, 1980; Shaw and Prepas, 1990; Orihel et al., 2017) of the region.

The unique conditions on the Canadian Prairies, including shallow, often eutrophic lakes, large predominantly agricultural watersheds, and potentially high rates of internal P loading create a critical situation for water quality in this region (Schindler and Donahue, 2006; Orihel et al., 2017). Within the Qu'Appelle River Watershed, the lakes are P-rich, dissolved reactive P concentrations are high ($0.38\text{--}3.85\text{ mg L}^{-1}$) and increase in downstream lakes (Hammer, 1971). These high P concentrations affect algal productivity (Vogt et al., 2015), contributing to recurrent blooms. Sediment P concentrations in these lakes are comparable to other Canadian Prairie lakes, and can be high to depths of 15 cm (Allan and Williams, 1978). Phosphorus forms associated with redox-sensitive metal cations in lake sediments within the watershed constitute a significant P fraction that can release phosphate under changing redox conditions and increased duration of thermal stratification (Allan and Williams, 1978; Doig et al., 2017). However, our current knowledge is limited regarding composition, bioavailability, and reactivity of P species in lake sediments at different depths, and the broader role of sediment metals on P cycling in hardwater lakes in the Northern Great Plains. Increased knowledge of sediment P forms will improve understanding of internal P loading, to better manage P in lake sediments (Shinohara et al., 2012; Giles et al., 2015),



especially in eutrophic bloom-affected lakes. This study addresses the research questions: What are the major forms of P present in eutrophic, hardwater lakes in the prairies? Are there differences in sediment P biogeochemistry across lakes? And, what factors are associated with these differences? Specifically, our objectives were to characterize and quantify P forms at different depths in sediments from several prairie lakes located within the Qu'Appelle River watershed using P-NMR, and to examine geochemical factors influencing these P forms. Lakes along the Qu'Appelle chain differ in their inputs (Saskatchewan Water Security Agency, 2018), morphometry, and ecology (Hammer, 1971; Hall et al., 1999), hence we hypothesized that the lakes would show 1) significant differences in sediment P species and sediment metal cation concentrations; and 2) sediment P species and associated metal cation concentrations will vary with depth, based on diagenetic processes.

Materials and methods

Study area

The Canadian Prairies have semi-arid conditions in the south and west with frigid winters and warm summers with low precipitation coupled with high evaporation (Hammer, 1971; Sauchyn et al., 2002). Snowmelt is the primary source of runoff sustaining most streams, lakes, and wetlands in this region. Drought can lead to cessation of surface runoff while snowmelt and spring rain occasionally cause extreme flood events (Sauchyn et al., 2002; Pomeroy et al., 2005; Wheeler

and Gober, 2013). The Qu'Appelle River Watershed in southern Saskatchewan, Canada, drains more than 53,000 km² of semi-arid agricultural land, and contains reservoirs, and lakes (McGowan et al., 2005) providing important ecosystem services including hydroelectricity, recreation and drinking water (Hall et al., 1999). The Qu'Appelle lakes are a chain of polymictic, hardwater, and naturally eutrophic prairie lakes in the lower Qu'Appelle River Watershed that range in depth (maximum depth 4.6–21.9 m) with short water residence times (0.05–0.7 years; Rawson and Moore, 1944; Hammer, 1971; Barica, 1993; Supplementary Table S1).

Four lakes from the Qu'Appelle lake chain were selected for this research (Figure 1; Supplementary Table S1). The first, Wascana Lake, is situated in the middle of the city of Regina, upstream of the Regional Regina Wastewater Treatment Plant (RRWTP). It was formed in the 1880s by damming an agriculturally-drained tributary, Wascana Creek. The lake was drained, dredged, and deepened in 1931 and 2003–2004 (Riddell, 1992; Hughes, 2004). Wascana Lake receives water flow directly from Wascana Creek and urban storm runoff from Regina, including road construction and residential development (Riddell, 1992). Pasqua Lake, Echo Lake, and Crooked Lake are in a series connected by the Qu'Appelle River and flow into each other. Pasqua Lake is the first, Echo Lake is second, connected to Pasqua Lake by a narrow, shallow channel, and Crooked Lake is further downstream and receives water from other lakes not included in this study. These three lakes are downstream of the RRWTP. Control structures along the Qu'Appelle River moderate water flow downstream so that Crooked Lake may receive less flow than the other lakes of this study (Pomeroy et al., 2005).

Sample collection and processing

Vertical lake profile measurements, including oxygen, temperature, pH, and specific conductance, were measured using YSI 556 Multi-Probe System (YSI Environmental, OH) to assess the ambient water conditions when samples were collected. Dissolved oxygen concentrations indicated that the lakes were well-oxygenated from the water surface to 8 m, the conductivity levels were homogenous, and the pH for the water column (8.39–8.74) was alkaline (Supplementary Table S2). Undisturbed sediment cores were collected within a 48-h period in September 2018 using a Glew gravity corer, John Glew, Kingston ON, Canada (Glew et al., 2001). Four replicate sediment cores were collected from two to four random sub-sites within 5 m of the deepest spots in each lake. Two sediment cores were designated as main lake cores, and the other two as duplicate lake cores. All samples were placed on ice and held upright during transport to the laboratory, where they were stored and refrigerated at 4°C in the dark until processing. Sediment cores were sectioned in 1-cm intervals for the first 5 cm

of each core, then one section each for the 5–10-cm and 10–12-cm increments. After sectioning, identical depths from each set of cores were combined to give duplicate samples for each depth for each lake. Sediments were then frozen, lyophilized using a Freezone Freeze-Dryer (Labconco, MO) and stored in the dark until analysis.

Geochemical analyses

A subset of sediment samples was submitted to the Analytical Chemistry Services Laboratory (ACS Lab) in Victoria, BC, for geochemical analyses. One 5–10-cm sample (from all but Pasqua Lake, where a 0–1-cm sample was used), was analyzed for particle size using the hydrometer method (Kroetsch and Wang, 2008) to determine percentages of silt, clay, and sand, and for pH with a 1:1 sediment: water ratio (Hendershot et al., 2008). Also at the ACS Lab, samples from all depths of one core per lake were analyzed for 1) total concentrations of major metal cations and P by Vaporized High Pressure (VHP) closed vessel microwave acid digestion followed by inductively coupled plasma mass spectrometry (ICP-MS; EPA 3051A; Agilent 7900 ICP-MS); and 2) extractable Al, Mn and Fe concentrations in separate extractions using sodium pyrophosphate (SP), acid ammonium-oxalate (AAO), and dithionite-citrate (DC), followed by inductively coupled plasma optical emission spectrometry analysis (Courchesne and Turmel, 2008; Teledyne Leeman Prodigy ICP-OES). Metal cations extracted with SP were considered to be organically-complexed (o-Al, o-Fe, o-Mn), the difference between AAO and SP concentrations was considered to represent amorphous metals (a-Al, a-Fe, a-Mn), and the difference between DC and AAO concentrations was considered to represent crystalline metals (c-Fe, c-Mn; Reddy and Delaune, 2008a; Jan et al., 2013). The concentrations of Fe, Mn, and Al in each extracted metal pool were converted to percentages of the total concentrations for each metal cation. At the Swift Current Research and Development Centre (SCRDC), samples from all depths for both cores from all lakes were analyzed for total P_o (TP_o) concentrations by the ignition method (Saunders and Williams, 1955; O'Halloran and Cade-Menun, 2008), calculated as the difference in P concentrations of extracts of ignited and unignited samples after colorimetric analysis (Murphy and Riley, 1962). Samples were weighed before and after ignition, before extraction, for loss on ignition to estimate OM (%), while the total P concentrations were estimated (eTP) by extraction and colorimetric analysis of ignited samples. Linear regression showed a positive and significant correlation ($p < 0.001$, $R^2 = 0.87$, $y = 0.69x + 0.32$) between the TP concentrations determined by digestion and the eTP concentrations determined by ignition; thus, only eTP concentrations are reported.

Solution phosphorus-31 nuclear magnetic resonance spectroscopy

At the SCRDC, a revised version of the Cade-Menun and Preston (1996) protocol was used to extract samples from all depths in both cores for all lakes for P-NMR analysis. The extractant solution was 0.5 M NaOH plus 0.1 M Na_2EDTA (NaOH-EDTA) with an extractant: sediment (dry weight) ratio of 25 ml: 2.5 g, extracted for 5 h at 20°C and 180 rpm in the dark, followed by centrifugation (20 min at 10,000 × g). A 1-ml aliquot of each supernatant, diluted to 10 ml with water, was analyzed by ICP-OES (Thermo Scientific ICAP 6300 Duo) for NaOH-EDTA-extracted total P (TP_{NE}), Fe, and Mn concentrations. The TP_{NE} concentration was compared to the eTP concentration to determine the percentage of recovered P (Recovered TP). In the remaining supernatants, pH was adjusted to near neutral with 6 M HCl (Cade-Menun et al., 2006), and then they were frozen and lyophilized. Lyophilized extracts were re-dissolved using D_2O (0.6 ml), water (0.6 ml), 10 M NaOH (0.8 ml) and the NaOH-EDTA extraction solution (0.8 ml), vortex-mixed (5 min; Johns Scientific Thermolyne Corp. United States), centrifuged (20 min at 3,260 × g; Thermo Scientific Sorval ST8, United States) and transferred to 10-mm NMR tubes. After preparation, samples were stored in a refrigerator for no more than 24 h before analysis with a Bruker Avance III HD 500 MHz spectrometer equipped with a 10-mm broadband observe probe. Experimental parameters were: 202.4 MHz; 45° pulse angle; 20°C; 0.4 s acquisition time; no proton decoupling; and 1,526–4,164 scans. Recycle delay times were determined as 4 times T_1 , with T_1 values estimated for each sample from the P: (Fe + Mn) ratio in each extract (McDowell et al., 2006; Cade-Menun and Liu, 2014) and ranged from 3 to 10 s. Spiking experiments to confirm peak identifications for *myo*-inositol hexakisphosphate (*myo*-IHP, phytate), DNA, pyrophosphate, α - and β -glycerophosphate, and adenosine monophosphate (AMP) were conducted after initial P-NMR analysis (Cade-Menun, 2015).

Spectra were processed with Acorn NMR Utility Transform Software (NUTS), using 7 Hz line broadening for the whole spectrum and 2 Hz line-broadening for specific regions. Chemical shifts were determined relative to an 85% phosphoric acid standard, and the orthophosphate peak in each spectrum was standardized to 6 ppm during processing. Peaks were identified from the literature (Cade-Menun, 2015) and confirmed from spiking experiments. The calculations for total orthophosphate monoesters and total orthophosphate diesters were corrected by subtracting the percentages of orthophosphate diester degradation products (α -glycerophosphate, β -glycerophosphate and mononucleotides) from the orthophosphate monoester region and adding these percentages to the orthophosphate diester region per spectrum (Schneider et al., 2016). Peak area percentages were multiplied by TP_{NE} concentrations for each sample to convert to mg P kg^{-1} .

TABLE 1 Organic matter (OM), estimated concentrations per dry weight of total P (eTP), total organic P (TP_o), NaOH-EDTA-extracted TP (TP_{NE}) and the proportion of eTP recovered in TP_{NE} extracts (Recovered TP) of sediments from the sampled Qu'Appelle lakes, Saskatchewan, Canada. Values are the concentration means (\pm SD); $n = 14$ (7 depths, duplicate sediment core samples that were evenly mixed per depth). Different letters indicate significant differences ($p < 0.05$) in concentrations of the nutrients, determined using Kruskal-Wallis tests followed by pairwise Wilcoxon tests with Bonferroni correction.

Analytes	Wascana Lake	Pasqua Lake	Echo Lake	Crooked Lake
OM (%)	11.5 \pm 1.14b	11.3 \pm 0.44b	15.2 \pm 0.84a	14.6 \pm 0.94a
eTP (mg P g ⁻¹)	0.92 \pm 0.05b	0.94 \pm 0.03b	1.29 \pm 0.12a	1.31 \pm 0.06a
TP _o (mg P g ⁻¹)	0.40 \pm 0.06b	0.43 \pm 0.08b	0.64 \pm 0.17a	0.54 \pm 0.05a
TP _{NE} (mg P g ⁻¹)	0.49 \pm 0.07a	0.35 \pm 0.04b	0.44 \pm 0.03a	0.47 \pm 0.03a
Recovered TP (%)	53.1 \pm 7.10a	37.5 \pm 3.37b	34.1 \pm 2.52c	36.1 \pm 2.31b

sediment. Examples of P-NMR spectra are shown in [Supplementary Figures S2–S4](#) and P compound chemical shifts are shown in [Supplementary Table S4](#).

Statistical analyses

Geochemical data were tested for normality with the Shapiro Wilks test and were log-transformed as needed. The P-NMR data were normalized by centred-log ratio transformation ([Abdi et al., 2015](#)). All statistical analyses were completed using R statistical software ([R Core Team, 2020](#)), with a significance level of $\alpha < 0.05$. Two-way Analysis of Variance (ANOVA) tests were conducted to evaluate relationships between depths and lakes ([Zar, 1999](#)). Tukey HSD post-hoc tests were performed when the ANOVA results were statistically significant. Kruskal-Wallis tests followed by a pairwise Wilcoxon test with Bonferroni correction were conducted for data sets that did not normalize after log-transformations (e.g., OM, TP_o). Pearson correlation analyses with Bonferroni correction were used to evaluate relationships among the P compounds determined by P-NMR, sediment metal cations, and other geochemical data.

Results

Sediment texture, pH, organic matter, total organic phosphorus and estimated total phosphorus

Sediment pH was 7.53–7.93 ([Supplementary Table S1](#)). Wascana Lake sediments were higher in clay than the other lakes, while Pasqua and Echo Lake sediments had more silt and sand than Wascana and Crooked Lake sediments

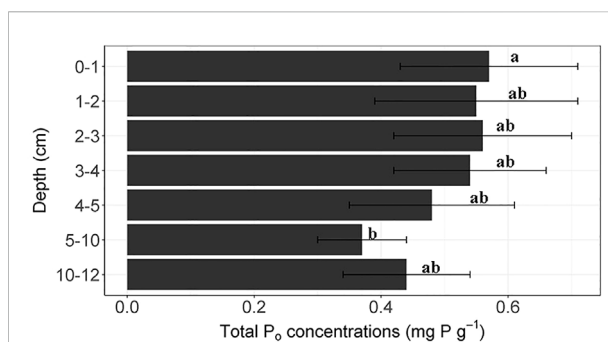


FIGURE 2

Total organic P (TP_o) concentrations (mg P g⁻¹ dry weight) in sediments by depth. Values are means (\pm SD); $n = 8$ (4 lakes, duplicate cores). Different letters indicate significant differences ($p < 0.05$) in the P_o concentrations among the depths and lakes, determined by Kruskal-Wallis tests followed by pairwise Wilcoxon tests with Bonferroni correction.

([Supplementary Table S1](#)). For OM, eTP and TP_o concentrations, the depth \times lake interaction in two-way ANOVAs was not significant, but there were highly significant differences ($p < 0.001$) among lakes ([Supplementary Table S3](#)). Mean OM, eTP, and TP_o concentrations were significantly higher in Echo Lake and Crooked Lake sediments than in Pasqua Lake and Wascana Lake ([Table 1](#)). There were also significant differences ($p < 0.05$) in TP_o concentrations with sediment depth, which were significantly higher at 0–1-cm than at 5–10-cm ([Figure 2](#)), using Kruskal-Wallis tests. There were highly significant differences ($p < 0.001$) among lakes for concentrations of TP_{NE} and Recovered TP ([Supplementary Table S3](#)) using Kruskal-Wallis tests. Mean TP_{NE} concentrations were significantly lower in Pasqua Lake sediments than the other lakes, while the greatest proportion of Recovered TP was from Wascana Lake sediments, and the lowest was from Echo Lake sediments ([Table 1](#)).

Sediment metals

Sediment total Ca concentrations were generally highest in Echo Lake (110–120 mg g⁻¹) and lowest in Wascana Lake (22.0–26.0 mg g⁻¹) and generally increased with sediment depth ([Figure 3](#)). Sediment total Mg concentrations (11.0–14.0 mg g⁻¹) were generally constant across depths among the Qu'Appelle lakes with 1 mg g⁻¹ fluctuations for Echo and Crooked Lakes ([Figure 3](#)). Total Al concentrations generally increased with depth for all lakes ([Figure 3](#)), with the highest concentrations in Wascana Lake (44.0–48.0 mg g⁻¹), followed by Crooked Lake (27.0–28.0 mg g⁻¹), then Pasqua Lake (18.0–21.0 mg g⁻¹), and Echo Lake (13.0–18.0 mg g⁻¹). Approximately 2.4%–

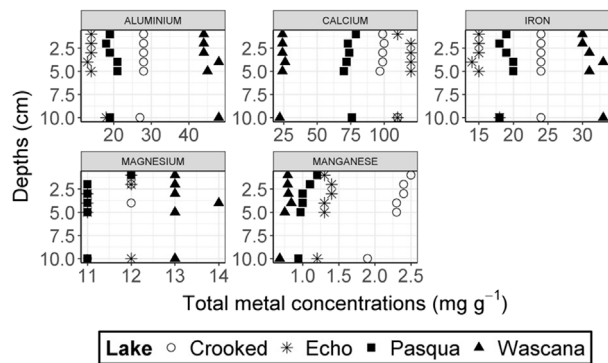


FIGURE 3 Concentrations of total sediment metal cations (mg g^{-1}) plotted against depth from the sampled Qu’Appelle lakes, Saskatchewan, Canada; $n = 6$ sediment samples per lake (no duplicates were analyzed). Each point corresponds to 0–1-cm, 1–2-cm, 2–3-cm, 3–4-cm, 4–5-cm, and 10–12-cm depth increments.

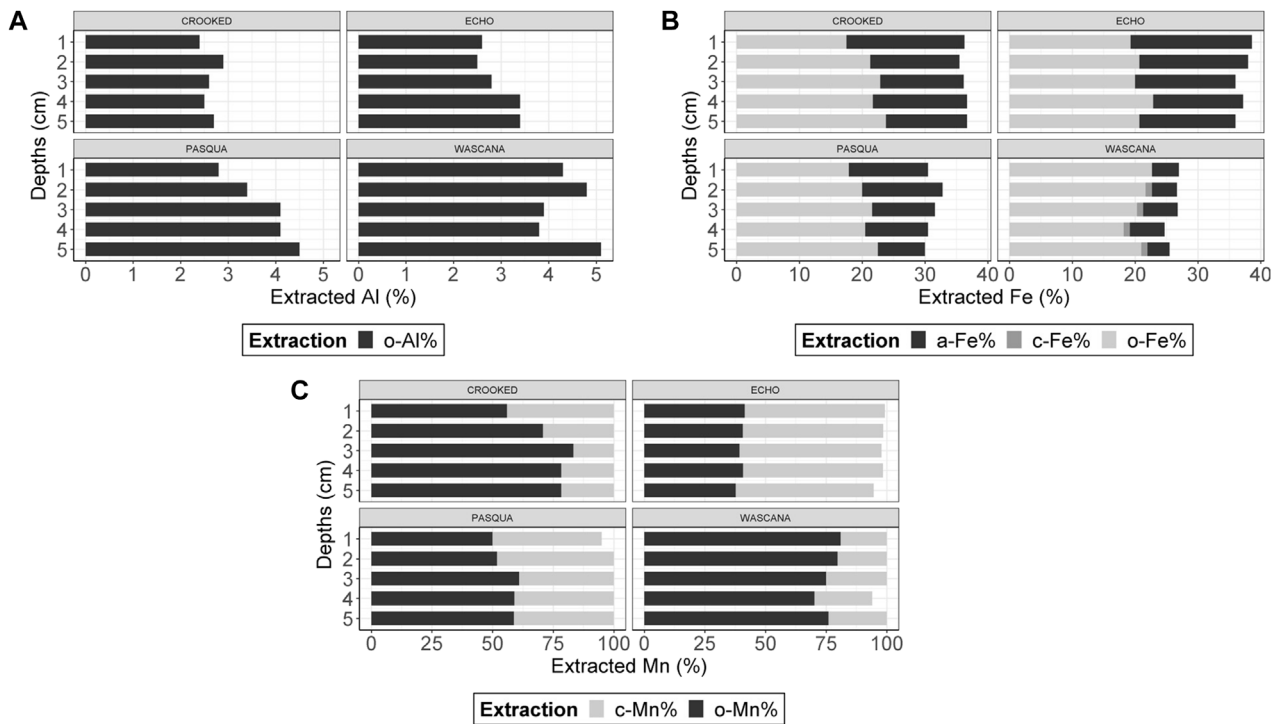


FIGURE 4 Extracted metal cation phase concentrations of (A) organically-complexed aluminum (o-Al) as a percentage of the total Al; (B) organically-complexed iron (o-Fe), amorphous Fe (a-Fe) and crystalline Fe (c-Fe) as percentages of the total Fe; and (C) organically-complexed manganese (o-Mn) and crystalline Mn (c-Mn) as percentages of the total Mn in sediments by depth (ranging from 0–5-cm); $n = 5$ depth samples per lake, (no duplicates were analyzed).

6.9% of the total sediment Al extracted from the sediments of the Qu’Appelle lakes was o-Al (Figure 4), with no detected a-Al. Wascana Lake sediments had the greatest

concentrations of extracted o-Al of the four studied lakes, and the concentrations increased with depth from 5.1% at 4–5-cm to 6.9% at 10–12-cm.

TABLE 2 Concentrations (mg P kg^{-1} dry weight) of orthophosphate and organic P compounds in NaOH-EDTA extracts of sediments analyzed by P-NMR spectroscopy. Values are means (\pm SD); $n = 2$ (duplicate cores) per depth. Different letters indicate significant ($p < 0.05$) differences in concentrations among depths and lakes for each P species, determined by two-way ANOVAs followed by Tukey HSD post-hoc tests using centred-log ratio data.

Lake	Depth (cm)	OrthoP ^a	<i>myo</i> -IHP	5 ppm	DNA	OthDi1
Wascana	0–1	296 \pm 15.2a	10.2 \pm 0.9a	2.6 \pm 1.5b	2.8 \pm 0.4b	25.7 \pm 4.5b
	1–2	340 \pm 39.6a	8.4 \pm 1.8a	3.6 \pm 0.4a	1.9 \pm 0.4b	22.3 \pm 8.2b
	2–3	271 \pm 53.6a	5.6 \pm 0.5b	1.9 \pm 0.7b	1.7 \pm 0.5b	9.0 \pm 0.4c
	3–4	296 \pm 126a	5.9 \pm 1.9b	1.9 \pm 0.4b	1.4 \pm 1.1b	9.5 \pm 0.6c
	4–5	323 \pm 8.0a	3.4 \pm 0.0b	1.7 \pm 0.3b	1.5 \pm 0.0b	12.7 \pm 4.9c
	5–10	302 \pm 11.6a	0.00c	3.2 \pm 0.1a	3.2 \pm 0.1b	9.2 \pm 3.7c
	10–12	322 \pm 22.9a	0.00c	1.7 \pm 0.5b	3.6 \pm 0.1b	18.2 \pm 3.7b
Pasqua	0–1	159 \pm 5.2c	5.7 \pm 0.4b	1.1 \pm 0.1b	49.4 \pm 6.1a	16.5 \pm 3.0b
	1–2	165 \pm 17.4b	3.7 \pm 0.2b	2.3 \pm 1.8b	38.1 \pm 0.6a	29.6 \pm 16.4a
	2–3	176 \pm 17.0b	4.1 \pm 0.8b	1.7 \pm 1.1b	29.3 \pm 7.5a	13.4 \pm 6.9b
	3–4	177 \pm 61.4b	3.7 \pm 1.1b	1.8 \pm 0.3b	27.6 \pm 10.4a	9.9 \pm 4.4c
	4–5	206 \pm 18.4b	3.9 \pm 0.8b	1.1 \pm 0.0b	29.5 \pm 7.8a	15.6 \pm 2.3b
	5–10	206 \pm 11.0b	3.1 \pm 0.3b	1.1 \pm 0.0b	34.0 \pm 6.5a	15.7 \pm 2.6b
	10–12	211 \pm 1.8b	1.5 \pm 2.1c	1.5 \pm 0.7b	22.8 \pm 1.3a	9.9 \pm 2.7c
Echo	0–1	188 \pm 25.4b	7.1 \pm 0.0a	3.7 \pm 1.5a	48.7 \pm 11.4a	30.1 \pm 9.7a
	1–2	205 \pm 19.4b	6.2 \pm 2.2b	2.4 \pm 0.1b	48.4 \pm 2.6a	31.6 \pm 8.6a
	2–3	179 \pm 12.6c	5.5 \pm 1.3b	2.2 \pm 0.1b	40.8 \pm 10.5a	24.4 \pm 6.7b
	3–4	217 \pm 18.7b	4.9 \pm 0.7b	2.4 \pm 0.2b	52.4 \pm 6.3a	33.4 \pm 7.4a
	4–5	222 \pm 6.7b	0.00c	2.4 \pm 0.3b	40.2 \pm 11.5a	28.5 \pm 1.8a
	5–10	282 \pm 40.8b	0.00c	2.7 \pm 0.0b	32.7 \pm 18.2a	10.5 \pm 7.9b
	10–12	222 \pm 5.9b	0.00c	2.4 \pm 0.1b	32.5 \pm 5.0a	29.6 \pm 0.9a
Crooked	0–1	249 \pm 10.1a	6.4 \pm 1.1b	2.6 \pm 0.3b	52.0 \pm 19.3a	24.8 \pm 11.3b
	1–2	241 \pm 18.1a	6.4 \pm 1.9b	2.1 \pm 0.9b	58.0 \pm 3.4a	16.0 \pm 9.0b
	2–3	245 \pm 27.8a	4.9 \pm 0.5b	1.9 \pm 0.6b	57.1 \pm 9.9a	22.1 \pm 0.7b
	3–4	252 \pm 43.5a	5.5 \pm 1.0b	1.4 \pm 0.2b	53.5 \pm 1.8a	19.6 \pm 5.9b
	4–5	278 \pm 23.2a	1.9 \pm 3.3c	1.6 \pm 0.1b	71.6 \pm 6.2a	28.6 \pm 10.8b
	5–10	384 \pm 132a	7.5 \pm 2.3a	1.9 \pm 0.6b	48.4 \pm 10.1a	26.9 \pm 7.1b
	10–12	255 \pm 8.3a	5.1 \pm 0.0b	2.0 \pm 1.1b	41.8 \pm 0.4a	26.1 \pm 4.3b

^aOrthoP, orthophosphate; *myo*-IHP, *myo*-inositol hexakisphosphate; 5 ppm, unidentified peak at 5 ppm; DNA, deoxyribonucleic acid; and OthDi1, region one of orthophosphate diesters.

Total Fe concentrations in sediments generally increased with depth (Figure 3), and the highest concentrations were observed in Wascana Lake (30–33 mg g^{-1}) followed by Crooked Lake (with constant concentrations of 24 mg g^{-1} from 0–1-cm to 10–12-cm), then Pasqua Lake (18–20 mg g^{-1}) and Echo Lake (14–18 mg g^{-1}). Approximately 15.0%–23.8% of the total Fe extracted was o-Fe, which increased with depth (Figure 4), a-Fe was a smaller proportion of total Fe (3.5%–19.3%) and decreased with depth, and c-Fe was the smallest proportion of total Fe (0.3%–0.6%). Percentages of a-Fe were similar in Crooked Lake (12.9–18.8%) and Echo Lake (10.0%–19.3%) and lower in Wascana Lake (3.5%–5.5%). However, Wascana Lake had more o-Fe (18.2%–22.7%) and was the only lake with c-Fe from 1–2-cm to 10–12-cm depths. Sediment total Mn concentrations were highest in Crooked

Lake (1.90–2.50 mg g^{-1} ; Figure 3), similar in Echo Lake and Pasqua Lake (1.20–1.40 mg g^{-1} and 0.94–1.20 mg g^{-1}), and lowest in Wascana Lake (0.68–0.84 mg g^{-1}), and were generally higher at the sediment surface. Of the total Mn, o-Mn was 37.7%–83.3%, c-Mn was 16.7%–58.6%, and a-Mn was not detected (Figure 4). The largest percentage of c-Mn (58.6%) and the lowest percentage of o-Mn (39.3%) were observed in Echo Lake (Figure 4).

Solution phosphorus-31 nuclear magnetic resonance analysis

The P-NMR results for P_i compounds will be presented first, followed by those for P_o compounds.

TABLE 3 Concentrations (mg P kg^{-1} dry weight) of sediment P species in NaOH-EDTA extracts of sediments analyzed by P-NMR spectroscopy. Values are means (\pm SD); $n = 14$ depths (7 depths, duplicate cores per lake). Different letters indicate significant ($p < 0.05$) differences in concentrations of P species among lakes, determined by two-way ANOVAs followed by Tukey HSD post-hoc tests using centred-log ratio data.

P Forms	Wascana Lake	Pasqua Lake	Echo Lake	Crooked Lake
Pyro ^a	19.9 \pm 5.7a	13.4 \pm 5.3ab	15.6 \pm 6.8ab	13.0 \pm 3.8b
2.3ppm	1.6 \pm 0.6b	2.8 \pm 0.6ab	3.5 \pm 1.7a	3.4 \pm 1.9a
scyllo-IHP	0.7 \pm 0.8a	0.2 \pm 0.4ab	0.4 \pm 0.9ab	0.1 \pm 0.4b
D-chiro-IHP	0.8 \pm 1.3ab	1.5 \pm 1.3a	1.6 \pm 2.5a	0.1 \pm 0.4b

^aPyro, pyrophosphate; unidentified peak at 2.3 ppm; scyllo-IHP, scyllo-inositol hexakisphosphate; and D-chiro-IHP, D-chiro-inositol hexakisphosphate.

TABLE 4 Concentrations (mg P kg^{-1} dry weight) of sediment P compound classes and P species in NaOH-EDTA extracts of sediments analyzed by P-NMR spectroscopy. Values are means (\pm SD); $n = 8$ (4 lakes, duplicate cores). Different letters indicate significant ($p < 0.05$) differences in concentrations of P compound class and P species among depths, determined by two-way ANOVAs followed by Tukey HSD post-hoc tests using centred-log ratio data.

P Forms	0–1-cm	1–2-cm	2–3-cm	3–4-cm	4–5-cm	5–10-cm	10–12-cm
TotPoly ^a	41.0 \pm 12.0a	33.0 \pm 8.0ab	35.0 \pm 9.0ab	29.0 \pm 8.0ab	27.0 \pm 7.0ab	21.0 \pm 5.0b	24.0 \pm 10.0b
TotPhn	5.0 \pm 2.0b	5.0 \pm 2.0b	5.0 \pm 1.9b	6.5 \pm 3.5a	6.9 \pm 2.7a	5.8 \pm 2.4a	5.8 \pm 2.8a
Diest	132 \pm 22.0a	126 \pm 26.0a	105 \pm 36.0ab	108 \pm 42.0ab	117 \pm 46.0ab	93.0 \pm 34.0b	83.0 \pm 26.0b
Pyro	21.4 \pm 7.1a	18.5 \pm 3.6a	17.3 \pm 3.7ab	15.5 \pm 4.1ab	14.2 \pm 4.8ab	11.1 \pm 4.5ab	9.8 \pm 6.2b
Poly	21.4 \pm 7.1a	18.5 \pm 3.6a	17.3 \pm 3.7ab	15.5 \pm 4.1ab	14.2 \pm 4.8ab	11.1 \pm 4.5ab	9.8 \pm 6.2b
neo-IHP	2.4 \pm 0.7a	1.5 \pm 0.4a	1.5 \pm 0.9a	1.6 \pm 0.7a	1.3 \pm 0.9a	0.4 \pm 0.6b	0.1 \pm 0.4c
g6P	1.5 \pm 0.8a	1.5 \pm 0.4a	1.1 \pm 0.4ab	0.8 \pm 0.6ab	0.4 \pm 0.6b	0.3 \pm 0.5b	0.5 \pm 0.6b
Mono3	5.0 \pm 1.2a	4.4 \pm 1.7a	4.2 \pm 2.4ab	4.2 \pm 1.4ab	4.4 \pm 2.6ab	3.7 \pm 1.6b	4.8 \pm 1.2ab
2.3ppm	3.6 \pm 2.1a	3.6 \pm 2.1a	2.3 \pm 0.7ab	2.3 \pm 0.9ab	2.2 \pm 0.5b	2.8 \pm 1.7a	2.7 \pm 1.1a

^aTotPoly, total polyphosphates; TotPhn, total phosphonates; Diest, orthophosphate diesters corrected for degradation during analysis; Pyro, pyrophosphate; Poly, polyphosphates; neo-IHP, neo-inositol hexakisphosphate; g6P, glucose 6-phosphate; Mono3, orthophosphate monoesters region three; and 2.3 ppm, unidentified peak at 2.3 ppm.

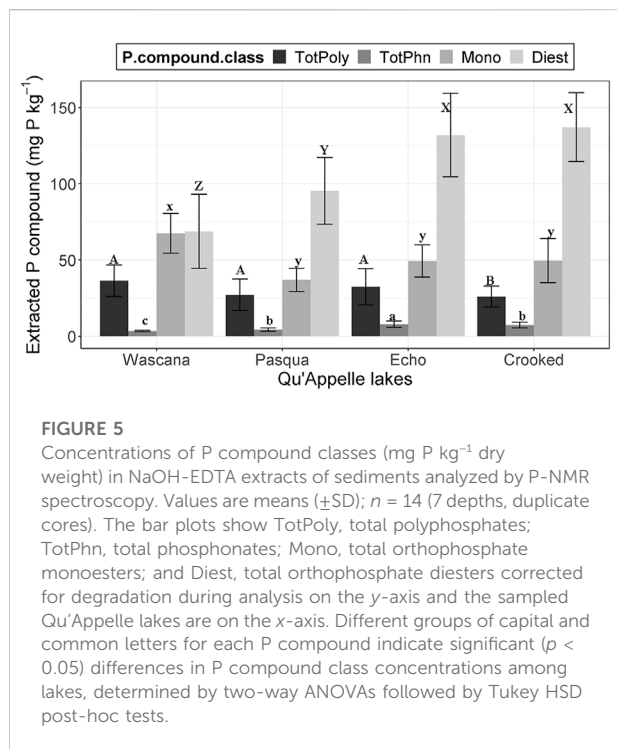
Orthophosphate, pyrophosphate, and polyphosphates

There was a significant lakes \times depth interaction in two-way ANOVAs for orthophosphate, significant differences with both lakes and depths but no interactions for total polyphosphates and pyrophosphate, and significant differences with depth for polyphosphate (Supplementary Table S5). Orthophosphate concentrations at all depths in Crooked and Wascana Lake sediments were significantly ($p < 0.05$) higher than in the other lakes, and were significantly lower at 0–1-cm and 2–3-cm in Echo and Pasqua Lake sediments than all other depths among the four lakes (Table 2). Recovered TP was 34.1 (\pm 2.52) to 53.1 (\pm 7.10) % of eTP (Table 1). Sediment P not extracted with NaOH-EDTA is likely insoluble mineral-bound orthophosphate (Chen et al., 2021), which accounted for 46.9%–65.9% of sediment P. Pyrophosphate concentrations in Wascana Lake sediments were significantly ($p < 0.01$) higher than those in Crooked Lake (Table 3), and pyrophosphate ($p < 0.01$) and polyphosphate ($p < 0.001$) concentrations at 0–1-cm and 1–2-cm were significantly higher than those at 10–12-cm (Table 4). Total

polyphosphate concentrations (pyrophosphate and polyphosphates combined) were significantly ($p < 0.001$) lower in Crooked Lake sediments compared to the other lakes (Figure 5), and concentrations at 0–1-cm were significantly higher ($p < 0.001$) than at 5–10-cm and 10–12-cm (Table 4).

Orthophosphate monoesters

There were differences among lakes in two-way ANOVAs for total orthophosphate monoesters (Supplementary Table S5). Concentrations of total orthophosphate monoesters were significantly ($p < 0.001$) higher in Wascana Lake sediments than in all other lakes (Figure 5). There were significant lakes \times depths interactions in two-way ANOVAs for *myo*-IHP, significant differences among lakes for *scyllo*-IHP and *D-chiro*-IHP, and significant differences with depth for *neo*-IHP (Supplementary Table S5). Concentrations of *myo*-IHP were significantly ($p < 0.01$) higher at 0–1-cm in Echo Lake sediment, at 0–1-cm and 1–2-cm in Wascana Lake, and at 5–10-cm in Crooked Lake than all other depths among the



lakes (Table 2). Concentrations of *scyllo*-IHP were significantly ($p < 0.05$) higher in Wascana Lake sediments than the other lakes (Table 3). Concentrations of *D-chiro*-IHP were significantly ($p < 0.01$) higher in Echo Lake and Pasqua Lake sediments and lowest in Crooked Lake (Table 3), while concentrations of *neo*-IHP were significantly lower ($p < 0.01$) at 5–10-cm and 10–12-cm than at all other depths, and significantly higher at 5–10-cm than at 10–12-cm (Table 4). There were significant lakes \times depths interactions for the unidentified peak at 5 ppm (Supplementary Table S5), concentrations of which were significantly higher ($p < 0.01$) at 0–1-cm in Echo Lake sediment and at 1–2-cm and 5–10-cm in Wascana Lake than all other depths among the four lakes (Table 2). There were significant differences with depth for g6P concentrations, which were significantly ($p < 0.05$) higher at 0–1-cm and 1–2-cm than at all other depths (Table 4; Supplementary Table S5). There were significant differences with depth for the orthophosphate monoester three region (Mono 3; Supplementary Table S5), with significantly ($p < 0.001$) higher concentrations at 0–1-cm and 1–2-cm than at 5–10-cm (Table 4).

Orthophosphate diesters

There were significant differences with both lakes and depths, but no interactions in two-way ANOVAs for total orthophosphate diester concentrations (Supplementary Table S5), which were significantly ($p < 0.001$) higher in Crooked

and Echo Lakes than in the other lakes (Figure 5) and were significantly ($p < 0.001$) higher at 0–1-cm and 1–2-cm than all other depths (Table 4). The only orthophosphate diester specifically identified in these sediments was DNA. There were significant lakes \times depths interactions in two-way ANOVAs for DNA concentrations (Supplementary Table S5), which were significantly ($p < 0.01$) higher in Pasqua, Echo and Crooked Lakes than in Wascana Lake and generally decreased with depth among the four lakes (Table 2). There were significant differences with both lakes and depths, but no interactions, for concentrations of the unidentified peak at 2.3 ppm (Supplementary Table S5), which were significantly ($p < 0.01$) higher in Crooked and Echo Lakes than in Wascana Lake (Table 3), and were significantly ($p < 0.001$) lower at 2–3-cm, 3–4-cm, and 4–5-cm (Table 4). There were significant lakes \times depth interactions in two-way ANOVAs for concentrations in the general orthophosphate diester one region (OthDi1; Supplementary Table S5), which were significantly ($p < 0.01$) higher at all depths in Echo Lake than the other lakes, except at 2–3-cm and 5–10-cm, and 1–2-cm in Pasqua Lake (Table 2).

Phosphonates

There were significant differences with both lakes and depths, but no interactions in two-way ANOVAs for total phosphonates (Supplementary Table S5). Total phosphonates were the lowest concentrations of all the P compound classes among the lakes, were significantly higher ($p < 0.001$) in Echo Lake and lowest in Wascana Lake sediments (Figure 5), and were significantly ($p < 0.05$) lower at 0–1-cm, 1–2-cm, and 2–3-cm than in the other depths among the four lakes (Table 4).

Relationships of phosphorus compounds to sediment organic matter, total organic phosphorus, and metals

Organic matter was significantly ($p < 0.01$) and positively correlated to TP_o, both of which were significantly and positively correlated to total phosphonates, total orthophosphate diesters and DNA, but negatively correlated to o-Al across depths among the lakes (Supplementary Table S6). Orthophosphate concentrations were significantly ($p < 0.01$) and positively correlated to total Al, total Fe, o-Al, and o-Fe (Supplementary Table S7). Total phosphonates were significantly ($p < 0.01$) and positively correlated to total Ca and c-Mn, but were negatively correlated to total Mg (Supplementary Table S7). Total orthophosphate monoester concentrations were significantly ($p < 0.01$) and positively correlated to total Al and Mg, and o-Fe and o-Al (Supplementary Table S7). Total orthophosphate diester concentrations were significantly ($p < 0.01$) and positively correlated to total Ca and Mn, and a-Fe and c-Mn, but were

negatively correlated to c-Fe and o-Al (Supplementary Table S7). Concentrations of DNA were significantly ($p < 0.01$) and positively correlated to total Ca and Mn, and a-Fe, o-Mn, and c-Mn, but were negatively correlated to total Al, Fe and Mg, and c-Fe and o-Al (Supplementary Table S7).

Discussion

Sediment chemistry

The mean sediment eTP concentrations ranged from 0.92 (± 0.05) to 1.31 (± 0.06) mg P g⁻¹ across the Qu'Appelle lakes used for this study, which is comparable to historical sediment TP concentrations in Pasqua Lake and Echo Lake (0.96–1.05 and 1.35 mg g⁻¹, respectively; Allan and Williams, 1978), and to TP concentrations of other prairie lakes, such as mesotrophic-eutrophic Lake Diefenbaker, a river-valley reservoir in the same watershed in Saskatchewan (0.91–1.24 mg g⁻¹; Doig et al., 2017). Although slightly lower, the study lakes sediment TP concentrations are also comparable to concentrations (0.19–2.86 mg g⁻¹) reported for Lake Erie in Ontario (Williams et al., 1976), Lake Simcoe (0.90–1.10 mg g⁻¹; Audette et al., 2018), and polymictic Nakamun Lake in Alberta (2.12 mg g⁻¹; Orihel et al., 2015). However, they are much lower than the surface sediment TP concentrations for the artificially P-amended Lake 227 in the Experimental Lake Area of Ontario (180–210 $\mu\text{mol g}^{-1}$, which is 5.6–6.5 mg g⁻¹; O'Connell et al., 2020). The mean TP_o concentrations [0.40 (± 0.06) to 0.64 (± 0.17) mg P g⁻¹] across the studied Qu'Appelle lakes are comparable to sediment TP_o concentrations (0.10–0.42 mg P g⁻¹) in seven mesotrophic-eutrophic lakes in China (Zhang et al., 2009), but were higher than 48 different sites in Lake Erie in Canada (<0.01–0.29 mg P g⁻¹; Williams et al., 1976).

Although sediment carbon is not the focus of this study, it is worth noting that the high OM in Echo Lake and Crooked Lake sediments may be due to higher concentrations of OM settling from the water column, or other drivers, such as lower mineralization rates. Although sediment accumulation rates reported across three of the lakes are high relative to much of Canada (Baud et al., 2021), they are fairly similar across the studied Qu'Appelle lakes (Pasqua, 5.7 ± 0.1 mm yr⁻¹; Echo, 4.3 ± 0.1 mm yr⁻¹; and Crooked Lakes, 5.72 ± 0.1 mm yr⁻¹; Dixit et al., 2000; Quinlan et al., 2002). Mineralization has not been directly studied in the lake chain; however, previous research showed that deep lakes have lower sediment OM mineralization than those with shallower depths (e.g., Canadian Shield lakes in Quebec; Den-Heyer and Kalff, 1998). Echo and Crooked Lakes are deeper than Wascana and Pasqua Lakes (Supplementary Table S1), suggesting lake depth effects on mineralization rates may be one driver of these differences.

Lake trophic status may also be associated with OM in lake sediments (Ahlgren et al., 2005). Mean sediment OM percentages of 11.3 (± 0.44) to 14.6 (± 0.94) across the studied Qu'Appelle lakes are comparable to the top 10 cm of seven eutrophic lakes in China with sediment OM of 5.3%–16.9% (Zhang et al., 2009), but are much lower than the sediment OM at depths of 0–2-cm and 32–24-cm in mesotrophic Lake Simcoe in Canada (27.4%; Audette et al., 2018), at 0–5-cm and 5–10-cm depths of seven dimictic lakes from the United States and Canada (23.3%–62.5%; Nürnberg, 1988), and in the top 15 cm of mesotrophic Lake Erken, Sweden (17.2%–21.3%; Reitzel et al., 2007). All of the Qu'Appelle lakes studied here are considered eutrophic; however, productivity is expected to vary across lakes and years, which may affect organic matter deposition.

Calcium was the dominant metal in the sediments of Echo, Crooked and Pasqua Lakes, but not Wascana Lake, the only dredged lake. Previous studies have shown differences in Ca-related mineralogy (calcite vs. dolomite) in water bodies of this lake chain, and have shown that calcite can precipitate from supersaturated water columns to increase sediment Ca (Ghebre-Egziabhier and Arnaud, 1983; Last and Last, 2012). Calcium dominance is not uncommon among Canadian lakes not located on the Canadian Shield; Ca compounds dominated the sediments of Lake Simcoe in Ontario, with total Ca concentrations >65 mg g⁻¹ (Audette et al., 2018), but lower sediment total Ca concentrations were reported for Nakamun Lake (25.4 mg g⁻¹; Orihel et al., 2015). Sediment total Mg concentrations were higher in the study lakes than in Nakamun Lake (6.94 mg g⁻¹; Orihel et al., 2015) and Lake Simcoe (4.5–5.1 mg g⁻¹; Audette et al., 2018). Elevated sediment Al concentrations that were noted in Wascana Lake were also reported for one site in the downstream region of Buffalo Pound Lake (an upstream Qu'Appelle lake), which resulted from long-term alum release (D'Silva, 2017). However, we are not aware of any alum release or application to Wascana Lake. Total Fe concentrations in Echo and Pasqua Lake are comparable to sediment Fe concentrations (17.1 mg g⁻¹) in Nakamun Lake (Orihel et al., 2015) and Lake Simcoe (13.3–14.8 mg g⁻¹; Audette et al., 2018). Low sediment total Mn concentrations in Wascana Lake were comparable to those in Nakamun Lake (0.81 mg g⁻¹; Orihel et al., 2015) and Lake Simcoe (0.47–0.84 mg g⁻¹; Audette et al., 2018). Total Al and Fe concentrations were generally greater across the lakes than Mn. Iron concentrations were generally greater in Wascana Lake and Mn concentrations were greater in Crooked Lake, suggesting that sediment P in these two lakes may be more susceptible to changes in reduction-oxidation processes because of these redox-sensitive metals (Boström et al., 1988; Reddy and Delaune, 2008b). Higher Al and Fe and lower Mn concentrations in Wascana Lake are likely due to the higher clay content (Reddy and Delaune, 2008a), which may be linked to dredging in this lake. Wascana Lake had higher Fe + Mn: Ca concentration ratios,

while the other three lakes had higher Ca: Fe + Mn concentration ratios (Supplementary Figure S1).

Phosphorus forms and cycling in lakes

Orthophosphate was the dominant extracted and reactive P_i form in sediments at all depths among the studied Qu'Appelle lakes, which concurred with results for mesotrophic-eutrophic Lake Erken (Ahlgren et al., 2005), Lake Simcoe (Audette et al., 2018), and eutrophic Lake Champlain at the USA-Canada border (Giles et al., 2015). High polyphosphate and pyrophosphate concentrations at the sediment surface in our study lakes are consistent with previous research on sediments of Lake Erken (Ahlgren et al., 2005), Lake Champlain (Giles et al., 2015), and eutrophic Lake Baldegg and oligo-mesotrophic Lake Lucerne in Switzerland (Hupfer et al., 1995). Functions of pyrophosphate and polyphosphates include energy and P storage, stress response, and enzyme activities in several organisms (Hupfer et al., 2007; Raven, 2015). These complex sediment P_i compounds were shown to have a short half-life (~1 decade) relative to P_o in Swedish lakes (Ahlgren et al., 2005; Reitzel et al., 2007) and are hydrolyzed to phosphates during early diagenesis *via* secreted phosphatases (Hupfer et al., 1995; Hupfer et al., 2004). Additionally, Mn^{4+} has a high electron affinity to sorb phosphates, can be more readily reduced to Mn^{2+} under low redox conditions at the SWI to desorb or solubilize phosphates (Mortimer, 1941; Reddy and Delaune, 2008b), and can catalyze the hydrolysis of polyphosphates to orthophosphate in the presence of different Mn oxides (e.g., α - MnO_2) and Ca^{2+} cations (Wan et al., 2019).

Orthophosphate monoesters identified in our study include inositol hexakisphosphates (IHP; with six phosphate groups; Giles et al., 2011), glucose 6-phosphate (g6P), choline phosphate, α - and β -glycerophosphate and mononucleotides (degradation products of phospholipids and RNA, respectively), and unidentified peaks either identified by their chemical shift (unknown 5 ppm) or grouped into general regions of the overall monoesters region of spectra as Monoesters 1, 2, and 3 (Cade-Menun, 2015; Supplementary Table S4) similar to Lake Kvie (Denmark; Paraskova et al., 2015), Lake Champlain (Giles et al., 2015), and Chaohu Lake (China; Zhang et al., 2017). Previous studies have reported that sediment P_o was predominantly orthophosphate monoesters in seven different lakes in China (Zhang et al., 2009) and a reservoir in Poland (Młynarczyk et al., 2013). However, these studies did not correct for orthophosphate diester degradation to orthophosphate monoesters during P-NMR extraction and analysis, which will overestimate the total orthophosphate monoester concentrations and underestimate total orthophosphate diester concentrations in the original sediment samples (Zhang et al., 2017).

Four IHP stereoisomers were identified in these lake sediments (*myo*, *scyllo*, *neo*, and *D-chiro*), similar to previous work in Lake Champlain (Giles et al., 2015). The *scyllo*-IHP concentrations among the study lakes were consistent with previous work in Danish lake

sediments, where it was one of the dominant orthophosphate monoesters (Jørgensen et al., 2011). Phytate (*myo*-IHP) is a P storage compound in higher plants (Raboy, 2003; Raven, 2015), but the origin of the other stereoisomers is unknown. In soils, the other stereoisomers are reported to be synthesized by microbes *de novo* or by the transformation of *myo*-IHP (Giles et al., 2011), but it is unclear if this is also true for aquatic sediments. All four stereoisomers have been identified in Saskatchewan soils, in both native grasslands and agriculturally-managed soils (Liu et al., 2018; Chen et al., 2021); therefore, they may have entered lakes *via* soil erosion (Giles et al., 2015). Decreases in IHP stereoisomers with depth suggest they may be mineralized by phytase in lake sediments (Giles et al., 2011), consistent with results in Lake Champlain (Giles et al., 2015). Further investigation is warranted to understand the origins and turnover of these important P compounds in Qu'Appelle lake sediments. The specific P_o compounds in the monoester 1, 2, and 3 regions are unknown, but they may include lower inositol phosphates and sugar phosphates (Giles et al., 2015). Glucose 6-phosphate is a sugar phosphate that functions in intermediate biochemical reactions (Raven, 2015). The origin and function of the P compound represented by the peak at 5 ppm are unknown.

Orthophosphate diesters were the predominant sediment P_o in our study after correction for degradation during analysis, consistent with Chaohu Lake (Zhang et al., 2017), Lake Simcoe (Audette et al., 2018), and Lake 227 (O'Connell et al., 2020). High sediment surface concentrations of DNA among the study lakes contrasted to Lake Champlain where DNA increased with depth (Giles et al., 2015). Bacteria can be a major contributor to DNA in lake sediments (Jørgensen and Jacobsen, 1996; Ishii et al., 1998; Zhang et al., 2009). In the studied Qu'Appelle lakes, DNA may have been extracted from intact microbes (algae and bacteria in these high productivity systems) or OM, but may also have been extracted from DNA sorbed to minerals (Giles et al., 2015; O'Connell et al., 2020). Intracellular and extracellular nucleases, bacteriovore grazing, and OM decomposition are responsible for mineralizing DNA in aquatic environments (Paul et al., 1987). Under algal breakdown and sedimentation, DNA and other biologically-derived P compounds are readily mineralized and released from sediment (Ahlgren et al., 2005) to supply phosphate to the water column, as may be the case in our studied Qu'Appelle lakes, Chaohu Lake (Zhang et al., 2017), and Lake Erken and eutrophic Lake Sønderby (Reitzel et al., 2006).

The unidentified peak at 2.3 ppm was separately quantified because it was prominent and present in most samples, and it may originate from lipoteichoic acid (Cade-Menun, 2015). The OthDi 1 region contains lipoteichoic acids, phospholipids, and RNA not degraded during extraction and NMR analysis (Cade-Menun, 2015; Giles et al., 2015), while the compounds producing peaks in the OthDi 2 region are unknown. As noted for the orthophosphate monoesters above, degradation products of phospholipids and RNA (α - and β -glycerophosphate and mononucleotides) were detected in these lake sediments, consistent with past work (Jørgensen et al., 2011; Giles et al.,

2015; Audette et al., 2018). Phospholipids and lipoteichoic acids are contained in cell membranes and are thought to represent microbial communities in sediments (Watts et al., 2002; Cade-Menun, 2015).

Low phosphonate concentrations at the sediment surface in our studied Qu'Appelle lakes agreed with several different southwestern and river channel lakes in China (Zhang et al., 2009) and mountain lakes in Sweden (Ahlgren et al., 2006). Phosphonates have very stable bonds that resist thermal, photolytic, and hydrolytic mineralization (Quinn et al., 2007; Kamat and Raushel, 2013; Sosa et al., 2019), and they exist in natural (e.g., ciliate, 2-aminoethyl phosphonate) and synthetic forms, including herbicides (e.g., glyphosate), antibiotics (phosphomycin, 1, two epoxypropyl phosphonic extracted from *Streptomyces* sp.), and detergent additives (Hilderbrand, 1983; Cade-Menun, 2015). The specific source of phosphonates in these lakes is unknown. However, snail shells were observed in Echo Lake sediments, and snails are known to synthesize phosphonates (Miceli et al., 1980), which may explain the higher phosphonate concentrations in that lake. Further investigation is warranted to determine if the phosphonates in these lakes come from natural or synthetic sources.

Sediment metal–P correlations

The positive and negative correlations between P compounds and metal cations presented in the results of this study indicate that metal associations play an important role in retaining P forms in sediments (Reddy and Delaune, 2008a). The correlations of sediment orthophosphate, Al and Fe concentrations among the studied Qu'Appelle lakes were consistent with past work in sediments of eutrophic constructed lakes in China (Cai et al., 2020) and eutrophic lakes in Denmark and Sweden (Reitzel et al., 2006). Total IHP did not correlate to any mineral pools in the studied lake sediments, and neither did any of the IHP stereoisomers, which contrasted with previous sediment studies reporting IHP sorption and precipitation with Ca, Mg, Al, and Fe (Jørgensen et al., 2011; Paraskova et al., 2015). Sediment DNA is the only orthophosphate diester that sorbs (Giles et al., 2015), although sorption is strongest below pH 5 (Condrón et al., 2005), well below the pH in these sediments. Phosphonates can adsorb or precipitate to soluble Ca compounds (Hilderbrand, 1983). They can also sorb to o-Fe and o-Al (Sprinkle et al., 1975), so we expected to see a correlation of phosphonates to Fe and Al pools, but this was not significant in our study.

Conclusion

Currently, knowledge is limited regarding P species in sediments of hardwater lakes on the North American Great Plains and the factors that control their cycling. This study is the first to use P-NMR to characterize lake sediment P forms in this region. In four lakes from the Qu'Appelle lakes chain in Saskatchewan, Canada, significant differences in sediment P forms were observed that

were not detected by measurements of sediment total P and total organic P concentrations alone. The main class of organic P compounds identified by P-NMR in extracts from all four lakes was orthophosphate diesters, typical of living biota, suggesting that P immobilized by microbes and algae is an important pool in these sediments of hardwater eutrophic lakes. Decreases in the concentrations of orthophosphate diesters and other organic P compounds with depth suggest that biological uptake and assimilation, decomposition and mineralization *via* enzyme hydrolysis and cell lysis appear to be important diagenetic processes at the SWI in these study lakes, either simultaneous with, or sequentially to redox processes and sedimentation. Significant differences were detected among the lakes for pools and concentrations of metal cations, suggesting there may be different processes controlling P cycling in these lakes. Of the total metal cation concentrations in these lakes, concentrations of Ca were greatest in Pasqua, Echo, and Crooked Lakes, while the concentrations of Al and Fe were greater in Wascana Lake. Crooked Lake had greater total Al and Fe concentrations than Pasqua and Echo Lakes, and the greatest total Mn concentrations of the lakes. In all four lakes, Al, Mn, and Fe were predominantly organically complexed. These metal cations appear to have considerable influence on the inorganic P forms (which formed 47%–66% of the eTP). Although total P and total organic P concentrations were highest in Echo and Crooked Lakes, the recovery of total P in extracts for P-NMR was low for these lakes and greatest for Wascana Lake. This suggests that P was loosely bound to Al and Fe compounds in Wascana Lake, but more tightly bound with Ca compounds of low solubility in the lakes with greater total Ca concentrations.

Significant differences were observed for P species among the lakes. Orthophosphate and orthophosphate monoester concentrations were greater in Wascana Lake than in the other lakes, while orthophosphate diesters were greater in Echo and Crooked Lakes. Differences with depth and some lakes and depths interactions were also observed, including increased orthophosphate concentrations and decreased orthophosphate diester concentrations with depth. Factors that may be responsible for the differences among these lakes include P retention by metal cations (including redox-sensitive processes) and variations in inputs, decomposition, and mineralization. It is not clear which of these processes most controls P in each lake, but it is clear that there are differences in factors controlling P cycling even within these four lakes, although they are all part of the same lake chain. These factors must be taken into consideration because they could affect P management and water quality control measures in these and other lakes within the Great Plains.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding authors.

Author contributions

MW-T: Conceptualization, Project funding, Analytical work, Data curation, Methodology, Writing original draft; BC-M: Conceptualization, Analytical work, Methodology, NMR interpretation, Writing original draft; HB: Conceptualization, Project funding, Methodology, Writing original draft. All authors have read and approved the final version of this manuscript prior to submission.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenvs.2022.928824/full#supplementary-material>

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