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Paleolimnological proxies reveal continued eutrophication issues in the St. Lawrence River Area of Concern

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Abstract

Recent surface-water surveys suggest that high nutrient concentrations and nuisance algae remain issues in the St. Lawrence River Area of Concern (AOC) at Cornwall, Ontario, specifically in the tributaries and nearshore zones of Lake St. Francis (LSF). In particular, it is unclear whether management actions designed to reduce nutrient inputs, first implemented in the 1990s as part of the Remedial Action Plan for the AOC, have reduced algal production or influenced assemblage composition. To address this issue, a paleolimnological approach was used to provide a historical context for the present-day nutrient concentrations and to quantify the extent of change in water quality in LSF since the early 1990s. A sediment core was collected near the north shore of LSF and was examined for changes in the concentrations and compositions of fossil diatoms and pigments, as well as stable isotope ($\delta^{15}N$ and $\delta^{13}C$) values. Analyses of diatom and pigment concentrations indicated that overall algal abundance has risen in the last few decades, including trends of increasing occurrences of potentially toxic cyanobacteria, despite ongoing remediation efforts. Temporal patterns of stable isotope signatures in the core suggest a steady increase in nutrient influx since the mid-20th century, with the post-1990 increase in algal production likely attributable to recent inputs associated with land-use changes in local contributing watersheds. These patterns suggest that the AOC delisting goals for the LSF tributaries will not be reached without a drastic change in land management practices.

Keywords

Eutrophication, paleolimnology, St. Lawrence River, pigments, diatoms, stable isotopes

Introduction

Within the Laurentian Great Lakes Basin, 43 Areas of Concern (AOCs) have been identified by the International Joint Commission as regions that have experienced environmental degradation as a result of biological, chemical, or physical changes in the aquatic ecosystem (Dreier et al., 1997; International Joint Commission, 2003a). The St. Lawrence River near Cornwall, ON, and Massena, NY, is the easternmost AOC where environmental issues arose from intensive industrial and agricultural activities, habitat loss and degradation, as well as from hydrodynamic changes from anthropogenic modifications to the waterway such as the construction of the St. Lawrence Seaway (Anderson et al., 1992). Two Remedial Action Plans (RAPs) were developed for the St. Lawrence River AOC at Cornwall and Massena, serving to identify and remediate beneficial use impairments (BUIs; International Joint Commission, 2012) in the Canadian and U.S. portions of the AOC, respectively. Within the Canadian section of the AOC, many of the identified environmental stressors have been mitigated through regulations and local action, including reductions in the concentrations of harmful bacteria, improved management of fish populations, and restrictions on industrial discharges to the waterway (Environment Canada and Ontario Ministry of the Environment, 2010). However, three BUIs remain impaired in this AOC, including eutrophication and the presence of undesirable algae (e.g., toxic cyanobacterial blooms), a problematic issue in the nearshore zones and tributaries of the fluvial lake known as Lake St. Francis (LSF; Environment Canada and Ontario Ministry of the Environment, 2010).

Increased nutrient loadings from the LSF watersheds, faulty septic systems in nearshore communities, changes to the hydraulics of the system from seaway construction, and climate change have all been suggested as contributing sources of the nuisance eutrophication and algal blooms in the AOC (Anderson et al., 1992; The St. Lawrence River (Cornwall) RAP Team, 1995). Although only 5% of the water in LSF originates in its tributaries (Anderson et al., 1992), the large proportion of agricultural land in the contributing watersheds could disproportionately affect nutrient loadings to LSF and impair water quality in nearshore areas. Remediation goals for eutrophication in the AOC originally included mean summer tributary and nearshore total phosphorus (TP) concentrations ≤ 30 μg/L and no eutrophication-related fish kills (Dreier et al., 1997). The targets for TP concentration in the tributaries were updated in 2009 to reflect proportional goals based on the amount of agricultural activity in each watershed, ranging from 35-60 μg/L (AECOM Canada Ltd., 2009; J. Ridal, pers. comm.). The TP target for the main body of LSF, beyond the 2-m isopleth, remains at 20 μg/L and is not currently considered impaired.

Since the early 1990s, efforts to reduce eutrophication in LSF have primarily targeted nutrients emanating from local farms and those from the city of Cornwall. Actions have included tributary restoration programs (including tree planting along tributary banks and fencing to restrict cattle access to streams), upgrades to septic systems, reductions in agricultural runoff through the *Nutrient Management Act* (2002), upgrades to the city of Cornwall wastewater treatment plant, and reductions in the number of combined sewers in the city of Cornwall (Environment Canada and Ontario Ministry of the Environment, 2010). Unfortunately, monitoring of the water-quality and ecological responses to these actions has been limited, hampering the ability to assess potential eutrophication declines in LSF. Monitoring data for both TP and algal abundance and community structure are sparse prior to the last decade (Pilon and Chrétien, 1991; Reavie et al., 1998; Richman et al., 1997), and it remains unclear if and how algal communities in the tributaries and nearshore zones of LSF have responded to remedial actions.

Provided that the sediment has remained relatively undisturbed, paleolimnological approaches can be applied to LSF to examine how algal assemblages have responded to the implementation of the RAP, and how those communities have changed over time. Previous paleolimnological characterisations of the eastern end of LSF, collected in the early 1990s, suggested that diatom communities responded to the known period of eutrophication in the Great Lakes in the mid-20th century, and additionally responded to well-documented macrophyte growth in the region (Reavie et al., 1998). However, less is known about historical changes in other groups of primary producers, including potentially toxin-producing cyanobacteria such as *Anabaena* and *Microcystis* (Carmichael, 2001), occurrences of which have been reported in this region in recent years (Bramburger, 2014; Waller et al., 2016). Paleolimnological techniques have been successfully applied to other AOCs (e.g., Alexson et al., 2017; Dixit et al., 1998), providing valuable information to stakeholders regarding historical environmental changes to the impacted systems.

The objective of the current study is to assess the degree to which the abundance and composition of algal communities in the nearshore areas of LSF have changed since the implementation of the RAP in the early-1990s. Although some surface-water sampling has been conducted in recent years, the response of algal assemblages to actions implemented as part of the RAP has not been examined, despite ongoing concerns regarding high nutrient concentrations and algal blooms in the AOC, including occurrences of toxin-producing cyanobacteria (Bramburger, 2014; Environment Canada and Ontario Ministry of the Environment, 2010; Savard et al., 2013, 2015). To address this issue, we quantified sedimentary concentrations of photosynthetic pigments known to reliably indicate historical changes in abundances of primary producers (Hall et al., 1999; Leavitt and Findlay, 1994), fossil diatom assemblages to infer past environmental conditions along the impacted northern shore of LSF (Battarbee et al., 2002; Reavie and Edlund, 2010), and carbon (C) stable isotopes to evaluate temporal changes in production and C sources (Hodell and Schelske, 1998; Savage et al., 2010). In addition, stable isotopes of nitrogen (N) were used to infer historical changes in nutrient sources arising from changes in aquatic production (N_2 fixation), agriculture within the watershed, or regional urban development (Bunting et al., 2016; Leavitt et al., 2006). These proxies can be used to provide a comprehensive overview of changes to algal abundance, production, and composition, suitable to evaluate water quality status. This information is valuable to the St. Lawrence River AOC, as beneficial uses must be restored to all 14 BUIs prior to delisting (International Joint Commission, 2012), including reductions in symptoms of eutrophication and the presence of undesirable algae.

Methods

Study Area

The St. Lawrence River at Cornwall, Ontario, Canada, marks the eastern end of the international section of the waterway and is located just downstream of the Moses-Saunders Power Dam. East of the city of Cornwall, the river widens into Lake St. Francis for 50 km before narrowing again as it passes around Grande-Île, near Salaberry-de-Valleyfield, Quebec (Fig. 1a). Lake St. Francis covers approximately 233 km^2, with a mean depth of 6 m (maximum 26 m), short hydraulic residence time (3 days) and a total volume of 2.8 km^3 (Anderson et al., 1992; Fortin et al., 1994). Water level is controlled in this portion of the St. Lawrence River by the Moses-Saunders Power Dam upstream and the Coteau works and Beauharnois hydroelectric generating station downstream (Anderson et al., 1992). Water levels in the St. Lawrence River are regulated by the International Joint Commission to stabilise Lake Ontario and to ensure adequate capacity for navigation, hydroelectric power generation, and flood control (Yee et al., 1990). In LSF, Hydro Quebec manages the downstream discharge through the Beauharnois dam such that water level variation is typically <20 cm (Morin and Leclerc, 1998). Approximately 95% of the flow in LSF comes from Lake Ontario, with the remainder originating from tributaries on the north and south shores (Anderson et al., 1992). Little mixing occurs across the main shipping channel, which divides the north and south portions of LSF, each of which is differently influenced by local inflow tributaries (International Joint Commission, 2003b). As a result, the main channel and the flows north and south thereof can be considered to be three distinct water bodies (Dreier et al., 1997). On the northern shore, nine Ontario watersheds drain into LSF, the largest of which, the Raisin River watershed, covers over 500 km^2 (Fig. 1b, c). Across the northern watersheds, the dominant agricultural products are corn and soybeans, accounting for 15% and 14% of land use, respectively, with other dominant land cover including forest (43%), pasture and forages (15%), and urban and developed areas (8%; 2015 annual crop inventory data from Agriculture and Agri-Food Canada, http://open.canada.ca/data/en/dataset/3688e7d9-7520-42bd-a3eb-8854b685fef3, accessed 25 July, 2017).

In the deep, fast-flowing channels of the river, sedimentation does not reliably occur (Carignan and Lorrain, 2000), making the collection of a sediment core representative of past conditions unlikely from deeper sites. Several areas in LSF also have been disturbed previously by dredging activities when the shipping channel was created as part of the construction of the St. Lawrence Seaway in the 1950s (Morin and Leclerc, 1998); such areas were avoided for the current study to ensure a continuous, undisturbed sedimentary record. In the AOC, five sedimentation basins have been described (Lorrain et al., 1993), two of which are on the northern side of the main channel of the St. Lawrence River and are likely to be influenced by flows from the northern tributaries. Sediment cores with reliable, continuous dating profiles have previously been collected from both of these basins (Carignan and Lorrain, 2000). The more westerly of these two basins, located just east of Lancaster, Ontario, is in a portion of the river that has seen extensive water-quality monitoring take place since 2010 (Bramburger, 2014; Savard et al., 2013, 2015). Both the availability of recent monitoring data and the known sedimentation characteristics of the basin influenced the selection of this site for sample collection.

Sediment Collection

A sediment core was collected on May 5, 2016 from the St. Lawrence River near Lancaster, Ontario, Canada (74°27’47”W, 45°08’07”N; Fig. 1b) using a modified gravity corer (Glew, 1989) with an internal diameter of 7.62 cm. The collection site was located approximately 900 m from shore, 2.5 km downstream from the outlet of the Raisin River (Fig. 1b). The core was collected from a depth of 5 m to minimise sediment mixing (Carignan and Lorrain, 2000; Lepage et al., 2000). Additionally, this location was selected for sample collection to best achieve proximity to tributary inputs while remaining deep enough to experience permanent sediment deposition without resuspension.

The collected core was sectioned in the field into 0.5-cm increments which were bagged, transported in the dark to Queen's University, and stored in the dark at ~4°C until analysis. Subsamples were taken for determination of sediment ages using gamma spectroscopy, pigment concentrations using high performance liquid chromatography (HPLC), organic matter content via loss-on-ignition (LOI), stable isotope analyses using mass spectrometry, and diatom assemblages using light microscopy.

Chronology

Gamma spectroscopy was used to measure the activities of total ^{210}Pb, ^{214}Pb and ^{214}Bi (proxies of supported ^{210}Pb), and ^{137}Cs following the methods of Schelske et al. (1994) in 25 intervals throughout the core. Sediments were freeze-dried, then approximately 1 g dry mass was sealed into counting tubes using 2-Ton® Epoxy. Samples were left for 2 weeks for in situ decay of ^{226}Ra to stabilise. The constant rate of supply (CRS) calculation of Appleby and Oldfield (1978) was used to estimate sediment ages using unsupported ^{210}Pb activity in conjunction with ^{137}Cs activity, an independent indicator of the year 1963 (Appleby, 2002).

Pigments

Frozen subsamples of whole sediments were taken for determination of photosynthetic pigment concentrations from 37 intervals throughout the core. Pigments were extracted and quantified using high performance liquid chromatography (HPLC) following the protocol outlined in Leavitt and Hodgson (2001). Briefly, frozen samples were freeze-dried, and approximately 0.05 g of dried sediment was extracted using a mixture of acetone:methanol:water (80:15:5, by volume) to extract chlorophylls, carotenoids, and their derivatives. Extracts were evaporated to dryness under a stream of N_2, then redissolved in injection solvent containing Sudan II dye as an internal standard. Pigment concentrations are reported as nmoles pigment/g organic matter. HPLC analyses were restricted to common taxonomically-diagnostic pigments including fucoxanthin (siliceous algae), diatoxanthin (mainly diatoms), alloxanthin (cryptophytes), phaeophytin *b* (chlorophytes), echinenone (total cyanobacteria), canthaxanthin (Nostocales cyanobacteria), and β-carotene (all phytoplankton). In addition, lutein (chlorophytes) and zeaxanthin (cyanobacteria) were not separable on our HPLC system and were used as an index of bloom-forming taxa (Leavitt et al., 2006; Leavitt and Hodgson, 2001).

Organic Matter and Stable Isotopes

Percent organic matter was determined through standard LOI procedures (Dean, 1974) in 25 intervals throughout the sediment core. Briefly, a known mass (~0.08 g) of freeze-dried sediment was tared and combusted at 550°C for 4 hours to determine organic content, then ignited at 950°C for 2 hours to determine carbonate content. Stable isotopes of N ($\delta^{15}N$) and C ($\delta^{13}C$), as well as elemental N and C contents, were determined using isotope ratio mass spectrometric (IRMS) analysis of 0.01-0.015 g of freeze-dried sediment following Savage et al. (2010). IRMS was performed using a Thermoquest (Finnigan-MAT) Delta Plus^{XL} mass spectrometer coupled with a Carlo Erba NC2500 elemental analyser (Savage et al., 2010). Isotope values are presented as per mille (‰) differences of samples to standard references for each element (Savage et al., 2010). Sediment elemental composition is reported as the mass ratio of C:N, as determined through the elemental analyser.

Diatoms

Diatom slurries were prepared for enumeration after removal of organic matter using an acid digestion procedure. Briefly, approximately 0.2-0.3 g of whole wet sediment was subsampled at 1-cm intervals into 20-mL glass scintillation vials. Known masses of sediment were mixed with a 50:50 (molar) solution of sulphuric and nitric acids overnight, then digested in a hot water bath at 70°C for 8 hours. Diatoms were allowed to settle for 24 hours, after which the supernatant above the settled diatoms was aspirated. Scintillation vials were then refilled with double-deionised water, and samples were agitated to resuspend the diatoms. Samples were rinsed until the pH was the same as deionised water, as verified with litmus paper (typically eight rinses). Samples were then spiked with a solution of microspheres (mean diameter = 7.9 μm) of known concentration (34,000 microspheres/mL). Samples were plated on coverslips in a series of four dilutions and allowed to evaporate, after which they were fixed permanently to slides using Naphrax®, a medium with a high refractive index (>1.7).

Diatom valves were identified and enumerated using a Leica (DMRB model) microscope fitted with a 100x fluotar objective (numerical aperture of objective = 1.3) and using differential interference contrast optics at 1000x magnification. Diatoms were identified to species wherever possible, or to the lowest possible taxonomic classification. Valves were counted until a minimum of 400 valves were enumerated, or, if the concentration of valves was exceptionally low, until five transects were completed. Primary taxonomic keys used for diatom identification were Krammer and Lange-Bertalot (1991a, 1991b, 1988, 1986) and Reavie and Smol (1998).

The main chronological zones of diatom species assemblages were estimated using a constrained incremental sum of squares analysis (CONISS; Grimm, 1987), performed in the R computing environment (R Core Team, 2015) and the *rioja* (Juggins, 2015) and *vegan* (Oksanen et al., 2015) packages. Diatom abundances were Hellinger-transformed (Rao, 1995) prior to CONISS analysis using Euclidean distance, to minimise distortions that can occur when zero values are present (Legendre and Legendre, 2012). A broken stick model (Bennett, 1996) was used to determine the number of significant zones in the stratigraphic sequence.

Results

Chronology

The total ^{210}Pb activity decreased from the top of the sediment core and followed an exponential decay ($r^2 = 0.83$; Fig. 2). Both ^{214}Pb and ^{214}Bi activities remained relatively constant throughout the core, and are consistent with previously collected sediment cores from LSF which have reported supported ^{210}Pb activities of approximately 20 Bq/kg (Carignan and Lorrain, 2000). ^{137}Cs activity reached a distinct peak at a depth of 18.25 cm.

Application of the CRS model to determine sediment ages and sedimentation rates from the unsupported ^{210}Pb activities suggested that dates were reliable until approximately 30-cm burial depth (ca. 1940; Fig. 2). Although local error estimates are large, sedimentation rates appear to have increased substantially between depths of approximately 25 and 20 cm (1955-1959) in the core. The depth at which the year 1963 occurred was agreed-upon by the ^{210}Pb model and the analysis of ^{137}Cs activity (~18 cm). Given this dating profile, approximate depths in the core for the designation of the AOC (1987) and the release of the Stage 1 (1992) and Stage 2 (1997) RAP reports are 9.75 cm, 8.75 cm, and 7.25 cm, respectively.

Pigments

Analysis of concentrations of all pigment biomarkers suggested a progressive increase in lake production during the 20th century (Fig. 3). In general, total phytoplankton abundance (as β-carotene) was stable from the base of the core to ca. 1960, after which time inferred abundance increased approximately twofold to an irregular plateau after ca. 1980. As ratios of labile to stable pigments (chlorophyll *a*:phaeophytin *a*) did not change in the ca. 1960-1980 interval, we infer that elevated concentrations of pigments reflect actual increases in mean water column standing stock, rather than alterations in the preservation environment. Although timing of the concentration change varies slightly among algal groups, concentrations of chemically-stable biomarkers from total (echinenone) and colonial cyanobacteria (canthaxanthin), chlorophytes (phaeophytin *b*), diatoms (diatoxanthin) and cryptophytes (alloxanthin) all exhibited similar patterns, with elevated abundance of these groups after the mid-1970s. In contrast, levels of labile pigments from siliceous (fucoxanthin) and total algae (chlorophyll *a*) declined exponentially with burial depth, suggesting rapid degradation following deposition, especially in the most recent 5 years. Finally, concentrations of many chemically-stable pigments increased sharply after ca. 2005, suggesting a recent increase in either algal abundance or changes in sedimentary preservation.

Organic Matter and Stable Isotopes

The organic matter content remained relatively constant throughout the core, varying between 8% and 13% of dry mass (Fig. 4). In contrast, $\delta^{15}N$ values were stable (~5‰) from the bottom of the core until the early 1960s (~20-cm depth) and then increased steadily towards 7‰ at the top of the core, in a pattern similar to the changes in total algal abundance (Fig. 3). The $\delta^{13}C$ values increased rapidly from approximately -23‰ at ~30-cm depth (early 20th century) to -16‰ at 25 cm (ca. early 1950s), before declining to consistent values of approximately -20‰ in sediments deposited in the upper 20 cm of the core (after 1960; Fig. 4). The C:N mass ratio followed a similar trajectory to that of $\delta^{13}C$, starting at approximately 15 at the base of the core, increasing to ~23 at a depth of 25 cm (ca. 1960), then gradually decreasing until the top of the core where it reached a value of 10 (Fig. 4).

Diatoms

Concentrations of diatoms increased exponentially from ~1 x 10^5 valves/g dry mass prior to ca. 1960 to greater than 4 x 10^6 valves/g dry mass in surface deposits (Fig. 5). After ca. 1970, diatom concentrations increased in a pattern moderately correlated ($r^2 = 0.57$, $p < 0.001$) with fossil concentrations of the labile biomarker of siliceous algae (fucoxanthin). Constrained cluster analysis using CONISS distinguished two main zones of diatom species assemblages, which appear to correspond to intervals before and after construction of the Moses-Saunders Power Dam (1954-1959; 23.25-cm depth). The older assemblage was characterised by higher abundances of *Fragilaria construens* (Ehrenberg) Grunow, *Sellaphora submuralis* (Hustedt) Wetzel, Ector, Van de Vijver, Compère, & Mann, *Achnanthes clevei* Grunow, and *Cocconeis neothumensis* Krammer. Above 23.25 cm, several taxa became much more prevalent, including *Achnanthidium minutissimum* (Kützing) Czarnecki, *F. capucina* Desmazières, *C. placentula* (Ehrenberg) Grunow, *Navicula cryptotenella* Lange-Bertalot, and *Nitzschia fonticola* Grunow. Other taxa, such as *Amphora pediculus* (Kützing) Grunow ex Schmidt, *Staurosirella pinnata* (Ehrenberg) Williams & Round, *Pseudostaurosira brevistriata* (Grunow) Williams & Round, and *Planothidium lanceolatum* (Brébisson ex Kützing) Lange-Bertalot, were present in relatively high abundances throughout the core. Diatoms identified were predominantly benthic taxa.

Discussion

Analyses of fossil pigments, diatoms, and stable isotopes revealed a progressive increase in the abundance of primary producers in this portion of LSF during the late-20th century, continuing into the 21st century (Figs. 3-5). In general, algal abundance and community composition were relatively stable prior to the 1954-1959 construction of the Moses-Saunders Power Dam and the St. Lawrence Seaway, with low and constant concentrations of biomarker pigments from diatoms (diatoxanthin) and chlorophytes (phaeophytin *b*, lutein-zeaxanthin), and lower abundances of total (echinenone) and colonial (canthaxanthin) cyanobacteria. Diatom assemblage composition changed after dam construction (ca. 1960), though assemblages before and after this period were both characterised by benthic taxa, none of which indicated a change to LSF trophic status. Total algal abundance appears to have increased after ca. 1970, with an approximate two-fold increase in fossil concentrations of most pigment biomarkers (Fig. 3), but no marked change in the preservation environment, as recorded by the degradation index of labile chlorophyll *a* to stable phaeophytin *a* (Leavitt and Hodgson, 2001). This increase in abundance occurs in parallel with elevated nutrient supply inferred from the $\delta^{15}N$ signal (Fig. 4). Microfossil and labile pigments from diatoms were particularly abundant after ca. 2005, as were concentrations of chemically stable carotenoids from total cyanobacteria (echinenone, lutein-zeaxanthin) and cryptophytes (alloxanthin) but not those from chlorophytes (phaeophytin *b*) or total algae (β-carotene). Overall, this pattern shows that water quality along the north shore of LSF did not improve as a result of local and regional remedial actions implemented in the early 1990s and suggests that substantial additional measures to curb nutrient influxes from regional and headwater sources are required if the AOC delisting goals relating to eutrophication and undesirable algae are to be achieved.

Baseline Conditions (pre-1950s)

Prior to the construction of the Moses-Saunders Power Dam and the St. Lawrence Seaway in the mid-1950s, conditions were stable, with relatively constant concentrations of most photosynthetic pigments, low and steady concentrations of diatoms, and diatom assemblages characterised by predominantly benthic taxa. Organic material in the aquatic environment was supplied by both autochthonous and allochthonous sources, as indicated by the moderate and stable molar ratio of C:N (Meyers and Ishiwatari, 1993; Fig. 4). An exact chronology is difficult to assign to this portion of the sediment core, as errors associated with sediment dating are large (Fig. 2); however, we are confident that the bottom four intervals represent a period of time prior to the 1950s. Although we cannot consider these records to represent pristine conditions, as industrial activity had been occurring upstream of our site in Cornwall, Ontario, since the late-19th century (Stein, 1995), we will refer to them as baseline conditions which represent a period prior to the major anthropogenic changes that occurred in our system during the second half of the 20th century.

St. Lawrence Seaway and Power Dam (mid-1950s)

Between 1954 and 1959, two major construction projects occurred in this portion of the St. Lawrence River: the construction of the Moses-Saunders Power Dam and the dredging of the St. Lawrence Seaway. These concurrent events appear to be represented in our paleolimnological record through marked changes in $\delta^{13}C$ values and C:N ratios, as well as diatom species composition. For example, although the $\delta^{15}N$ values remained relatively stable through the 1950s, the C:N ratio increased quickly at this time, indicating a substantial increase in the terrestrial fraction of organic matter entering the system (Meyers and Ishiwatari, 1993). At the same time, a sharp increase in the $\delta^{13}C$ signal (Fig. 4) to values characteristic of regional terrestrial plants suggests an increase in organic matter subsidies from adjacent farms (Meyers and Ishiwatari, 1993). Elevated influxes of terrestrial organic matter most likely arose from the construction of the Moses-Saunders Power Dam, which flooded more than 75 km^2 of land, much of it agricultural, on July 1, 1958 (Macfarlane, 2014). High sedimentary $\delta^{13}C$ values in the 1950s may be additionally driven by an elevated proportion of C4 plants such as corn in the watershed. At present, corn is a predominant crop within the local catchment area (2015 annual crop inventory data from Agriculture and Agri-Food Canada, http://open.canada.ca/data/en/dataset/3688e7d9-7520-42bd-a3eb-8854b685fef3, accessed 25 July, 2017), although we recognise that it is difficult to distinguish among potential plant sources of C from an analysis of bulk sediment isotopic values.

Analysis of the fossil diatom assemblages using stratigraphically constrained hierarchical cluster analysis revealed only a single transition in species assemblages, which occurred in the late-1950s, coinciding with the construction of the Moses-Saunders Power Dam and the St. Lawrence Seaway (Fig. 5). Previous research at the eastern end of LSF has suggested that an increase in epiphytic diatom taxa and inferred higher macrophyte coverage occurred in the early- to mid-20^{th} century, possibly attributable to a decrease in the variability of the water level resulting from Seaway construction and the construction of water control structures at the eastern end of LSF (Reavie et al., 1998). Seasonal water level variability in LSF was known to exceed 0.5 m in the first half of the 20^{th} century, but this variability was reduced to less than 0.2 m after the construction of the Moses-Saunders Power Dam (Morin and Leclerc, 1998). Although some epiphytic diatom taxa (e.g., *Cocconeis placentula*) were observed in the current study to be more abundant after the construction of the Moses-Saunders Power Dam, possibly attributable to higher macrophyte coverage due to stabilisation of water levels, many of the diatom taxa that were abundant following dam construction (e.g., *Fragilaria capucina*, *Amphora pediculus*) can be commonly found on other substrata (e.g., rocks; Reavie and Smol, 1997). The diatom assemblages before and after the late-1950s share many characteristics, such as being predominantly benthic taxa with no strong trophic status affiliations, with some epiphytic taxa present. It seems likely that the two major construction projects in the St. Lawrence River in the 1950s caused a substantial disturbance to the aquatic environment (as indicated by the abrupt terrestrial loading suggested by the C:N ratio), which allowed a slightly different diatom assemblage to settle and thrive once the disturbance was over.

20^{th} Century Eutrophication (1960s-1970s)

In the 1960s and 1970s, the lower Laurentian Great Lakes were characterised by intensive eutrophication and related algal blooms and hypoxia (Beeton, 1965; Mortimer, 1987; Schelske, 1991), events which are represented in our core by increases in photosynthetic pigments and diatoms. The pigment data suggest that production increased first in the early- to mid-1970s, indicated particularly by biomarkers derived from bloom-forming cyanobacteria (canthaxanthin), chlorophytes (phaeophytin *b*), diatoms (diatoxanthin), and total production (β-carotene). This trend is supported by an increase in diatom production between the early-1960s and 1970s, during which a 4-fold increase in fossil frustule concentration occurred, and a previously reported mid-20th century increase in eutrophic diatom taxa at the eastern end of LSF (Reavie et al., 1998). At present, we cannot easily distinguish between elevated production in LSF due to inputs of nutrient- and phytoplankton-rich waters from the upstream Great Lakes, and elevated production due to eutrophication of the LSF basin from local nutrient influx, as historical surface water-quality monitoring data are limited. However, nutrient monitoring of the Raisin River, a major tributary near the sampling location of the current study, indicates that, after 1976, high (>30 μg/L) and variable TP concentrations have occurred (data from Ontario Ministry of the Environment and Climate Change, https://www.ontario.ca/data/provincial-stream-water-quality-monitoring-network, site 12007300302, accessed 19 December, 2016).

N influx to LSF appears to have increased markedly during the 1960s and 1970s, as indicated by persistent increases in sedimentary $\delta^{15}N$ values (Fig. 4). As noted elsewhere (Leavitt et al., 2006; Savage et al., 2010; Bunting et al., 2016), the addition of anthropogenic reactive N to terrestrial and aquatic systems often results in the enrichment of adjoining water bodies due to microbial processing of added N and loss of depleted N to the atmosphere. Similarly, the values of $\delta^{15}N$ in aquatic food webs (Anderson and Cabana, 2005) and stream nitrate (Harrington et al., 1998) have been positively correlated with agricultural land use in the surrounding catchment. Consistent with this mechanism, the sharp increase in fertilisation of Ontario farmlands with N between the 1960s and 1980s (Smith, 2015) is expected to have favoured the elevation of both flux and isotopic values of N in runoff into the St. Lawrence River.

Response to Modern Management (post-1990s)

Since the designation of the St. Lawrence River at Cornwall, Ontario, as an AOC, remediation efforts have successfully targeted many of the BUIs. For example, water quality has improved through upgrades to the Cornwall wastewater treatment plant, remediation of decommissioned industrial sites (e.g., chemical manufacturing facilities), and legislation restricting concentrations of harmful substances in wastewater effluent from industrial facilities (Environment Canada et al., 2007; Environment Canada and Ontario Ministry of the Environment, 2010). Similarly, progress has been made on improving fish and wildlife biodiversity and condition through wetland construction, habitat protection programs, and changes to fishing regulations (Environment Canada et al., 2007). As well, many remedial actions in the AOC have targeted the issue of eutrophication and undesirable algae. For example, a tributary restoration program initiated in 1994 has led to the planting of over 300,000 trees in riparian areas, increased buffer zones and cattle exclusion fencing along waterways, upgraded manure storage facilities and rural septic systems, increased well protection projects, and more (Environment Canada et al., 2007). However, despite these efforts, our data suggest that the eutrophication and undesirable algae BUI remains impaired, with continuously elevated algal abundance (as pigment and diatom concentrations) since the 1990s and no evidence of recovery to lower abundances.

Pronounced increases in sedimentary pigment content during the past 10 years were observed for echinenone, a chemically stable biomarker for total cyanobacteria (Leavitt and Hodgson, 2001), and are consistent with increased reports of potentially toxic cyanobacteria in recent years (Bramburger, 2014; Savard et al., 2013, 2015). Elevated cyanobacterial abundance could be attributable to several factors, including high nutrient concentrations (Downing et al., 2001); although lotic TP concentrations from the Raisin River have not increased in recent years, values have remained persistently high (> 30 μg/L) since the early-1990s (data from Ontario Ministry of the Environment and Climate Change, https://www.ontario.ca/data/provincial-stream-water-quality-monitoring-network, site 12007300302, accessed 19 December, 2016), and similarly high TP concentrations have been reported in the nearshore areas of tributary mouths (Savard et al., 2015). Given these consistently high TP values and the evidence of persistent increases in sedimentary nutrient influx in LSF ($\delta^{15}N$ in Fig. 4), it appears likely that recent cyanobacterial growth has been influenced by nutrient inputs. Upstream of our study location, surface-water chlorophyll *a* concentrations collected at Kingston and Brockville have dropped substantially since the 1980s, from approximately 2-5 μg/L to < 1 μg/L (data from Ministry of the Environment and Climate Change, https://www.ontario.ca/data/lake-water-quality-drinking-water-intakes, stations 020170010 and 020180011, accessed 3 September 2017), suggesting that production has not increased in the main river channel flowing into LSF and supporting local nutrient inputs as an influence to cyanobacterial growth. In general, modelling of nutrient fluxes in St. Lawrence River catchments shows that net anthropogenic inputs of nitrogen and phosphorus have increased throughout the 20th century, with pronounced effects of agricultural fertilisers during the past 50 years (Goyette et al., 2016), which may be particularly relevant given the high proportion of agricultural lands in the contributing watersheds to our study site (Fig. 1c). Unfortunately, without refined hydrologic models of water flow in the LSF nearshore region, it is difficult to identify which catchments may be fertilising waters in the AOC. In particular, combining flow modelling with nutrient modelling (Goyette et al., 2016) might allow for the determination of priority areas for nutrient monitoring in the LSF nearshore.

It is possible that other factors have also affected the recent cyanobacterial growth in our study area, though these influences are difficult to assess without in-depth analyses. Recently, persistent eutrophication issues have been described in areas where monitoring data suggest that nutrient concentrations have declined (Alexson et al., 2017), which may be explained in lakes by hypoxia-induced internal phosphorus loading resulting from stronger thermal stratification related to climate change (North et al., 2014). Although it is unlikely that internal phosphorus loading is providing an additional source of nutrients at our shallow, well-oxygenated, fluvial site, hydrologic changes relating to catchment land use and climate change may have altered nutrient delivery to LSF. For instance, pronounced land-use changes in the Raisin River watershed have occurred between 1990 and 2010, with urban areas increasing by 12% and the extent of treed and forested areas decreasing by 20% (data from Agriculture and Agri-Food Canada, http://open.canada.ca/data/en/dataset/02202cec-b4a1-4a1d-9997-edcbaca92d41, http://open.canada.ca/data/en/dataset/9e1efe92-e5a3-4f70-b313-68fb1283eadf, accessed 3 September, 2017). Although land use devoted to crops in this watershed has only increased by 0.5%, deforestation and urbanisation could have increased runoff (Hundecha and Bárdossy, 2004), facilitating the transport of nutrients from the watershed to LSF. Climate change may have also favoured the proliferation of cyanobacteria, either directly (i.e., increased water temperatures; Paerl and Huisman, 2008) or indirectly (e.g., increased frequency of droughts and floods; Paerl et al., 2011). Temperature and precipitation trends in the Great Lakes-St. Lawrence River Basin have climbed throughout the 20th century (Magnuson et al., 1997), and temperature increases and hydrologic changes are expected to continue to occur in St. Lawrence River tributaries throughout the 21st century, particularly in the winter and spring months (Boyer et al., 2010). Though it is impossible to assess the influences of land-use change and climate change on cyanobacterial abundance within the confines of the current study, it is unlikely that these factors have not affected cyanobacterial growth and should be more thoroughly investigated.

Conclusion

Though numerous actions have targeted reducing nutrient inputs to LSF in the past 20 years, we found that algal abundance has not decreased in response to remediation efforts, and that, in fact, populations of cyanobacteria appear to have expanded during the past decade. The causal mechanism for this increase in not immediately clear, but is likely related to continuously high nutrient concentrations in major LSF tributaries, possibly combined with major land-use changes and climate change. The potential for toxin-producing cyanobacterial blooms is particularly troubling for both local and downstream residents, and the cyanobacterial communities of LSF and its tributaries should be monitored closely for the presence of potentially toxin-producing species. As the AOC committee works toward delisting, it is important to recognise that, despite successes in other areas, the sediment record demonstrates continuing impacts to water quality in LSF over the past two decades, indicating that the eutrophication and undesirable algae BUI remains in need of remediation.

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References

AECOM Canada Ltd., 2009. Evaluation of remedial action plan tributary nutrient delisting criteria for the St. Lawrence River, Cornwall, Area of Concern. Bracebridge, ON.

Agriculture and Agri-Food Canada, 2016. Annual Crop Inventory 2015 - Open Government License - Canada.

Alexson, E.E., Reavie, E.D., Axler, R.P., Yemets, S.V., Krasutsky, P.A., Edlund, M.B., Pillsbury, R.W., Desotelle, D., 2017. Paleolimnology of a freshwater estuary to inform Area of Concern nutrient delisting efforts. J. Paleolimnol. https://doi.org/10.1007/s10933-017-0014-8

Anderson, C., Cabana, G., 2005. δ15N in riverine food webs: effects of N inputs from agricultural watersheds. Can. J. Fish. Aquat. Sci. 62, 333–340.

Anderson, J., de Barros, C., Drouillard, J., Eckersley, M., Helliar, B., Lickers, H., Marsden, J., Milnes, J., Pritchard, K., Richman, L., 1992. Remedial action plan for the St. Lawrence River (Cornwall) area of concern. Stage 1 report: environmental conditions and problem definitions.

Appleby, P.G., 2002. Chronostratigraphic techniques in recent sediments, in: Last, W.M., Smol, J.P. (Eds.), Tracking Environmental Change Using Lake Sediments, Developments in Paleoenvironmental Research. Springer Netherlands, pp. 171–203. https://doi.org/10.1007/0-306-47669-X_9

Appleby, P.G., Oldfield, F., 1978. The calculation of lead-210 dates assuming a constant rate of supply of unsupported 210Pb to the sediment. Catena 5, 1–8. https://doi.org/10.1016/S0341-8162(78)80002-2

Battarbee, R.W., Jones, V.J., Flower, R.J., Cameron, N.G., Bennion, H., Carvalho, L., Juggins, S., 2002. Diatoms, in: Smol, J.P., Birks, H.J.B., Last, W.M., Bradley, R.S., Alverson, K. (Eds.), Tracking Environmental Change Using Lake Sediments, Developments in Paleoenvironmental Research. Springer Netherlands, pp. 155–202. https://doi.org/10.1007/0-306-47668-1_8

Beeton, A.M., 1965. Eutrophication of the St. Lawrence Great Lakes. Limnol. Oceanogr. 10, 240–254.

Bennett, K.D., 1996. Determination of the number of zones in a biostratigraphical sequence. New Phytol. 132, 155–170.

Boyer, C., Chaumont, D., Chartier, I., Roy, A.G., 2010. Impact of climate change on the hydrology of St. Lawrence tributaries. J. Hydrol. 384, 65–83. https://doi.org/10.1016/j.jhydrol.2010.01.011

Bramburger, A.J., 2014. Transport and differential influences of phosphorus fractions on algal community dynamics in the nearshore zone of Lake St. Francis, St. Lawrence River. Prepared by the SLRIES for the Ontario Ministry of the Environment and Climate Change.

Bunting, L., Leavitt, P.R., Simpson, G.L., Wissel, B., Laird, K.R., Cumming, B.F., St. Amand, A., Engstrom, D.R., 2016. Increased variability and sudden ecosystem state change in Lake Winnipeg, Canada, caused by 20th century agriculture. Limnol. Oceanogr. 61, 2090–2107. https://doi.org/10.1002/lno.10355

Carignan, R., Lorrain, S., 2000. Sediment dynamics in the fluvial lakes of the St. Lawrence River: accumulation rates and characterization of the mixed sediment layer. Can. J. Fish. Aquat. Sci. 57, 63–77. https://doi.org/10.1139/f99-246

Carmichael, W.W., 2001. Health effects of toxin-producing cyanobacteria: "The CyanoHABs." Hum. Ecol. Risk Assess. Int. J. 7, 1393–1407. https://doi.org/10.1080/20018091095087

Dean, W.E.J., 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. J. Sediment. Res. 44, 242–248. https://doi.org/https://doi.org/10.1306/74D729D2-2B21-11D7-8648000102C1865D

Dixit, A.S., Dixit, S.S., Smol, J.P., Keller, W.B., 1998. Paleolimnological study of metal and nutrient changes in Spanish Harbour, north channel of Lake Huron (Ontario). Lake Reserv. Manage. 14, 428-439. https://doi.org/10.1080/07438149809354349

Downing, J.A., Watson, S.B., McCauley, E., 2001. Predicting cyanobacteria dominance in lakes. Can. J. Fish. Aquat. Sci. 58, 1905–1908.

Dreier, S.I., Anderson, J., Biberhofer, J., Eckersley, M., Helliar, R., Hickey, M.B.C., Richman, L., Stride, F., 1997. Remedial action plan for St. Lawrence River (Cornwall) area of concern. Stage 2 report: The recommended plan.

Environment Canada, Ontario Ministry of the Environment, 2010. St. Lawrence River area of concern (Canadian Section): status of beneficial use impairments.

Environment Canada, Ontario Ministry of the Environment, Ontario Minstry of Natural Resources, St. Lawrence River Restoration Council, 2007. Great lakes, great river: an update to the stage 2 report for the St. Lawrence River (Cornwall) remedial action plan.

Fortin, G., Leclair, D., Sylvestre, A., 1994. Synthèse des connaisances sur les aspects physiques et chimiques de l'eau et des sediments du Lac Saint-Francois: Rapport technique, zones d'intervention prioritaire 1 et 2. Centre Saint-Laurent, Environnement Canada - Région du Québec.

Glew, J., 1989. A new trigger mechanism for sediment samplers. J. Paleolimnol. 2, 241–243. https://doi.org/10.1007/BF00195474

Goyette, J.-O., Bennett, E.M., Howarth, R.W., Maranger, R., 2016. Changes in anthropogenic nitrogen and phosphorus inputs to the St. Lawrence sub-basin over 110 years and impacts on riverine export. Glob. Biogeochem. Cycles 30, 2016GB005384. https://doi.org/10.1002/2016GB005384

Grimm, E.C., 1987. CONISS: a FORTRAN 77 program for stratigraphically constrained cluster analysis by the method of incremental sum of squares. Comput. Geosci. 13, 13–35. https://doi.org/10.1016/0098-3004(87)90022-7

Hall, R.I., Leavitt, P.R., Quinlan, R., Dixit, A.S., Smol, J.P., 1999. Effects of agriculture, urbanization, and climate on water quality in the northern Great Plains. Limnol. Oceanogr. 44, 739–756.

Harrington, R.R., Kennedy, B.P., Chamberlain, C.P., Blum, J.D., Folt, C.L., 1998. 15N enrichment in agricultural catchments: field patterns and applications to tracking Atlantic salmon (Salmo salar). Chem. Geol. 147, 281–294. https://doi.org/10.1016/S0009-2541(98)00018-7

Hodell, D.A., Schelske, C.L., 1998. Production, sedimentation, and isotopic composition of organic matter in Lake Ontario. Limnol. Oceanogr. 43, 200–214.

Hundecha, Y., Bárdossy, A., 2004. Modeling of the effect of land use changes on the runoff generation of a river basin through parameter regionalization of a watershed model. J. Hydrol. 292, 281–295. https://doi.org/10.1016/j.jhydrol.2004.01.002

International Joint Commission, 2012. Revised Great Lakes Water Quality Agreement of 1978 as amended by Protocol signed September 7th, 2012. Retrieved June 13th, 2016 from http://www.ijc.org/en_/Great_Lakes_Water_Quality.

International Joint Commission, 2003a. Status of restoration activities in Great Lakes areas of concern: a special report.

International Joint Commission, 2003b. St. Lawrence River Area of Concern, Status Assessment. Submitted to the Governments of the United States and Canada. Retrieved July 17th, 2016 from www.dec.ny.gov/docs/water_pdf/massenarapstat0513.pdf.

Juggins, S., 2015. rioja: Analysis of Quaternary Science Data, R package version (0.9-6). (http://cran.r-project.org/project=rioja).

Krammer, K., Lange-Bertalot, H., 1991a. Bacillariophyceae. 3: Teil: Centrales, Fragilariaceae, Eunotiaceae, in: Ettl, H., Gärtner, G., Gerloff, J., Heynig, H., Mollenhauer, D. (Eds.), Su¨ßwasserflora von Mitteleuropa, Band 2/3. Stuttgart.

Krammer, K., Lange-Bertalot, H., 1991b. Bacillariophyceae. 4: Teil: Achnanthaceae, in: Ettl, H., Gärtner, G., Gerloff, J., Heynig, H., Mollenhauer, D. (Eds.), Su¨ßwasserflora von Mitteleuropa, Band 2/4. Stuttgart.

Krammer, K., Lange-Bertalot, H., 1988. Bacillariophyceae. 2: Teil: Bacillariaceae, Epithmiaceae, Surirellaceae, in: Ettl, H., Gärtner, G., Gerloff, J., Heynig, H., Mollenhauer, D. (Eds.), Su¨ßwasserflora von Mitteleuropa, Band 2/2. Stuttgart.

Krammer, K., Lange-Bertalot, H., 1986. Bacillariophyceae. 1: Teil: Naviculaceae, in: Ettl, H., Gärtner, G., Gerloff, J., Heynig, H., Mollenhauer, D. (Eds.), Su¨ßwasserflora von Mitteleuropa, Band 2/1. Stuttgart.

Leavitt, P.R., Brock, C.S., Ebel, C., Patoine, A., 2006. Landscape-scale effects of urban nitrogen on a chain of freshwater lakes in central North America. Limnol. Oceanogr. 51, 2262–2277. https://doi.org/10.4319/lo.2006.51.5.2262

Leavitt, P.R., Findlay, D.L., 1994. Comparison of fossil pigments with 20 years of phytoplankton data from eutrophic lake 227, Experimental Lakes Area, Ontario. Can. J. Fish. Aquat. Sci. 51, 2286–2299. https://doi.org/10.1139/f94-232

Leavitt, P.R., Hodgson, D.A., 2001. Sedimentary pigments, in: Smol, J.P., Birks, H.J.B., Last, W.M., Bradley, R.S., Alverson, K. (Eds.), Tracking Environmental Change Using Lake Sediments, Developments in Paleoenvironmental Research. Springer Netherlands, pp. 295–325. https://doi.org/10.1007/0-306-47668-1_15

Legendre, P., Legendre, L.F.J., 2012. Numerical Ecology. Elsevier.

Lepage, S., Biberhofer, J., Lorrain, S., 2000. Sediment dynamics and the transport of suspended matter in the upstream area of Lake St. Francis. Can. J. Fish. Aquat. Sci. 57, 52–62. https://doi.org/10.1139/f99-238

Lorrain, S., Jarry, V., Guertin, K., 1993. Répartition spatiale et évolution temporelle des biphényles polychlorés et du mercure dans les sédiments du Lac Saint-Francois; 1979-1989.

Macfarlane, D., 2014. Negotiating a River: Canada, the U.S., and the Creation of the St. Lawrence Seaway. University of British Columbia Press, Vancouver, B.C.

Magnuson, J.J., Webster, K.E., Assel, R.A., Bowser, C.J., Dillon, P.J., Eaton, J.G., Evans, H.E., Fee, E.J., Hall, R.I., Mortsch, L.R., Schindler, D.W., Quinn, F.H., 1997. Potential effects of climate changes on aquatic systems: Laurentian Great lakes and Precambrian shield region. Hydrol. Process. 11, 825–871. https://doi.org/10.1002/(SICI)1099-1085(19970630)11:8<825::AID-HYP509>3.0.CO;2-G

Meyers, P.A., Ishiwatari, R., 1993. Lacustrine organic geochemistry-an overview of indicators of organic matter sources and diagenesis in lake sediments. Org. Geochem. 20, 867–900. https://doi.org/10.1016/0146-6380(93)90100-P

Ministry of the Environment and Climate Change, 2014. Provincial (Stream) Water Quality Monitoring Network [WWW Document]. URL https://www.javacoeapp.lrc.gov.on.ca/geonetwork/srv/en/metadata.show?id=13826 (accessed 12.19.16).

Morin, J., Leclerc, M., 1998. From pristine to present state: hydrology evolution of Lake Saint-François, St. Lawrence River. Can. J. Civ. Eng. 25, 864–879. https://doi.org/10.1139/l98-019

Mortimer, C.H., 1987. Fifty years of physical investigations and related limnological studies on Lake Erie, 1928–1977. J. Great Lakes Res. 13, 407–435.

North, R.P., North, R.L., Livingstone, D.M., Köster, O., Kipfer, R., 2014. Long-term changes in hypoxia and soluble reactive phosphorus in the hypolimnion of a large temperate lake: consequences of a climate regime shift. Global Change Biol. 20, 811-823. https://doi.org/10.1111/gcb.12371

Nutrient Management Act, S.O. 2002, c.4. Retrieved June 1st, 2017 from https://www.ontario.ca/laws/statute/02n04.

Oksanen, J., Blanchet, F.G., Kindt, R., Legendre, P., Minchin, P.R., O'Hara, R.B., Simpson, G.L., Solymos, P., Stevens, M.H.H., Wagner, H., 2015. vegan: Community Ecology Package. R package version 2.2-1. http://cran.R-project.org/package=vegan.

Paerl, H.W., Hall, N.S., Calandrino, E.S., 2011. Controlling harmful cyanobacterial blooms in a world experiencing anthropogenic and climatic-induced change. Sci. Total Environ. 409, 1739–1745. https://doi.org/10.1016/j.scitotenv.2011.02.001

Paerl, H.W., Huisman, J., 2008. Blooms like It Hot. Science 320, 57–58.

Pilon, R.E., Chrétien, R.-M., 1991. St. Lawrence beaches study: 1990 summary report. Report prepared for the Raisin Region Conservation Authority. Retrieved March 15th, 2016 from http://agrienvarchive.ca/download/RBS-St_Lawrence_beaches90.pdf.

R Core Team, 2015. R: A language and environment for statistical computing.

Rao, C.R., 1995. A review of canonical coordinates and an alternative to correspondence analysis using Hellinger distance. Qüestiió 19, 23–63.

Reavie, E.D., Edlund, M.B., 2010. Diatoms as indicators of long-term environmental change in rivers, fluvial lakes, and impoundments, in: Smol, J.P., Stoermer, E.F. (Eds.), The Diatoms: Applications for the Environmental and Earth Sciences. Cambridge University Press, Cambridge, UK, p. 667.

Reavie, E. D., Smol, J. P., 1997. Diatom-based model to infer past littoral habitat characteristics in the St. Lawrence River. J. Great Lakes Res. 23, 339-348.

Reavie, E.D., Smol, J.P., 1998. Freshwater diatoms from the St. Lawrence River, in: Lange-Bertalot, H., Kociolek, P. (Eds.), Biblioteca Diatomologica: Band 41. Gebruder Borntraeger, Stuttgart.

Reavie, E.D., Smol, J.P., Carignan, R., Lorrain, S., 1998. Diatom paleolimnology of two fluvial lakes in the St. Lawrence River: a reconstruction of environmental changes during the last century. J. Phycol. 34, 446–456.

Richman, L.A., Rupert, G., Young, H., 1997. St. Lawrence River Remedial Action Plan: Technical Report #8.

Savage, C., Leavitt, P.R., Elmgren, R., 2010. Effects of land use, urbanization, and climate variability on coastal eutrophication in the Baltic Sea. Limnol. Oceanogr. 55, 1033–1046. https://doi.org/10.4319/lo.2010.55.3.1033

Savard, L., Marty, J., Waller, M.E., Bramburger, A.J., 2013. Mapping water quality in Lake St Francis nearshore areas of the St. Lawrence River. Prepared by the SLRIES for the Ontario Ministry of the Environment and Climate Change.

Savard, L., Razavi, R., Ridal, J., 2015. Characterization of tributary phosphorus inputs to Lake St. Francis nearshore areas of the St. Lawrence River. Prepared for the SLRIES for the Ontario Ministry of the Environment and Climate Change. St. Lawrence River Institute of Environmental Sciences, Cornwall, Ontario.

Schelske, C., Peplow, A., Brenner, M., Spencer, C., 1994. Low-background gamma counting: applications for 210Pb dating of sediments. J. Paleolimnol. 10, 115–128. https://doi.org/10.1007/BF00682508

Schelske, C.L., 1991. Historical nutrient enrichment of Lake Ontario: paleolimnological evidence. Can. J. Fish. Aquat. Sci. 48, 1529–1538. https://doi.org/10.1139/f91-181

Smith, P.G.R., 2015. Long-term temporal trends in agri-environment and agricultural land use in Ontario, Canada: transformation, transition and significance. J. Geogr. Geol. 7, 32–55. https://doi.org/10.5539/jgg.v7n2p32

Stein, J., 1995. Time, space and social discipline: factory life in Cornwall, Ontario, 1867–1893. J. Hist. Geogr. 21, 278–299. https://doi.org/10.1006/jhge.1995.0020

The St. Lawrence River (Cornwall) RAP Team, 1995. Addendum to stage 1 report: St. Lawrence River remedial action plan, Cornwall/Lake St. Francis area.

Waller, M.E., Bramburger, A.J., Cumming, B.F., 2016. Bi-weekly changes in phytoplankton abundance in 25 tributaries of Lake St. Francis, Canada: evaluating the occurrence of nuisance and harmful algae. J. Great Lakes Res. 42, 1049–1059. https://doi.org/10.1016/j.jglr.2016.07.003

Yee, P., Edgett, R., Eberhardt, A., 1990. Great Lakes - St. Lawrence River regulation: What it means and how it works. Retrieved November 29th, 2016 from http://ijc.org/files/tinymce/uploaded/ISLRBC/Great%20Lakes-St.%20Lawrence%20River%20Regulation_1993_e.pdf.

Figure Captions

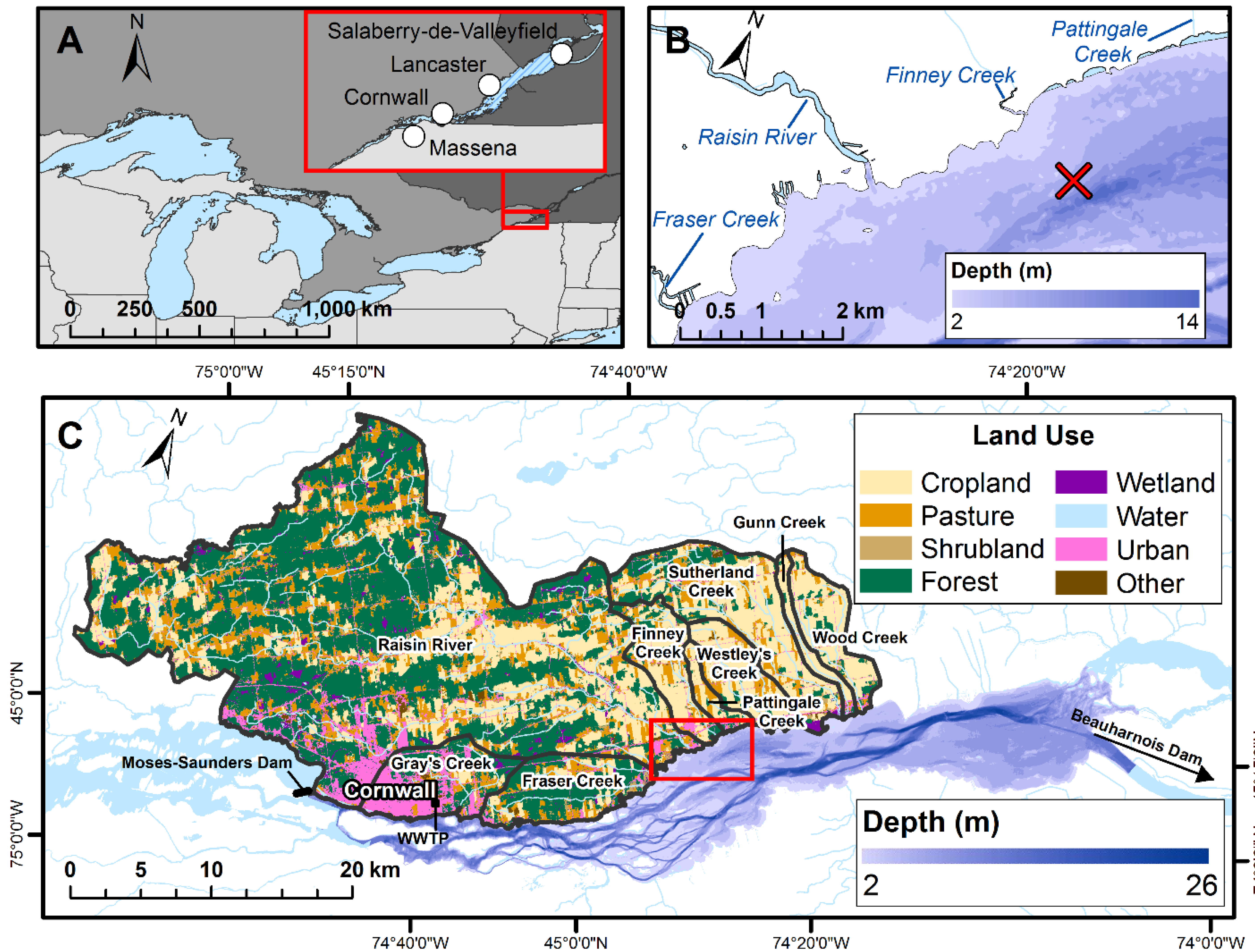
Figure 1. A) The Laurentian Great Lakes and St. Lawrence River with inset indicating towns of interest and the Area of Concern (the hatched area). B) Sampling location (indicated by the “X”), Lake St. Francis bathymetry, and nearby tributaries. C) Bathymetry of Lake St. Francis within the Area of Concern, land use of the nine major watersheds in Ontario that contribute to the St. Lawrence River Area of Concern, and locations of nearby dams and Cornwall wastewater treatment plant (WWTP); the extent of panel B is indicated by the rectangle.

Figure 2. A) Activities and errors of the four radioisotopes, by depth in the sediment core, measured through gamma spectroscopy. B) Inferred year, sedimentation rate, and associated errors as calculated through the constant rate of supply (CRS) model.

Figure 3. Concentrations of photosynthetic pigments (per gram organic matter) throughout the sediment core. Secondary y-axis indicates year inferred from the constant rate of supply (CRS) dating model. Top panel: more stable pigments, defined as a category 1 (Leavitt and Hodgson, 2001). Bottom panel: more labile pigments, defined as a category 2, 3, or 4 (Leavitt and Hodgson, 2001) and ratio of chlorophyll *a* to phaeophytin *a*, an indicator of the extent of pigment degradation.

Figure 4. Percent organic matter, per mille ratios of stable isotopes, and mass ratio of carbon to nitrogen by depth and year inferred through the constant rate of supply (CRS) dating model.

Figure 5. A) Diatom valve concentrations by depth and year inferred through the constant rate of supply (CRS) dating model. B, C) Relative abundances of the dominant (B) and subdominant (C) diatom species observed in the core. The dotted line represents the significant assemblage change identified by the broken stick model and constrained incremental sum of squares.



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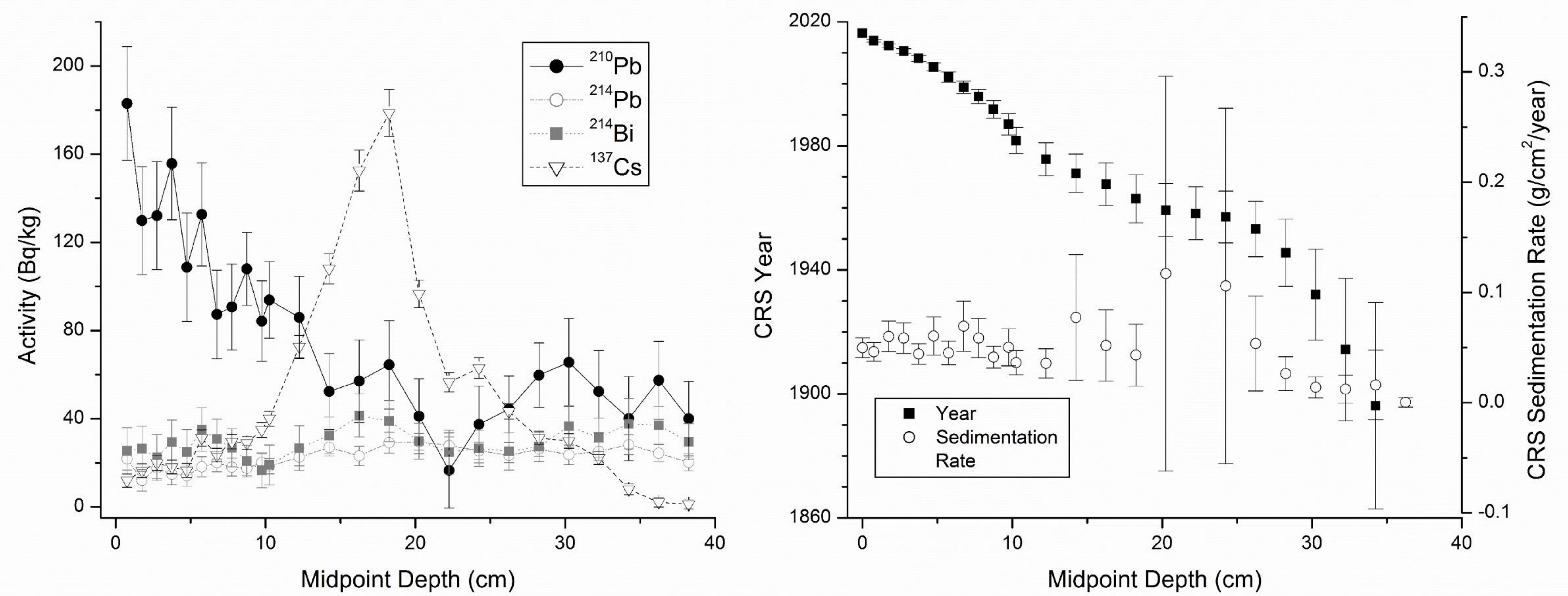

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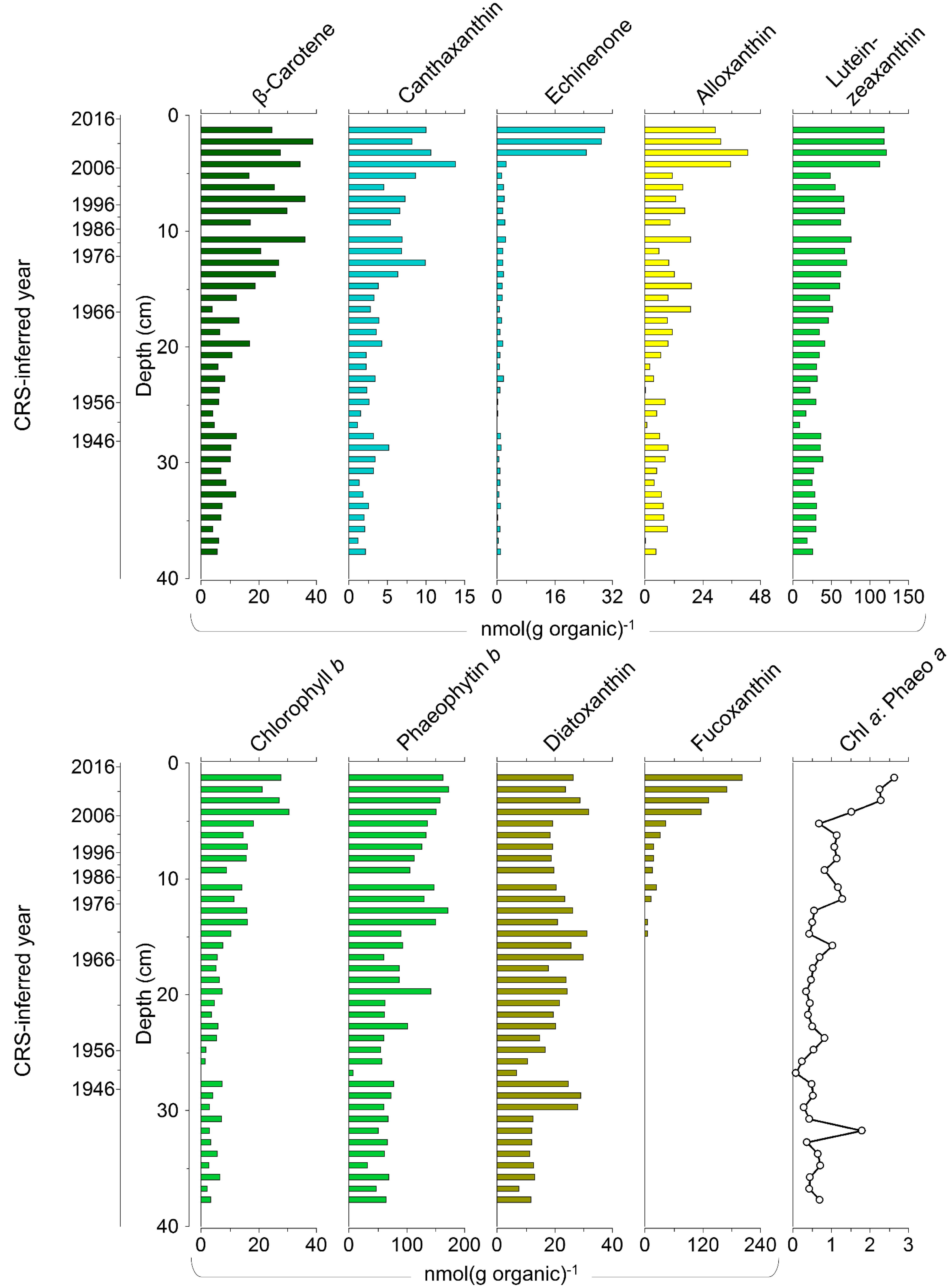

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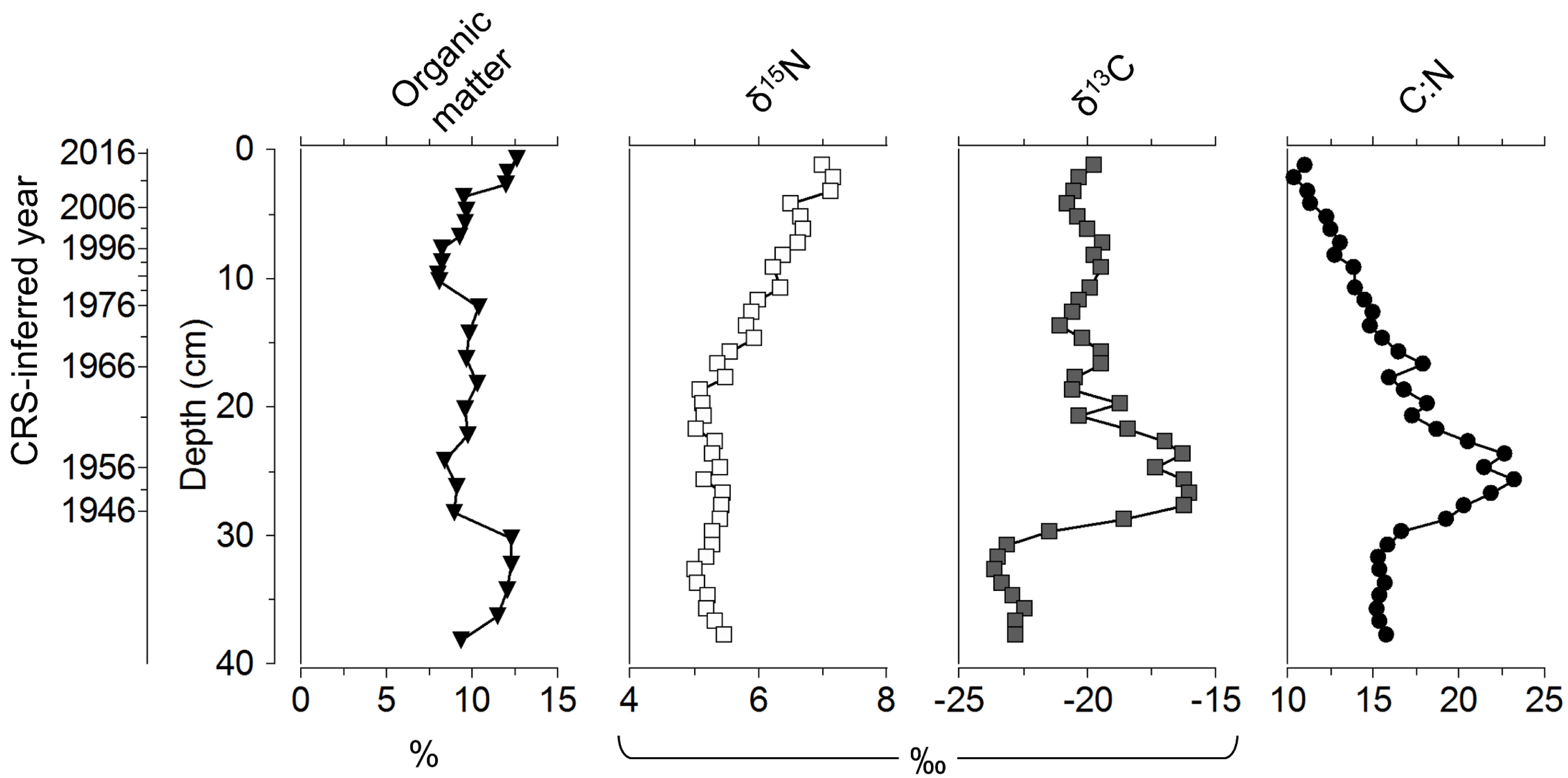

Figure 4. Percent organic matter and ratios of stable isotopes by depth and year inferred through the constant rate of supply (CRS) dating model. The box indicates inferred years during which the Moses-Saunders Power Dam was constructed (1954-1959).

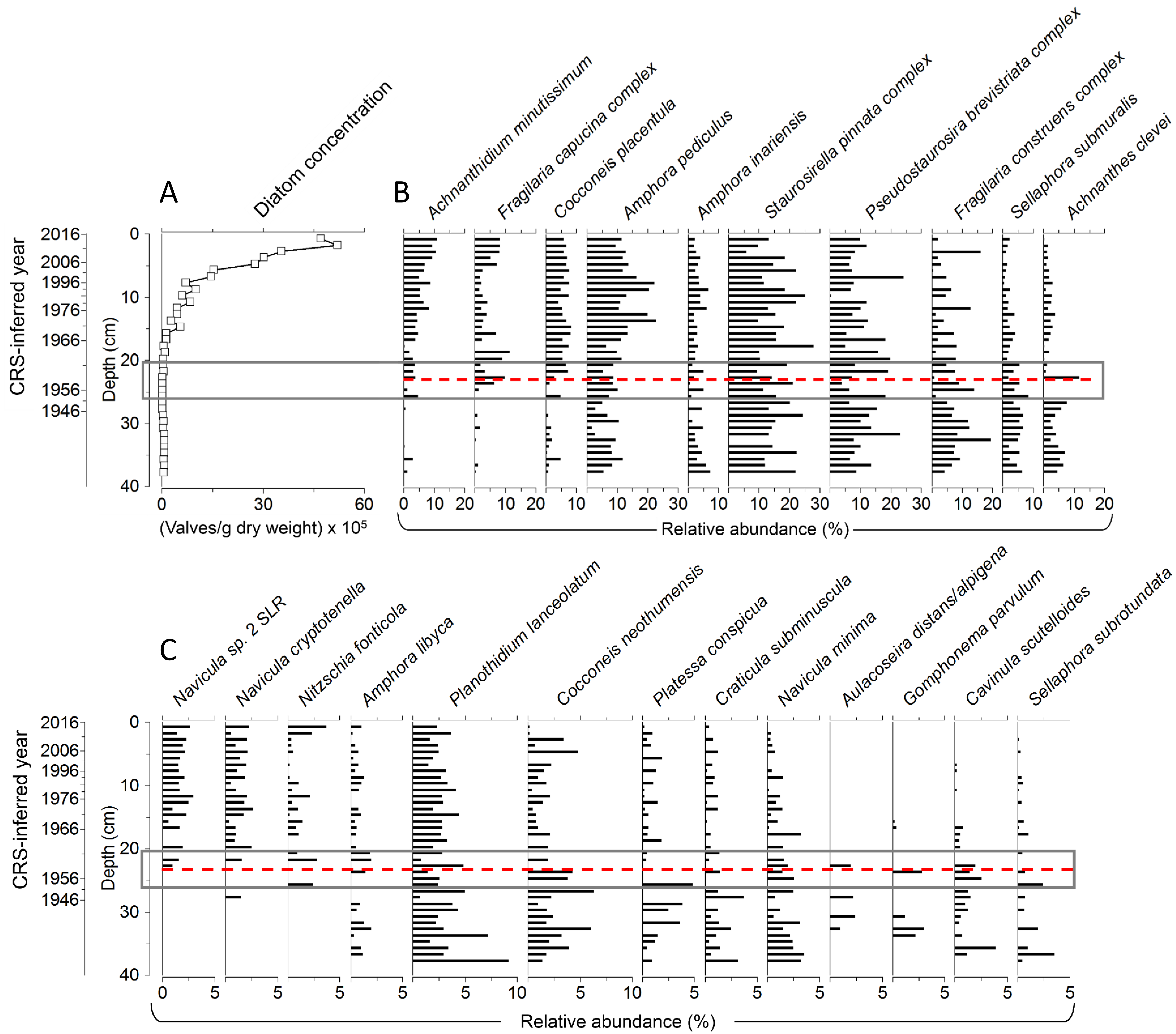

Figure 5. A) Diatom concentrations by depth and year inferred through the constant rate of supply (CRS) dating model. B, C) Relative abundances of the dominant (B) and subdominant (C) diatom species observed in the core. The dotted line represents the significant assemblage change identified by the broken stick model and constrained incremental sum of squares. The box indicates inferred years during which the Moses-Saunders Power Dam was constructed (1954-1959).