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The relative roles of point and nonpoint phosphorus sources in the eutrophication of Lake Champlain as recorded in sediment cores

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Abstract

Thirteen sediment cores from Lake Champlain (Vermont-New York- Quebec) were analyzed for sediment accumulation rate and eleven indicators of trophic status to reconstruct eutrophication history and relate it to phosphorus inputs from soil erosion, urban point sources, and agricultural runoff including P extracted from phosphate ore and brought to the catchment in fertilizer and livestock feed. Although the catchment was severely deforested and grazed by sheep and cattle in the 19th century, ten of thirteen sites accumulated excess sediment only in the 20th century, a consequence of slow sediment transport through the catchment. Of the three sites that received extra sediment, one remained oligotrophic, while two exhibited mild eutrophication. All sites underwent eutrophication in the 20th century. Three reached their current trophic status before agriculture's intensification, while point-source P input was maximal (1950-1980), four stayed in the reference state until agriculture intensified in the 1970s, and six responded incrementally first to point and then to agricultural P input. Pigment accumulation rates diminished at the surface of seven cores, evidence that the 1990s expansion of P removal from point sources reduced phytoplankton biomass. Additional water quality improvement depends on P management at the catchment border to balance inputs and outputs, and thus avoid P accumulation in soil that saturates phosphate sorption capacity, increasing the proportion of runoff P that is highly-bioavailable orthophosphate. Erosion control is of lower priority because the P native to the catchment's soil is of relatively low bioavailability, and retention structures do not retain dissolved P.

Introduction

Eutrophication brought on by human activity continues to expand globally in freshwater despite increasingly aggressive management of phosphorus point and nonpoint sources (ILEC, 1994; US EPA, 2010). Where point sources contribute most excess P, eutrophication has been slowed, even reversed, through sewage diversion, phosphate precipitation from wastewater, and restrictions on the P content of detergents (Guillizoni et al., 2012; Schindler and Vallentyne, 2008; Søndergarrd et al., 2007), but today's P loading increasingly arises from nonpoint sources (ILEC, 1994; Søndergarrd et al., 2007; US EPA, 2010), and few lakes affected by non-point loading have been restored through their management alone (Jarvie et al., 2013; Jeppesen et al. 2005; US EPA 2010). Low success may be temporary if there are lag times between source manipulations and reduced P supply to phytoplankton associated with the nutrient's transport through the catchment (Cassell et al., 1995; Meals et al., 2010; Sharpley et al., 2003) or to the processing in the lake of biologically-unavailable dissolved organic and particulate P (DOP and PP) into orthophosphate (PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$; abbreviated PO_4), the P form that is transported across the phytoplankton cell membrane (Reynolds, 2006). In these circumstances, the lake will respond to the new catchment source output once legacy P has been removed from the catchment-lake system via outflow or burial in bottom sediment (Cassell et al., 1995; Meals et al., 2010; Sharpley et al., 2003). However, if the nonpoint sources targeted include substantial biologically-unreactive P, their management will not be as effective as the control of equal amounts of point-source P which is predominantly PO_4 (Dueñas et al., 2003), and is discharged directly into the phytoplankton habitat.

Historically, nonpoint source P has been largely in particulate (Meybeck, 1982; Reynolds and Davies, 2001) form from eroded soil and detritus although where wetlands are abundant, P may reside primarily in colloidal humus-metal complexes (DeHaan and DeBoer, 1986; Meili, 1992). Orthophosphate generally is scarce, except where runoff passes over exposed phosphate rock, because it sorbs readily to particles and is taken up by microorganisms and plants (Reddy et al., 2010; Reynolds and Davies, 2001; Sharpley et al., 2003). The average PO_4 content of stream flow may have increased, however, (Meybeck 1982; Seitzinger et al., 2005) as a consequence of the liberal application of commercial fertilizer to urban-suburban landscapes and cropland, and wastewater discharge to streams following secondary, but not tertiary, treatment. Phosphate fertilizer and many industrial P products are manufactured from mined phosphate rock, which is crushed and acidified to release PO_4 (Gowarikar et al., 2009). Phosphate mining is relatively new, developed primarily after 1960 as part of agriculture's Green Revolution, which doubled food production globally over four decades, in part by increasing P supplementation of cropland to thirteen times the traditional rate (Tilman, 1999). With 11% of Earth's landmass cropland, the overall P demand has been high and most easily met through the manufacture of mineral phosphate (Gowarikar et al., 2009). By 2000, enough P was extracted from inert rock to increase the mass of the global P cycle by three- to five-fold (Falkowski et al. 2000; Smil 2000). The fate of this extra P may be pertinent to the eutrophication crisis that has recently emerged worldwide, and its effect likely most intense in agricultural areas (US EPA, 2010).

Only a portion of the P amendment to cropland is absorbed by the harvested crop; a larger portion is usually retained in the soil through sorption, microbial uptake and other mechanisms (Carpenter, 2005). Initially P immobilization may be nearly complete, but with repeated fertilizer addition, the soil retention sites saturate, so that newly introduced PO_4 can flush into overland flow or infiltrate to groundwater (Bennet et al., 2001; Carpenter, 2005; Daniels et al., 1998). Global soil surveys carried out around 2000, found P saturation in about

70% of cropland soil (MacDonald et al., 2010). The time needed for agricultural P to deplete soil sorptive capacity may explain why the eutrophication crisis in rural areas emerged in the 1980s or later (Gakstatter et al., 1978; Ryding et al., 1990; US EPA, 1990), decades after Hasler (1947) warned of the effects of domestic sewage influx on lake trophic status.

Much of the P captured in crops reaches agricultural soil as well, although generally in a different catchment, through the disposal of livestock manure and urban sewage sludge (biosolids) on farmland (Naylor et al., 2006; Pimentel and Pimentel, 2008). Underground septic systems, which handle roughly half of human waste in the United States (US Census Bureau, 2013), also rely on soil P retention capacity to protect groundwater from PO_4 input, and when operated for decades, eventually P-saturate the soil in leach fields (Gold and Sims, 2000). Moore et al. (2003) have documented the eutrophication of suburban Seattle lakes through septic P contamination of the groundwater, for example. Because animal wastes are alkaline, and hydroxyl ion competes with PO_4 for shared sorption sites on soil, their addition to soil reduces the overall P retention capacity as well as adding new P (Iyamuremye and Dick, 1996; Lijklema, 1980; Olila and Reddy, 1995).

The hypothesis that mined P is primarily responsible for surging lake eutrophication is currently popular (Bennet et al., 2001; Carpenter, 2005; Daniels et al., 1998), but challenged by the more traditional view that the P output from lake catchments is from internal sources. The global P cycle is, in fact, parsed into catchment units by the strong linkage of P transport to water flow, and mass balance studies indicate that soil erosion rates have been historically high in recent decades (Pimentel, 2006). The principal issue with this hypothesis is the uncertain bioavailability of soil sediment PP. Orthophosphate is the only P molecule small enough to be transported across cell membranes; therefore, PP must be transformed into soluble PO_4 before it can contribute to lake eutrophication. There are many processes in lakes that can accomplish this transformation, e.g. desorption, mineral dissolution, the decomposition of organic matter, and waste elimination from detritivores (Jensen and Andersen, 1992; Pettersson, 1998; Søndergaard et al., 2003). Each of these processes must occur as PP sinks through the water column, however, and may not be completed before the particulate matter is buried in bottom sediment. Furthermore, all are sensitive to environmental conditions that may or may not be favorable. For example, the dissolution of iron oxy-hydroxides with sorbed PO_4 occurs when the sediment-water interface is anoxic (Nürnberg, 1984), not if dissolved oxygen is abundant, and PO_4 desorption occurs when pH is rising, because OH^- and PO_4 compete for sorption sites, but is unlikely at neutrality (Lijklema, 1980; Olila and Reddy, 1995). In short, considerable information about lake ecology is needed to predict the impact of soil sediment loading to a lake on its level of primary production. Nonetheless, catchment P management based on the total P (TP) content of the P sources present is common practice.

The dynamics of sediment transport in overland flow and streams (Gordon et al., 2013; Leopold et al., 1995) also complicates catchment P management. Orthophosphate and dissolved P are fully integrated into water flow, and thus spend only a few days in runoff before spreading out into the surface waters of a downstream lake. By contrast, particles require the turbulent lift generated by high current velocity to travel in suspension or bedload traction. For many streams, this critical velocity is attained only during spring snowmelt and storm events and subsides quickly. Consequently, the average sized particle often spends much more time deposited on the stream bottom than in transit. For example, Beach (1994) examined the fate of soil eroded from three Minnesota catchments during a forest clear cut 137 years earlier, and found 63 to 87% of the eroded material downhill, but still in the parent catchment. The late start of the eutrophication crisis in lakes that do not have a point-source P influx might be explained by the addition of particle travel time to soil erosion that began acceleration in the middle of the 20th century.

Although eutrophication by P species other than PO_4 should be explored through experimentation, much can be learned ahead of time through the monitoring of lakes impacted by excess erosion or agricultural importation of P. Regular water sampling to monitor trophic status change has been available only since the 1960s, too short a time for some of the processes involving PP mobilization to play out. Consequently, a blend of paleolimnology and neolimnology is necessary, at least in the early stages of research when hypotheses about processes evolve. Sediments collect remnants of past environments that can be quantified in the dated layers of sediment cores (Batterbee and Bennion, 2012; Smol, 2008), and related to recorded land use events. In this work, we analyze thirteen sediment cores from Lake Champlain (Vermont, New York, Quebec) for indicators of trophic status, including total phosphorus (TP), total nitrogen (TN), organic carbon (OC), fossil pigments, biogenic silica (BSi), and diatoms, over up to three centuries. Initially settled by Europeans in the 18th century, the lake catchment was severely deforested and eroded in the 19th century before sewage discharge began around 1900. Reforestation occurred during the 20th century, and reductions in the P content of point sources began around 1980. The intensification of agriculture to include fertilizer and CAFOs (concentrated animal feeding operations) began in the 1970s, but has been especially intense since 1990. We have previously presented data for four cores analyzed from the lake's highly eutrophic and hydrologically isolated northeastern arm (Levine et al., 2012) and focus here on nine cores collected elsewhere. In the final discussion, we evaluate the trophic history of all thirteen study locations to reach conclusions about the roles the major nonpoint and point sources of P have had in driving an initially oligotrophic water body towards eutrophy. The land use history for the catchment, and physical, chemical and biological characteristics of the lake pertinent to the observations made here are provided in Electronic Supplementary Material (ESM) Appendix S1.

Methods

Core Acquisition and Sampling

Short cores were retrieved at the locations shown in Figure 1 using a gravity-corer fitted with a 2.5” OD PVC tube, wrapped in black plastic (for pigment preservation), and kept upright and cold during transport to the laboratory. After core stratigraphy was recorded, sediments were extruded at 1 cm intervals. Samples for pigments and diatoms were processed wet, while those for ^{210}Pb dating and geochemistry were freeze-dried and pulverized prior to analysis (details in Levine et al., 2012). The dry mass of each section was determined from its volume and bulk density, the latter measured by collecting precisely 1 cc of sediment into a syringe, drying and weighing the sample.

Chronology and Sediment Accumulation Rate Determination

Sediment chronology was determined using the ^{210}Pb gamma spectrometric method of Engstrom et al. (2006) and a constant rate of supply model (Appleby, 2001). This method is accurate for sediment up to 150 to 200 years old. To estimate sediment accumulation rates (SAR), the dried mass of each sediment layer was divided by the number of years required for deposition as indicated by the ^{210}Pb radio-chronology. The SAR value for the oldest datable ^{210}Pb layer was used to estimate the deposition dates of deeper segments.

Geochemistry

Organic carbon (OC) and total nitrogen (TN) were measured by combusting dried sediment in sealed tin capsules and releasing the gas formed into a CE Instruments NC 2500 elemental analyzer (details in Levine et al. (2012)). For total phosphorus (TP) measurement, sediment was combusted then treated with a hot HCl solution (Andersen, 1976), before its concentration was determined on an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) or by spectroscopy (Strickland and Parsons, 1968). TP was not analyzed for Cole Bay and Pt. Au Roche. Biogenic silica (BSi) measurement followed the procedure of DeMasters (1981) in which hot (85 °C) 1% sodium carbonate is added to powered sediment and the appearance of silica in solution measured over a time course. Silica concentrations were regressed against time to determine ambient concentration as the y-intercept of the resulting equation. The OC, TN, TP and BSi concentrations in sediment layers were multiplied by corresponding sediment accumulation rates (SAR) to estimate rates of mass accumulation (OCAR, NAR, PAR, and BSiAR, respectively).

Fossil Pigments

Forril pigment analysis began with the third core collected, Port Henry (after Cole Bay and Pt. Au Roche), which was analyzed at the University of Saskatchewan, Regina, using the method of Leavitt and Hodgson (2001). Samples from the remaining six cores were sent frozen to the CNR-IES facility in Pallanza-Verbania, Italy, where analysis followed the procedures of Lami et al. (2000). Both methods involve pigment extraction into a degassed mixture of organic solvents (acetone, methanol) and water under an inert N_2 atmosphere, filtration through 0.45-μm pore membrane filters, and injection into an HPLC system with a C18 column and operated in reversed phase for separation and detection of chlorophylls, carotenoids and their derivatives. Calibration was with pigments extracted from uni-algal cultures and separated by thin layer chromatography or standards provided by the U.S. Environmental Protection Agency. The compounds isolated included chlorophylls *a*, *b* and *c* and their derivatives, β-carotene (a total algae indicator), and carotenoids diagnostic of particular algal groups, e.g., alloxanthin for cryptophytes, diatoxanthin for diatoms and siliceous chrysophytes, echinenone for cyanobacteria (all types), and myxoxanthophyll for colonial cyanobacteria. The pigments that we provide data for here were both more abundant and more stable than alternative choices (Lami et al., 2000; Leavitt and Hodgson, 2001). Pigment concentrations were multiplied by rates of sediment accumulation to estimate their individual accumulation rates (μmol pigment/m^2/y).

Diatoms

Sediment for diatom analysis was clarified through treatment with hot H_2O_2 (30%) followed by soaking in CH_3COOH (95%) (Bates et al., 1978; Morley et al., 2004), and the cleaned frustules mounted on slides with Naphrax. At least 300 valves or stomatocysts were identified to the lowest taxonomic level possible and counted. Data are reported as species relative abundance, although only values for the five most common indicator species are shown in plots.

Data Presentation

To reduce the volume of data presented and avoid over-interpretation of inter-annual variations in the measured parameters, we present decadal means rather than the data from each core segment in our figures. The complete data set is available on request (slevine@uvm.edu). The data are further aggregated into periods representing reference conditions (1700-1850), large-scale soil erosion

(1850-1900), maximum point-source P influx (1950-1980), and the intensification of agriculture to include fertilizers and CAFOs (1980-2000). Correlation analysis (liner regression) was carried out on all pairs of variables, the results available on request (slevine@uvm.edu); here we consider only the chl *a* + pheo *a* AR- SAR relationship.

Results

Chronology and Stratigraphy

Excess ^{210}Pb activity was found in the upper layers of all cores, facilitating the dating of sections deposited since 1800 using the constant rate of supply(CRS) model. ESM Figure S1 shows inferred dates plotted against sediment depth. Dating error was low (SD, 0.1-3 y) for layers lain down after 1950, but increased down-core to 5-15 y SD around 1900, 10-40 y SD around 1850 and 25-40 y SD around 1800.

The stratigraphy of individual cores is described in Appendix S2. Common features pertinent to trophic history included a rust-colored organic floc at the top of each core, representing recent deposition under oxic conditions, and at depth, pre-eutrophication sediment consisting mostly of plain grey or olive grey clay (7 of 9 cores). Six of nine cores included sections with dark organic inclusions that were dissected to reveal decomposing plant detritus (Palmer, 2012), while one core, Cole Bay, was unique in including at these depths ten centimeters of black mud over an equal length of alternating layers of grey clay and black mud, before transition to grey clay only. Pt. Au Roche contained an intermediate (1907 to 2000) layer of greenish-grey gyttja with abundant plant microfibers. The cores with unusual basement layers were Outer Malletts Bay, which at its 1850 horizon changed deposition from coarse silt below to clay above, a transition that may be contemporaneous with the construction of a causeway at its northern boundary, and the Schuyler

Island core which ended with a stiff crust containing a machined object.

Sediment Accumulation Rates

Sediment mass accumulation rates (Figure 2A) were low and relatively constant through the 19th century at six of nine sites, averaging just 0.07 $kg/m^2/y$ at seiche-impacted Juniper Basin, up to 0.2 to 0.3 $kg/m^2/y$ at Port Henry, Cole Bay, Schuyler Island, Shelburne Bay, and Pt. Au Roche. Inner Malletts Bay was among the three cores that recorded an early SAR augmentation, first a minor two-fold increase (from 0.3 to 0.6 $kg/m^2/y$) during logging close to the shoreline between 1800 and 1820, and after 1850, gradual long-term increase to a 0.9-$kg/m^2/y$ peak at the turn of the 20th century. SAR increases over the latter half of the century occurred at Outer Malletts Bay and Elm Pt., as well, but peaked sooner, from the 1880s to 1890s, the maxima being 0.7 and 1.1 $kg/m^2/y$, respectively.

Juniper Basin sustained its SAR baseline below 0.1 $kg/m^2/y$ beyond the 19th century up to the time of core collection, with the exception of a brief excursion to 0.14 $kg/m^2/y$ during the 1920s to 1930s, when hurricanes severely eroded area streams. Pt. Au Roche's SAR also resisted change as its decadal mean rose very gradually from 0.3 to 0.4 $kg/m^2/y$ over all of the 20th century. However, following the dredging of nearby Cumberland Bay in 2000, its SAR increased abruptly to 0.7 $kg/m^2/y$. Shelburne Bay showed an SAR trajectory that spanned the 20th century, describing a flattened bell with a rate maximum of 0.5 to 0.6 $kg/m^2/y$ that continued from the 1920s through the 1980s. The trajectories at Port Henry and Schuyler Is. were more compressed, SAR increase beginning in the 1920s, and attaining brief maxima of 0.9 and 0.7 $kg/m^2/y$, respectively, during the 1960s.

SAR dynamics that hinted at in-lake as well as catchment influences were observed at the

Outer Malletts Bay, Elm Pt. and Cole Bay sites. Between 1850 and 1890, the SAR trajectories of the two cores from Malletts Bay were nearly identical. Subsequently, the two diverged, Inner Malletts Bay recorded a gradual rate decline after 1910 to a baseline of 0.4 kg/m^2/y after 1960; whereas Outer Malletts Bay maintained its SAR at about 0.6 kg/m^2/y henceforth, except for major diversions to 1.1 and 1.4 kg/m^2/y during the hurricane decades of the 1920s and 1930s, respectively. Elm Pt. followed its late-19th century SAR peak, with two more cycles of increase and decline in the 20th century, the new maxima, 1.3 kg/m^2/y in the 1910s and 1.0 kg/m^2/y in the 1960s. Curiously, Cole Bay, a few kilometers away, recorded similar cycles to Elm Pt. but offset in time so that the maxima and minima at the two sites were juxtaposed, as might occur if they share an unequally-distributed sediment source. Cole Bay's SAR maxima occurred in the 1950s and 2000s, both 1.1 kg/m^2/y.

Phosphorus

Total P (TP) concentration (Figure 2B) varied minimally in the 1700 to 1900 deposition of the Port Henry, Elm Pt., Schuyler Is., Juniper Basin, and Shelburne Bay cores, the range of means, 0.7 to 0.9 mg/g. The Malletts Bay cores were more P-rich over this interval, their period means around 1.1 mg/g, and a higher value, 1.3 mg/g, measured during 1800-1820 logging. The Schuyler Is. crust bore the most P, however, 1.4 mg/g. TP increased at all sites during all or a portion of the 20th century, the site maxima between 1.4 and 2.1 mg/g. TP was often greater yet in 21st century deposition, but this enhancement may include P stored in live organisms that on death, cell lysis and organic matter decomposition is returned to the water column.

The spatiotemporal pattern of PAR (Figure 2C) was different than that of TP because SAR impacted its value. Although TP was mid-range in the Juniper Basin core, its PAR was normally in the neighborhood of 0.1 g/m^2/y, the single exception, a temporary increase to 0.4 g/m^2/y during the hurricane decades of 1920s and 1930s. Port Henry, Schuyler Is. and Shelburne Bay recorded relatively steady PAR of from 0.2 to 0.3 g/m^2/y during the 19th century, but these rates began to increase in early 20th century as a result of sewage P inputs and the delayed arrival of sediment eroded during earlier land use. Peak PAR at Port Henry was 0.9 g/m^2/y in the 1940s to 1960s, whereas it was 1.1 g/m^2/y at Shelburne Bay in the 1970s to 1980s, and 0.8 g/m^2/y at Schuyler Is. in the 1970s to 1990s. The late 19th century SAR peaks at the Elm Pt., Outer Malletts Bay and Inner Malletts Bay sites, brought PAR up to 0.9, 0.8 and 1.1 g/m^2/y (rates on par with the late 20th century maxima at most sites). As with SAR, PAR cycled up and down at Elm Pt. during the 20th century; but, because TP increased here over time, its 1910s' peak measured 0.8 g/m^2/y whereas that of the 1960s was nearly three times greater, 2.3 g/m^2/y. In the Inner Malletts Bay core, PAR initially decreased with SAR; but, after a mid-century minimum of 0.5 g/m^2/y mid-century, its value rose to 0.8 g/m^2/y in the 1990s, based only on TP increase. Outer Mallets Bay's PAR ranged between 0.7 and 0.8 g/m^2/y over most of the 20th century, but increased to 1.3 and 1.9 g/m^2/y during the 1920s and 1930s, when hurricane runoff temporarily accelerated erosion, and to 1.0 g/m^2/y in the 1990s, when TP enrichment of the sediment occurred.

Nitrogen and N: P Ratio

Similar to TP, total N concentration (TN) was relatively constant in sediment deposited between 1700 and 1900 (Figure 2D), the means ranging from a low of 0.15% at Port Henry to a high of 0.27% at Inner Malletts Bay. The Schuyler Is. crust, however, contained very little TN, about 0.05%. TN increase was first apparent in 1920s deposition and increased over all of the 20th century, even where TP declined. For the 1990s, sediment TN was up to between 0.31% at Elm Pt. and

0.60% at Pt. Au Roche. TN:TP ratios, by weight (not shown), ranged between 1.5:1 and 4.5:1 over the three centuries sampled by the cores.

Nitrogen accumulation rates (NAR) during the 19th century (Figure 2E) ranged between 0.2 and 0.4 $g/m^2/y$ at Juniper Basin, Schuyler Is. and Port Henry, and between 0.6 and 0.7 $g/m^2/y$ at Cole Bay, Shelburne Bay and Pt. Au Roche. When SAR increased at Elm Pt., Outer Malletts Bay and Inner Malletts Bay during the latter half of this century, NAR increased as well, to 2.0, 1.5 and 2.3 $g/m^2/y$, respectively. In the 20th century, NAR varied greatly between sites, the lowest values measured at the mid-lake sites, Juniper Basin and Schuyler Is., with their maxima during this century, just 0.3 and 0.7 $g/m^2/y$, in the 1920s and 1960s, respectively. NAR increased throughout the 20th century at Port Henry, Elm Pt., Shelburne Bay, Outer Malletts Bay, Inner Malletts Bay and Pt. Au Roche, attaining 1990s maxima of 2.3 to 3.3 $g/m^2/y$. Cole Bay recorded two NAR maxima to match its two SAR peaks, 3.3 $g/m^2/y$ in the 1950s and 5.0 $g/m^2/y$ in the 1990s. For comparison, St. Albans Bay and Missisquoi Bay, recorded 1990s NAR of 5.1 and 6.7 $g/m^2/y$, respectively (Levine et al., 2012).

Organic C

As observed for TN, the organic carbon (OC) content of sediment was relatively constant within cores between 1700 and 1900, but showed a positive gradient from the southern to the northern end of the lake (Figure 2F). The means for Port Henry, Elm Pt., Cole Bay and Schuyler Is. were between 1.0 and 1.6% OC, for example, while those for Shelburne Bay and Juniper Basin were from 2.0 to 2.2%, and those of Outer Malletts Bay, Inner Malletts Bay and Pt. Au Roche, between 2.4 and 2.7%. The Schuyler Is. crust had an OC content of just 0.4%. General OC increase was observed over the 20th century, the 1990s means were between 2.3 and 2.5%

OC at Port Henry and Elm Pt., between 3.6 and 4.1% OC at Cole Bay, Shelburne Bay, Juniper Is., Outer Malletts Bay, and Inner Malletts, and greatest, 4.7%, at Pt. Au Roche, the sediment of which included microscopic macrophyte fibers (ESM Appendix S2).

OCAR during the 19th century (Figure 2G) was very low at Juniper Basin and Port Henry, just 1.6 and 2.6 g/m^2/y, on average. By contrast, Cole Bay, Schuyler Is., Shelburne Bay, and Pt. Au Roche had mean rates of 5 to 6 g/m^2/y. Elm Pt., Outer Malletts Bay and Inner Malletts had mid-century rates of 7 to 8 g/m^2/y; but during peak SAR at the turn of the century, OCAR was up to from 11 to 13 g/m^2/y at these sites. In the 20th century, OCAR continued below 3 g/m^2/y at Juniper Basin. At Schuyler Is., where NAR was very low, OCAR peaked at 13 g/m^2/y in the 1970s. Most sites showed OCAR increase over most of the 20th century to attain maxima of 19 to 25 g/m^2/y in the 1990s, but Cole Bay, rose higher, to 36 g/m^2/y. For comparison, the 1990s means for St. Albans Bay and Missisquoi Bay were much higher, 62 and 66 g/m^2/y respectively (Levine et al., 2012).

C: N Ratio and C Stable Isotopes

C: N ratios in the cores stayed below 12 (Figure 2H), as generally is the case when phytoplankton or submerged macrophytes rather than terrestrial plants produce most of the organic matter that accumulates in sediment (Kaushal and Binford, 1999). For the period 1700 to 1850, ratios at the southernmost sites (Port Henry, Elm Pt. Cole Bay) were so low (6.2 to 7.6) that exclusive production by algae (C: N << 10) can be posited. At most other sites, ratios between 8.7 and 9.2 were typical, although the means for Juniper Basin and Outer Malletts Bay were higher, 9.9 and 10.5, respectively. Most sites recorded C: N ratio increase over several decades between the mid-19th and mid-20th centuries, then reversed course to undergo major decline. The turnaround was earliest at the Port Henry and Cole Bay sites, before the end of the 19th century, but occurred in the 1900s-1920s at Juniper Basin, Shelburne Bay, Pt. Au Roche and Outer Malletts Bay, in the 1930s at Inner Malletts Bay; and in the 1950s-1960s at Elm Pt. and Schuyler Is. C: N declined to 5.8 to 7.2 in the southern lake by the end of the 20th century, but hovered around 7.8 at the central lake sites, and measured 8.7 and 9.2. at Inner Mallets Bay and Outer Malletts Bay, respectively.

Biogenic Silica

Biogenic silica concentration (BSi), a proxy for diatoms and siliceous chrysophytes, showed more spatial heterogeneity than most measured parameters (Figure 3A), probably because these phytoplankton require specific conditions that are more favorable in some places than others. The means for 1700-1900 ranged from an exceptionally low 6 mg/g at Elm Pt., to between 13 and 16 mg/g at Port Henry, Juniper Basin, and Inner Malletts Bay, and between 21 and 22 mg/g at Cole Bay, Schuyler Is., Shelburne Bay, Outer Malletts Bay and Pt. Au Roche. Again, the Schuyler Is. crust was highly aberrant, with BSi concentrations no greater than 3 mg/g. BSi increase was generally apparent in core sediments from the 1920s onward, although not at Port Henry and Elm Pt., where this augmentation was delayed until the 1960s.

BSiAR (Figure 3B) in the 19th century was between 1 and 3 g/m^2/y at Juniper Basin and Port Henry, from 5 to 8 g/m^2/y at Elm Pt., Schuyler Is., Shelburne Bay, Outer Malletts Bay, Inner Malletts Bay and Pt. Au Roche, and a phenomenal 23 g/m^2/y in the Cole Bay core. In the 20th century, BSiAR increase brought the 1990s means (in g/m^2/y) up to 4 at Juniper Basin, 14-15 at Inner Malletts Bay and Outer Malletts Bay, 20- 26 at Port Henry, Elm Pt and Shelburne Bay, 49 at

Pt. Au Roche, 101 at Schuyler Is., and 214 at Cole Bay. St. Albans Bay and Missisquoi Bay showed more middling values, their 1990s means, 35 and 54 g/m^2/y, respectively (Levine et al., 2012).

Algal Pigments

Chl *a* + pheo *a* concentration (Figure 3C), our proxy for phytoplankton biomass (although it includes periphyton and macrophytes as well), was, like most variables, relatively constant in the deposition of 1700 to 1900 in five of the seven cores analyzed for pigments. The period means for Elm Pt., Port Henry, and Schuyler Is. were 0.3, 0.8 and 1.1 nmol/g, respectively, whereas Juniper Is. and Shelburne Bay bore 2.0 and 2.3 nmol/g, and the Schuyler Crust, not even 0.1 nmol/g. Chl *a* + pheo *a* increased to 3.9 and 5.0 nmol/g at the Inner Malletts Bay and Outer Malletts Bay sites, respectively, during the logging of the bay sub-catchment in early-19th century, then plunged to 2 nmol/g for a few decades, before rising to 5.9 and 3.0 nmol/g over the second half of this century. During the 20th century, chl *a* + pheo *a* increased to maxima (in nmol/g) of 3 at Port Henry, 8 at Elm Pt., 17-18 at Schuyler Is., Juniper Basin and Shelburne Bay, 40 at Inner Malletts Bay and 43 at Outer Malletts Bay.

Chl *a* + pheo *a* AR showed a baseline rate of 0.2 to 0.3 µmol/m^2/y at most sites during the 19th century (Figure 3D), but was 0.4 µmol/m^2/y at Inner Malletts Bay (data missing for Outer Malletts Bay) and Shelburne Bay. During the 1800-1820 SAR peak at Inner Malletts Bay, chl *a* + pheo *a* AR was amplified five-fold, reaching 2.3 µmol/m^2/y temporarily. During its second, larger SAR increase, this site recorded a chl *a* + pheo *a* AR of 5.2 µmol/m^2/y, a maximum for cores up to this point in time. At Outer Malletts Bay, chl *a* + pheo *a* AR attained an 1880s peak of 2.0 µmol/m^2/y, whereas Elm Pt., with a much higher SAR, presented a 19th-century maximum of just

0.5 µmol/m^2/y.

All sites recorded one or more periods of chl *a* + pheo *a* AR augmentation in the 20th century, although for Juniper Basin, the highest value was just 1.4 µmol/m^2/y, measured in the 1990s. Shelburne Bay recorded a 1970s peak of 10 µmol/m^2/y, whereas the maxima at Schuyler Is., Elm Pt. and Port Henry, all in the 1980s to 1990s, were 6, 10 and 11 µmol/m^2/y, respectively. The chl *a* + pheo *a* AR records of the Malletts Bay cores were more complex, with two peaks in the 20th century, for Outer Malletts Bay, 14 µmol/m^2/y between the 1930s and 1950s, and 25 µmol/m^2/y between the 1980s to the 1990s, and for Inner Malletts Bay, 13 µmol/m^2/y between the 1950s and 1960s, and 17 µmol/m^2/y during the 1980s-1990s. For comparative purposes, St. Albans Bay, Missisquoi Bay, Cheney Pt. and Savage Is. recorded 1990s maxima of 55, 49, 18 and 4 µmol/m^2/y, respectively.

Pigments of Specific Algal Taxa

Data on the rates of accumulation of pigments other than chlorophyll *a* and pheophytin *a* in the cores are presented in ESM Appemdix S3 and Fig.S2, documenting changes in the biomass of cyanobacteria, cryptophytes, diatoms, and chlorophytes over time. Figure 4 compares the mean relative abundances of echinenone (cyanobacteria), alloxanthin (cryptophytes), diatoxanthin (diatoms and siliceous chrysophytes) and chlorophyll *b* + pheophytin *b* (chlorophytes) before eutrophication, from 1800 to 1899, and between 1950 and 2010. In all but one core, alloxanthin was the most abundant pigment over both periods, although it became less dominant over time. By contrast, diatoms and cyanobacteria gained in relative abundance between the two periods. Port Henry, in the shallowest water, was unique for this study in containing primarily chlorophyte pigment. In the lake's northeastern arm, however, we found chlorophytes dominant at three of four study locations (Levine et al., 2012).

Diatoms

Diatom microfossils were identified and enumerated in 20 or more segments from each of five cores. More than 100 species were observed, five of which are well-known indicators of trophic state, and whose specific relative abundance is included in Figure 5. Schuyler Is., Juniper Basin and Shelburne Bay, cores taken well offshore in deep water, contained, as expected, primarily planktonic species, in particular, the colonial pennates *Fragilaria crotenensis* and *Tabellaria flocculosa*. The ratio of *Fragilaria* to *Tabellaria* increased during the latter half of the 20th century at the Schuyler Is. and Juniper Basin sites, likely reflecting biomass-induced reductions of average light intensity and dissolved silica concentration unfavorable to thick-frustuled *Tabellaria* (Reynolds et al., 2002). Centric diatom composition also changed at these sites, generally-oligotrophic *Cyclotella bodanica* giving way to meso-eutrophic *Stephanodiscus niagarae* at Schuyler Is. and Juniper Is. Shelburne Bay was exceptional in its maintenance of *Cyclotella* as the dominant centric diatom.

Because the southern lake sites were either in or near littoral habitat where benthic diatoms do well, the heavy centric diatom *Aulacoseira ambigua* was abundant in the Cole Bay and Port Henry cores before 1920. Thereafter, *Stephanodiscus niagarae* increased its share of centric diatom biomass at Cole Bay, while at both Cole Bay and Port Henry, the ratio of pennate to centric species increased. *Fragilaria crotenensis* dominated at Port Henry in the late 20th century, as also was the case throughout the lake's northeastern arm. Nevertheless, for reasons unknown, *Tabellaria flocculosa* was the dominant pennate in Cole Bay and Shelburne Bay.

*Summary*Tables 1A and 1B display the means for the twelve trophic status indicators measured in cores during four periods: the reference period (1700-1850), the decades of maximum catchment deforestation when SAR was expected to (but did not) peak (1850-1900), the three decades when sewage influx was greatest (1950-1980), and the final decades of the 20th century (1980-2000) when P removal from wastewater was substantial but agriculture intensified to add fertilizer and waste P to catchment soil.

Discussion

The Lake before Eutrophication

Lake Champlain was considerably more oligotrophic than at present when European settlers arrived ca. 1760, and in most lake regions, remained so until the late-19th to middle-20th century. The 1700-1850 means for TP, TN, OC, BSi and chl *a* + pheo *a* in the thirteen cores were between 31 and 84, 22 and 61, 25 and 65, 15 and 59, and 1 and 30%, respectively, of the means obtained for 1980-2000 deposition, and because SAR generally increased between 1850 and 1980 as well, the 1800-1850 means for PAR, NAR, OCAR, BSiAR and chl *a* + pheo *a* AR (Tables 1A and 1B) were even smaller percentages of the modern values, from 16 to 33, 11 to 31, 16 to 41, 7 to 25 and 1 to 8%, respectively. Also, consistent with early oligotrophy, the diatom dominants of 1700-1850 included *Tabellaria flocculosa*, *Aulacoseira ambigua* and *Cyclotella bodanica*, highly-siliceous species with benthic stages that require high water clarity (Reynolds 2006). During subsequent lake eutrophication, less-siliceous, more-planktonic species, such as *Fragilaria crotenensis*, partially replaced these species as dominants (Figure 5; Levine et al., 2012).

A degree of spatial heterogeneity was observed within the reference-period lake (1700-1850). Sediment organic matter content increased from its southern to the northern end (mean OC rising from 0.9 to 2.9%; mean TN, from 0.15 to 0.29%), and sediment TP was greater inside than outside the lake's bays (the means, 0.9-1.2 vs. 0.7-0.8 mg/g) (Figure 2 B, D and F). Baseline chl *a* + pheo *a* AR (Figure 3D, Tables 1A and 1B) was higher in the bays as well, with St. Albans Bay > Malletts Bay > Missisquoi Bay > Shelburne Bay. This ranking may not indicate real differences in primary production, however, because pigment deposition is affected by water circulation patterns that can focus biomass at some locations and disperse it at others (e.g., minimal deposition at Juniper Basin), and more pigment is preserved rather than degraded where sediment burial is rapid (as at Missisquoi Bay, St. Albans Bay and Malletts Bay) or the pigment sinks into a dark, cool and anoxic hypolimnion (modern Malletts Bay) (Leavitt and Hodgson, 2001). This point is illustrated by comparing the mean chlorophyll concentrations recorded at the Juniper Basin, Shelburne Bay and Outer Malletts Bay monitoring sites by the Vermont DEC between 1992 and 2010 (ESM appendix S1and Table S1), 3.9, 3.7 and 3.3 µg/L, respectively, with the 1980-2000 means for chl *a* + pheo *a* AR recorded in cores taken near these sites (Tables 1A and 1B), 1.4, 6.4 and 19 µmol/m^2/y.

The trophic-state indicators varied minimally at most sites between 1700 and 1850, but the Shelburne Bay core recorded several decades of simultaneous chl *a* + pheo *a*, OC and TN decrease that may indicate prolonged stress on phytoplankton and primary production The Little Ice Age in New England was especially cold during the latter half of the 18th century (Mann et al., 1999), and may have narrowed the phytoplankton growth season through prolonged ice cover or seasonal mixing to depths with inadequate light for photosynthesis.

The relative abundances of the pigments specific to phytoplankton groups in the cores (ESM Appendix S3, Figure S2) suggest that the phytoplankton community has changed minimally over the past two centuries with regard to biomass distribution among the major groups, all groups having responded positively to eutrophication. Cryptophytes were initially slightly better represented than at the turn of the 21st century; whereas, diatoms and cyanobacteria seem to have become somewhat more common over time.

Spatiotemporal Pattern of Sediment Accumulation in the Lake

Despite intensive land use and up to 70% catchment deforestation during the 19th century, SAR continued at its baseline levels into the 20th century at ten of thirteen study sites (Figure 2A). Landscape photography confirms extensive erosion in late 19th century (Bierman et al. 2005), and aerial photography from the 1930s and 1940s (Vermont State Archives, Series USSCS-01) captures images of large sediment plugs migrating down lake tributaries. These results suggest residence times for sediment in the local tributaries of several decades, as was the case with Beach's (1994) assessment of mass transport in Minnesota catchments. To obtain closer estimates of travel times, we can measure the time elapsed between the catchment's deforestation maximum ca. 1870 and the maxima for SAR in those cores whose SAR trajectories over time describe a bell-shaped curve. Trajectories of this shape occur when sediment is mobilized over limited area and for a short duration, and the dislodged particles are sorted by size during transport (small particles are suspended more easily and take longer to resettle). At Inner Malletts Bay, SAR peaked shortly after 1900, or about three decades after maximum deforestation. At Port Henry and Schuyler Is., the peak was in the 1960s, suggesting a nine-decade delay for particles of modal size. Shelburne Bay's SAR trajectory was shaped more like a flattened bell, with rates nearly constant (declining slightly) from the 1920s through the 1980s, suggestive of more prolonged high erosion in its sub-catchment. Finally, in the northern lake, SAR increased up to the time of core collection. Whether this time course reflects later settlement of the northern than the southern catchment, or the concentration of intensive agriculture around the northeastern lake arm is uncertain. Yet another contributing factor could be the mobilization of stream alluvium in many Vermont streams, especially in the drainage of the northeastern arm.

A basic feature of stream evolution is continual adjustment of the stream channel volume to maximize the efficiency of both water and sediment transport, with the equilibrium condition achieved when channel volume accommodates the average annual high flow event, but no more (Kline and Cahoon, 2010; Leopold et al., 1998). Land use in the Lake Champlain Basin has not only eroded soil, but altered the local hydrology. Streams were straightened for log runs in the 18th and 19th centuries, and later provided greater water loads through surface paving, pond and wetland filling, vegetation removal and extensive installation of drainage, especially on farmland (Albers, 2000; Sims et al., 1998). Geomorphic assessment of the tributaries in Vermont indicates that about 70% of total stream length is actively adjusting to “flashy” hydrology (rapid change in discharge after precipitation) through incision and bank collapse (Kline and Cahoon, 2010), and subsequent downstream transport of old deposits. The recent catchment P model of Tetra Tech (2015), attributes 18% of the P influx to Lake Champlain to streambank collapse alone.

The exception that may prove the rule regarding slow sediment transport to Lake Champlain is the SAR response of Inner Malletts Bay to near-shore logging in the early 19th century; with minimal distance to travel, sediment arrived coincident with the soil disturbance. Other oddities in the SAR trajectories of cores demonstrate the importance of internal processes in moving incoming sediment to deposition sites that need not be at river mouths. The Elm Pt. and Cole Bay cores recorded cycles of SAR increase and decline that were opposed to one another at the two sites, as if they shared a sediment source that divided deposition between them unequally. For example, SAR exceeded 1.0 $kg/m^2/y$ at Elm Pt. in the 1880s-1890s, 1910s, and 1970s-1990, during sediment deposition about half this rate at Cole Bay, but between times, during the 1920s to 1950s and the 2000s, Cole Bay, not Elm Pt. boasted the higher SAR. Also, consistent with there being multiple circulation patterns in the southern lake, were alternating layers of black mud and grey clay in the 1800-1950 section of the Cole Bay core. Meteorological factors such as prevailing wind direction might alter gyre position or direction.

Outer Malletts Bay recorded changes in SAR that can be related to an alternation of internal hydrology as well as, in this case, the placement of causeways along its northern and western perimeter between 1847 and 1898 (Albers, 2000). The Lamoille River carries a heavy sediment load into Malletts Bay, which apparently was partially removed through current flow north and south before blockage of the transport. Three consequences were recorded in the core, one an abrupt change in the texture of deposited sediment ca. 1850, from coarse silt deposition initially to clay deposition after the 1847 causeway installation. The others were SAR increase after 1850 to a baseline for the 1880s to 2000s that was twice the previous level (0.6 vs. 0.3 $kg/m^2/y$), and upward excursion during the decades with hurricanes, the 1920s and 1930s, to average 1.1 and 1.6 $kg/m^2/y$, respectively, while at most other lake sites the means were between 0.3 and 0.6 $kg/m^2/y$. Finally, the Juniper Basin and Savage Is. sites documented the importance of the lake's internal seiche to sediment distribution, generally recording low (< 0.1 $kg/m^2/y$) and consistent SAR over two centuries. An exception to this generalization was a brief doubling of the decadal SAR mean at Juniper Basin during the flooding associated with hurricanes in the 1920s and 1930s.

The crust layer in the Schuyler Is. core may be of exotic origin. Many barges carried iron ore out of the lake in the middle of the 19th century (Albers, 2000), and may have occasionally lost part of the load. The layer was too old to date with ^{210}Pb, had a geochemistry very different from the sediment above it, and contained a small machined object.

Phytoplankton Response to Soil Sediment Influx

Opportunities to evaluate the impact of soil sediment PP on phytoplankton biomass and primary production in the absence of point source P input were limited by the extended period sediment spent in transit. Just three cores, Malletts Bay, Outer Malletts Bay and Elm Pt., recorded periods of heightened SAR and PAR before sewage discharge began around 1900. Inner Malletts Bay captured two events, the first coincident with the nearshore logging of 1800 to 1820, and the second, a gradual rate increase from the 1850s to the site's all-time maximum of 0.9 kg/m^2/y at the turn of the century. The Outer Malletts Bay and Elm Pt. cores recorded single peaks coincident with the second event at Inner Malletts Bay but with their maxima (0.7 and 1.1 kg/m^2/y) between the 1880s and 1890s. For pigment accumulation, the response at Inner Malletts Bay far exceeded that at Elm Pt. Chl *a* + pheo *a* AR increased almost five-fold, from 0.5 to 2.3 µmol/m^2/y, during the first SAR-PAR augmentation, and reached 5.2 µmol/m^2/y during the second, both increases disproportional to smaller changes in SAR. Chl *a* + pheo *a*/TP, our indicator of P use efficiency, was 1.4 µmol/µg at this site between events, but 3.9 and 4.8 µmol/µg during the SAR peaks (Figure 6A). The increases in this ratio suggest the introduction of a P source not well-represented initially, such as horse manure or human-waste contamination of runoff near the logging camp and or from the village of Malletts Bay, which was founded in 1763.

The Outer Mallets Bay core also included pigment data for early 19th century, but lacked the SAR data needed to calculate fluxes. We note, however, that its chl *a* + pheo *a*/TP during the 1800-1820 SAR peak at its nearest neighboring site, was 4.8 µmol/µg. During the 1880s-1890s

SAR maximum at the site, chl *a* + pheo *a* AR measured 2.1 µmol/m^2/y, and chl *a* + pheo *a*/TP, 3.9 µmol/µg. Elm Pt., by contrast, recorded a very low chl *a* + pheo *a* AR of 0.2 µmol/m^2/y in the middle of the 19th century, to peak at 0.5 µmol/m^2/y in the 1880s, although its SAR at the time was 60% greater than that at Outer Malletts Bay. A simple interpretation of these results is that the allochthonous PP brought to Elm Pt. in the 19th century was largely recalcitrant, its principal fate being burial in sediment. However, this need not be true, if the forcing factors determining the distribution of inorganic sediment and pigment deposits are different. Briefly, because mineral sediment is heavy it settles quickly and thus patchily within the lake. By contrast, PO_4 released from sediment does not stay adjacent to it, but instead enters large-scale water circulation. It may be distributed within a large gyre, and thus nourish pigment-producing phytoplankton over many square kilometers. In this case, the pigment accumulation measured at Elm Pt. may have been determined by P input to a large lake region not just by deposition rates around the collection site. Consistent with this suggestion, the chl *a* + pheo *a* AR means for 1850-1900 at Port Henry, Schuyler Is. and Elm Pt. were within 15% of one another, whereas their PAR means differed by up to 300% (Tables 1A and 1B).

The ten cores that recorded relatively-constant SAR over the 19th century also recorded consistent trophic status (Tables 1A and 1B). The 1850- 1900 means for PAR, NAR, OCAR, BSiAR and chl *a* + pheo *a* AR were between 19 and 36, 14 and 33, 15 and 41, 8 and 25, and 1 and 11%, respectively, of the means for 1980-2000, ranges just slightly offset from the comparison made with 1800-1850 sediment (above). During the 20th century, SAR and PAR at Shelburne Bay, Schuyler Is, and Port Henry peaked in the 1930s to 1950s, 1950s to 1970s and 1960s to 1970s, respectively, whereas the chl *a* + pheo *a* AR peaks at these sites were in the 1970s, the 1980s to 1990s, and the 1990s, respectively, the discrepancies in timing related to the growing importance of P point sources over the first seven decades of the century, and to the introduction of substantial agricultural nutrient to the catchment after 1980. Inner Malletts Bay provides a more interesting history yet. SAR stayed at baseline here between 1960 and 2010, whereas chl *a* + pheo *a* AR showed two unusually high peaks, 13 and 17 µmol/m^2/y, in the 1960s and 1980s, respectively. Chl *a* + pheo *a*/TP during these peaks was 27 and 30 µmol/g, about six times greater than during the sites early-century SAR-PAR peak. Malletts Bay presents a challenge to P management because it has no direct sewage inflows. Excess PO_4 might be brought in by the Lamoille River, which receives sewage from villages along its length, but more likely originates in septic systems in the village of Malletts Bay and along the water front. This is a site that would benefit from more extensive monitoring and core collection.

The regression of the decadal means of chl *a* + pheo *a* AR against the corresponding SAR means over the interval 1800 to 2000 (11 cores included) indicated a significant relationship (r^2 = 0.203, n = 122, $p < 0.05$; Fig. 6B). However, prudence in interpretation is suggested by the possibility of a spurious relationship. For example, in the northern catchment, intensified animal agriculture has added substantial manure P to soil, but also raised erosion rates because row-corn production has greatly increased (Smeltzer et al., 2012). The clusters of points above the regression line in the middle and at the right side of the graph represent chl *a* + pheo *a* AR in Malletts, Missisquoi, and St. Albans bays towards the end of the 20th century, when fertilizer and human and animal waste inputs were elevated (Smeltzer et al., 2012).

Phytoplankton Response to Phosphorus from Point Sources and Intensive Agriculture

Outside of Malletts Bay, eutrophication began as early as the first decade of the 20th century (Shelburne Bay) and as late as the 1960s to 1970s , e.g. at Elm Pt., Missisquoi Bay and

Cheney Pt. Comparison of the means for the trophic state indicators over the intervals 1950 to 1980 and 1980 to 2000, indicates that Inner Malletts Bay and Outer Malletts Bay were near full-eutrophy, and Shelburne Bay at its most eutrophic, during the first interval, when point source P influx was maximal, whereas the intensification of agriculture was still modest. Elm Pt., Port Henry, and Cole Bay in the southern lake and Missisquoi Bay at the lake's most northern reach, recorded the opposite pattern, low and consistent biomass indicators before 1980, followed by major increase between 1980 and 2000, as agriculture brought commercial fertilizer and feed into the catchment. The remaining six cores exhibited increased productivity over both periods. In this assessment, we have plotted but hitherto avoided discussion of data for the most recent (2000 to 2010) deposition because this material includes live organisms that may decompose before permanent burial of remaining pigment and nutrient. Consequently, it is significant that all of the cores taken from the central and southern lake, record chl a + pheo a AR decrease, rather than the expected gain, at the sediment surface. This finding may be evidence that tertiary treatment of wastewaters, mostly initiated in the 1990s, has reduced primary production in areas where agricultural inputs of bioavailable P have not grown faster than the reductions.

Conclusions and Recommendations

Sediment core assessment indicates that for Lake Champlain, eutrophication was largely a 20th century phenomenon, driven initially by point sources of P, principally domestic sewage, but toward the end of the century also by runoff from agriculture. The role of eroded soil in providing P for eutrophication remains uncertain, although the observation that sediment accumulation rate has generally peaked decades before the productivity maximum suggested by pigment accumulation rates, suggests that this P is at best partially exploited. In any case, sediment travel through the catchment proved long enough to temper expectations that urban and agricultural BMPs focused on soil conservation, streambank stabilization, and the trapping of sediment in suspension will improvement lake trophic status quickly. Phytoplankton biomass reductions near the top of the cores, on the other hand, is consistent with the large point source P reductions of the 1990s eliciting a rapid response. The data provided are available for further analysis and use in hypothesis testing if a more spatially and temporally detailed land use history for the catchment is made available in the future. For now, we recommend focusing on managing P exchange at the catchment boundary i.e. on reducing the importation of commercial P enough to avoid soil P saturation, although the local soil may already be overloaded in some areas; maps of soil P content made by MacDonald and Bennett (2009) show the northern Lake Champlain Basin in their most P-rich category, > 1200 kg P/ha. Once soils are P saturated, the potential for nonpoint-source P driven eutrophication increases greatly; PO_4 is not held back by soil retention, is transported to the lake in days rather than decades, and is immediately available to phytoplankton on lake entry rather than requiring prior processing. With reduced P import to the catchment, however, the excess will purge, although possibly over decades (Cassell et al., 1995). The goal of agricultural land use should be to balance P import with P export in agricultural products thereby reducing risk that excess dissolved P will be transported to waterways.

A larger sample of lake eutrophication histories is needed to generalize about the relative roles that soil erosion and industrial agriculture using P derived from phosphate ore have had as drivers of eutrophication on the global stage. We encourage sediment core analysis similar to ours in other lakes, but also strongly encourage experimentation to learn more about the fate and bioavailability of P brought into lakes in forms other than PO_4. Orthophosphate was the standard P species added to mesocosms and whole lakes in the 1960s to 1980s to evaluate the lacustrine P cycle and the dynamics of eutrophication (Elser et al., 1990; Levine et al., 1986; Schindler and Vallentyne, 2008). In contrast, catchment research has simplified its task by focusing on only TP measurement and tracking (Søndergaardet al., 2007). Linking the two efforts to understand how terrestrial P impacts lakes requires that we learn more about the P forms reaching lakes and about the fate and bioavailability of each form in the lake. On the positive side pragmatically, controlling P movement along the roadways into and out of lake catchments is less costly and laborious than managing the entire area within each catchment.

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List of Tables

Table 1A. Period means for sediment accumulation rate (SAR) and the corresponding means for ten indicators of lake trophic status in the thirteen Lake Champlain cores. Ref = the reference period, 1700-1850; Def = period of maximum deforestation,1850-1900; Sew = the period of maximum sewage P influx, 1950-1980; and Ag = the period of intensified agriculture, 1980-2000.

Table 1B. Continuation of Table 1.

Figure Legends

Figure 1. Core collection sites in Lake Champlain, with solid dots indicating the sites analyzed here, and solid triangles, sites assessed in Levine et al. (2012).

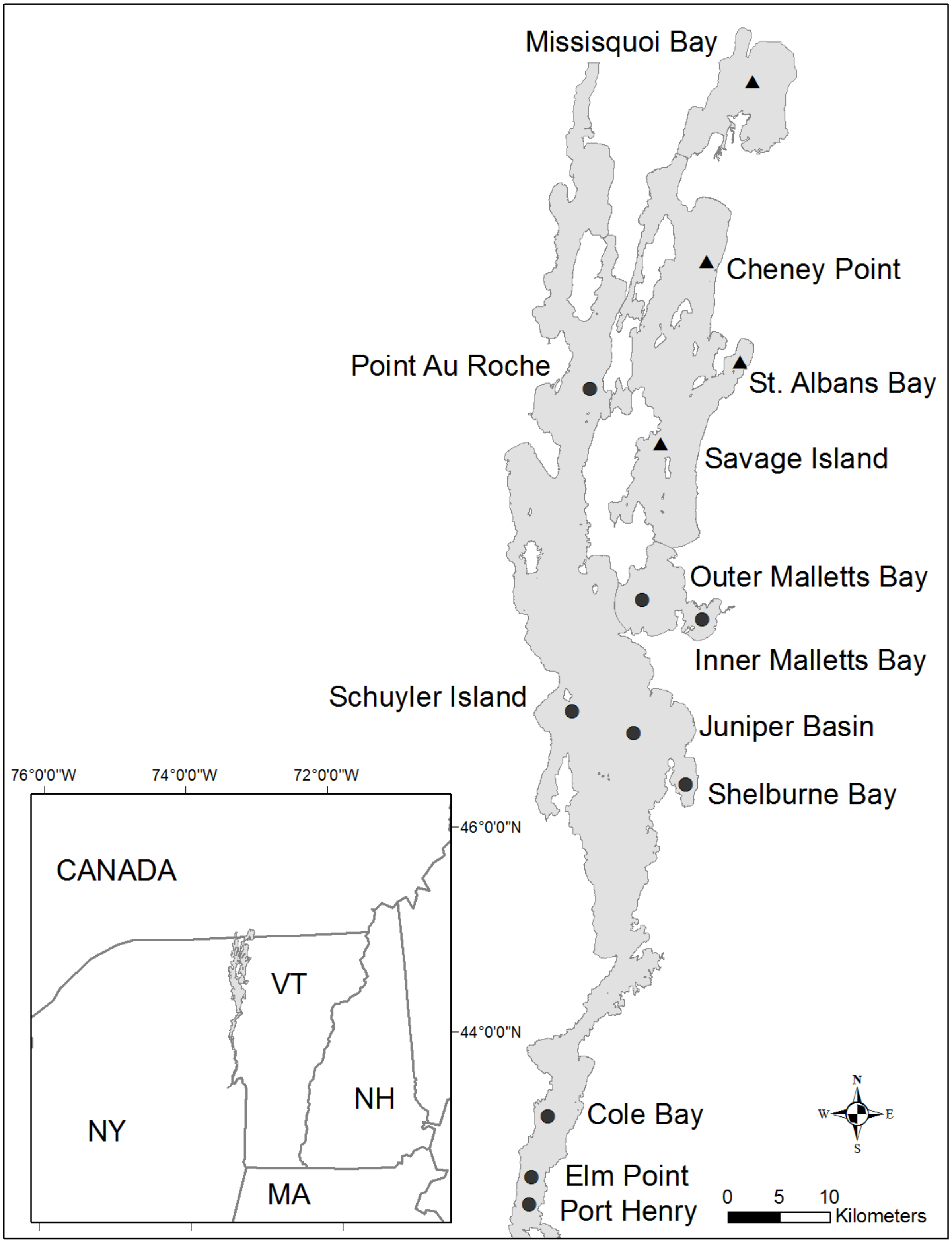
Figure 2. Decadal means for A) sediment accumulation rate (SAR), B) total phosphorus concentration (TP), C) phosphorus accumulation rate (PAR), D) total nitrogen concentration (TN), E) nitrogen accumulation rate (NAR), F) organic carbon concentration (OC), G) organic carbon accumulation rate (OCAR), and H) C: N weight ratio (values < 10 suggest algal dominance of primary production; Kemp 1971).

Figure 3. Decadal means for A) biogenic silica concentration (BSi), B) biogenic silica accumulation rate (BSiAR), C) chlorophyll *a*+ pheophytin *a* concentration (chl *a* + pheo *a*), and D) chlorophyll *a*+ pheophytin *a* accumulation rate (chl *a* + pheo *a* AR).

Figure 4. Comparison of the average relative distributions of pigments in core segments deposited between 1800-1899 and between 1950-2010. Chlorophyll *b* + pheophytin *b* represents chlorophytes and higher plants; alloxanthin, cryptophytes; diatoxanthin, diatoms and siliceous chrysophytes; and echinenone, cyanobacteria. Because pigments occur in algae at different concentrations, these graphs do not directly reflect biomass distribution.

Figure 5. The relative abundance of fossil diatom species in cores. Not all core layers were analyzed, thus the unequal spacing of decadal labeling on the x-axis. “Centrales sideways” indicates fossils of *Aulacoseira ambigua* and *Stephanodiscus nigarae* that could not be distinguished due to position.

Figure 6. A) Decadal means for chlor *a*+ pheo *a*/ TP, an indicator of phytoplankton phosphorus use efficiency. B) Chl *a* + pheo *a* AR plotted against SAR for all data attained for the period 1800-2000 (the new data and from the four northeastern arm cores). The r^2 is 0.203 for n = 122.


Missisquoi Bay
Cheney Point
Point Au Roche
St. Albans Bay
Savage Island
Outer Malletts Bay
Inner Malletts Bay
Schuyler Island
Juniper Basin
Shelburne Bay
Cole Bay
Elm Point
Port Henry
76°0'0"W
74°0'0"W
72°0'0"W
46°0'0"N
44°0'0"N
CANADA
VT
NH
NY
MA
N
W
E
S
0
5
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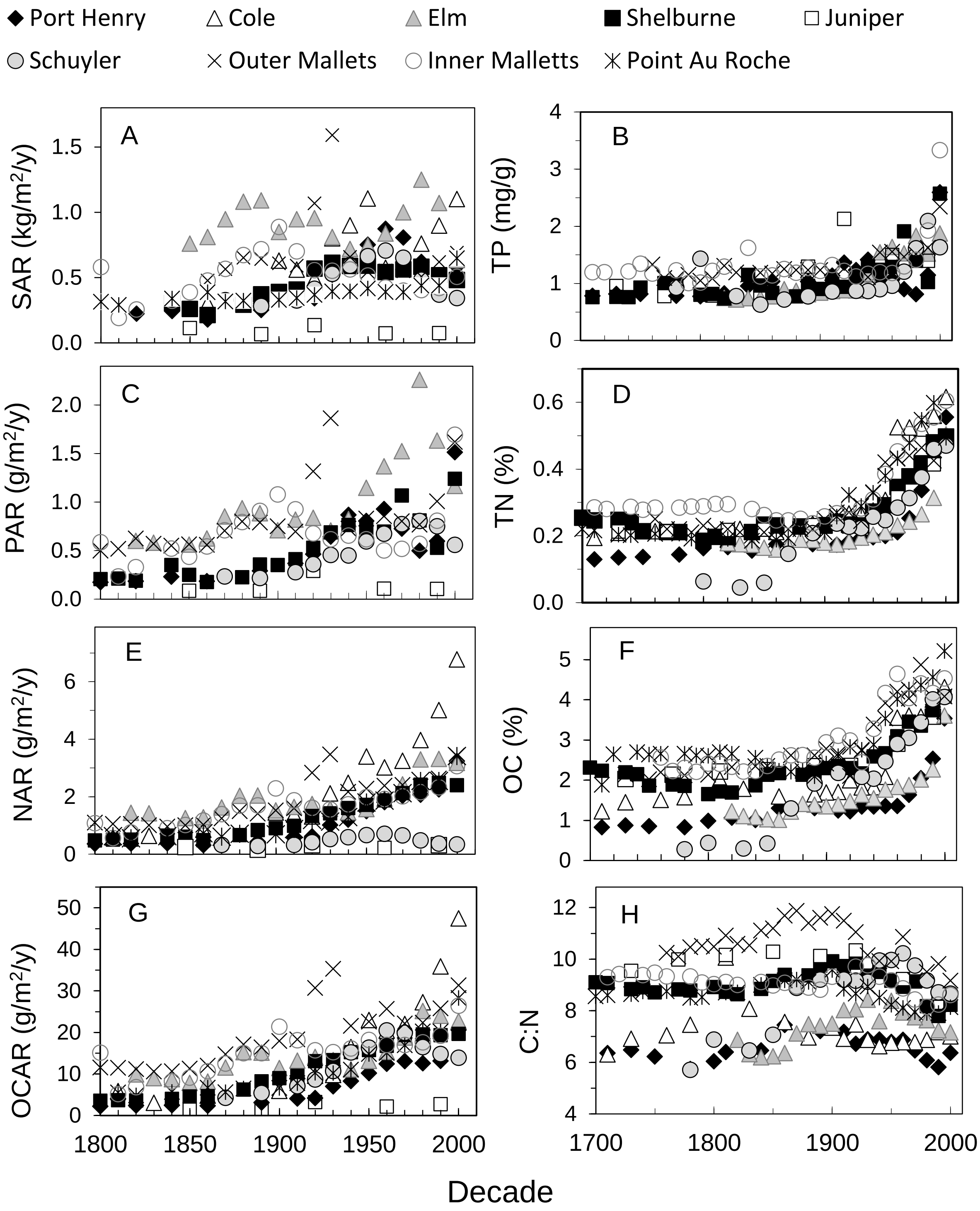
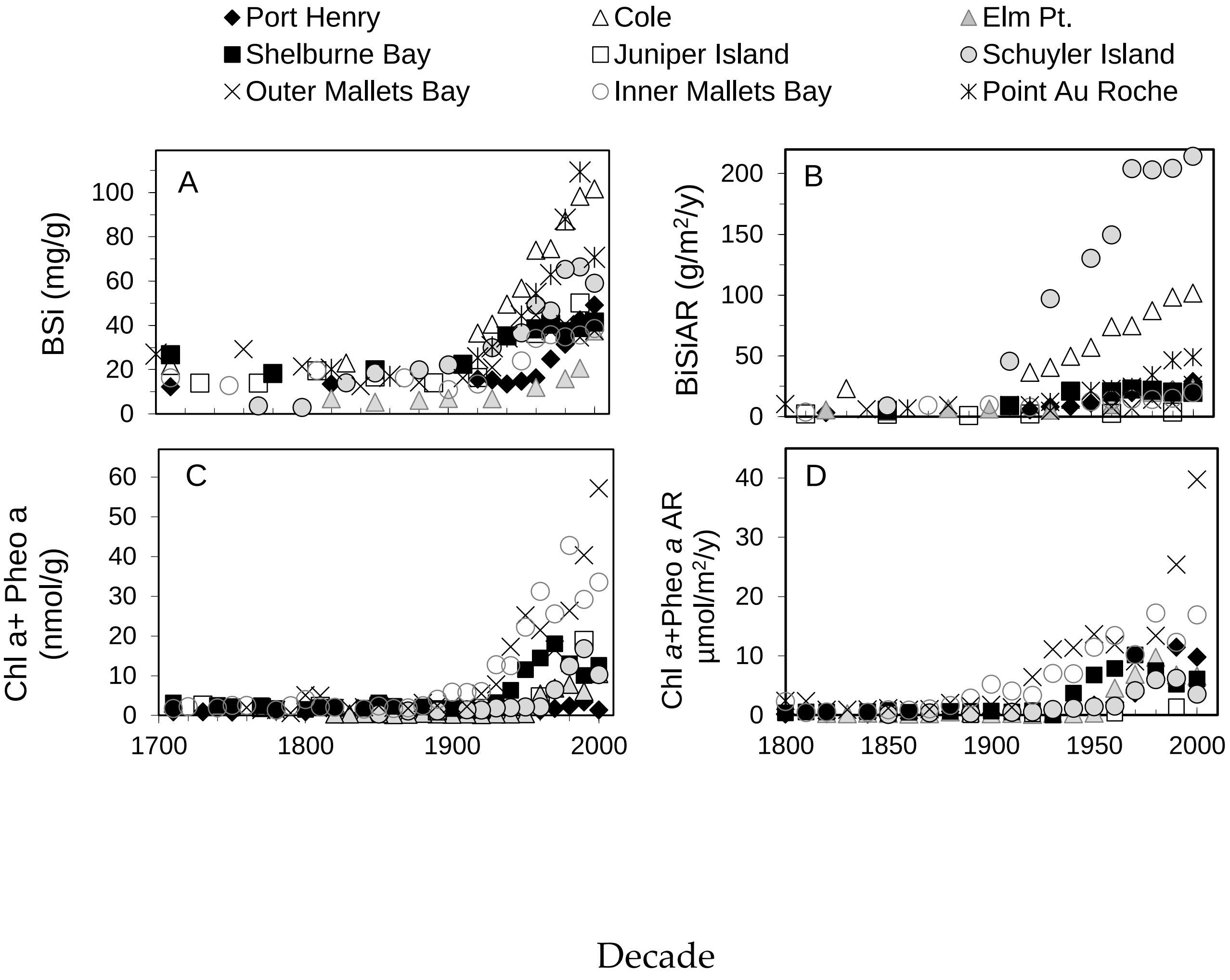
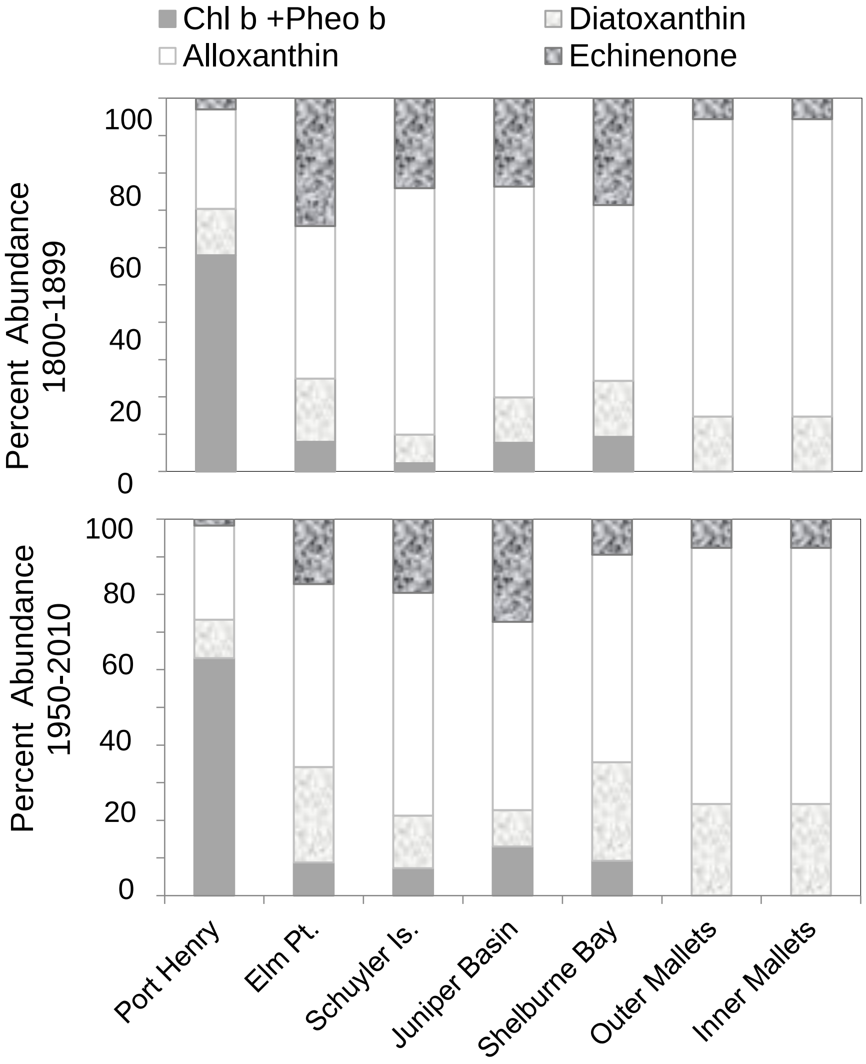
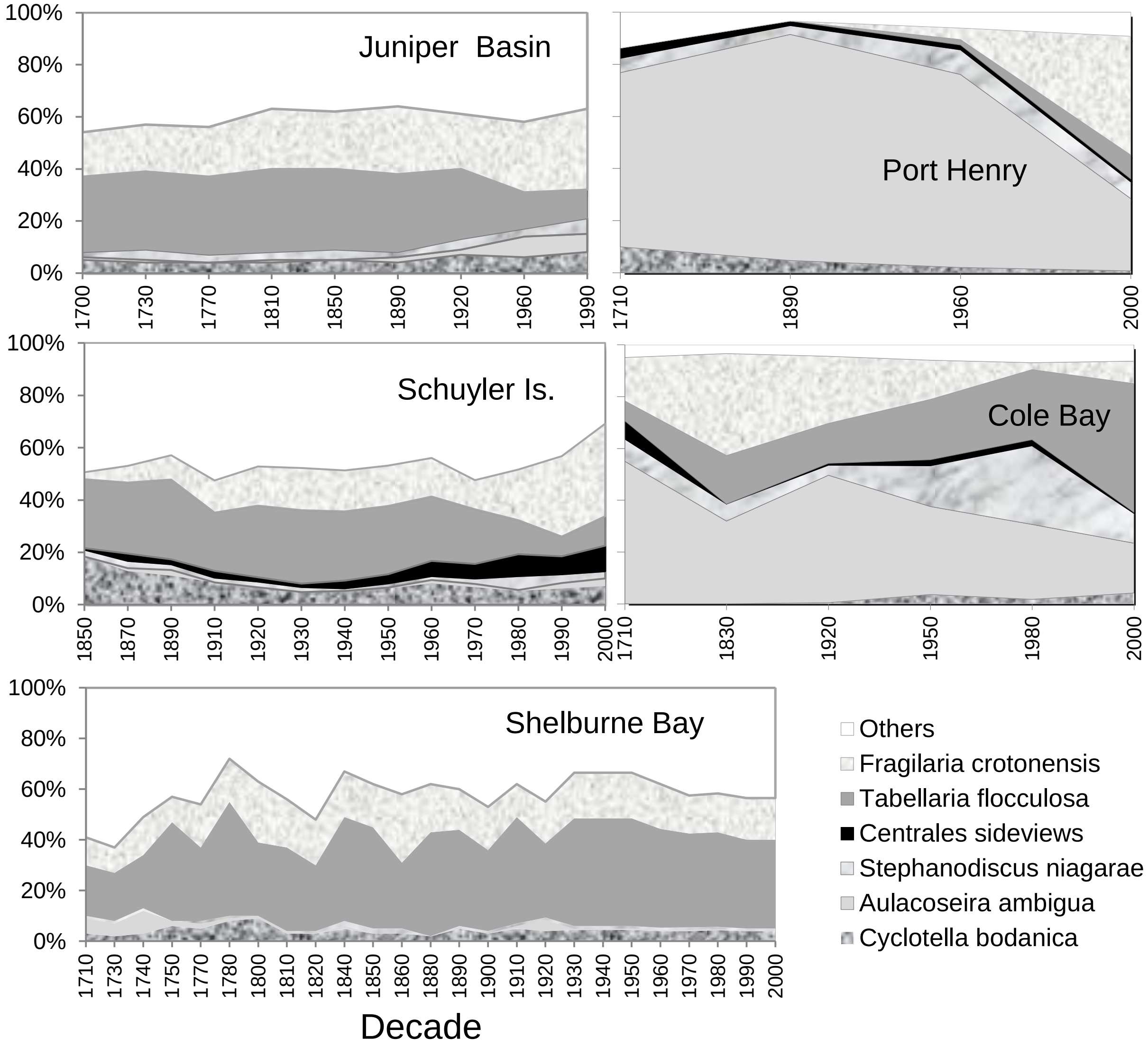
Kilometers


◆ Port Henry
△ Cole
▲ Elm
■ Shelburne
☐ Juniper
● Schuyler
× Outer Mallets
○ Inner Malletts
✳ Point Au Roche
A
SAR (kg/m²/y)
0.0
0.5
1.0
1.5
B
TP (mg/g)
0
1
2
3
4
C
PAR (g/m²/y)
0.0
0.5
1.0
1.5
2.0
D
TN (%)
0.0
0.2
0.4
0.6
E
NAR (g/m²/y)
0
2
4
6
F
OC (%)
0
1
2
3
4
5
G
OCAR (g/m²/y)
0
10
20
30
40
50
H
C:N
4
6
8
10
12
1800
1850
1900
1950
2000
1700
1800
1900
2000
Decade


◆ Port Henry
△ Cole
▲ Elm Pt.
■ Shelburne Bay
☐ Juniper Island
● Schuyler Island
× Outer Mallets Bay
○ Inner Mallets Bay
⋇ Point Au Roche
A
BSi (mg/g)
0
20
40
60
80
100
B
BiSiAR (g/m²/y)
0
50
100
150
200
C
Chl a+ Pheo a (nmol/g)
0
10
20
30
40
50
60
1700
1800
1900
2000
D
Chl a+Pheo a AR µmol/m²/y)
0
10
20
30
40
1800
1850
1900
1950
2000
Decade


Chl b +Pheo b
Diatoxanthin
Alloxanthin
Echinenone
Percent Abundance 1800-1899
Percent Abundance 1950-2010
0
20
40
60
80
100
Port Henry
Elm Pt.
Schuyler Is.
Juniper Basin
Shelburne Bay
Outer Mallets
Inner Mallets


100%
80%
60%
40%
20%
0%
Juniper Basin
1700
1730
1770
1810
1850
1890
1920
1960
1990
Port Henry
1710
1890
1960
2000
Schuyler Is.
1850
1870
1890
1910
1920
1930
1940
1950
1960
1970
1980
1990
2000
Cole Bay
1710
1830
1920
1950
1980
2000
Shelburne Bay
1710
1730
1740
1750
1770
1780
1800
1810
1820
1840
1850
1860
1880
1890
1900
1910
1920
1930
1940
1950
1960
1970
1980
1990
2000
Decade
Others
Fragilaria crotonensis
Tabellaria flocculosa
Centrales sideviews
Stephanodiscus niagarae
Aulacoseira ambigua
Cyclotella bodanica

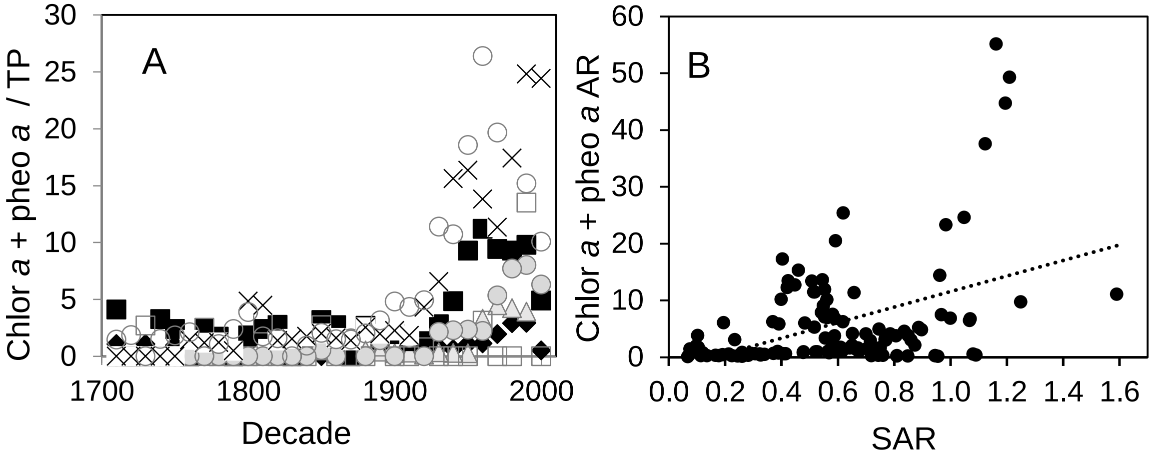
A
Chlor *a* + pheo *a* / TP
0
5
10
15
20
25
30
1700
1800
1900
2000
Decade
B
Chlor *a* + pheo *a* AR
0
10
20
30
40
50
60
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
SAR

Table 1A. Period means for sediment accumulation rate (SAR) and the corresponding means for ten indicators of lake trophic status in the thirteen Lake Champlain cores. Ref = the reference period, 1700-1850; Def = period of maximum deforestation,1850-1900; Sew = the period of maximum sewage P influx, 1950-1980; and Ag = the period of intensified agriculture, 1980-2000.

							Total Algae	Cyanobacteria	Cryptophytes	Diatoms	Chlorophytes	
							Chl a+Pheo a				Chl b+Pheo b	
	Era	SAR	PAR	NAR	OCAR	BSiAR	AR	Echin. AR	Allox AR	Diax AR	AR	C: N
Port Henry	Ref	0.23 (0.01)	0.20 (0.03)	0.37 (0.01)	2.3 (0.1)	3.0	0.19 (0.03)	0.004 (0.001)	0.04 (0.01)	0.02 (0.01)	0.10 (0.00)	6.2 (0.3)
	Def	0.22 (0.05)	0.24 (0.08)	0.37 (0.08)	2.7 (0.6)	-	0.28 (0.09)	0.01 (0.01)	0.07 (0.02)	0.04 (0.02)	0.15 (0.04)	7.3 (0.2)
	Sew	0.81 (0.06)	0.82 (0.10)	1.8 (0.3)	12 (2)	15 (4)	2.5 (1.1)	0.08 (0.03)	0.79 (0.50)	0.44 (0.26)	1.3 (0.7)	6.7 (0.2)
	Ag	0.57 (0.07)	0.67 (0.09)	1.2 (0.7)	13 (0)	21 (2)	8.8 (3.7)	0.15 (0.07)	2.5 (1.1)	1.1 (0.2)	6.6 (3.2)	5.9 (0.2)
Elm Pt.	Ref	-	-	-	-	-	-	-		-	-	6.4 (0.4)
	Def	0.94 (0.15)	0.77 (0.17)	1.6 (0.4)	12 (4)	5.3 (1.5)	0.30 (0.14)	0.29 (0.15)	0.61 (0.19)	0.12 (0.06)	0.07 (0.08)	6.9 (0.6)
	Sew	0.86 (0.13)	1.3 (0.2)	2.0 (0.4)	16 (3)	9.6	3.9 (3.3)	0.42 (0.26)	1.1 (0.5)	0.65 (0.46)	0.34 (0.25)	8.0 (0.3)
	Ag	1.2 (0.1)	2.0 (0.4)	3.3 (0.0)	25 (1)	21 (1)	8.2 (2.1)	1.7 (0.5)	2.8 (0.5)	2.4 (0.8)	0.22 (0.09)	7.4 (0.3)
Cole Bay	Ref	-	-	-	-	-	-	-	-	-	-	7.6 (1.3)
	Def	0.33 (0.04)	-	0.85	4.8	-	-	-	-	-	-	7.3 (0.4)
	Sew	0.77 (0.29)	-	3.2 (0.2)	22 (1)	68 (10)	-	-	-	-	-	6.8 (0.0)
	Ag	0.83 (0.10)	-	4.5 (0.7)	32 (6)	93 (8)		-	-	-	-	7.0 (0.2)
Shelburne Bay	Ref	0.31	0.24 (0.07)	0.54 (0.08)	3.7 (0.2)	-	0.49 (0.08)	0.10 (0.04)	0.24 (0.04)	0.06 (0.01)	0.03 (0.01)	8.9 (0.1)
	Def	0.28 (0.07)	0.25 (0.08)	0.65 (0.14)	5.9 (1.7)	5.2	0.63 (0.13)	0.13 (0.04)	0.31 (0.01)	0.06 (0.02)	0.04 (0.02)	9.4 (0.3)
	Sew	0.56 (0.02)	0.83 (0.20)	1.9 (0.2)	17 (2)	22 (2)	8.2 (1.7)	0.68 (0.09)	3.6 (1.0)	2.0 (0.6)	0.21 (0.08)	9.1 (0.1)
	Ag	0.55 (0.05)	0.67 (0.20)	2.5 (0.1)	19 (0)	21 (1)	6.4 (1.6)	0.55 (0.02)	3.2 (1.4)	1.4 (1.1)	0.25 (0.01)	8.0 (0.3)
Juniper Basin	Ref	-	-	-	-	-	-	-	-	-	-	9.9 (0.3)
	Def	0.09 (0.03)	0.09 (0.00)	0.20 (0.07)	1.6 (0.0)	1.4 (0.7)	0.16 (0.12)	0.05 (0.05)	0.11 (0.09)	0.02 (0.02)	0.04	10 (0)
	Sew	0.07	0.11	0.23	2.1	2.6	0.33	0.05	0.10	-	0.01	9.2
	Ag	0.08	0.10	0.31	2.7	3.8	1.4	0.17	0.30	0.08	0.09	8.7
Schuyler Is.	Ref	-	-	-	-	-	-	-		-	-	-
	Def	0.30 (0.03)	0.23 (0.01)	0.30 (0.03)	4.8 (0.8)	8.7	0.26 (0.14)	0.08 (0.04)	0.18 (0.07)	0.05 (0.00)	0.008 (0.004)	8.4 (0.3)
	Sew	0.67 (0.03)	0.68 (0.09)	0.67 (0.03)	19 (2)	161 (38)	2.3 (1.6)	0.55 (0.11)	1.2 (0.12)	0.29 (0.03)	0.14 (0.06)	10 (0)
	Ag	0.43 (0.08)	0.78 (0.20)	0.65 (0.05)	16 (1)	203 (1)	6.1 (0.2)	0.60 (0.00)	1.4 (0.1)	0.35 (0.04)	0.19 (0.10)	8.0 (0.3)

Table 1B. Continuation of Table 1A.

							Total Algae Chl a+Pheo a	Cyanobacteria	Cryptophytes	Diatoms	Chlorophytes Chl b+Pheo b	
	Era	SAR	PAR	NAR	OCAR	BSiAR	AR	Echin. AR	Allox AR	Diax AR	AR	C: N
I. Malletts Bay	Ref	0.34 (0.17)	0.42 (0.16)	0.60 (0.22)	8.8 (4.4)	3.7	0.92 (0.90)	0.14 (0.12)	0.24 (0.20)	0.05 (0.04)	0.06 (0.07)	9.2 (0.2)
	Def	0.56 (0.14)	0.68 (0.19)	0.68 (0.30)	12 (3)	9.2	1.4 (0.9)	0.24 (0.08)	0.57 (0.32)	0.10 (0.06)	0.08 (0.03)	8.9 (0.1)
	Sew	0.45 (0.06)	0.54 (0.06)	2.0 (0.1)	17 (1)	13 (1)	12 (2)	0.57 (0.12)	1.4 (0.7)	0.64 (0.46)	0.20 (0.03)	8.9 (0.4)
	Ag	0.41 (0.01)	0.69 (0.17)	2.6 (0.1)	18 (1)	15 (1)	15 (4)	0.71 (0.15)	1.1 (0.4)	0.31 (0.19)	0.29 (0.07)	8.2 (0.1)
O. Malletts Bay	Ref	-	-	-	-	-	-	-	-	-	-	10.5 (0.3)
	Def	0.58 (0.08)	0.68 (0.12)	1.4 (0.2)	14 (3)	9.2	1.3 (0.5)	0.23 (0.05)	0.55 (0.16)	0.18 (0.08)	0.13 (0.06)	12 (0)
	Sew	0.55 (0.00)	0.83 (0.03)	2.4 (0.1)	23 (2)	7.3 (1.0)	12 (2)	1.1 (0.3)	4.0 (0.9)	3.0 (1.0)	0.30(0.11)	10 (1)
	Ag	0.56 (0.08)	0.89 (0.17)	2.2 (0.2)	24 (2)	12 (2)	19 (8)	1.8 (0.5)	5.1 (1.7)	3.6 (1.6)	0.72 (0.06)	8.9 (0.2)
Pt. Au Roche	Ref	0.32 (0.02)	-	0.60 (0.04)	5.3 (0.4)	-	-	-	-		-	8.7 (0.2)
	Def	0.34 (0.04)	-	0.68 (0.06)	6.2 (0.6)	6.6	-	-	-		-	9.2 (0.1)
	Sew	0.40 (0.02)	-	1.9 (0.2)	16 (1)	23 (2)	-	-	-		-	8.1 (0.1)
	Ag	0.44 (0.00)	-	2.6 (0.0)	20 (0)	40 (5)	-	-	-		-	7.9 (0.0)
Savage Is.	Ref	-	-	-	-	-	-	-	-	-	-	8.3
	Def	0.17	0.14	0.22	1.8	1.9	0.27	0.006	0.11	0.12	0.82	7.6
	Sew	0.10	0.11	0.46	3.1 (0.7)	4.0	1.9	0.030	0.29	0.15	12	7.4
	Ag	0.10	0.21	0.47	-	6.3	3.8	0.20	0.63	2.5	14	7.4
St. Albans Bay	Ref	0.27	0.26	0.73	7.7	-	2.0	0.10	0.16	0.13	1.4	10.4 (0.0)
	Def	0.28 (0.05)	0.30 (0.05)	0.94 (0.22)	9.3 (2.0)	2.6	3.1	0.20	0.3	0.26	10	9.9 (0.3)
	Sew	0.90 (0.27)	1.1 (0.4)	4.2 (1.5)	34 (13)	24 (6)	27 (12)	3.9 (1.7)	2.8 (1.1)	2.7 (1.2)	16 (6)	9.1 (0.2)
	Ag	1.2 (0.0)	1.6 (0.1)	6.5 (0.2)	57 (1)	34 (1)	50 (7)	4.2 (0.7)	4.4 (0.6)	5.0 (1.1)	20 (1)	8.7 (0.2)
Cheney Pt.	Ref	0.26	0.12	0.34	2.8	0.9	0.14	0.05	0.11	0.03	0.02	8.4 (0.1)
	Def	0.19 (0.10)	0.15 (0.09)	0.38 (0.14)	3.1 (1.2)	1.5 (0.4)	0.29 (0.24)	0.06 (0.00)	0.12 (0.01)	0.03 (0.01)	0.14 (0.15)	8.1 (0.3)
	Sew	0.20	0.28	1.6	12	8.7	6.1	0.65	2.2	0.66	1.6	7.3
	Ag	0.27	0.63	2.4	18	12.4	18	0.88	1.9	0.69	4.0	7.4
Missisquoi Bay	Ref	0.68	0.63	1.3	16	-	0.98	0.07	0.16	0.09	1.3	11.9 (0.3)
	Def	0.68 (0.13)	0.67 (0.05)	1.4 (0.2)	16 (2)	5.5	2.4 (1.1)	0.11 (0.02)	0.32 (0.01)	0.13 (0.02)	2.6 (0.4)	12 (0)
	Sew	0.94 (0.06)	1.2 (0.2)	2.7 (0.5)	25 (3)	12 (7)	8.9 (8.8)	1.0 (0.4)	1.1 (0.6)	0.72 (0.42)	5.9 (3.3)	10 (1)
	Ag	1.3 (0.1)	1.9 (0.4)	4.3 (1.1)	39 (8)	47 (11)	37 (17)	2.7 (1.9)	3.8 (1.3)	2.9 (1.3)	15 (3)	9.1 (0.4)