Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec)

Article *in* Journal of Great Lakes Research · July 2020

DOI: 10.1016/j.jglr.2020.07.010

CITATIONS
2

READS
142

3 authors, including:

Milton L Ostrofsky
Allegheny College
41 PUBLICATIONS **1,012** CITATIONS

SEE PROFILE

Suzanne Nanette Levine
University of Vermont
34 PUBLICATIONS **1,333** CITATIONS

SEE PROFILE

Journal of Great Lakes Research xxx (xxxx) xxx

Contents lists available at ScienceDirect

Journal of Great Lakes Research

journal homepage: www.elsevier.com/locate/ijglr

Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec)

Milton L. Ostrofsky [a,*], Suzanne N. Levine [b], Andrea Lini [c]

[a] Biology Department, Allegheny College, Meadville, PA 16335, United States
[b] Rubenstein School of Environment and Natural Resources, University of Vermont, Burlington, VT 05405, United States
[c] Department of Geology, University of Vermont, Burlington, VT 05405, United States

ARTICLE INFO

Article history:
Received 25 February 2020
Accepted 16 July 2020
Available online xxxx
Communicated by Joseph Makarewicz

Keywords:
Lake Champlain
Paleolimnology
Sediment
Phosphorus species
Eutrophication

ABSTRACT

We tested the hypothesis that the analysis of operationally defined sedimentary phosphorus species gives a finer resolution of historical land-use changes in lake watersheds than does total phosphorus alone. We measured loosely sorbed/interstitial, reductant soluble, aluminum-bound, apatite, organic and total phosphorus in eleven cores taken from heterogeneous regions of Lake Champlain using sequential extraction. During the pre-settlement period (before 1770 C.E.) concentrations of all P species were low, stable, and dominated by apatite P. With the exception of apatite P, sediment concentrations of all P species increased from pre-settlement times to the present. When accumulation rates were examined, the three P species least susceptible to post-depositional migration (apatite, aluminum-bound, and organic P) were unaffected by deforestation and the development of small, family-scale farms in the 19th century. Increases in accumulation rates were only detected in the early 20th century coincident with afforestation of the watershed as marginal farms were abandoned. By mid-20th century, the accumulation rate of apatite P decreased in all but the lake regions most affected by the industrialization of agriculture and urban development. Aluminum-bound and organic P rates continued to increase in all regions.

Introduction

The eutrophication of lakes remains a persistent environmental problem despite major strides in understanding made by limnologists over the past several decades (Schindler, 2006). As a rule, phosphorus influx to lakes is the principal controller of productivity and biomass accumulation, although other nutrients, light, and grazing often are influential as well. Because the lake water concentration of total phosphorus (TP) is often the sole independent variable in a number of models that predict the biomass and productivity of different trophic levels (phytoplankton, zooplankton, benthos, fish) in lakes (Peters, 1986), the historical change in lake-water TP concentrations from pre-settlement times to present is our best indicator of the onset, rate, and extent of eutrophication. However, in the absence of historical water quality records, the eutrophication history of lakes can only be inferred from their sedimentary records (Carey and Rydin, 2011; Davidson and Jeppesen, 2013; Hiriart-Baer et al., 2011; Schelske and Hodell, 1995). Consequently, sedimentary profiles of phosphorus are of considerable interest to limnologists and lake managers.

There is substantial literature on total phosphorus in lake sediments. In addition, sequential extraction with increasingly aggressive solvents has made the measurement of operationally defined P species routine. Studies of the distribution of sedimentary P species strive to: 1) assess the potential for internal P loading, 2) characterize the P speciation of allochthonous sources, or 3) evaluate trophic status (e. g., Carey and Rydin, 2011; Gikuma-Njuru et al., 2010; Kisand, 2005; Mayer et al., 2006; Nõges and Kisand, 1999; Olila et al., 1995; Ostrofsky and McGee, 1991; Penn et al., 1995; Pettersson and Istvanovics, 1988; Ruban and Demare, 1998; Rydin, 2000; Søndergaard et al., 1993; Søndergaard et al., 1996; Trolle, et al., 2009; Williams et al., 1976). The first objective is straightforward; several studies have linked P release to total sediment P or to particular operationally defined P species (Nürnberg, 1988; Ostrofsky et al., 1989; Ostrofsky and Marbach, 2019; Petticrew and Arocena, 2001; Rydin, 2000; Smith et al., 2011; Søndergaard et al., 1993; Søndergaard et al., 2001). The second is frequently accomplished as well although only if an assumption of minor post-depositional diagenetic transformations is made. The third objective is most problematic, largely due to demon-

* Corresponding author.
E-mail address: mostrofs@allegheny.edu (M.L. Ostrofsky).

https://doi.org/10.1016/j.jglr.2020.07.010
0380-1330/

strated post-depositional mobility of dissolved species within the sediment pore water (Carignan and Flett, 1981). The widely observed large increase in total sedimentary P near the surface of a sediment core has alternatively been interpreted as evidence for the increased P loading and subsequent eutrophication of a lake (e. g., Lucas et al., 2015) or as the accumulation of upward migrating nutrient released at depth through desorption, redox-mediated Fe and Mn reduction that dissolves sorptive oxy-hydroxides, and the mineralization of organic matter. Consequently, limnologists have been cautious in interpreting sedimentary P profiles unless apparent trends are corroborated by other proxies. For example, historical lake water TP concentrations have been inferred from diatom-based transfer functions. This approach also has problems, such as a scarcity of reliable lake training sets, the need for advanced taxonomic skills, the presence of species with broad tolerances, the confounding effect of secondary variables, and little predictive power beyond the immediate geographic area (Davidson and Jeppesen, 2013; Juggins, 2013; Juggins et al., 2013). However, much of the surface increase in total sediment P can be attributed to a reductant-soluble fraction, whereas other sedimentary P species seem not to be mobile at all (Ostrofsky, 2012) and are therefore potentially useful markers in the sedimentary record of historic changes in a lake and its watershed.

Walker and Syers (1976) presented a conceptual model of the evolution of phosphorus geochemistry in soils that may be explanatory for lake sediments as well. Initially, phosphorus is associated with the primary mineral apatite [Ca_5 $(PO_4)_3$(OH, F, Cl)]. Apatite degrades through carbonation weathering from CO_2 in precipitation, from bacterial decomposition of organic matter, and from organic acids released by plant roots (Schlesinger, 1991). This newly "available" P is converted to organic P through biological uptake or is occluded by mineral oxyhydroxides (Al, Fe, Mn) in the soil. With time, total soil P is reduced through losses to ground- or surface-water transport, and remaining P is largely in the organic-bound or occluded fractions. The acidification of young soils is largely due to the development of vegetation (Boyle, 2007) and forested soils typically have lower pH than non-forested soils (Grossman and Mladenoff, 2008). These shifts in soil P speciation can occur relatively quickly. Chen et al. (2008) and Garcia-Montiel et al. (2000) found that deforestation leads to an increase in soil pH and abrupt increase in HCl extractable P (mainly apatite) and that reforestation of previously open sites decreases soil pH which leads to apatite decline. Noll et al. (2009), on the other hand, presented evidence that agricultural land exports more NaOH-P than HCl-P to Conesus Lake, New York, but found that stream processes retain the former so that nearshore lake sediments are richer in HCl-P.

These shifts in soil P speciation can be reflected in a lake's sedimentary profile. For example, the sedimentary P fractions in Sargent Mountain Pond, Maine, measured by Norton et al. (2011), show maximum apatite-P concentration in sediment deposited immediately after deglaciation. The apatite likely originated in adjacent soils without vegetation that tends to acidify soil through organic acid secretion from root hairs and organic matter decomposition. Further, the absence of vegetative cover would have facilitated soil erosion and particle transport to the lake. As forest cover later developed in the Sargent Mountain Pond watershed, apatite P decreased concurrent with aluminum and iron oxyhydroxide-bound P increases, with corresponding changes reflected in the lake's sediment.

Filippelli et al. (2010) have argued that this process is reversible through land disturbance. Their core from Laguna Zoncho, Costa Rica, captured changes in the distribution of P species coincident with alternating periods of agriculture/deforestation and land abandonment/afforestation. Periods of intense agricultural activity were marked by elevated organic and apatite P content and less metal-bound P. Land abandonment allowed afforestation to occur, which acidified soils resulting in lower apatite P content and reduced soil erosion, the end result a lowering of apatite P export to the lake sediments. If this pattern has general application, we would expect to see similar changes in other lakes' sediments, i.e. increasing deposition in lakes of apatite- and organic-P during periods of deforestation and agricultural development, and decreasing apatite- and organic-P deposition during land abandonment and afforestation.

The two studies cited above were done on lakes with simple morphometry in small watersheds. Here we examine the sedimentary P species in large, multibasin Lake Champlain whose watershed has undergone settlement, deforestation, subsistence agriculture, afforestation, urbanization, and intensified mechanized agriculture since the end of the 18th century. Our goal was to quantify phosphorus species in the surface sediments that are correlated with internal P loading, and to determine historical changes in phosphorus species concentrations and flux rates as they are related to land use/cover changes. A description of other paleolimnological proxies in these cores (C, N, TP, biogenic Si, pigments, metals) has been presented in Levine et al. (2012, 2018) and are not further discussed here.

Methods

Description of study area

Lake Champlain is a large (1,127 km^2), deep (max. depth 122 m, mean depth 19.5 m) lake that occupies the northern portion of a narrow valley that extends from the St. Lawrence River near Montreal, PQ to the mouth of the Hudson River at New York, NY. Its watershed (21,326 km^2) is bounded on the west by the Adirondack Mountains and on the east by the Green Mountains. The lake forms most of the border between the states of Vermont and New York and extends eight km into the Province of Québec. The lake naturally drains north via the Richelieu River but in 1823 was connected in the south to the Hudson River by way of the Hudson-Champlain Canal. The lake has a rich history of anthropogenic influences. It is generally assumed that because indigenous populations were sufficiently small, there was only minimal effect, if any, on the lake's trophic status.

The estimated population of the Champlain Valley in 1600 was only around 4000, composed largely of hunter-gatherers; the growing season was too short and unpredictable for maize cultivation (Albers, 2000; Haviland and Power, 1994). Following the resolution of hostilities between European powers for control of the area in the 1760 s, settlers from southern New England began moving into the Champlain basin from south to north. Due to more favorable soils and topography, the eastern Champlain lowlands (now Vermont) attracted more settlers than did the west (New York). Populations initially grew rapidly; by 1810 there were 86,762 inhabitants in the Champlain basin, mostly on small subsistence farms (Henson and Gruendling, 1977). Population growth slowed during the early 19th century due to war fears (1812) and the opening of agriculturally more favorable western lands with the completion of the Erie Canal (1825). Nevertheless, the region became an important source of timber with Burlington becoming a major lumber exporting port. Sheep were introduced in 1811. By 1840 all commercially valuable timber was gone, although deforestation continued for fuel wood and to clear pastures for sheep, and later for dairy cattle. By 1850 sheep farming was no longer economically viable, and gradually farms converted to dairy cattle although farms remained small and unmechanized well into the latter half of the 20th century. Maximum deforestation (~70%) was reached in 1870 in Vermont and around 1900 in

Please cite this article as: M. L. Ostrofsky, S. N. Levine and A. Lini, Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec), Journal of Great Lakes Research, https://doi.org/10.1016/j.jglr.2020.07.010

the New York portion of the watershed. Eventually afforestation began as hill farms were abandoned due to short growing seasons, competition with western agricultural products made available to eastern markets by expanding railroads, and alternative employment opportunities in manufacturing and mining.

For almost a century the basin population grew very slowly at about 0.5% per year – 238,229 in 1870, 363,236 in 1950 (Henson and Gruendling, 1977). During this time, municipalities with sewerage systems discharged untreated sewage directly into streams and the lake. The city of Burlington initiated primary sewage treatment only in the 1930 s and secondary treatment in 1950. Populations grew more rapidly after 1960 with the completion of interstate highways and the development of a strong tourist economy. Increased population has promoted suburbanization, impermeable surfaces leading to increased storm water discharge, and more domestic waste. As late as 1970, 60% of all municipalities in the Champlain basin were discharging untreated sewage into surface waters; only 25% had primary treatment. The Clean Water Act (1972) mandated secondary treatment of municipal sewage. By 2001 all municipalities discharging sewage had secondary treatment, and half had tertiary treatment (P removal). In 1978 Vermont enacted a phosphate detergent ban, and significant progress has been made to reduce non-point sources of P from farms. However, there has been a shift from small family-operated dairy farms to larger industrial farms that rely on imported feed grains and artificial fertilizers and result in increased animal waste.

Approximately 571,000 people currently live within the watershed with about 35% depending on the lake for domestic water supply. The lake is also used extensively for transportation, commerce, domestic and industrial waste disposal, and recreation. Current land cover in the watershed is 70% forest, 13% grass/pasture, 6% row crops and 6% developed. The lake is generally mesotrophic, but the basin is of such complex morphology containing over 70 islands and numerous shallow sills, and more recently road and rail causeways, that it is divided into five distinct areas, each with different physiochemical characteristics (Fig. 1a, b): the South Lake, the Main Lake, Malletts Bay, Northeast Arm (or the Inland Sea), and Missisquoi Bay [Lake Champlain Basin Program (LCBP)].

The riverine South Lake, extending north from the south end of South Bay to Crown Point, is approximately 60 km in length, 0.1 to 2 km wide, but nowhere deeper than 9.5 m (NOAA Nautical Charts 14781–14784, 1:40,000 scale, 1980). This area of the lake contains only 0.6% of the lake volume and is most eutrophic with TP normally ranging from 30 – 50 μg L^{-1} (LCBP).

Malletts Bay is a figure "8″-shaped bay isolated from the Main Lake by a natural sill (<1 m deep) and a rail causeway (no longer in use) and separated from the Northeast Arm by a natural sill (<1 m deep) and a highway causeway. Each causeway has a narrow opening to the Main Lake or the Inland Sea. The Outer Bay [43.3 km^2, maximum depth (z_{max}) 32 m] and the Inner Bay (10.7 km^2, z_{max} 27 m) combined contain 2.8% of the lake's total volume but receive runoff from 8.6% of the basin area, largely by way of the Lamoille River, one of the largest lake tributaries. The isolation by causeways and sills, and the hydrologic loading suggest that the Bay behaves more like an "upstream lake" than a bay. At present this is the most oligotrophic region of Lake Champlain with mean TP ~ 10 μg L^{-1}.

Missisquoi Bay is a broad, shallow (80 km^2, z_{max} 4.5 m) bay in the northeastern-most region of the lake. It is isolated from the Northeast Arm by a sill and a highway causeway. It receives drainage from another of the largest lake tributaries, the Missisquoi River (catchment area 2234.5 km^2, about 10.5% of the total lake watershed area), but contains only 0.9% of the lake's total volume. Land cover is largely agricultural (30.2% with grass/pasture + culti vated crop) and the bay is consequently eutrophic with TP greater than 40 μg L^{-1} and frequently hosts blooms of toxic cyanobacteria (Shambaugh, 2008; Smeltzer et al., 2012).

The Northeast Arm is a heterogeneous region of the lake containing both the shallow, mesoeutrophic St. Albans Bay (TP ~ 25 μg L^{-1}) and the deeper mesotrophic central region of the Arm (10 < TP < 20 μg L^{-1}). It has no major direct tributaries, receiving most of its hydrologic loading from Missisquoi and Malletts Bays to the north and south, respectively. It is separated from those bays as described above and from the Main Lake directly by two natural sills and causeways, one at Pelot's Point (between the Alburg Tongue and North Hero Island) and at Tromp Point (between North Hero Island and Grand Isle (South Hero Island)). Maximum depth of the Inland Sea is 48 m and it contains 13.5% of the lake's total volume.

With the above areas excluded, the remainder is the large (682.5 km^2) heterogeneous Main Lake, extending 118 km from Crown Point north to the Richelieu River. This portion of the lake has a maximum depth of 122 m, and contains 82% of the total lake volume. It is mesotrophic, with 10 < TP < 20 μg L^{-1}.

Analysis

Cores were collected over several years (2005–2010) using a Glew gravity corer from four of the five regions listed above. We did not core the riverine South Lake area where extensive dredging has occurred to permit commercial and private boat traffic and where the pulp and paper industry had discharged 945,000 m^3 of waste solids (Myers and Gruendling 1979). The Main Lake was represented by five cores (Port Henry, Elm Point, Shelburne Bay, Juniper Basin, and Schuyler Island), Malletts Bay by two cores (Inner Malletts Bay and Outer Malletts Bay), the Northeast Arm (Inland Sea) by three cores (Savage Island, St. Albans Bay, and Cheney Point), and Missisquoi Bay by a single core (Missisquoi Bay). Core site descriptions are given in Table 1.

Cores were extruded in the lab in 1-cm segments and partitioned for analyses (stable isotopes, pigments, diatoms, nutrients, ^{210}Pb dating, etc.). The results of these analyses have been reported elsewhere (Levine et al., 2012, 2018). Dating of core segments was done using the ultra-low background gamma spectrometry protocol and the constant rate of supply (CRS) model (Engstrom et al., 2006). Freeze-dried samples were used for phosphorus analyses. For total sediment P, analysis followed the combustion technique of Andersen (1976) followed by spectrophotometry (Murphy and Riley, 1962) (Elm Point, Shelburne Bay, Schuyler Island, Port Henry, Inner and Outer Malletts Bay, Cheney Point, Juniper Basin) or the acid digestion technique of Anschutz et al. (1998) followed by ICP-OES (Savage Island, Port Henry, St. Albans Bay, Missisquoi Bay). The Port Henry core total P was analyzed using both techniques to determine if results were comparable. The mean ratio (Andersen/ICP) of 38 paired total P samples was 0.976 with a standard error of 0.015. We concluded that this ratio was not significantly different from 1.0 and that the two methods give similar results. Analysis of phosphorus species followed a modification of the sequential extraction technique described by Hupfer et al. (1995). Here, 75-mg samples were extracted with 1 M NH_4Cl (2 hr), 0.1 M bicarbonate/dithionite (BD) (1 hr), 1 M NaOH (16 hr), and 0.5 M HCl (24 hr). All extracts were centrifuged (5 min, 3000 RPM) and aliquots of the supernatant were analyzed using spectrophotometry (Murphy and Riley, 1962). The NH_4Cl extract measures P in the interstitial water and P loosely adsorbed to mineral surfaces. The BD extract measures P bound to redox-sensitive iron and manganese oxyhydroxides. The NaOH extract measures P bound to aluminum and any residual iron oxides. The HCl extract measures P bound with calcium that was not removed in the NH4Cl extraction and apatite. The difference between total sediment P and the sum of these inorganic fractions is assumed to be

Please cite this article as: M. L. Ostrofsky, S. N. Levine and A. Lini, Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec), Journal of Great Lakes Research, https://doi.org/10.1016/j.jglr.2020.07.010

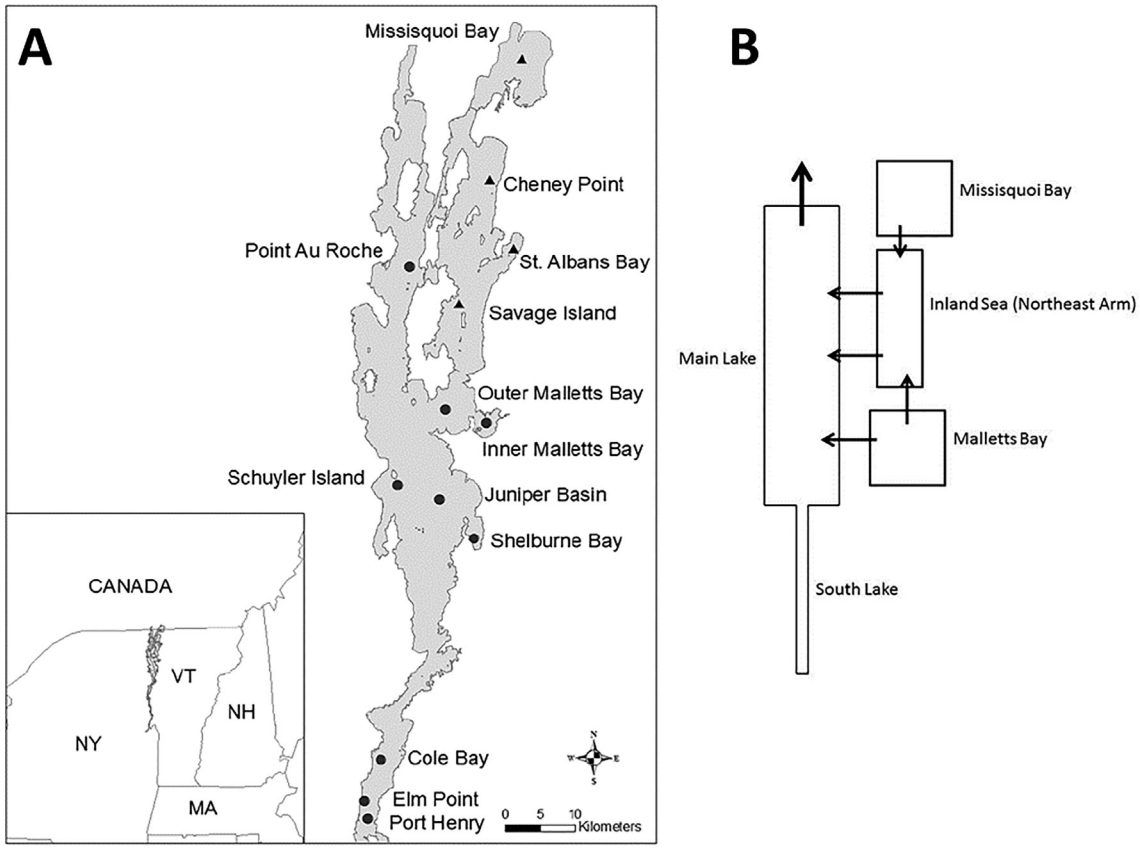

Fig. 1. Panel A - Map of Lake Champlain showing coring sites. Panel B - Schematic of Lake Champlain showing the hydrologic relationships among the 5 lake areas (not drawn to scale).

Table 1
Core locations in Lake Champlain.

Core Site	Latitude	Longitude	Water Depth (m)
Cheney Point	44.876	−73.191	26
Elm Point	44.0759	−73.4397	14
Inner Malletts Bay	44.5636	−73.2083	19
Juniper Basin	44.4649	−73.2954	86
Missisquoi Bay	45.0367	−73.130	4
Outer Malletts Bay	44.5820	−73.2669	32
Port Henry	44.0518	−73.4346	9
Savage Island	44.7173	−73.2460	11
Schuyler Island	44.4853	−73.3704	46
Shelburne Bay	44.4143	−73.2357	27
St Albans Bay	45.788	−73.161	6

organic P and any refractory P bound in mineral lattices. P species accumulation rates were estimated as the product of sediment accumulation rates (Levine et al., 2012, 2018) as indicated by ^{210}Pb dating and P species concentration.

Results and discussion

Collected cores varied in length from 24 to 69 cm, and ^{210}Pb activity allowed dating as early as the first decade of the 19th century in three of the cores (Inner Malletts Bay, Cheney Point, and St. Albans Bay) and from the middle of the 19th century for the remainder. Sediment accumulation rates varied widely in different regions of the lake, with the ^{210}Pb date of 1900 ranging from 28 cm in depth in Outer Malletts Bay to only 3 cm in depth at Cheney Point and Juniper Basin. In eight of the cores the recovered sediment extended well beyond the earliest date possible using ^{210}Pb activity. If we assume that sediment accumulation rate calculated at the oldest ^{210}Pb-dated section of each core is representative of the rate preceding that date, then four cores (Inner Malletts Bay, Outer Malletts Bay, Shelburne Bay, and Schuyler Island) captured lake history to the middle of the 18th century. The Cheney Point, Juniper Basin, and Savage Island cores were apparently collected from locations frequently swept by large seiches (Manley et al. 1999) and sediment accumulation rates were very low. The earliest ^{210}Pb dates for the three cores were found at 5–6 cm (1804), 4–5 cm (1846), and 4–5 cm (1874), respectively. Consequently, the post-settlement historic records here are too compressed to be useful. The three cores do, however, give a long record of the pre-settlement period. Extrapolated dates to the bottom of these cores suggest that each contains at least a 10^3 yr. record. While this approach may be common practice, we do not make specific inferences from analyses of sediments of any of the cores older than the earliest ^{210}Pb dates beyond noting that these cores have captured sediments deposited well before the onset of European settlement in the Champlain basin.

The areas of Lake Champlain examined spanned a trophic continuum from oligotrophic (Malletts Bay) to eutrophic (Missisquoi Bay), and concentrations of phosphorus in the sediments varied both spatially and historically. The stratigraphic profiles of P species at all cored locations are shown in Figs. 2–12. At the sediment surface, total P in the 11 cores varied from about 1300 to 3500 μg P g^{-1} sediment dry weight, similar to concentrations reported from other studies on large lakes (Gikuma-Njuru et al., 2010; Mayer et al., 2006; Olila et al., 1995; Pettersson and Istvanovics, 1988; Tõnno et al., 2013; Trolle et al., 2009; Williams et al., 1976). There was no correlation between surface sediment total P concentrations and median lake water TP concentrations reported by the

Please cite this article as: M. L. Ostrofsky, S. N. Levine and A. Lini, Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec), Journal of Great Lakes Research, https://doi.org/10.1016/j.jglr.2020.07.010

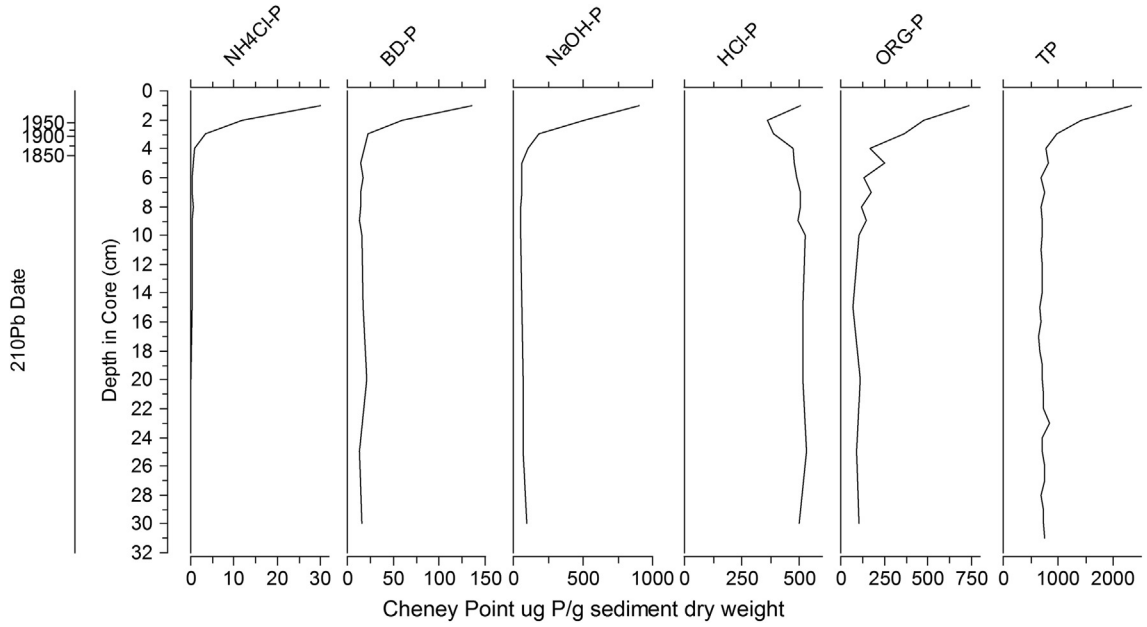

Fig. 2. Stratigraphic distribution of P species in Cheney Point core. All units are μg P g^{-1} sediment dry weight. See Methods for description of P species.

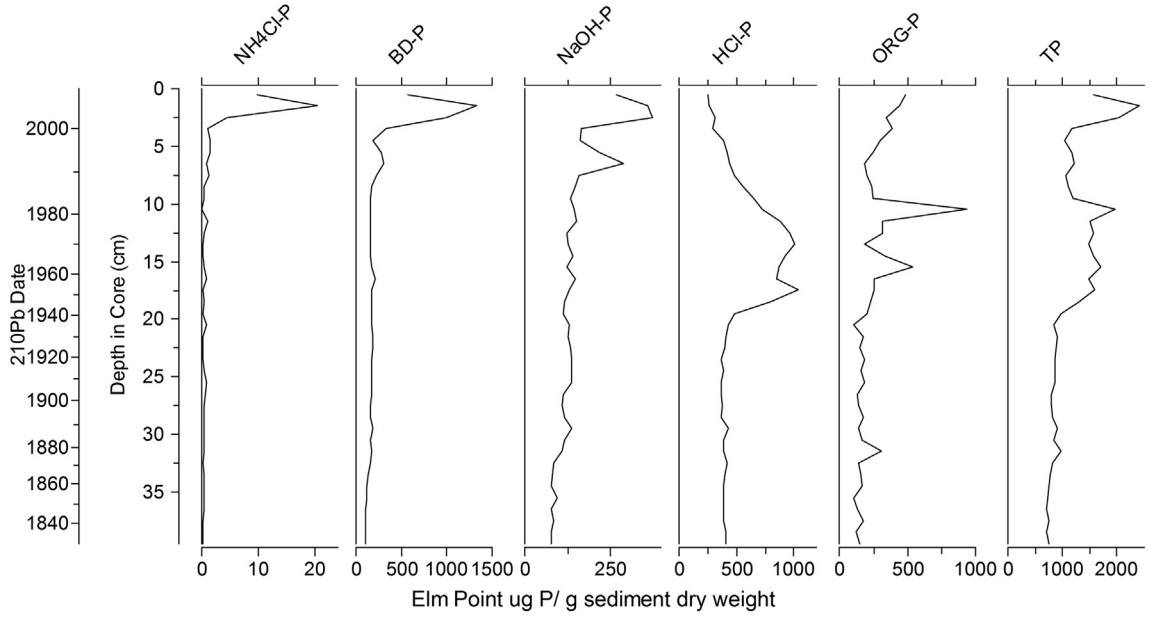

Fig. 3. Stratigraphic distribution of P species in Elm Point core. Units as in Fig. 2.

Lake Champlain Basin Program based on annual sampling since 1992 (LCBP). The lack of any correlation has been frequently reported in the literature (McColl, 1977; Ostrofsky, 1987; Trolle et al., 2009) and is due at least in part to differences in P retention among and within lakes, to rapid early mineralization of much of the sedimented organic P (Hupfer et al., 1995), and to post depositional mobility (Carignan and Flett, 1981; Ostrofsky, 2012) of some P species within the sediment column. The concentrations of the P fractions we report are also well within ranges observed in other lakes.

Although Lake Champlain is not a homogeneous water body due to numerous islands and sills that isolate significant areas, there were some common patterns observed in the historical distribution of P species in its sedimentary record. Throughout the pre-settlement period most P species are relatively constant, and in low concentrations compared to the post-settlement concentrations. The exception is HCl-P which has relatively constant concentrations throughout both the pre-settlement and post-settlement periods at all areas of the lake for which we have core data. Surface or near subsurface concentrations were generally the greatest in each core, with often steep declines in concentration with increasing sediment depth. In all cores the NH_4Cl-extractable P was only a minor contributor to total sediment P, with core average concentrations ranging from 1.4 to 11 μg P g^{-1} sediment dry weight, and typically making up < 0.1 to 1% by weight of total sediment P. This fraction represents interstitial P and P loosely adsorbed to mineral (e. g., Fe, $CaCO_3$) surfaces. The increase in its concentration near the surface in all cores may be due to rapid mineralization of

Please cite this article as: M. L. Ostrofsky, S. N. Levine and A. Lini, Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec), Journal of Great Lakes Research, https://doi.org/10.1016/j.jglr.2020.07.010

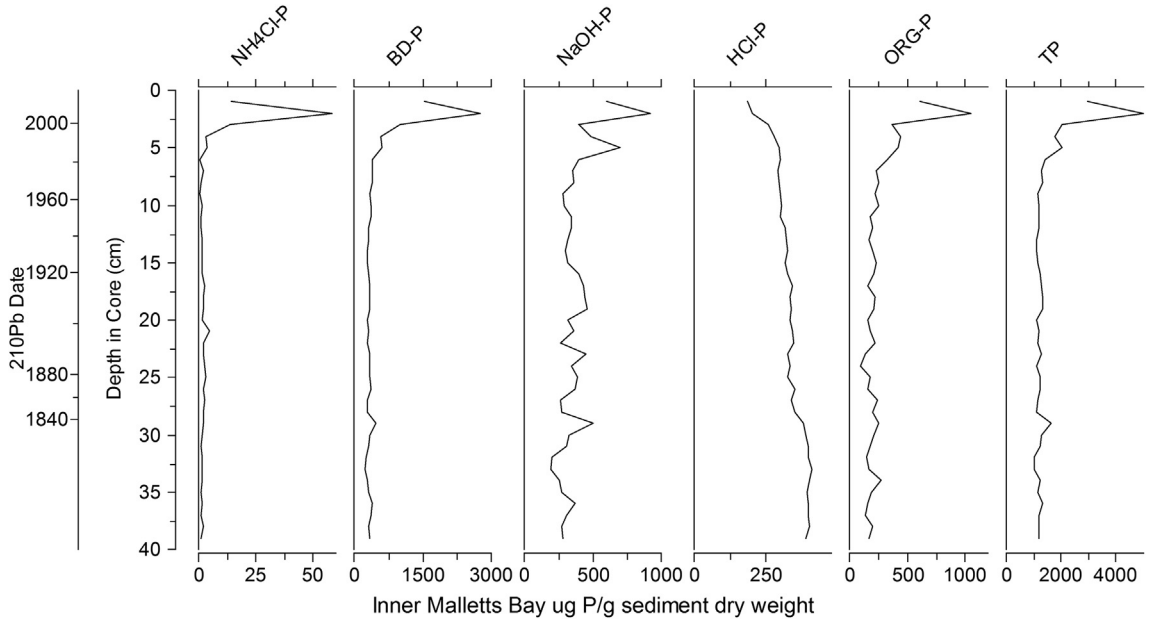

Fig. 4. Stratigraphic distribution of P species in Inner Malletts Bay core. Units as in Fig. 2.

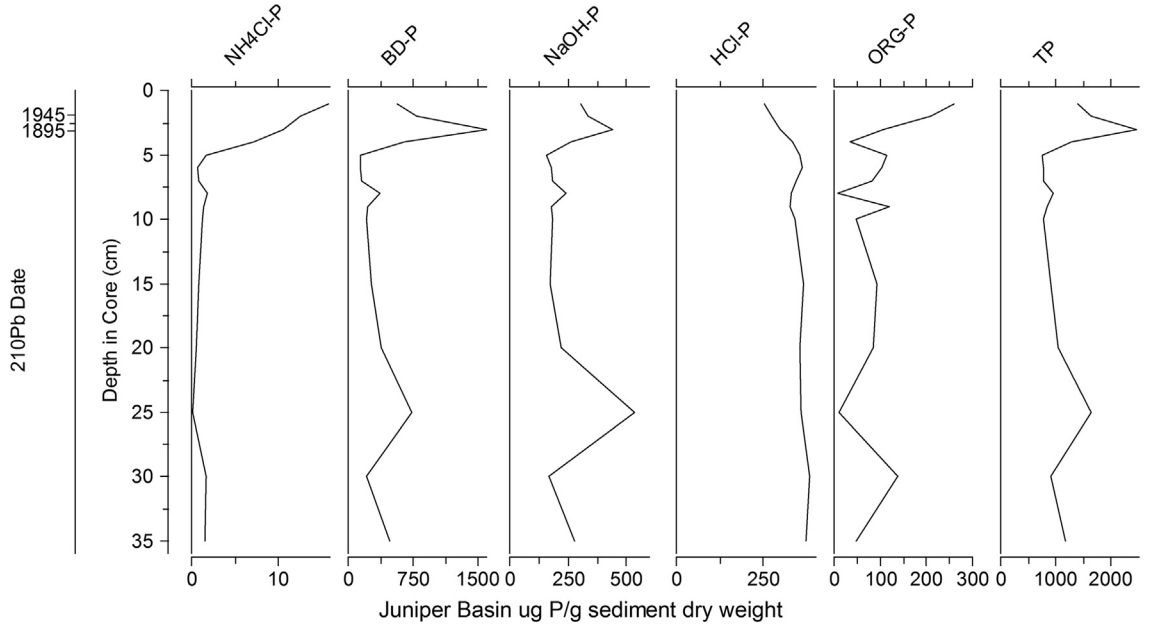

Fig. 5. Stratigraphic distribution of P species in Juniper Basin core. Units as in Fig. 2.

freshly settled organic matter, the temporary adsorption of water column dissolved P on settling particles or the sediment surface (Hupfer et al., 1995), and to the greater interstitial water content of surficial sediments. Some of this P fraction can diffuse into the overlying water mass during periods of hypolimnetic anoxia and be the principal source of internal loading (Nürnberg, 1984). With longer burial time and sediment compaction, much of this P may permanently bind to metal oxyhydroxides or be immobilized in heterotrophic bacterial biomass and contribute to other P fractions. The absence of oxygen and low concentrations of alternate electron acceptors (e. g., Fe^{3+}, NO_3, SO_4) in deeper sediments, however, precludes the continued mineralization of sedimented organic matter.

BD-extractable P was a significant component of total P contributing 20 to 40% of the total sediment P except in the Cheney Point core where an anomalously low core average of only 3.1% was measured. Concentrations generally increased from the oldest to the more recent sections of each core. The single exception to this pattern was seen in the Cheney Point core where concentrations of BD-P were very low (<25 μg P g^{-1} sediment dry weight), made up less than 5% of total P, and even in the most recent sediments accounted for <10% of total P. In most cores, the surficial increase in BD-P concentration was abrupt, occurring only in the most recently deposited, upper few centimeters of sediment. However, in Shelburne, Missisquoi and St. Albans bays, the increase was gradual, beginning in the mid- to late-19th century and may be related to expanding population centers and agricultural development adjacent to the lake in these areas. The BD-P fraction represents P bound to reducible iron and manganese oxyhydroxides,

Please cite this article as: M. L. Ostrofsky, S. N. Levine and A. Lini, Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec), Journal of Great Lakes Research, https://doi.org/10.1016/j.jglr.2020.07.010

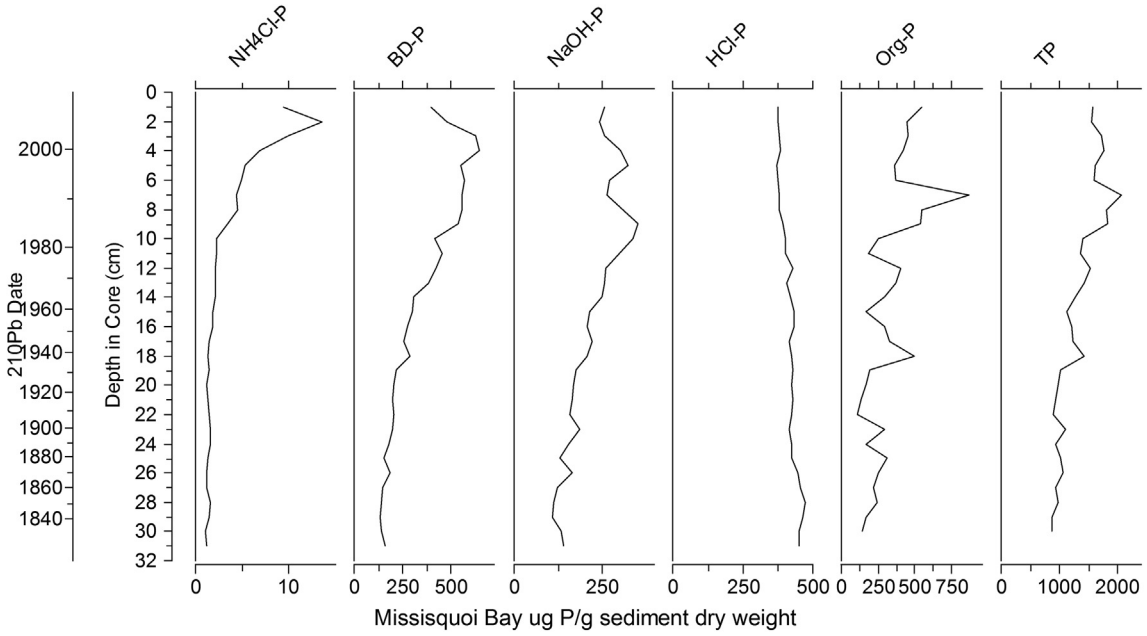

Fig. 6. Stratigraphic distribution of P species in Missisquoi Bay core. Units as in Fig. 2.

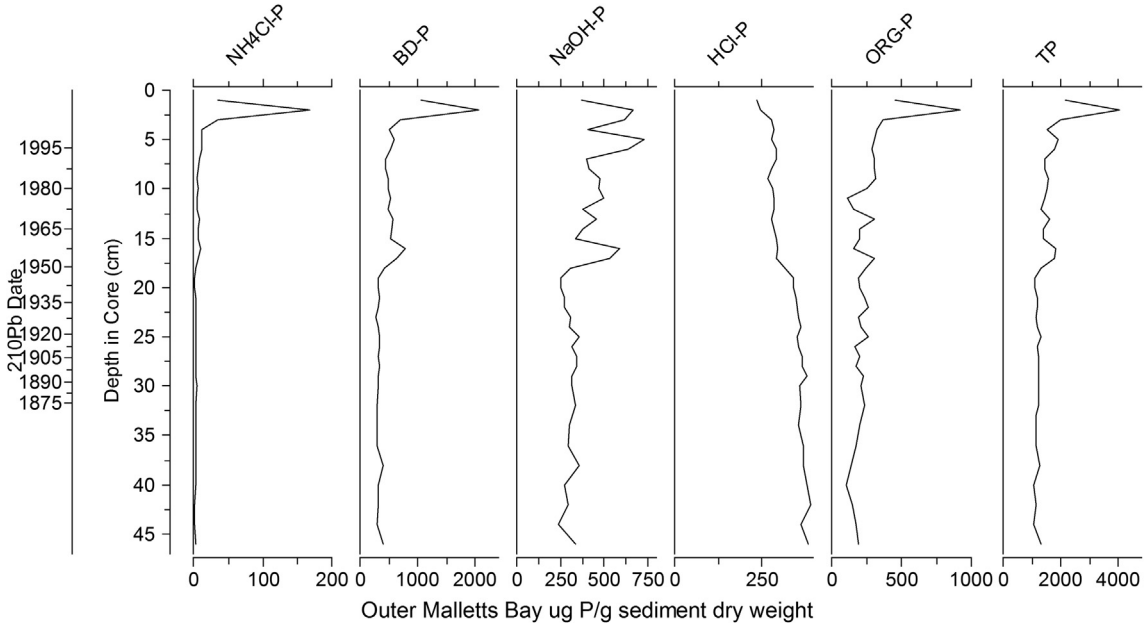

Fig. 7. Stratigraphic distribution of P species in Outer Malletts Bay core. Units as in Fig. 2.

although the BD reagent creates stronger reducing conditions than occur naturally and likely overestimates reducible P. BD-P is not a reliable proxy for paleolimnological reconstructions of lake trophic history. Dissolved P in sediment interstitial water resulting from desorption, redox-mediated release, and mineralization of solid P phases can migrate within the core along a concentration gradient and re-precipitate in the surficial sediments in the presence of Fe^{3+} and oxygen, giving a false signal that is often attributed to increased trophic status (Łukawska-Matuszewka et al., 2013). This post-depositional mobility of P in sediment profiles first identified by Carignan and Flett (1981) is due almost exclusively to BD-P (Ostrofsky 2012). This fraction is a fair proxy for P that may be released at low redox, however, and has been significantly correlated with rates of internal P loading in stratified lakes (Nürnberg, 1988; Ostrofsky et al., 1989; Ostrofsky and Marbach, 2019). All cores except Cheney Point and St. Albans Bay have peak BD-P concentrations in the surface sediments in excess of 1000 μg P g^{-1} sediment dry wt, suggesting that should anoxic conditions develop significant internal loading would occur in these areas.

NaOH-P represents that fraction of P that is bound to aluminum (Kopáček et al., 2005). The lake management literature is replete with comments that aluminum will "permanently bind" sedimentary P and prevent redox-mediated release. Because Al-P is in particulate form. dissolved PO_4 is not released to the sediment interstices to migrate upward along a concentration gradient and accumulate at the sediment surface. Its relative immobility makes

Please cite this article as: M. L. Ostrofsky, S. N. Levine and A. Lini, Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec), Journal of Great Lakes Research, https://doi.org/10.1016/j.jglr.2020.07.010

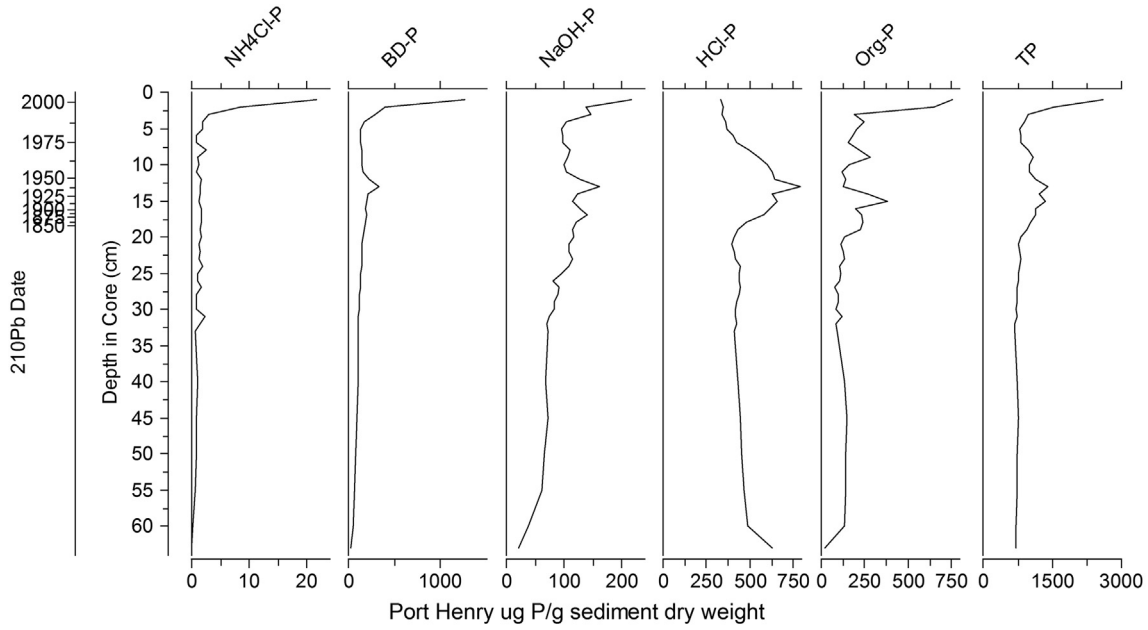

Fig. 8. Stratigraphic distribution of P species in Port Henry core. Units as in Fig. 2.

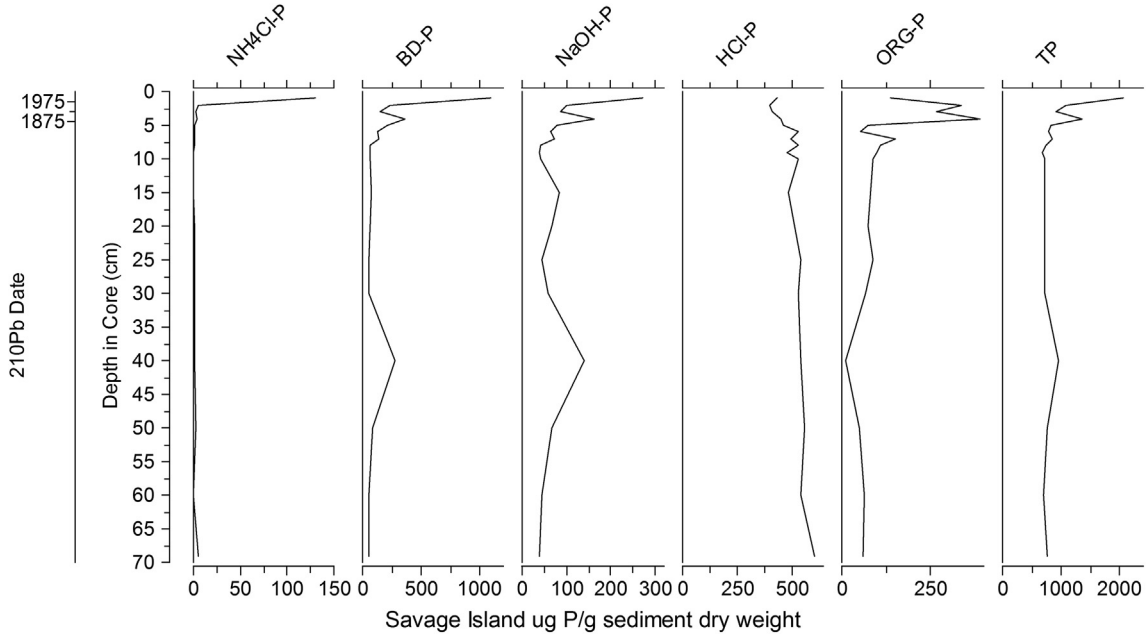

Fig. 9. Stratigraphic distribution of P species in Savage Island core. Units as in Fig. 2.

NaOH-P a reliable proxy for paleolimnological interpretations (Rydin, 2000).

Core average NaOH-P made up from 10 to 25% of total sediment P and tended to be relatively constant within each core at all depths or with only slight increases toward the surface. The exceptions to this pattern included the Savage Island and the Cheney Point cores where NaOH-P showed a surface spike. Based on the relative contribution of NaOH-P to total P, the cores fell into two groups: the Port Henry, Savage Island, St. Albans Bay, and Cheney Point cores had NaOH-P contributing, on average, 10% or less of total sediment P, whereas in the Schuyler Island, Juniper Basin, Shelburne Bay, Missisquoi Bay, Inner Malletts Bay, and Outer Malletts Bay cores NaOH-P made up between 20 and 30% of total P. The NaOH-P content of the Elm Point core fell between these groups, 10–20%.

HCl-P concentrations were the least variable among the cores; mean values ranged from 325 to 513 μg P g^{-1} sediment dry weight. Its percent contribution to TP, however, ranged from 20 to almost 60%. With only two exceptions, HCl-P concentrations decreased very gradually from the oldest to the more recent sections of cores. The exceptions were in cores from Elm Point and Port Henry, in the southern main lake where there was a mid-core peak in concentration about twice that of historical levels. At Elm Point, HCl-P concentrations abruptly increased starting about 1940, whereas at Port Henry the increase occurred a century earlier. In both cores, concentrations fell back to earlier levels around 1970–80. When

Please cite this article as: M. L. Ostrofsky, S. N. Levine and A. Lini, Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec), Journal of Great Lakes Research, https://doi.org/10.1016/j.jglr.2020.07.010

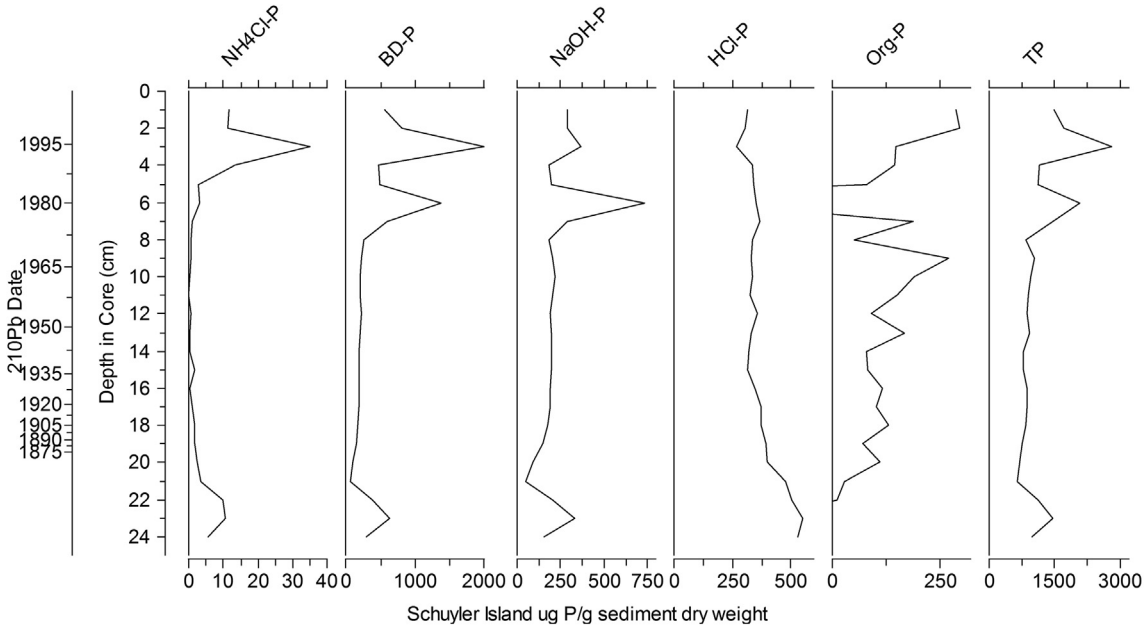

Fig. 10. Stratigraphic distribution of P species in Schuyler Island core. Units as in Fig. 2.

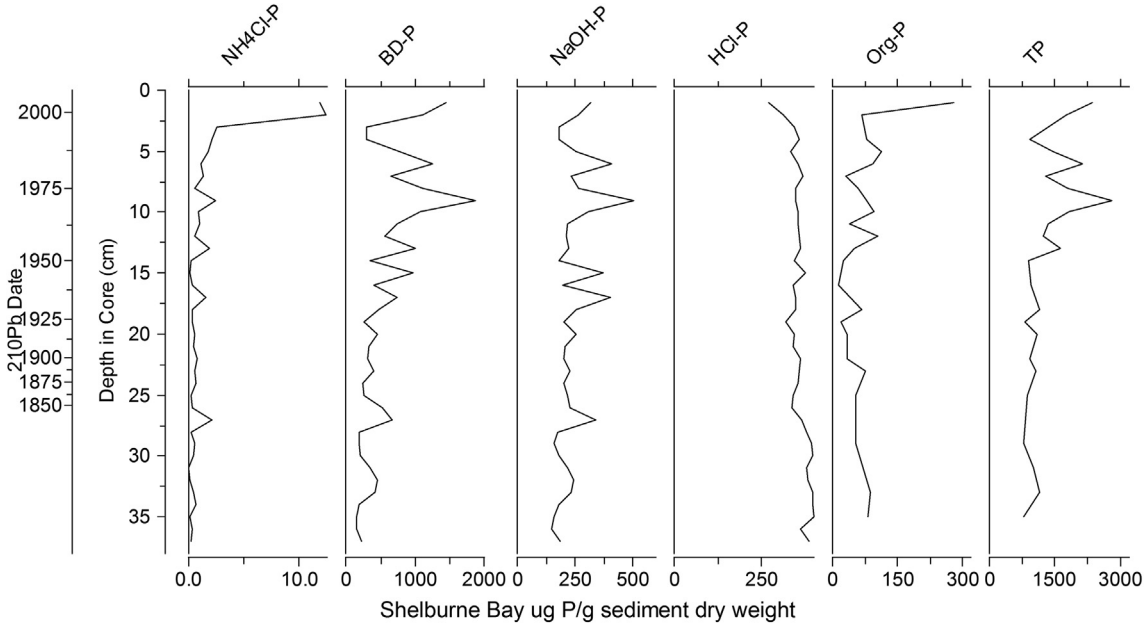

Fig. 11. Stratigraphic distribution of P species in Shelburne Bay core. Units as in Fig. 2.

HCl-P was expressed as a percentage of total sediment P, it was the dominant fraction in all cores historically, only decreasing in the recent sections in the core as BD-P increased.

HCl-extractable P represents P bound in apatite, largely of detrital origin (e. g., Lucas et al., 2015). The formation of authigenic apatite would be limited in view of the low alkalinity and calcium concentrations in the four regions of the lake where cores were obtained, due to a large portion of the watershed lying on crystalline silicate rocks of the Adirondack and Green Mountains. All regions of the lake except the South Lake have alkalinities of 50 mg·L^{-1} or less and calcium concentrations <20 mg·L^{-1} (LCBC) classifying them as "soft" (Biesecker and George, 1966). No whitings have been observed in Lake Champlain by the crew of the RV Melosira between 1966 and 2011 (R. Furbush, Captain, RV Melosira, University of Vermont, personal communication 2019), and the calculated calcium carbonate saturation indices (Kufel and Rymuza, 2014) ranged from 0.07 to 0.39, well below the threshold for calcite precipitation. These indices were calculated using the median values of Ca, alkalinity, and pH reported for sampling stations nearest our core sites (LCBC). Calcium concentrations within the sediments are also low, <1% by weight (Lini, unpublished data).

Because HCl-P is largely detrital, permanently bound (Rydin, 2000), and non-mobile (Ostrofsky, 2012), it is a reliable proxy for paleolimnological interpretations. For this reason, Hiriart-Baer et al. (2011) have suggested that increasing contributions of HCl-P indicate land-use changes that favor the export of apatite by way of erosion from agricultural landscapes to streams and ulti-

Please cite this article as: M. L. Ostrofsky, S. N. Levine and A. Lini, Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec), Journal of Great Lakes Research, https://doi.org/10.1016/j.jglr.2020.07.010

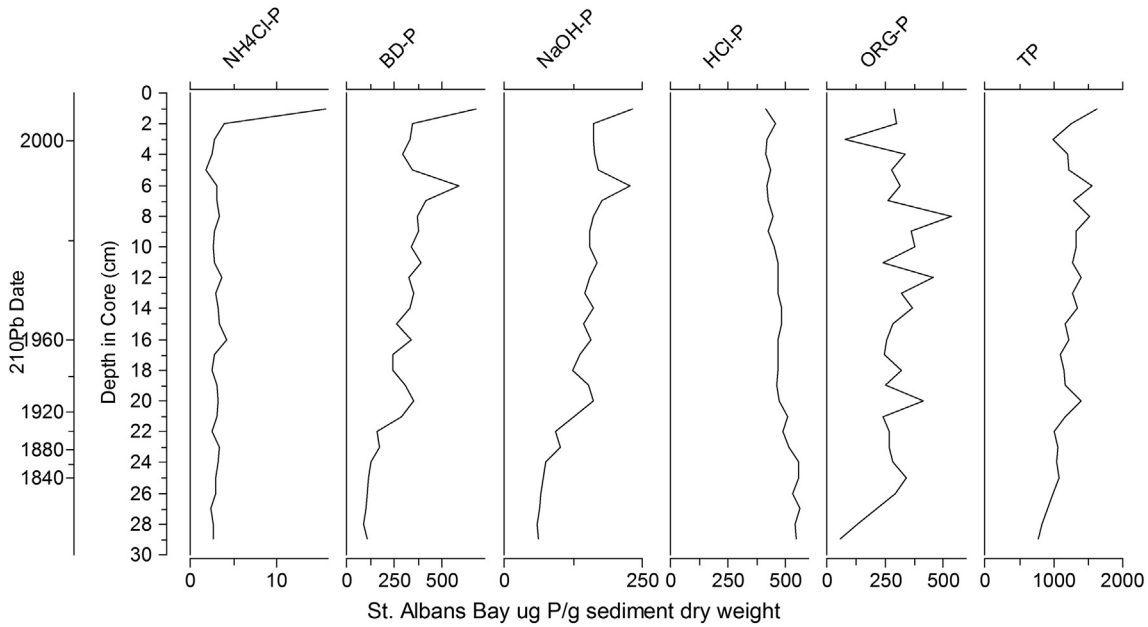

Fig. 12. Stratigraphic distribution of P species in St. Albans Bay core. Units as in Fig. 2.

mately lakes, consistent with the findings of Filippelli et al. (2010) from Laguna Zoncho and of Norton et al. (2011) from Sargent Mountain Pond as previously noted.

Org-P was not measured directly but calculated as the difference between TP and the sum of the inorganic fractions. We acknowledge that this fraction also contains some refractory mineral P not extracted in the previous steps; however, in eight of the eleven cores, Org-P was significantly correlated ($p < 0.001$) with estimates of total organic matter based on our %C data (Levine et al., 2012; 2018). The exceptions were cores from Savage Island, Shelburne Bay, and St Albans Bay ($0.1 < p < 0.2$). Org-P contributed between 5 and 25% of total sediment P. In six of the cores (Elm Point, Shelburne Bay, Cheney Point, Savage Island, Missisquoi Bay, Port Henry) there was a surface or near-surface increase in Org-P. Concentrations were invariably greater near the core surface but rapidly decreased with depth due to rapid breakdown of much labile organic matter during early diagenesis (Hupfer et al., 1995). The persistence of organic matter throughout the deeper sedimentary profile has been used by many authors (e. g., Hiriart-Baer et al., 2012) to suggest that microbial oxidation is much reduced due to low concentrations of oxygen and alternate electron acceptors.

We assumed that below the sediment surface spike in TP and component P species that their concentrations were relatively stable. Carey and Rydin (2011) argue that there exists a stabilization depth, a depth at which phosphorus diagenesis processes have stabilized. This depth is below the surface spike in concentrations.

Accumulation rates

To facilitate comparisons among the cores, we calculated accumulation rates of the three P species least likely to be affected by post-depositional mobility (Ostrofsky, 2012) as the product of the P species concentration (μg P g^{-1} sediment dry weight) and the sediment accumulation rates ($g \cdot cm^{-2} \cdot yr^{-1}$) from ^{210}Pb analysis (Levine et al., 2012; 2018).

The decadal average accumulation rates of NaOH-P (Fig. 13a) on a common time axis for the eleven cores all show increases toward the surface sediment with only slight declines noted at Schuyler Island and Shelburne Bay. There is a surge in accumulation around the turn of the 20th century in Inner Malletts Bay. Increases in accumulation rates may be, in part, a consequence of regional acidic precipitation mobilizing aluminum in soils, leading to increased particulate Al deposition in lake sediments where Al is a strong competitor for P released from Fe under reducing conditions (Huser and Rydin, 2005). We note that the damaging effects of acid precipitation were first documented in the Green and Adirondack Mountains in the Lake Champlain watershed (Siccama et al., 1982). There are conspicuous anomalous peaks in accumulation rate in the Juniper Basin and Outer Malletts Bay cores that may be a consequence of a devastating flood in 1927 in which up to 24 cm of rain fell over a 2-day period on already saturated soils in central Vermont. The subsequent flooding washed out 1285 bridges and countless kilometers of roads and railroads. Cores lacking this spike in NaOH-P accumulation rates are sites some distance from major affected tributaries.

Fig. 13b shows the decadal average accumulation rates of HCl-P. Patterns here are more varied, but in most cases it is clear that in spite of gradually falling concentrations in the sediments over most or all of the record available (Figs. 2–12), the accumulation rate has generally increased over time starting mid-20th century in Elm Point, Port Henry, and St. Albans Bay cores, and a decade or two earlier in the Inner Malletts Bay, Shelburne Bay, and Schuyler Island cores. In five of these cores accumulation rates have fallen in the most recent sediments whereas in St. Albans and Missisquoi Bay cores the accumulation rate remains high or continues to increase. Both latter cores are from areas most affected by intensified agriculture.

Finally, accumulation rates of Org-P (Fig. 13c) show increases from the oldest to the most recent sediments of all cores except Juniper Basin and Savage Island where the sedimentary records are too compressed to draw reliable conclusions. In almost all of the remaining cores, Org-P and HCl-P accumulation rates increase in tandem from pre-settlement to modern times. The two exceptions, Inner Malletts Bay and Port Henry cores, show peak HCl-P accumulation rates in the early- and mid- 20th century, respectively, but Org-P accumulation rates increasing only in the most recent samples.

In no case could accumulation rates be calculated for the pre-settlement period due to the lack of ^{210}Pb dates before the begin-

Please cite this article as: M. L. Ostrofsky, S. N. Levine and A. Lini, Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec), Journal of Great Lakes Research, https://doi.org/10.1016/j.jglr.2020.07.010

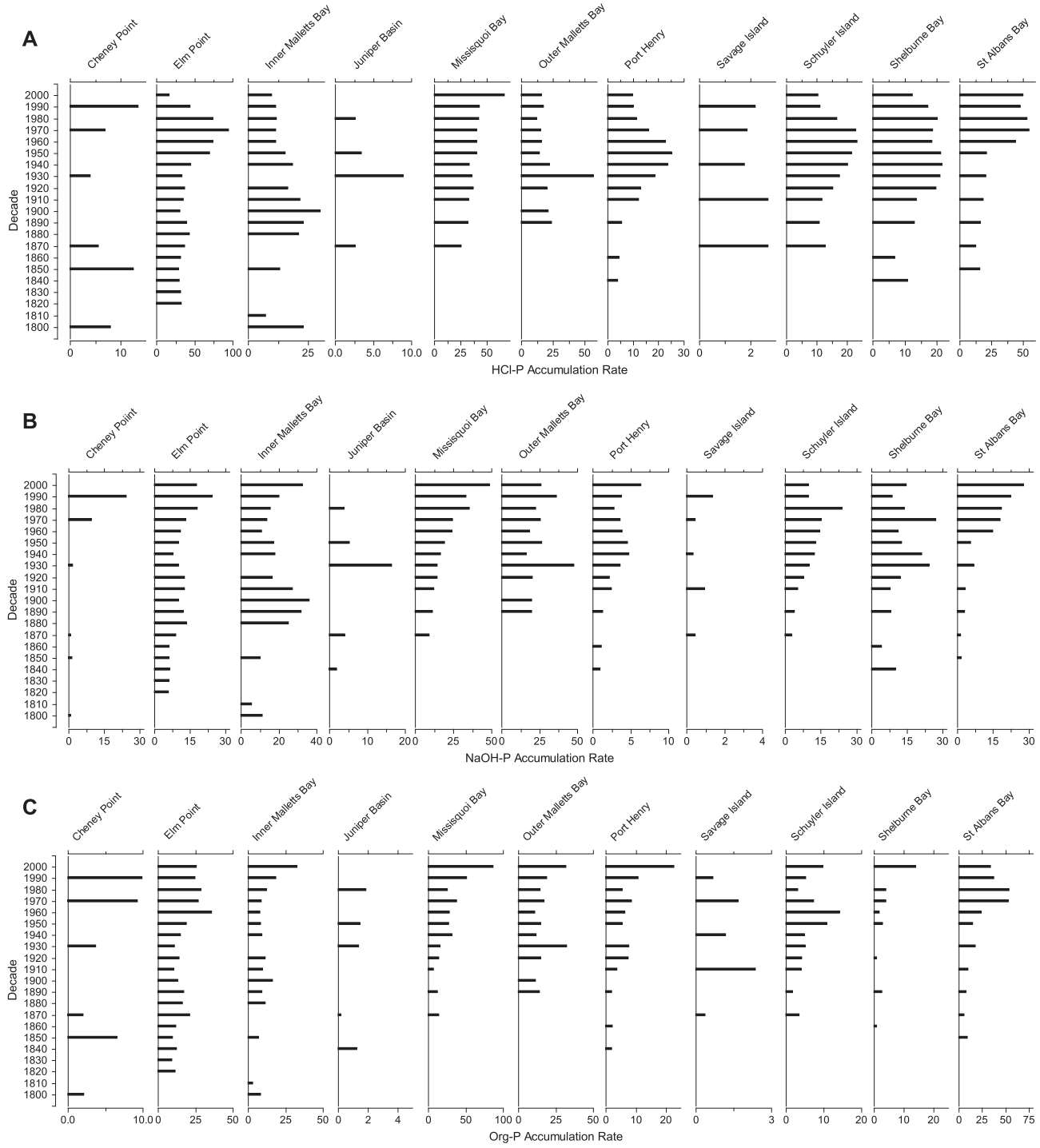

Fig. 13. Decadal average of P species accumulation rate (μg P·cm^{-2}·yr^{-1}) with all cores shown on a common time axis. Panel A: NaOH-P; Panel B: HCl-P; Panel C: Org-P.

ning of the 19th century. It is clear, however, that accumulation rates for these three P species are substantially greater in more recent sediments than in the past.

Intervals of cultural development

Pre-settlement (before 1770)

Five of the eleven cores (Cheney Point, Inner Malletts Bay, Juniper Basin, Port Henry, and Savage Island) contained sediment from the pre-settlement period before deforestation and agriculture. These sections of each core had uniformly low concentrations of total sediment P and of each of the P fractions. Mean total sediment P concentrations ranged from 700 (Cheney Point) to 1200 (Inner Malletts Bay) μg P g^{-1} sediment dry weight. Among the P fractions, HCl-P was the least variable, ranging from 350 to 550 μg P g^{-1}. The remaining fractions were in lower concentrations with BD-P ranging from 15 to 350 μg P g^{-1}, NaOH-P from 60 to 300 μg P g^{-1}, and Org-P from 70 to 170 μg P g^{-1}. In all cases during this pre-settlement period, HCl-P was the largest fraction, making up over 60% of total sediment P in the Cheney Point, Port Henry, and Savage

Please cite this article as: M. L. Ostrofsky, S. N. Levine and A. Lini, Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec), Journal of Great Lakes Research, https://doi.org/10.1016/j.jglr.2020.07.010

Island cores and 35% in both Inner Malletts Bay and Juniper Basin cores.

Early Settlement (1770–1870)

During this early settlement period, from the resolution of European territorial claims to the approximate date of maximum deforestation in the Lake Champlain watershed, the population in the basin increased from 4000 to about 240,000 with most involved in farming and logging. During this time there was very little change in concentrations of any P fractions in nine of the eleven cores. These results are consistent with the absence of responses in the concentrations of other chemical proxies (total nitrogen, % organic C, biogenic Si) and photosynthetic pigments (chlorophyll-α, β-carotene) presented in Levine et al. (2012; 2018). The exceptions included an increase in Org-P in the St. Albans Bay core and the beginnings of an increase in both HCl-P and NaOH-P in the Port Henry core. Only in the St Albans core, there is weak evidence for increases in pigments. It is during this interval where we anticipated increases in HCl-P and Org-P in all cores as forest clearing for agriculture increased erosion and transport of humic forest soils and apatite minerals to the lake. During this interval there was no significant increase in sediment accumulation rate (Levine et al., 2012, 2018) over pre-settlement rates in eight of the eleven cores, the exceptions being the cores from Elm Point, Inner Malletts Bay, and Outer Malletts Bay where sediment accumulation rates started to increase around 1850. There are at least two possible explanations for this apparent delay. The first is that eroded particles from anthropogenically modified watersheds can be retained in river channels and in flood plains for considerable lengths of time before entering lakes. Beach (1994) examined three watersheds in Minnesota drained by 3rd to 5th order streams and determined that no more than 13–36.5% of all sediments had travelled more than 25 km downstream in 137 years. Meade et al. (1990) found that less than 10% of eroded soils were exported out of the basin by Coon Creek, Wisconsin, and in their review of the literature on sediment storage in streams concluded that 70–80% of the sediment eroded from land surfaces is stored in rivers and floodplains and that retention times may be on the order of centuries to millennia. Chen et al. (2015) estimated that 8 – 58% of annual TP export from six catchments in eastern China was "legacy" P and suggested a continual yield of 0.04 – 1.71 kg $P \cdot ha^{-1} \cdot yr^{-1}$ for the next 16 – 100 years. There is a considerable area of lowlands between the Lake Champlain and the foothills of the Green Mountains. The four largest tributaries to the lake, all in Vermont, combined make up 47% of the lake's total watershed area. These tributaries, the Winooski R., Otter Creek, the Missisquoi R. and the Lamoille R., have gradients of only 1.52, 1.71, 1.50, and 1.89 m/km, respectively over the last 81, 97, 62, and 65 km, respectively, before entering the lake. In the lower reaches all of these rivers are sinuous in mature channels. These same lowlands were most conducive to forest removal and agricultural development. For the most part, the smaller tributaries on the New York side do have steeper gradients due to the nearness of the Adirondack foothills, but as a consequence there is less level arable land for agriculture, the exception being the watershed of the Great Chazy River that enters the lake less than eight km from the lake's outlet to the Richelieu R. Wigham (1970) presents data showing a precipitous decrease in sediment production (transport) in rivers with increasing watershed size. The above four Lake Champlain tributaries have watershed areas ranging from 2000 to 2800 km^2. This decrease is attributed to wider flood plain areas for deposition and bed storage. Retention of P in river channels and flood plains contribute to "legacy" P that hampers lake remediation efforts (Jarvie et al., 2013). A second possible reason is that prior to the mid-20th century most Champlain valley farms were small and un-mechanized, having a much smaller impact than current industrial farms with greater acreage under tillage and larger herd size.

Mid-Settlement (1870 – 1945)

This interval extends from the date of maximum forest clearance and the onset of gradual afforestation as unproductive hill farms were abandoned, to the advent of commercial inorganic fertilizers following WWII. During this interval the basin population increased from 240,000 to 350,000 although farms remained small and largely unmechanized. In most cores there was no evidence for any significant increases in either P species concentrations or accumulation rates. Exceptions were conspicuous spikes in NaOH, HCl, and Org-P accumulation in Outer Malletts Bay, a peak in NaOH and HCL-P accumulation consistent with increased sediment accumulation (Levine et al., 2018) in Inner Malletts Bay, and very gradual increases in P species concentrations in St Albans and Missisquoi Bays and at Port Henry. In spite of these modest and inconsistent increases in P species concentrations and accumulation rates other chemical proxies and pigments increased in all cores, especially in Missisquoi, St Albans, and Outer Malletts Bays (Levine et al., 2012; 2018). Here our expectations for decreasing HCl-P consistent with afforestation was tempered by the increased population largely occupied in agriculture, and in increased erosion.

Modern (1945 – present)

This interval is characterized by increased urbanization, industrialization of agriculture, and continued afforestation. With the exception of HCl-P the concentrations of all P species increased during this period, often sharply, and all cores showed markedly higher concentrations in the top few cm. Sediment accumulation rates showed large increases during this time at the St. Albans Bay and Missisquoi Bay sites, but showed no further increases over the previous period at most other locations (Levine et al., 2012; 2018). Sediment accumulation rates decreased at Port Henry, Shelburne Bay, and Schuyler Island. HCl-P accumulation rates showed increases over the previous interval only at Missisquoi Bay and Cheney Point. At other locations HCl-P flux held steady or decreased compared with the previous period. NaOH-P accumulation rates increased at most locations. Other chemical proxies and pigments increased in all cores, with very large increases in Missisquoi, St Albans, and the two Malletts Bay cores. These observations suggest that changes in farming practices were having a large effect on erosion and export of sediment and HCl-P from agricultural landscapes only where practices were most intense; whereas, 70% deforestation in the previous century had only minimal effect.

The changes in sedimentary P speciation are summarized across the four intervals of development (Fig. 14). There has been little change in any core over time in either NaOH-P or Org-P as measured as a percent of total P. On the other hand, there has been a decline, often precipitous, in the contribution of HCl-P that is matched with a corresponding increase in BD-P in all cores.

There have been considerable changes in land use/cover in the Lake Champlain basin over the past two and a half centuries. Early settlement began near the end of the 18th century with subsistence farming and logging as principal commercial activities with attendant deforestation that reached its peak at the end of the 19th century. Since then, abandonment of unprofitable hill farms and alternate employment opportunities allowed afforestation, but this was accompanied by increased population growth and urbanization, and more recently, the industrialization of agriculture characterized by larger herd size and importation of fertilizers and feed grains. Based on these changes we anticipated a clear sedimentary record of trophic changes in Lake Champlain. However, analysis of both chemical and biological proxies indicated little change during the century-long early settlement period (1770–1870) from either concentrations or accumulation rates measured

Please cite this article as: M. L. Ostrofsky, S. N. Levine and A. Lini, Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec), Journal of Great Lakes Research, https://doi.org/10.1016/j.jglr.2020.07.010

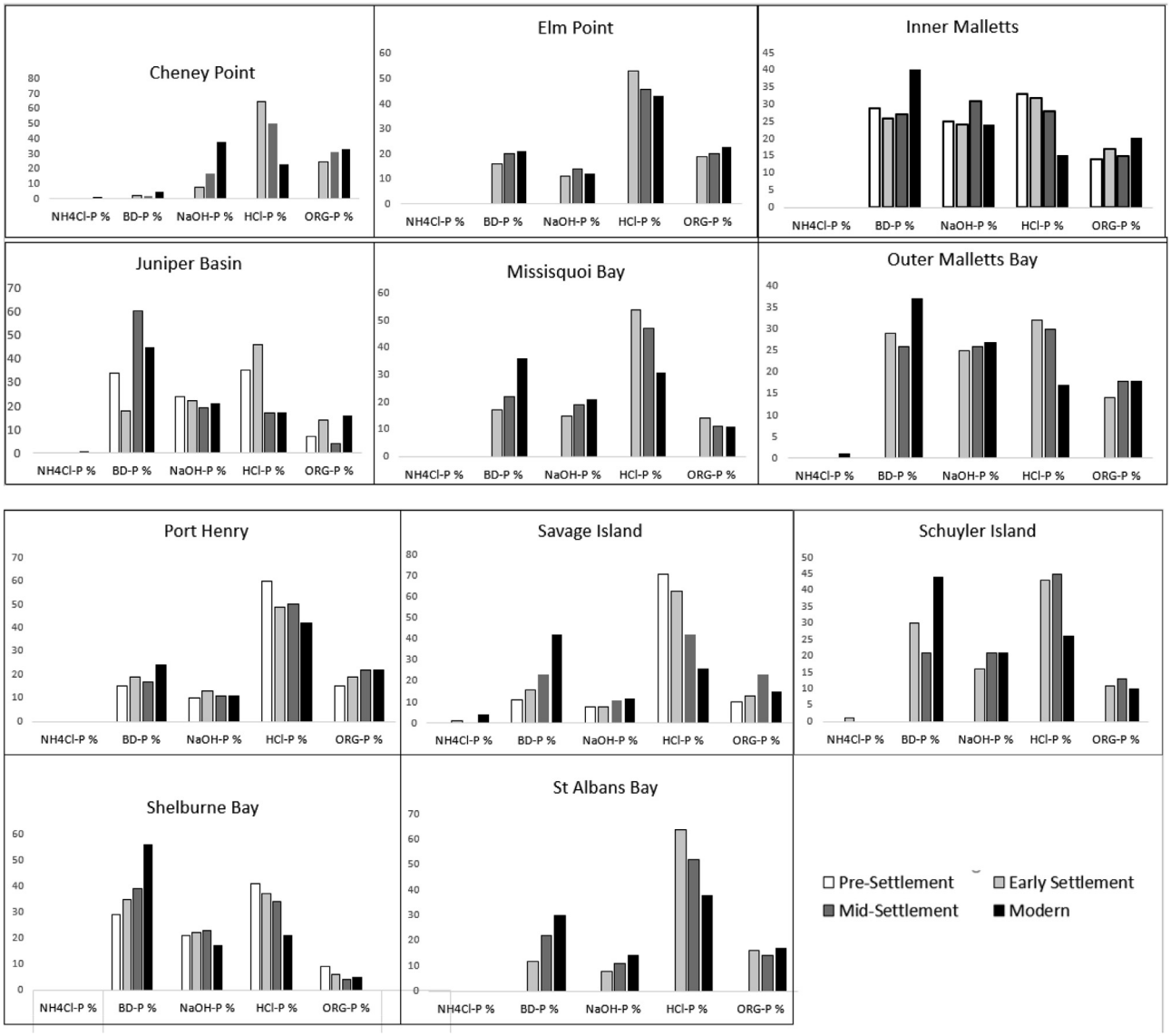

Fig. 14. P species as a percentage of total P averaged for each of the four development intervals (pre-settlement – before 1770, Early Settlement – 1770–1870, Mid-Settlement – 1870–1945, and Modern – 1945-present). Note scale changes on Y axis.

during the pre-settlement period. Sediment total P concentrations showed no significant change from pre-settlement values until the beginning of the modern period (1945). Sediment total P accumulation increased at only a few sites (Inner and Outer Malletts Bay and Elm Point), but these increases were closely tied to increased sedimentation rates rather than changes in concentration (Levine et al., 2018). Data presented by Filippelli et al. (2010) and Norton et al. (2011) suggested that lake sediments accumulating in deforested landscapes would show increases in HCl-P with corresponding decreases in NaOH-P and that these trends would be reversed with afforestation. In all of the Lake Champlain cores HCl-P concentrations were stable across two centuries of marked land use changes, and showed significant declines in percent contribution to total P. In most cores, NaOH-P increased in concentration only in the modern period. These results are similar to those of Tõnno et al. (2013) where neither HCl-P nor NaOH-P increased in cores from Lake Võrtsjärv, Estonia in spite of accelerated urbanization and intensification of agriculture in the watershed. We conclude that in Lake Champlain the analysis of P fractions in the sedimentary record is of limited use in revealing historical trends in trophic status.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The USGS Water Centers Program and NOAA SeaGrant (Emerging Threats to Lake Champlain) funded this project. H. Burgess-Grant, H. Carr, G. Druschel, N. Kamman, E. Marsden, E. Ostrofsky, and L. Schwartig-Miller assisted in collecting and sectioning the cores. We thank two anonymous reviewers for their valuable suggestions to improve the manuscript.

References

Albers, J., 2000. Hands on the Land: A History of the Vermont Landscape. MIT Press, Cambridge Mass.
Andersen, J.M., 1976. An ignition method for determination of total phosphorus in lake sediments. Water Res. 10, 329–331.

Please cite this article as: M. L. Ostrofsky, S. N. Levine and A. Lini, Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec), Journal of Great Lakes Research, https://doi.org/10.1016/j.jglr.2020.07.010

Anschutz, P., Zhong, S.J., Sundby, B., Mucci, A., Gobei, l C, 1998. Burial efficiency of phosphorus and the geochemistry of iron in continental margin sediments. Limnol. Oceanogr. 43, 53–64.
Beach, T., 1994. The fate of eroded soil: Sediment sinks and sediment budgets of agrarian landscapes in southern Minnesota, 1851–1998. Ann. Assoc. Amer. Geogr. 84, 5–28.
Biesecker, J. E. and George, J. R. 1966. Stream quality in Appalachia as related to coal-mine drainage, 1965. Geological Survey Circular 526. Washington.
Boyle, J.E., 2007. Loss of apatite caused by irreversible early-Holocene lake acidification. Holocene 17, 543–547.
Carey, C.C., Rydin, E., 2011. Lake trophic status can be determined by the depth distribution of sediment phosphorus. Limnol. Oceanogr. 56, 2051–2063.
Carignan, R., Flett, R.J., 1981. Postdepositional mobility of phosphorus in lake sediments. Limnol. Oceanogr. 26, 361–366.
Chen, C.R., Condron, L.M., Xu, Z.H., 2008. Impacts of grassland afforestation with coniferous trees on soil phosphorus dynamics and associated microbial processes: A review. For. Ecol. Manag. 255, 396–409.
Chen, D., Hu, M., Guo, Y., Dahlgren, A., 2015. Influence of legacy phosphorus, land use, and climate change on anthropogenic phosphorus inputs and riverine export dynamics. Biogeochem. 123, 99–116.
Davidson, T.A., Jeppesen, E., 2013. The role of palaeolimnology in assessing eutrophication and its impact on lakes. J. Paleolimnol. 49, 391–410.
Engstrom, D.R., Schottler, S.P., Leavitt, P.R., Havens, K.E., 2006. Reevaluation of the cultural eutrophication of Lake Okeechobee using multiproxy sediment records. Ecol. Appl. 16, 1194–1206.
Filippelli, G.M., Souch, C., Horn, S.P., Newkirk, D., 2010. The pre-Colombian footprint on terrestrial nutrient cycling in Costa Rica: insights from phosphorus in a lake sediment record. J. Paleolimnol. 43, 843–856.
Garcia-Montiel, D.C., Neill, C., Melillo, J., Thomas, S., Steudler, P.A., Cerri, C.C., 2000. Soil phosphorus transformations following forest clearing for pasture in the Brazilian Amazon. Soil Sci. Soc. Am. J. 64, 1792–1804.
Gikuma-Njuru, P., Hecky, R.E., Guildford, S.J., 2010. Surficial sediment phosphorus fractions along a biogeochemical gradient in Nyanza (Winam) Gulf, northeastern Lake Victoria and their possible role in phosphorus recycling and internal loading. Biogeochem. 97, 247–261.
Grossman, E.B., Mladenoff, D.J., 2008. Farms, fires, and forestry: Disturbance legacies in the soils of the Northwest Wisconsin (USA) Sand Plain. For. Ecol. Manag. 256, 827–836.
Haviland, W.A., Power, M.W., 1994. The Original Vermonters, Native Inhabitants. Past and Present. University Press of New England, Hanover, NH.
Henson, E.B., Gruendling, G.K., 1977. Trophic status and phosphorus loading of Lake Champlain. Ecological Research Series 600/3-77-106, U. S. Environmental Protection Agency, Corvallis, OR.
Hiriart-Baer, V.P., Milne, J.E., Marvin, C.H., 2011. Temporal trends in phosphorus and lacustrine productivity in Lake Simcoe inferred from lake sediment. J. Great Lakes Res. 37, 764–771.
Hiriart-Baer, V.P., Milne, J.E., Marvin, C.H., 2012. Response to comment on 'Temporal trends in phosphorus and lacustrine productivity in Lake Simcoe inferred from lake sediment'. J. Great Lakes Res. 38, 830–833.
Hupfer, M., Gachter, R., Giovanoli, R., 1995. Transformation of phosphorus species in settling seston and during early sediment diagenesis. Aquat. Sci. 57, 305–324.
Huser, B.J., Rydin, E., 2005. Phosphorus inactivation by aluminum in Lakes Gårdsjön and Härsvatten sediment during the industrial acidification period in Sweden. Can. J. Fish. Aquat. Sci. 62, 1702–1709.
Jarvie, H.P., Sharpley, A.N., Spears, B., Buda, A.R., May, L., Kleinman, P.J.A., 2013. Water Quality Remediation Faces Unprecedented Challenges from "Legacy Phosphorus". Env. Sci. Technol. 47, 8997–8998.
Juggins, S., 2013. Paleolimnological transfer functions: new paradigm or sick science? J. Quat. Res. 64, 20–32.
Juggins, S., Anderson, N.J., Ramstack Hobbs, J.M., Heathcoate, A.J., 2013. Reconstructing epilimnetic total phosphorus using diatoms: statistical and ecological constraints. J. Paleolimnol. 49, 373–390.
Kisand, A., 2005. Distribution of sediment phosphorus fractions in hypertrophic strongly stratified Lake Verevi. Hydrobiol. 547, 33–39.
Kopáček, J., Borovec, J., Heizlar, J., Ulrich, K.-U., Norton, S.A., Amirbahman, A., 2005. Aluminum control of phosphorus sorption by lake sediments. Environ. Sci. Technol. 39, 8784–8789.
Kufel, L., Rymuza, K., 2014. Comparing the effect of phytoplankton and charophyte on calcite precipitation in lake water: experimental approach. Polish J. Ecol. 62, 431–439.
LCBP. Lake Champlain Basin Program. www.lcbp.org/
Levine, S.N., Lini, A., Ostrofsky, M.L., Bunting, L., Burgess, H., Leavitt, P.R., Reuter, D., Lami, A., Guilizzoni, P., Gilles, E., 2012. The eutrophication of Lake Champlain's northeastern arm: Insights from paleolimnological analyses. J. Great Lakes Res. 38, 35–48.
Levine, S.N., Lini, A., Ostrofsky, M.L., Burgess-Grant, H., Lami, A., Collyer-Gilles, E., Reuter, D., Schwarting-Miller, L., Kamman, N., 2018. The relative roles of point and nonpoint phosphorus sources in the eutrophication of Lake Champlain as recorded in sediment cores. J. Great Lakes Res. 44, 1043–1056.
Lucas, B.T., Liber, K., Doig, L.E., 2015. Spatial and temporal trends in reservoir physicochemistry and phosphorus speciation within Lake Diefenbaker, a Great Plains reservoir, as inferred from depositional sediments. J. Great Lakes Res. 41, 67–80.
Łukawska-Matuszewska, K., Vogt, R.D., Xie, R., 2013. Phosphorus pools and internal loading in a eutrophic lake with gradients in sediment geochemistry created by land use in the watershed. Hydrobiol. 713, 183–197.
Manley, T.O., Hunkins, K.L., Saylor, J., Miller, G., Manley, P.L., 1999. Aspects of summertime and wintertime hydrodynamics of Lake Champlain, in: Manley, T. O., Manley, P. L. (Eds.), Lake Champlain in Transition: From Research toward Restoration. American Geophysical Union Monograph, Water Science and Application 1, pp. 67-116.
Mayer, T., Simpson, S.L., Thorleifson, L.H., Lockhart, W.L., Wilkinson, P., 2006. Phosphorus geochemistry of recent sediments in the South Basin of Lake Winnipeg. Aquat. Ecosyst. Health Manag. 9, 307–318.
Meade, R. H., Yuzyk, T. R., Day, T. J., 1990. Movement and storage of sediment in rivers of the United States and Canada, in: Wolman MG, Riggs HC (Eds.). Surface water hydrology. The Geology of North America Vol. 0-1. Geological Society of America, Bolder CO.
McColl, R.H.S., 1977. Chemistry of sediments in relation to trophic conditions of eight Rotorua lakes. N. Z. J. Mar. Freshwat. Res. 11, 509–523.
Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27, 31–36.
Myers, G.E., Gruendling, G.K., 1979. Limnology of Lake Champlain. Champlain Basin Study. New England River Basin Commission, Burlington, VT.
Nõges, P., Kisand, A., 1999. Horizontal distribution of sediment phosphorus in shallow eutrophic Lake Võrtsjärv (Estonia). Hydrobiol. 408 (409), 167–174.
Noll, M.R., Szatkowski, A.E., Magee, E.A., 2009. Phosphorus fractionation in soil and sediments along a continuum from agricultural fields to nearshore lake sediments: Potential ecological impacts. J. Great Lakes Res. 35, 56–63.
Norton, S.A., Perry, R.H., Saros, J.E., Jacobson Jr., G.L., Fernandez, I.J., Kopáček, J., Wilson, T.A., SanClements, M.D., 2011. The controls on phosphorus availability in a Boreal lake ecosystem since deglaciation. J. Paleolimnol. 46, 107–122.
Nürnberg, G.K., 1984. The prediction of internal phosphorus load in lakes with anoxic hypolimnia. Limnol. Oceanogr. 29, 111–124.
Nürnberg, G.K., 1988. Prediction of phosphorus release rates from total and reductant-soluble phosphorus in anoxic lake sediments. Can. J. Fish. Aquat. Sci. 45, 453–462.
Olila, O.G., Reddy, K.R., Harris, W.G., 1995. Forms and distribution of inorganic phosphorus in sediments of two shallow eutrophic lakes in Florida. Hydrobiol. 302, 147–161.
Ostrofsky, M.L., 1987. Phosphorus species in the surficial sediments of lakes of eastern North America. Can. J. Fish. Aquat. Sci. 44, 960–966.
Ostrofsky, M.L., 2012. Differential post-depositional mobility of phosphorus species in lake sediments. J. Paleolimnol. 48, 559–569.
Ostrofsky, M.L., Marbach, R.L., 2019. Predicting internal phosphorus loading in stratified lakes. Aquat. Sci. 81, 18.
Ostrofsky, M.L., McGee, G.G., 1991. Spatial variation in the distribution of phosphorus species in the surficial sediments of Canadohta Lake, Pennsylvania: implications for internal phosphorus loading estimates. Can. J. Fish. Aquat. Sci. 48, 233–237.
Ostrofsky, M.L., Osborne, D.A., Zebulske, T.J., 1989. Relationship between anaerobic sediment phosphorus release rates and sedimentary phosphorus species. Can. J. Fish. Aquat. Sci. 46, 416–419.
Penn, M.R., Auer, M.T., VanOrman, E.L., Korienek, J.J., 1995. Phosphorus diagenesis in lake sediment: investigations using fractionation techniques. Mar. Freshwat. Res. 46, 89–99.
Peters, R.H., 1986. The role of prediction in limnology. Limnol. Oceanogr. 31, 1143–1159.
Pettersson, K., Istvanovics, V., 1988. Sediment phosphorus in Lake Balaton – forms and mobility. Arch. Hydrobiol. Beih. Ergebn. Limnol. 30, 25–41.
Petticrew, E.L., Arocena, J.M., 2001. Evaluation of iron-phosphate as a source of internal lake phosphorus loadings. Sci. Tot. Environ. 266, 87–93.
Ruban, V., Demare, D., 1998. Sediment phosphorus and internal phosphate flux in the hydroelectric reservoir of Bort-les-Orgues. France. Hydrobiol. 373 (374), 349–359.
Rydin, E., 2000. Potentially mobile phosphorus in Lake Erken sediment. Wat. Res. 34, 2037–2042.
Schelske, C.L., Hodell, D.A., 1995. Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication of Lake Erie. Limnol. Oceanogr. 40, 918–929.
Schindler, D.W., 2006. Recent advances in the understanding and management of eutrophication. Limnol. Oceanogr. 51, 356–363.
Schlesinger, W.H., 1991. Biogeochemistry: An Analysis of Global Change. Academic Press, San Diego, CA.
Shambaugh, A., 2008. Historical phytoplankton densities at Missisquoi Bay, Station 50. Lake Champlain Basin Program Report, Vermont ANR, Waterbury, VT.
Siccama, T., Bliss, M., Vogelmann, H.W., 1982. Decline of red spruce in the Green Mountains of Vermont. Bull. Torrey Bot. Club 109, 162–168.
Smeltzer, E., Shambaugh, A.D., Stangel, P., 2012. Environmental change in Lake Champlain revealed by long-term monitoring. J. Great Lakes Res. 38, 6–18.
Smith, L., Watzin, M.C., Druschel, G., 2011. Relating sediment phosphorus mobility to seasonal and diel redox fluctuations at the sediment-water interface in a eutrophic freshwater lake. Limnol. Oceanogr. 56, 2251–2264.
Søndergaard, M., Jensen, J.P., Jeppesen, E., 2001. Retention and internal loading of phosphorus in shallow, eutrophic lakes. The Scientific World 1, 427–442.
Søndergaard, M., Kristensen, P., Jeppesen, E., 1993. Eight years of internal phosphorus loading and changes in the sediment phosphorus profile of Lake Søbygaard. Denmark. Hydrobiol. 253, 345–356.
Søndergaard, M., Windolf, J., Jeppesen, E., 1996. Phosphorus fractions and profiles in the sediment of shallow Danish lakes as related to phosphorus load, sediment composition and lake chemistry. Wat. Res. 30, 992–1002.

Please cite this article as: M. L. Ostrofsky, S. N. Levine and A. Lini, Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec), Journal of Great Lakes Research, https://doi.org/10.1016/j.jglr.2020.07.010

Tõnno, I., Kirsi, A.-L., Freiberg, R., Alliksaar, T., Lepane, V., Kõiv, T., Kisand, A., Heinsalu, A., 2013. Ecosystem changes in large and shallow Võrtsjärv, a lake in Estonia – evidence from sediment pigments and phosphorus fractions. Boreal Environ. Res. 18, 195–208.

Trolle, D., Guangwei, Z., Hamilton, D., Luo, L., McBride, C., Zhang, L., 2009. The influence of water quality and sediment geochemistry on the horizontal and vertical distribution of phosphorus and nitrogen insediments of a large, shallow lake. Hydrobiol. 627, 31–44.

Walker, T.W., Syers, J.K., 1976. The fate of phosphorus during pedogenesis. Geoderma 15, 1–19.

Wigham, J.M., 1970. Sediment Transportation. In: Gray, D.M. (Ed.), Handbook on the Principles of Hydrology. Section XI, National Research Council of Canada.

Williams, J.D.H., Jaquet, J.-M., Thomas, R.L., 1976. Forms of phosphorus in the surficial sediment of Lake Erie. J. Fish. Res. Bd Can. 33, 413–429.

Please cite this article as: M. L. Ostrofsky, S. N. Levine and A. Lini, Spatial and temporal variation in sedimentary phosphorus species in Lake Champlain (Vermont, New York, Québec), Journal of Great Lakes Research, https://doi.org/10.1016/j.jglr.2020.07.010