A Whole-Basin Reconstruction of Sediment and Phosphorus Loading to Lake St. Croix

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BY

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ABSTRACT

Lake St. Croix is a natural impoundment of the lowermost 37 kilometers of the St. Croix River in Minnesota and Wisconsin, making this one of a few large river systems in the world possessing a long-term depositional basin at its terminus. The river's relatively pristine condition led to its designation as a National Scenic Riverway in 1968, but increasing urbanization in its lower reaches has raised concerns about impacts on water quality. This study was initiated to reconstruct historical loadings of suspended sediment and phosphorus (P) from the sediment record in Lake St. Croix.

Twenty-four piston cores, with an average length of 2 meters, were collected along eight transects of the lake. Dated chronologies from ^{210}Pb, ^{137}Cs and ^{14}C were used to calculate the rate of sediment accumulation in the lake over the past 100+ years. Diatom microfossil analysis was used to reconstruct historical lakewater P concentrations over the same time period, and sediment P analysis quantified the amount of P trapped in lake sediments. Using a whole-basin mass balance approach, the loading of sediment and P to Lake St. Croix over the last 100+ years was calculated.

Beginning in 1850, sediment accumulation increased dramatically to a peak in 1950-1960 of eight times background rates prior to European settlement. The peak is driven largely by sediment contributions from small side-valley catchments tributary to the downstream half of the lake. The total P load to the lake increased sharply after 1940 and remains high, at around four times the level of pre-European settlement conditions. The timing of peak sediment and P loading to the lake shows that early settlement activities, such as logging and the conversion of forest and prairie to agricultural land between 1850-1890, had only modest impacts on the lake. By contrast, the mid-1900s brought major increases in sediment and P loading to the lake, suggesting that relatively recent activities on the landscape and changes to nutrient balances in the watershed have caused the current eutrophic condition of this important recreational and natural resource.

INTRODUCTION

Large temperate rivers around the world have been significantly impacted by recent human activities (Meybeck and Helmer 1989; Meybeck et al. 1990; Bernhardt 1995; Saeijs and Van Berkel 1995; Zhang et al. 1999; Bennett et al. 2001; Smith 2003), but because of relatively short periods of water quality monitoring there is not a good understanding of the magnitude of change in these systems. To protect these resources with sound management strategies, their 'natural', or pre-disturbance, condition must be understood. In most places, regular and reliable testing of environmental variables did not begin until 1950 or later, after major industrial and social changes had already affected waterways and landscapes. Furthermore, sediment transport in most riverine systems is too episodic and complex to allow accumulation of continuous sedimentary sequences, so historical water quality cannot be reconstructed from sedimentary records, as is more commonly done for lakes. However, several studies of the Mississippi River's natural impoundment at Lake Pepin (Maurer et al. 1995; Engstrom and Almendinger 1998; Balogh et al. 1999) demonstrated that these types of deposits can be interpreted as effectively as those from more typical (non-riverine) lakes.

The St. Croix River, a major tributary to the upper Mississippi River, is one of a very few large rivers in the world that has a natural lake, or long-term depositional basin, at its terminus. Fine-grained sediments have accumulated on the lake bottom in a conformable, continuous manner since the lake's formation around 9,000 years ago (Eyster-Smith et al. 1991), thus, paleolimnological techniques using stratigraphic analysis of sediment cores can be applied to evaluate the historical conditions of the river. Specifically, the changes in sediment and phosphorus flux to the lake can be reconstructed from the sediment record, thereby inferring how changes on the landscape have been reflected in the aquatic environment.

To fully elucidate the history of phosphorus loading to Lake St. Croix, it is necessary to account for spatial variability in the depositional basin. By analyzing sedimentary phosphorus (total-P_{sed}) in multiple cores throughout the lake basin, a whole-lake flux of phosphorus (P) to the sediment can be calculated (Evans and Rigler 1980; Moss 1980; Anderson and Rippey 1994). When combined with historical lakewater phosphorus (total-P_{lake}) reconstructed from diatoms using multivariate transfer function techniques (Hall and Smol 1992; Anderson et al. 1994; Bennion et al. 1996), a quantitative whole-basin P mass balance can be established. This approach was described by Rippey and Anderson (1996) and has been used and refined by others including Hall and Smol (1992) and Jordan et al. (2002).

SITE DESCRIPTION

The St. Croix River drains an area of 22,200 km^2 in Minnesota and Wisconsin (Fig. 1) before it joins the Mississippi River at Prescott, Wisconsin. The northern part of the watershed consists of northern boreal forest, bogs and peatlands (Curtis 1959). The southern sub-watersheds were originally vegetated by prairie and northern mixed hardwoods but have come to be dominated by agricultural land uses (Curtis 1959; Troelstrup et al. 1993a).

The lowermost 37 km of the St. Croix River function as a lake (Lake St. Croix) due to its impoundment by a delta of the Mississippi River. The delta formed around 9500 ^{14}C years B.P. when reduced outflow from Glacial Lake Agassiz allowed sediment loads from the Chippewa River to dam the upper Mississippi at Lake Pepin (Eyster-Smith et al. 1991;Wright et al. 1998). Lake Pepin originally extended 120 km north to St. Paul and at least several kilometers into the St. Croix valley. Almost immediately, the Mississippi River began depositing a delta at the head of Lake Pepin which eventually prograded across the mouth of the St. Croix River. Similarly, the St. Croix River began depositing a delta at what was then the head of Lake St. Croix, likely about 40 km upstream of its current position at Stillwater, Minnesota (Cahow 1985).

Before European settlement, Native Americans lived in the St. Croix watershed and influenced vegetation by intentional and unintentional burning (Curtis 1959). However, their activities probably had negligible impacts on the river and lake water quality. Europeans first settled in the St. Croix valley in the 1830s (Dunn 1979; Osh et al. 1996; McMahon and Karamanski 2002); logging and milling were well underway by the late 1840s and "there was a nearly complete occupation of the prairies" by 1880 (Curtis 1959). Agricultural utilization continued unabated through the 1900s, although principal products changed from wheat to dairy to corn through time. Human population in the watershed increased to 250,000 by 1920, then remained static until the 1970s when it began to increase again; by 1992 there were 400,000 people living in the St. Croix watershed (Mulla et al. 1999). Counties bordering the lower St. Croix continue to experience strong urban- and suburbanization pressure because of their proximity to the rapidly-growing Minneapolis/St. Paul metropolitan area. The lower St. Croix River is particularly accessible to metro-area residents, and over 1 million visitors boat, swim, fish or camp along the river each year (Lenz et al. 2003).

Today, Lake St. Croix occupies a narrow (0.5 to 2 km wide) riverine basin that is divided into four sub-basins by the deltas of side-valley tributaries along its course: the Willow River, Valley Branch Creek and the Kinnickinnic River (Fig. 2). The maximum depth in these sub-basins is between 10 and 22 m and the water residence time in the lake as a whole is on the order of 20-50 days depending on season and precipitation. The average annual total phosphorus (TP) concentration in the lake is around 50 µg PO_4-P L^{-1}, alkalinity is near 90 mg L^{-1}, and average total suspended solids concentration is on the order of 4 mg L^{-1}. Dissolved organic carbon is high due to the pine forests and peatlands in the upper watershed, so that light attenuation is rapid and Secchi depths are small (0.21-1.8 m) (Robertson and Lenz 2002). Lake St. Croix is considered to be eutrophic by most measures (MPCA 2003).

The St. Croix River is valued highly as a recreational and environmental resource and is commonly regarded as nearly pristine. Parts of the river were designated as National Scenic Riverway in 1968 and 1972, and more than 60 endangered and threatened species live in the Riverway (Lenz et al. 2003). However, the eutrophic condition of Lake St. Croix and continuing urbanization of the lower watershed have prompted concern among government officials and citizen groups determined to protect the St. Croix's unique character. In response, the St. Croix Interagency Basin Team (1998), comprised of regional, state and federal agencies, began a program to monitor and model the river/lake system to help develop future water quality goals and management policies. Several studies have used water quality monitoring data from 1970-2000 to examine recent nutrient dynamics and trends in the St. Croix River. Relative to the Minnesota and upper Mississippi rivers, the St. Croix has the lowest total-P_{lake} concentration (Kroenig and Andrews 1997) and "general water quality within the St. Croix River is good relative to other river systems within the region" (Troelstrup et al. 1993a). Furthermore, there appears to be a statistically significant, though small, decrease in total-P_{lake} concentrations over the past three decades. Lenz et. al (2003) performed one year of intensive monitoring to examine how much P each sub-watershed contributes to the whole St. Croix River system, and Robertson and Lenz (2002) constructed numerical models to simulate how the lake would respond to reduced phosphorus loads.

Eyster-Smith et al. (1991) took advantage of the lake-like conditions in the lower St. Croix River to retrieve a 19 m long sedimentary sequence extending back to the formation of the lake in late-glacial times. This core was used primarily to analyze changes in terrestrial vegetation and climate variation in the Holocene, and the recent sediments (i.e. the last 200 years) were analyzed only at coarse resolution. More recently, Troelstrup et al. (1993b) used three sediment cores to look for post-settlement human impacts on the river. They found that concentrations of pigment derivatives in Lake St. Croix sediments increased dramatically from deeper to surficial sediments, indicating that primary productivity had increased significantly in the last 40-50 years.

METHODS

Coring

Twenty-four sediment cores were collected from 1999 to 2001 along eight east-west transects of the lake (i.e. aligned perpendicular to the flow direction). Two transects were located in each of the four sub-basins and are numbered from 1 to 8 going upstream (Fig. 2). The three cores along each transect were approximately evenly-spaced between the two shores and were located on the flat bottom of the lake, carefully avoiding the steep side-slopes and anomalous bathymetric features; the cores along each transect are labeled A to C from west to east. The locations of all core sites were recorded by differentially-corrected GPS. One core from each transect was chosen for detailed analysis, and these eight are hereafter described as "primary" cores; the other two cores in each transect were analyzed in less detail and are considered to be "secondary" cores.

All cores were collected from a boat using piston corers operated by rigid drive rods from the lake surface. At each core site, a continuous 2-m section of the surface sediments was collected using a surface corer with a 7-cm diameter polycarbonate core barrel (Wright Jr 1991). This method allows collection of undisturbed, watery upper sediments, which is crucial to successful ^{210}Pb dating. These core sections were kept upright until the topmost 20-26 cm of uncompacted sediment had been extruded at 2-cm intervals into polypropylene sample jars on shore. The stiffer sediment in the remainder of each core was capped in the core tube and transported to the lab in a horizontal position.

At some sites, 1-m Livingstone cores were also taken to extend the sediment record further into the lake bottom, for a total core length of 2.5 to 3.5m. These deeper core sections were collected using a square-rod Livingstone corer (Wright Jr et al. 1983), and overlapped the adjacent surface core by about 20 cm. Magnetic susceptibility was used to confirm stratigraphic splicing of the Livingstone and surface core sections. At sites where rapid sediment accumulation was anticipated, these Livingstone cores were taken at the same time as the surface core. At other sites, the Livingstone cores were collected at a later date using GPS to relocate the original core site after initial analyses showed that the record contained in the surface cores was too short. Livingstone cores were extruded immediately following collection and were wrapped in polyethylene film (food wrap) and aluminum foil. All cores were stored at 4°C.

Depositional Area

The depositional area of the basin was defined as those regions of the lake bottom where fine-grained sediment accumulates conformably. It excludes shallow-water areas with sand and cobble substrates as well as deltas at river mouths and submerged paleo-islands. The delineation of depositional versus non-depositional areas of the lake was based primarily on GIS-based bathymetric maps provided by the Minnesota Department of Natural Resources. The steep walls of the lake basin make this a fairly straightforward exercise, but it was "ground-truthed" by gravity-core samples of sediment taken in transects along representative sections of the lake's side slopes and delta fronts. To calculate whole-lake fluxes, the lake was divided into eight sections, each represented by one transect of cores.

Magnetic Susceptibility

Whole-core magnetic susceptibility measurements were made on all cores using a Geotek LTD multi-sensor core logger with a Bartington MS2 loop sensor in the Limnological Research Center (LRC) at the University of Minnesota. The logger has an automated track feeder that can accommodate 1.6 m sections of core. Cores were brought to room temperature; surface cores were extruded from the core tube onto a rigid tray (a split polycarbonate tube) and cut into 1.6 m (or shorter) sections for logging. Susceptibility measurements were taken at 1 cm intervals through a 10 cm diameter loop. After susceptibility analysis, down-core smearing was removed from the core exterior and cores were sectioned into 2 cm intervals. Sediment samples were placed in 120-ml screw-top polypropylene jars for storage at 4°C.

Loss-on-ignition

Standard loss-on-ignition (LOI) techniques (Dean 1974) were used to determine dry density and the weight-percent of water, organic matter and carbonate of the sediments. All depth intervals in the primary cores were homogenized then sub-sampled for LOI analysis, while every fourth sample in the secondary cores was analyzed. Samples of 2-4g (wet mass) were dried overnight at 100°C, then ignited sequentially at 550°C and 1000°C for one hour each with mass measured between each step. Dry density was calculated from each sample's water content and fixed density values for organic, carbonate and inorganic matter.

Lead-210 Dating

Alpha spectrometry

The primary core from each transect was used for ^{210}Pb dating analysis to establish chronology and calculate sediment accumulation rates. Lead-210 activity was measured by the activity of its daughter product ^{210}Po, considered to be in secular equilibrium with its parent, in 18-25 samples per core. Polonium-209 was added to each freeze-dried sample as an internal yield tracer. Samples were treated with HCl to remove carbonate, then Po isotopes were distilled at 550°C and plated onto silver planchets directly from the HCl solution (adapted from Eakins and Morrison, 1978). Activity was measured for 0.8 to $3x10^5$ s using an Ortec alpha spectrometry system. Supported ^{210}Pb was determined from the asymptotic activity of the lowermost samples in the core and then subtracted from measured total activity in the upper samples to obtain the unsupported activity at each interval. Dates and sedimentation rates were calculated using the constant rate of supply (CRS) model (Appleby and Oldfield 1978).

Gamma spectrometry

Determination of the supported ^{210}Pb activity is crucial to this dating method. In three of the primary cores, the total activity did not decline monotonically with depth but instead co-varied with changes in magnetic susceptibility. This covariance suggested that supported ^{210}Pb activities were affected by changes in sediment lithology at these locations in the lake. Gamma spectrometry was thus used to directly and independently measure supported (^{214}Pb) and total ^{210}Pb activities in these three cores.

Because dates could not initially be calculated for three of the cores analyzed by alpha spectrometry, these cores were subsequently analyzed for ^{210}Pb and ^{214}Pb by gamma spectrometry. Freeze-dried sediment samples were sealed with epoxy resin and ingrown for a minimum of 30 days to achieve secular equilibrium between the native ^{226}Ra and its decay products. Isotopic activities were measured for 0.6 to $3x10^5$ s using a high-resolution germanium well detector and multichannel analyzer, Ortec Corporation, Oakridge Tennessee. Supported ^{210}Pb was measured as ^{214}Pb (multiple energies), a short-lived intermediary in the radioactive decay sequence from ^{226}Ra to ^{210}Pb. Unsupported ^{210}Pb was calculated as the difference between total ^{210}Pb (measured directly as ^{210}Pb at 46.52 kev) and supported ^{210}Pb. An efficiency curve for the detector was generated using a sediment matrix spiked with known activities of ^{210}Pb, ^{137}Cs, ^{7}Be, ^{54}Mn, and ^{109}Co, and was corrected for the small amount of native ^{210}Pb. This method is similar to that described by Schottler and Engstrom (2003).

Cesium-137 Dating

Freeze-dried sediment samples from the 8 primary cores were analyzed for ^{137}Cs to identify the 1963-1964 peak in atmospheric nuclear bomb testing. Samples were measured at 661.62 kev using a high-resolution germanium well detector multichannel analyzer, as described above. Four to eight samples were analyzed from each core with selection based on initial results from ^{210}Pb dating.

Radiocarbon Dating

Terrestrial (woody) organic matter samples were collected from near the bottom of four cores for radiocarbon dating. Sample depths were chosen to correspond with a distinctive feature in the magnetic susceptibility profile of the core so that the ^{14}C dates could be correlated to other cores. The woody pieces were converted to graphite targets at the LRC, and were analyzed by accelerator mass spectrometry (AMS) at the University of Arizona in Tucson. The CALIB program v. 4.3 (Stuiver et al. 1993a) and the atmospheric sample dataset from Stuiver et al. (Stuiver et al. 1998a) were used to convert ^{14}C dates to calendar years.

Grain size

Wet sediment samples were treated with 30% H_2O_2 and 11 M HNO_3 in an 85°C water bath for ~30 minutes to eliminate organic matter. Residues were rinsed and centrifuged three times until pH-neutral, then the solution was siphoned off. Residues were returned to the water bath and treated with 1M NaOH for 30 minutes to eliminate biogenic silica. Samples were then rinsed and centrifuged three times, the solution was siphoned off, and centrifuge tubes were filled with $(NaPO_3)_6$ solution and shaken overnight to deflocculate the grains.

Samples were analyzed on a Horiba LA-920, a laser-scattering particle size distribution analyzer with automated sampler. Particles were measured in the range of 0.02-2000 μm and were divided into 85 size fractions. The analyzer uses a He-Ne laser with a 632.8 nm wavelength and a tungsten lamp with 405 nm wavelength. Grain size distribution was measured at concentrations with between 85-90% laser/light transmittance and modeled using a relative refraction index of 1.57. Data are described here as median grain size for each sample.

Sediment P

Freeze-dried sediments were extracted for phosphorus determinations according to fractionation procedures adapted from Hieltjes and Lijklema (1980) and Engstrom and Wright (1984). Total phosphorus was measured as the ortho-P extracted by sequential digestion with 30% hydrogen peroxide (1 hr at 85°C) followed by 0.5 M HCl (0.5 hr at 85°C). Iron- and aluminum-bound phosphorus (NaOH-P) was measured by extracting a second subsample in 0.1 M NaOH (16 hr at 25°C). The sediment residue from the hydroxide extraction was further treated with 0.5 M HCl (20 hr at 25°C) to determine the calcium-bound pool of phosphorus (HCl-P). Finally the residual (organically-bound) phosphorus was estimated from the difference between the total-P and the inorganic-P. Extracts were analyzed with a Lachat QuikChem 8000 flow-injection autoanalyzer using the ascorbic acid method. Extraction temperatures for total-P were maintained in a hot-water bath, and extracts were separated from sediment residue by centrifugation. All dilutions were done according to weight on an electronic balance. Replicated extractions of 20 samples had an average relative difference of 1.8% for total-P, 1.2% for NaOH-P and 1.4% for HCl-P.

Biogenic silica

Twenty freeze-dried samples from each core were digested for biogenic silica analysis using 40 ml of 1% (w/v) Na_2CO_3 solution heated at 85°C in a reciprocating water bath for five hours (DeMaster 1979; Conley and Schelske 2001). Aliquots (0.5 g) of the supernatant were removed at 3, 4, and 5 h, and after cooling were neutralized with 4.5 g of 0.021N HCl solution. Dissolved silica was measured as SiO_2 on a Lachat QuikChem 8000 colorimeter as molybdate reactive silica (McKnight 1991).

Diatom analysis and lakewater P reconstruction

Two sediment cores (1B and 6B) were analyzed for diatom microfossils to reconstruct a detailed history of total-P_{lake} concentrations (Edlund and Engstrom 2001). Freeze-dried sediments from 21 and 23 intervals, respectively, were treated first with H_2O_2 at 150°C for 30 minutes, followed by concentrated HNO_3 at 175°C for 1 hour. After cooling and rinsing the samples six times with distilled water, the material was dried onto cover slips (Battarbee 1973), and these were mounted onto microslides with Naphrax.

Diatom valves and chrysophyte cysts along one or more random transects of each microslide were counted on an Olympus BX50 microscope using full oil immersion optics, until 500 diatom microfossils were tabulated. The counts were grouped into species and ecological groups, and the raw data were converted to absolute abundance of microfossils per gram of dry sediment.

Historical water column total P (total-P_{lake}) was reconstructed using weighted averaging calibration. Although Lake St. Croix is a riverine system, most of the diatom flora is lacustrine, and a diatom training set based on 55 Minnesota lakes (Ramstack 1999) was used. Some riverine species that were relatively abundant in the sediments are not part of the Ramstack training set and so were not used. To develop that training set, Ramstack collected surface sediment from those 55 lakes and measured environmental variables including total-$P_{lake.}$ Four hundred diatom microfossils were classified in each sediment sample. These data were analyzed using weighted average regression software (CALIBRATE; Juggins 1998) to determine total-P_{lake} optima for 108 diatom taxa, providing potential reconstructions of total-P_{lake} values from 0.009 to 0.105 mg L^{-1}.

Pigments

Cores from transects 1 and 6 were analyzed for fossil pigments. Because pigments degrade in oxic conditions, sediments from the primary cores 1B and 6B - collected in 1999 - were deemed too old (and likely too degraded) for pigment analysis. Secondary cores in those transects were collected in 2001, so samples from cores 1A and 6C were analyzed instead. Fifteen wet sediment samples from each of the two cores were frozen in containers with no airspace and were sent for analysis to the University of Regina. There, samples were freeze-dried and extracted using acetone, methanol, and water. A Waters HPLC system was used to measure fossil pigment concentrations (Swain 1985; Leavitt 1993; Leavitt and Findlay 1994). Chronologies from the dated primary cores were correlated to the secondary cores using visual inspection of the magnetic susceptibility profiles.

RESULTS AND DISCUSSION

Core lithology

i. Magnetic Susceptibility

Magnetic susceptibility in all the cores shows a common pattern: relatively constant and low values in the oldest sediments, followed by a sharp increase to peak values and a subsequent decrease to the present (Fig. 3). The oldest sediment in each core ranges from 25 to 35 SI, although cores from transect 8 have slightly higher background levels (30-40 SI). There are two notable exceptions to this pattern. First, the lower half of core 4C records pronounced fluctuations between 30 and 60 SI that are likely due to post-depositional sediment disturbance such as scouring or slumping; this core was not used for detailed analysis and correlation. Second, the three cores in transect 1 follow the general pattern described above but they also record two large magnetic susceptibility peaks well before the lake-wide peak described above. These earlier peaks at the downstream end of the lake may correspond to sediment back-washed into the St. Croix basin by major pre-historic flood events of the Mississippi River.

Cores within a given transect have highly similar magnetic susceptibility profiles indicating that the pattern of sediment deposition across the width of the lake is quite uniform. This similarity also confirms that sediments are not significantly remixed after deposition, because mixing would likely cause irregular fluctuations in the magnetic profiles from core to core. Consequently, chronologies constructed for the primary core in each transect can be translated with confidence to the other cores in that transect. Likewise, because the general pattern holds throughout the lake, some correlations can be made among transects as well.

In the upstream half of the lake, the magnetic susceptibility peaks are stronger in transects 8 and 7 (45-60 SI) and are more muted in transects 6 and 5 (~33 SI). This down-stream trend likely results from the progressive settling of sediment from the mainstem of the river as water moves through the lake basin. However, beginning with transect 4 there is a pronounced increase in peak intensity (70 SI) with transects 3 and 2 showing the highest peak intensities in the entire lake (135 and 118 SI, respectively).

Differences in magnetic susceptibility are due to differences in sediment mineralogy, grain size, and/or concentration of magnetic grains. Therefore, the stronger peaks in the downstream cores suggest a different sediment provenance than the muted upstream peaks. This is the first indication that side-valley tributaries flowing directly into the downstream half of the lake have at times contributed large amounts of sediment to the basin.

ii. Loss-on-ignition

Lake St. Croix sediments are consistently between 80 and 90% inorganic matter by weight as determined from LOI analysis (Fig. 4). This largely explains the detail and sensitivity of the magnetic susceptibility: ferromagnetic minerals are not diluted by large amounts of organic matter and carbonate. Carbonate comprises the smallest proportion of the sediment, ranging from 3-8% by weight. All cores show a peak in inorganic content of 82 to 91% at the time of highest magnetic susceptibility, confirming that a change in sediment character – and likely in sediment provenance – happened at that time.

Organic matter generally ranges from 7-15% with the highest values found in the upper 30-50 cm of the cores. Some of this up-core increase may be due to incomplete post-depositional diagenesis (compared to older strata in the core). The larger proportion of organic matter in recent sediments may also be due to increased productivity in the lake. The depth at which organic matter began to increase is deepest at the upstream end of the lake (52 cm, core 8C) and shallowest at the downstream end of the lake (30 cm, core 1B). Regardless of lake position, the increase always dates to about 1960, suggesting that an increase in productivity occurred throughout the lake at that time.

iii. Grain size analysis

The median grain size in all analyzed core sediments falls in the “clay” size fraction (<63 µm). Before European settlement, the median ranged from 4 µm (3B) to 14 µm (8C). In cores 8C, 6B, 5B and 1B there was a decrease in median grain size in the early- to mid-1900s, then a slight increase in recent years (Fig. 5). Cores 4B, 3B and 2B show little to no increase from 1800 to around 1930, then a sharp increase in median grain size through the second half of the 1900s. Core 2B has relatively large grains (relatively), with a peak of 21 µm in the mid-1980s. In other cores, the peak ranged from 5 to 12 µm.

Dating

i. Cesium-137

Cesium-137 activities in all eight primary cores had distinct peaks (Fig. 6) allowing for precise dating of those depth intervals. The burial depth for these maxima in ^{137}Cs ranged from 24-26 cm in core 1B to 62-66 cm in core 8C. Peak intensities ranged from 1.18 pCi/g (core 3B) to 2.70 pCi/g (core 5B).

ii. Lead-210 dating by alpha spectrometry

The ^{210}Pb activity profiles for five of the eight primary cores (8C, 7B, 6B, 5B, 1B) show roughly monotonic declines down-core, while the other three (4B, 3B, 2B) exhibit more complicated activity profiles (Fig. 7). Surface activities in all cores are relatively low, ranging from 5.5 to around 14.0 pCi/g, with no apparent spatial pattern to the variation. In the five cores modeled successfully with alpha spectrometry data, the background (supported) ^{210}Pb activities are between 1.2 and 2.1 pCi/g, as defined by 4-9 intervals with near-constant ^{210}Pb values at depth.

The inventory of supported ^{210}Pb in these five cores ranges from 51 pCi cm^{-2} (1B) to 103 pCi cm^{-2} (8C) which is equivalent to a ^{210}Pb flux of 1.7 – 3.3 pCi cm^{-2} yr^{-1}. The lake-wide average ^{210}Pb flux to Lake St. Croix sediments (2.3 pCi cm^{-2} yr^{-1}) is significantly larger than the atmospheric ^{210}Pb flux directly to the lake surface (0.45 pCi cm^{-2} yr^{-1}) (Urban et al. 1990) indicating that much of the lake's ^{210}Pb inventory is delivered by the St. Croix River. However, the riverine ^{210}Pb input represents only a small fraction (about 1%) of the total ^{210}Pb mass delivered to the watershed from atmospheric deposition. This indicates that most of the ^{210}Pb deposited on the landscape is trapped in the watershed soils and sediments where it decays away.

All the dated cores have ^{210}Pb activity profiles showing changes in slope due to changes in sediment flux to those core sites. These types of profiles are best interpreted using the constant rate of supply (CRS) model, which allows for changes in sediment accumulation while assuming constant flux of ^{210}Pb to the core site. This assumption of constant ^{210}Pb flux may be suspect in Lake St. Croix because much of the ^{210}Pb load comes, not from direct atmospheric deposition, but instead is delivered by the St. Croix River. Furthermore, unsupported activities are very low in Lake St. Croix sediments because of dilution by high sediment influx. Therefore, while the CRS model can be used to date most of these cores, additional dating markers must also be used to independently verify the chronology.

The ^{137}Cs peaks can be used to check the ^{210}Pb dating models. The ^{210}Pb dates at the depths of the ^{137}Cs peaks ranged from 1962 ±3 yr (5B) to 1975 ±8 yr (4B) (in the six cores dated by ^{210}Pb). The mean of those six dates is 1966, two or three years younger than the expected date of the peak, 1963-1964 (Fig. 8). Excluding core 4B, which has a larger error because it was counted by gamma assay, the average date is 1965. In either case, the ^{210}Pb dates are reasonably close to the ^{137}Cs date, confirming the reliability of the ^{210}Pb chronology from mid-century onward.

In contrast to coherence with the ^{137}Cs marker, the ^{210}Pb dates for the base of the magnetic susceptibility rise (approximately European settlement) vary from 1792 ± 51 yr (core 6B) to 1853 ± 48 yr (core 4B), with a mean of 1841 (Fig. 9). This is a wide range of dates for a signal of land clearance that should be nearly synchronous throughout the lake and could not have begun much before 1840 when the first European settlers arrived in the region. Despite this problem, there are good reasons to associate the rise in magnetic susceptibility with land clearance. First, the uncertainty in down-core ^{210}Pb dates is large; with a half-life of 22.3 years, there is little unsupported ^{210}Pb left in sediment 150 years old so it becomes difficult to distinguish from background levels (Oldfield et al. 1999). Second, many studies have noted a rise in magnetic susceptibility due to anthropogenic impacts in other locations (Oldfield et al. 1978; Dearing et al. 1981; Oldfield et al. 1989). Whether the initial susceptibility rise is due to logging in the upper watershed or to the nearly contemporaneous initiation of agriculture in the lower part of the watershed, the timing is within the margin of error for the ^{210}Pb dates and so can be considered a single time-stratigraphic horizon throughout Lake St. Croix.

iii. Lead-210 dating by gamma spectrometry

Three of the eight primary cores from the lower lake transects (2B, 3B, and 4B) had ^{210}Pb profiles (from alpha spectrometry) that were uninterpretable using any available dating model. Lead-210 activities are generally low throughout these cores, indicating dilution by extremely high sedimentation rates. More importantly, the lowest total ^{210}Pb values are found mid-core, rather than in the deeper (pre-settlement) strata that are normally used to estimate supported ^{210}Pb. These low mid-core activities coincide with peak values in magnetic susceptibility, implying that supported ^{210}Pb is variable in these cores and that the variation is related to major changes in sediment lithology and provenance. Therefore, supported ^{210}Pb could not be estimated from the asymptote of total ^{210}Pb at depth, but was instead measured directly for each sediment interval by gamma assay of ^{214}Pb. Unsupported ^{210}Pb was estimated by difference between total ^{210}Pb (also measured by gamma spectrometry) and ^{214}Pb.

The results from gamma assay of cores 2B, 3B, and 4B confirm that supported ^{210}Pb (^{214}Pb) is lower in the mid-core strata where total ^{210}Pb activities are at a minimum (Fig. 10). In core 4B, the point-transformed estimates of unsupported ^{210}Pb range from 1.8 to 12.2 pCi/g, with a local minimum between 52 and 78 cm where the peak in magnetic susceptibility would indicate a high input of eroded sediment. Core 4B had less variability in the supported ^{210}Pb activity than did cores 2B and 3B, so the 4B gamma values were used in the CRS model. To do this, the unique supported activity from each sample was subtracted from that sample's total activity to obtain the unsupported activity. Because the errors of gamma assay are substantially higher than those of alpha counting, the uncertainty of the CRS model dates for 4B are also larger.

In cores 2B and 3B, the estimates of unsupported ^{210}Pb (by difference) are so low – relative to analytical uncertainty – that a reliable ^{210}Pb chronology cannot be modeled. For these cores, an alternative chronology was derived by correlation of magnetic susceptibility profiles with the ^{210}Pb-dated cores from adjacent transects. Core 2B dates were derived by correlation with 1B, and 3B dates by correlation with 4B. In both cases, the ^{137}Cs peak also provided a reliable dating marker (1963). Core 1B is located downstream of 2B within the same depositional basin, and because there are no significant tributaries between the two sites, core 1B is a muted replica of 2B. The ^{210}Pb CRS model for 1B is coherent, without the extremely high sediment accumulation rates seen in 2B and with a regular ^{210}Pb activity profile. Therefore, dates for the base of the 1B magnetic susceptibility rise (1838), the top of that rise (1922) and a secondary peak (1952) were applied to the 2B sediment profile (Fig 11).

Core 3B was treated in a similar manner by correlation with core 4B. In this case, 3B is downstream of 4B and appears from the magnetic susceptibility profiles to be strongly impacted by Trout Brook, which enters the lake between these two transects (Fig. 2). Despite the differences in magnetic character (and sediment provenance), the general pattern of land-use change and sediment delivery should be broadly contemporaneous between these two depositional areas. Therefore, ^{210}Pb dates for the main magnetic features in 4B can provide dates for those features in 3B. Specifically, the base of the 4B magnetic susceptibility rise (1872), the top of that rise (1946), and a secondary peak (1955) were applied to the 3B magnetic profile.

For both 2B and 3B, dates between magnetic markers were interpolated assuming a constant dry-mass accumulation rate (g cm^{-2} yr^{-1}) for the given section of core.

iv. Carbon-14

Carbon-14 dates were obtained from cores 8C, 5B, 3A and 1B (Table 1). The date from core 8C was the most problematic, with five possible calendar dates returned by CALIB (Stuiver et al. 1993a). The 1940 and 1950 dates are not likely to be real based on ^{210}Pb and ^{137}Cs dating of the upper core, so these were eliminated and the median date of the remaining options (1760) was used. Three possible dates were returned by CALIB for the 5B sample. In this case, none of the possibilities overlapped with ^{210}Pb dates so the median of the three dates (1350) was used. CALIB returned only 1 possible date for each of the 3A and 1B samples, so these were used without modification.

Table 1: Carbon-14 ages and calibrated dates

CORE AND SAMPLE DEPTH (cm)	**^{14}C DATE (BP) ± 1 s.d.**	**1σ - CALIBRATED DATES (AD): maximum (intercepts) minimum**
1B – 124	528 ± 49	1329 (1413) 1438
3A – 238	670 ± 45	1284 (1297) 1387
5B – 142	602 ± 51	1300 (1330, 1350, 1390) 1400
8C – 230	167 ± 61	1660 (1680, 1760, 1800, 1940, 1950) 1950

Calibrated ^{14}C dates in cores 8C, 5B, 3A and 1B were used to calculate a single pre-European settlement sediment accumulation rate for each core, representing the period from the ^{14}C sample depth to settlement (initial magnetic susceptibility rise). These rates ranged from 0.28-2.81 kg m^{-2} yr^{-1}, with the highest value from core 8C at the upstream end of the lake. Based on the magnetic susceptibility profiles, the calibrated ^{14}C dates in these four cores were applied to the other two cores within their respective transects, and also to cores from adjacent transects without ^{14}C dating. The 5B date was applied to transects 7, 6 and 4, and the 1B date was translated to transect 2. The 8C date was only used to date transect 8 cores because it is the youngest ^{14}C sample and has the largest error. The 3A date was only used to date transect 3 cores because its associated magnetic feature was not identifiable in other transects.

Finally, the ^{14}C date from 1B was used to determine a pre-settlement date on core 2B. The magnetic feature associated with the 1B date was not identifiable in transect 2 cores. Instead, the ratio of post- to pre-settlement sediment accumulation was calculated for 1B, where post-settlement is defined as 1838 (magnetic susceptibility rise) to present, and presettlement as 1838 to the ^{14}C calibrated date of 1413. That ratio was applied to 2B, assuming that the magnitude of change would be the same in these two proximal transects. Although we would have preferred to date core 2B directly, we were unable to find a suitable ^{14}C sample (terrestrial macrofossil) in any of the transect 2 cores.

Sediment accumulation

Sediment accumulation rates for each core were defined as the accumulated dry mass between dated sediment intervals divided by the elapsed time. All cores show increased sediment accumulation after 1850, coincident with the magnetic susceptibility rise and

European settlement. Most cores have a peak sediment accumulation in the 1950s and 1960s (Fig. 12), with maximum values ranging from 2.61 kg m^{-2} yr^{-1} (5B) to 36 kg m^{-2} yr^{-1} (3B). The sediment accumulation peak in core 2B also extends into the 1940s, but this may be due to the dating uncertainty for that core. After the 1960s, sediment accumulation in all cores declined. Present-day sediment accumulations are still well above pre-European settlement accumulation, ranging from a 2.6-fold increase in transect 8 to an 11-fold increase in transect 4.

There is spatial, as well as temporal, variability in sediment accumulation. Rates in the upstream end of the lake should be higher than those further downstream if the mainstem of the river is the dominant source of sediment. Where the river first widens and deepens into a lake, sediment will quickly settle out of the decelerating water leaving less to be deposited downstream. Pre-European settlement data support this depositional model: before 1850, transect 8 had a sediment accumulation of 2.3 kg m^{-2} yr^{-1} and all other transects had sediment accumulations between 0.2 and 0.8 kg m^{-2} yr^{-1}. However, around 1940 transects 4, 3 and 2 suddenly began recording huge inputs of sediment with maxima from 11 kg m^{-2} yr^{-1} (4B) to 36 kg m^{-2} yr^{-1}(3B). Because upstream cores do not reflect such a dramatic increase in sediment load, it appears that this sediment was being contributed by the side-valley tributaries in the lower half of the lake, namely Valley Creek, Trout Brook and the Kinnickinnic River. Magnetic susceptibility and preliminary geochemical analyses confirm that the sediment pulses in these downstream transects have a different mineralogy, and thus likely have a different provenance, than contemporaneous upstream sediments.

While sediment accumulation rates vary among transects, cores within each transect have very similar magnetic susceptibility profiles (Fig. 3). This similarity demonstrates comparable sediment accumulation between cores in a transect, requiring that only one of the three cores be dated in detail. There is an exception in transect 8 where the dated core (8C) has magnetic susceptibility trends similar to 8A and 8B, but the profile is compressed into a shorter core length. The uneven sediment distribution across the river at this most upstream transect is likely due to asymmetric growth of the river's delta at the head of the lake. For this transect, separate sediment accumulation rates were estimated for 8A and 8B as proportions of 8C based on the magnetic susceptibility profiles.

Sediment Phosphorus

The total P in sediment (total-P_{sed}) is comprised of P in various chemical forms distinguished by their respective extractions: iron- and aluminum-bound P (NaOH-P), calcium-bound P (HCl-P) and organic-bound P (Org-P). In cores 8C, 7B and 1B, the NaOH-P and HCl-P fractions comprised equal proportions (~40%) of the total sediment P before 1900 (Fig. 13). After 1900, the proportions diverged and by 1950 NaOH-P was between 50-60% of the total sediment P while HCl-P was ~20%. In cores 6B, 5B, 4B and 3B, NaOH-P was initially around 50% of the total-P_{sed} versus 30% HCl-P. Around 1950, NaOH-P began increasing gradually to a peak of 70%, while HCl-P decreased to barely 10% of the total-P_{sed}. Core 2B is unique in that there is no clear trend in the proportion of NaOH-P, while HCl-P and Organic-P are essentially equally abundant since 1900. In all cores, Organic-P is about 20% of the total-P_{sed}, though in the surficial sediments of each core it rises slightly, possibly because of incomplete diagenesis of organic matter. Some cores have more scatter than others, making the NaOH-P increase and HCl-P decrease less clear in those cases.

Prior to European settlement, total-P_{sed} concentrations were fairly uniform at all core sites, around 1.5 ± 0.5 mg g^{-1}. The concentration of total-P_{sed} began to gradually increase between 1800 and 1900 and, in most cores, increased sharply from 1950 to the present. However, concentrations in core 2B changed little because of dilution from increased sediment loading.

Delivery of P to the sediments is better characterized by the P flux, the product of total-P_{sed} concentration and the concurrent sediment accumulation rate. For example, during 1940-1950 the core 3B total-P_{sed} concentration was 2.07 mg g^{-1} (111% of the pre-1850 concentration), while during the same decade the total-P_{sed} flux was 21.66 g $m^{-2}yr^{-1}$ (1400% of the pre-1850 flux and orders of magnitude larger than the total-P_{sed} flux in other cores for that time interval). Thus, total-P_{sed} flux is more indicative of loading changes than is total-P_{sed} concentration.

The total-P_{sed} flux in pre-settlement times ranges from 0.4 g m^{-2} yr^{-1} (7B) to 3.3 g m^{-2} yr^{-1} (8C). In all cores, the flux increased slightly around 1920 to between 2.8 g m^{-2} yr^{-1} (4B) and 9.2 g m^{-2} yr^{-1} (8C), peaks in the 1950s and 1960s at 5.2 g m^{-2} yr^{-1} (1B) to 67 g m^{-2} yr^{-1} (3B), then plateaus after 1980 in a range from 4.5 g m^{-2} yr^{-1} (1B) to 13.3 g m^{-2} yr^{-1} (8C).

Biogenic silica

Biogenic silica (bSi) analysis measures the mass of diatom and chrysophyte microfossils and is thus a proxy for biotic productivity within the lake. Most of the Lake St. Croix cores had a significant increase in bSi concentration in the sediment after 1950 (Fig. 14). Cores 8C and 2B are the exceptions, showing a more subtle increase in bSi concentration at that time and also more fluctuations in the trend.

As with total-P_{sed}, the concentration of bSi in these two cores was likely diluted by large changes in sediment flux. Therefore, the product of concentration and sediment accumulation better characterizes changes in the lake's bSi production. Prior to European settlement, bSi flux was much higher in core 8C (185 g m^{-2} yr^{-1}) than in the rest of the lake (ranging from 7 g m^{-2} yr^{-1} in core 4B to 55 g m^{-2} yr^{-1} in core 3B). In most cores, bSi flux increased sharply around 1940, rising to peak values of 119 g m^{-2} yr^{-1} (1B) to 654 g m^{-2} yr^{-1} (8C) sometime within the last few decades. The increase appears to begin somewhat earlier in core 2B, around 1920, but this difference may be due to uncertainty in that core's chronology. Cores 8C and 7B have local maxima (350-654 g m^{-2} yr^{-1}) in the 1960s, then the bSi flux decreased slightly and plateaued to the present at three to eight times presettlement fluxes. Downstream cores show more variability but have a present-day bSi flux (135-360 g m^{-2} yr^{-1}) that is four to sixteen times presettlement values.

Pigments

Fossil pigments measured in cores 1A and 6C increased significantly beginning between 1940 and 1970. In core 6C some pigments, such as canthaxanthin (from cyanobacteria) and diatoxanthin (from diatoms), first increased around 1940, declined, then increased again after 1960. Others, such as echinenone and lutein-zeaxanthin (also cyanobacteria), first increased around 1970 (Fig. 15). In core 1A, increases in all pigments began near 1950, including canthaxanthin, lutein-zeaxanthin and echinenone. The increase in all pigments and derivatives indicates a general increase in productivity after 1950. Fossil pigments from cyanobacteria, a common indicator of eutrophy, increase at a rapid rate comparable to the pigments from other algae. For further discussion of these results see Edlund et al. (2003, in review).

Whole-lake fluxes

To understand the cumulative effects of human activity on the sediment and P loads to Lake St. Croix, the information from all cores must be integrated. Eighteen to twenty samples from each of the eight primary cores were analyzed for total-P_{sed} and biogenic silica. In addition, two sediment samples from each of the sixteen secondary cores were analyzed for those parameters: the “top”, or most recent 4 cm of sediment, and the “bottom”, or the 4 cm immediately preceding the increase in magnetic susceptibility marking European settlement. The “top” and “bottom” values from the secondary cores were weighted proportionally and averaged into the flux calculations to account for within-transect variation and thus better constrain the fluxes during those two important time intervals. The flux of each sediment fraction to a core site was calculated as the product of the sediment accumulation rate and the concentration of that fraction in different strata. Subsequently, fluxes for the whole lake were determined by weighting the flux of each transect of cores by the portion of the depositional basin represented by that transect.

The resolution of the dating models limits the resolution at which these stratigraphic changes can be examined. Cores 2B and 3B in particular have coarse chronological resolution because of the inapplicability of the ^{210}Pb dating method. Instead of reporting annual changes in lake-wide fluxes, data are integrated as decadal averages for the period 1930-2000, and as twenty-year averages during 1850-1930 where dating uncertainty increases (Oldfield et al. 1999). Data before 1850 imply an average of the 100-700 years prior to 1850 when the respective ^{14}C samples were deposited. All graphs are truncated at 1800 to simplify visual interpretation of the data, but the 1800-1850 values actually extend back to the respective ^{14}C sample depth. This strategy harmonizes the chronologies among cores with different dating resolutions, yet provides sufficient resolution of major trends in the data over the past 150 years.

The whole-lake sediment accumulation began to increase shortly after European settlement from 15,000 t yr^{-1} to a peak in the 1950s of 130,000 t yr^{-1}, eight times the pre-settlement rate (Fig. 16). The whole-lake sediment accumulation then declined rapidly to a current level of 60,000 t yr^{-1}, around four times the pre-settlement rate. The sharp peak in the 1950s is driven in large part by sediment deposited in transects 4, 3 and 2.

The whole-lake accumulation of the major sedimentary fractions – inorganic, organic and carbonate – follows closely the whole-lake sediment accumulation trend. From 1850 to the 1950s there was a nearly exponential increase in all fractions, with inorganic flux to the lake bottom peaking in the 1950s at 112,000 t yr^{-1}, organic matter at 11,000 t yr^{-1} and carbonate at 6,000 t yr^{-1}. The up-core increase in organic matter observed in individual core analysis is overwhelmed by the massive sediment flux changes in the 1950s and is not seen in the whole-lake flux calculation.

Total-P_{sed} flux also follows closely the temporal and spatial patterns in sediment accumulation from pre-1850 to the 1950s. Total-P_{sed} flux rose from 23 t yr^{-1} before 1850 to a peak of 181 t yr^{-1} in the 1950s, an eight-fold increase. After 1950, however, total-P_{sed} did not decrease as much as the sediment accumulation but instead stayed near six times the pre-1850 level at 133 t yr^{-1} (Figs. 17 and 18). That is, post-1950 sediment had more P per sediment mass, and/or the proportion of P-rich organic matter increased in the sediment. This abrupt switch from a close correlation between P and sediment delivery to a distinct offset in that relationship strongly suggests that there was a new P source in the watershed after 1950.

Whole-lake biogenic silica accumulation began to rise after 1910 and continued to increase steadily until it plateaued at around 5,000 t yr^{-1} in the 1960s. Present-day levels remain near 5,500 t yr^{-1}. During the 1960s, bSi was ~5% of the sediment load (92,200 t yr^{-1}) but was greater than 9% of the sediment load (58,500 t yr^{-1}) by the 1990s.

<u>Lakewater P reconstruction</u>

Diatom microfossil analysis was performed on cores 6B and 1B, but only the downstream core (1B) is described here. All microfossil results from both cores are described in detail by Edlund and Engstrom (2001; Edlund et al., 2003, in review).

Three hundred and fifty-one diatom taxa were identified in Lake St. Croix sediments and these can be divided into benthic and planktic groups. From 1955 to 1975, absolute abundance of both diatom groups increased (Fig. 19). However, the relative ecological importance of the groups shifted: benthic species dominated the diatom flora before 1920, but by 1950 the relative abundance of planktic species was 77%.

Thirty-three of the diatom taxa in core 1B, representing a minimum of 55% and a maximum of 85% of the diatoms counted in each sample, were used with the Ramstack training set for P reconstructions (Ramstack 1999). Because some riverine and lacustrine species that were relatively abundant in the sediments are not part of the Ramstack model, Edlund et al. (2003, in review) also attempted a reconstruction using a combination of the Ramstack model and two other training sets containing some of these missing taxa. The trends in the data were unchanged, although the combination reconstruction consistently returned TP values ~0.010 mg L^{-1} lower than the Ramstack-only reconstruction. Because the Ramstack-only reconstruction was more statistically-sound, only those results are presented here. (For a detailed discussion of this issue, see Edlund et al.; 2003, in review).

Pre-settlement total-P_{lake} varied from 0.02 to 0.025 mg L^{-1}, and did not begin to rise until about 1920 (Fig. 20). The most dramatic increase began about 1950, and levels remained near the maximum value 0.06 mg L^{-1}, with some variation, through the 1980s and 1990s. The most recent diatom-inferred TP values (1990-2001 average = 0.064 mg L^{-1}) match closely those from direct monitoring (1990-2001 non-winter average = 0.056 mg L^{-1}; Johnson, MPCA, pers. comm.), providing further validation of the model results.

P mass balance

Phosphorus flux out of the lake to the Mississippi River was calculated as the product of the river's hydrologic discharge and the reconstructed total-P_{lake} concentration (core 1B) at the downstream end of the lake. The first consistent flow data for the St. Croix River were recorded at St. Croix Falls, Wisconsin beginning in 1892. The mean of all flow data from 1892 to 2001 ($4x10^9$ m^3 yr^{-1}) was used for pre-1892 flux calculations. Three large tributaries (the Apple, Willow and Kinnickinnic Rivers) enter the river and lake downstream of St. Croix Falls, increasing the flow through Lake St. Croix by about 11%. To account for that increase, measured and estimated flows for the tributaries were added to the St. Croix Falls data. Seventy-five years of flow data exist for the Apple River, but flows for the other two tributaries (and for unmonitored years on the Apple River) were estimated using representative ratios of tributary flow to mainstem flow, or tributary to Apple River flow. The Apple River has a good correlation with mainstem flows (R^2=0.70), and the Willow and Kinnickinnic River flows were estimated to be 0.30 and 0.36 of the Apple River flow based on 1-3 years of flow data.

As discussed above, reconstructed total-P_{lake} concentrations increased dramatically after 1950. When multiplied by flow to become mass flux, P export from the St. Croix River to the Mississippi more than doubled from 127 t yr^{-1} before 1850 to 285 t yr^{-1} in the 1990s. Flows from 1940 to 2000 did not vary significantly (Fig. 21), so the increase in P flux is due solely to increased P concentrations in the river.

The major phosphorus losses from Lake St. Croix are thus quantified as (1) P burial in the sediments (whole lake total-P_{sed} flux), and (2) P outflow to the Mississippi River (reconstructed total-P_{lake} from core 1B). Because there are no significant losses of P through other pathways (e.g. volatilization), the sum of the sedimented and discharged P equals the historical P loading to the lake system. That is,

(P loading to the lake) = (P trapped in sediment) + (P in outflow)
(Vollenweider 1975; Rippey and Anderson 1996)

Total P loads to the lake averaged 166 t yr^{-1} before European settlement. P input increased slightly during 1890-1910 to 210 t yr^{-1}, then increased sharply from the 1940s onward (Fig. 22). During the 1990s the total P load to the lake was 459 t yr^{-1}, a three-fold increase from the presettlement load and the highest P load the lake has received during the period of study (~200 years). This upward trend was driven by increasing total-P_{lake} concentrations which, in turn, were driven by the proliferation of anthropogenic P sources in the watershed from 1940 to 2000.

The proportion of P trapped in the sediment versus P discharged to the Mississippi River (sediment P retention rate) has not been constant through time (Fig. 23). Before 1850, 13% of the P input to the lake was trapped in the sediment while 87% was discharged to the Mississippi. The sediment retention increased gradually to 24% in 1890-1910 and peaked at 47% in the 1930s. Phosphorus retention remained above 40% through the 1960s, then decreased to the present rate of 29%. The trend in sediment retention does not parallel that of P input (R^2=0.13, linear regression), but is related more closely to sediment accumulation rate in the lake (R^2=0.60). This suggests that sediment-P retention is linked to burial rate and/or flux of sediment through the water column (scavenging P from the lakewater) rather than to absolute loading of P to the system.

In some systems, anoxic bottom water releases significant amounts of P from the sediments to the overlying water. While periods of anoxia have been documented in parts of the Lake St. Croix hypolimnion (Johnson 2001), an analysis reported by Robertson and Lenz (2002) suggests that the amount of P released from Lake St. Croix sediments would be small, on the order of 6% of the total P load to the lake. The relatively high sediment accumulation in the lake likely insures that most P delivered to the lake bottom is buried before it can be remobilized. Regardless of magnitude, P recycling does not affect the P mass balance because all P inputs are, eventually, buried in the sediment or discharged from the lake.

SYNTHESIS

In the 170 years since European settlement of the St. Croix watershed, significant changes have occurred in sediment accumulation, phosphorus loading and algal production and ecology in Lake St. Croix. With the multiple-core, whole-basin record developed in this study, these changes can be quantified and observed lake effects linked to specific anthropogenic causes.

Sediment

The sediment accumulation in Lake St. Croix increased gradually during the first century after European settlement, then rose sharply after 1930 to a peak of 129,000 t yr^{-1} in the 1950s. Today the lake accumulates around 60,000 t yr^{-1} of sediment, about four times the pre-settlement rate. The sediment accumulation increase is presumably due to increased topsoil or stream-bank erosion from the watershed (Schottler and Engstrom 2003). Importantly, the distribution of the sediment load among Lake St. Croix's four sub-basins varies through time. In its "natural" pre-European state, the lake's most upstream sub-basin (D) received the largest proportion of the total sediment load (51-56%), as expected where the river velocity decreases suddenly upon entering the lake. This pattern shifted dramatically between 1940 and 1960 when the two downstream sub-basins (A and B) became the primary depositional centers and together received 56-61% of the total sediment load (Fig. 24). These downstream spikes in sediment accumulation almost certainly originated in the small side-valley tributaries, specifically Valley Branch Creek, Trout Brook and the Kinnickinnic River. Despite the relatively small size of these watersheds (120 km^2, 45 km^2 and 520 km^2, respectively) they were able to deliver large amounts of sediment to the lake due to their steep gradients, proximity to the depositional basin and possibly because of locally-high erodibility of soil and glacial outwash (Dearing and Foster 1993; Mulla et al. 1999).

In summary, Lake St. Croix sediment accumulation responded only modestly to initial logging of northern forests and conversion of southern prairie and woodlands to agricultural uses during 1840-1880. Sediment eroded from land distant from the lake may have been temporarily stored in the river channel (including sloughs, sandbars, etc.) or behind impoundments such as the multitude of wing dams constructed along the river from 1850-1890 and the hydropower dam at St. Croix Falls built in 1904. For this reason, the amount of sediment accumulated in the lake does not directly equal that eroded from upstream landscapes after the original land conversion. It is clear, however, that the lake was strongly affected by land-use changes in the lower watershed during the mid-1900s, possibly including increased road-building, urbanization and the mechanization of agriculture. After 1970 the sediment accumulation declined, suggesting that agricultural soils and streambanks were stabilized and/or the local, episodic disturbances of the 1950s and 1960s have not occurred since.

Phosphorus

In calculating the total P load to the lake, it is apparent that total-P_{lake} is at all times a larger component than total-P_{sed}. That is, the majority of the P load (between 52-78%) is not trapped in lake sediments but is instead discharged to the Mississippi River. The P load to the lake increased after 1940 with a maximum during 1980-2000 of three times the average pre-settlement load. The increase began after land conversion was complete and was not due simply to eroded soils entering the lake.

Further detail is provided by total-P_{sed}, which followed closely the whole-lake sediment accumulation trend from pre-settlement to 1950. After 1950, total-P_{sed} diverged as more P or P-rich organic matter began accumulating (Figure 17). This shift to more P-rich sediments strongly suggests that a significant component of the total-P_{sed} came from a new source after 1950. This higher P:sediment ratio most likely resulted from increased inputs of dissolved P, which in turn increased biologic productivity in the lake and resulted in a higher proportion of organic matter in the sediment. Furthermore, while total-P_{sed} increased steadily from 1850 to 1950, total-P_{lake} began to increase only after 1940, indicating that there was a change in the proportion of non-particulate P (dissolved or soluble reactive phosphorus (SRP)) to particulate (sediment-bound) P at this time.

Today there are over 50 permitted point source discharges in the watershed, a few of which are large municipal wastewater treatment plants (WWTPs). However, even during a dry year (when non-point inputs are normally low) the P input from point sources represents less than 30% of the total P load to the lake (Robertson and Lenz 2002). In addition, P discharges from WWTPs in the nearby Upper Mississippi watershed peaked in the 1960s and 1970s (~1000 t/yr), then decreased significantly (~800 t/yr in 1992) after the ban on phosphate detergents (Mulla et al. 1999). The ban applied equally to WWTPs in the St. Croix watershed, so it can be assumed that a similar trend occurred in these discharges.

A more significant cause of the increased P load is likely the importation of phosphorus into the watershed via inorganic fertilizers and livestock feed supplements, leading to accumulation of P in watershed soils (Mulla et al. 1999). Foy et. al (1995) reported an increase in soluble reactive phosphorus (SRP) loading to an Irish lake despite reductions in point-source P discharges and a constant use of phosphate fertilizer in that watershed. The continued rise of SRP resulted from the buildup of P in the watershed and a decreasing ability of the soils to bind the additional P. This phenomenon has been observed in other locations as well (Mulla et al. 1999; Jordan et al. 2001; Baker and Richards 2002; Richards et al. 2002; Jordan and Rippey 2003). The situation in the St. Croix watershed, where phosphate fertilizer applications have remained steady since the 1970s (Mulla et al. 1999), is similar. As soil-P is increasing on a global scale (Bennett et al. 1999; Bennett et al. 2001) and there is evidence that soils in the St. Croix watershed are already high in P (Laboski and Lamb 2003), agricultural phosphorus (fertilizers and feed supplements) is likely a major source of P to the lake.

Ecological Impacts

The most significant consequence of increased P loading to the lake is the change in algal abundance and community structure. Since 1950, the sedimentary accumulation of diatoms from all ecological groups has increased 20- to 50-fold, while whole-lake biogenic silica accumulation has risen five times. The close correspondence between whole-lake TP and bSi trends confirms that there is increased productivity, but also demonstrates another fundamental relationship. While lakewater TP increased 2.5 times from 1850 to the present, bSi increased 5.5 times over the presettlement flux. That is, one unit of P input sustains multiple generations of algal productivity. In addition, the planktic diatom population increased more rapidly than did that of benthic species and so became the dominant ecological group in the system by 1950. Finally, fossil pigments show that the productivity of all algal groups, including cyanobacteria, has increased dramatically since 1960.

Uncertainties

Three components of this study have the most potential for introducing uncertainty to the calculations. First, the lack of flow data before 1892 means that earlier outflow-P calculations are estimated based on an average of 20^{th} century flows. Sediment transport is also correlated to flow. The flow in the St. Croix has certainly changed less since European settlement than in other major rivers such as the Minnesota, where extensive drainage of wetlands and installation of agricultural draintile has significantly increased the rate of water runoff to the river (Mulla et al. 1999). However, variations in flow due to climate are still not accounted for by using the average 20^{th} century flow, so this value is only a best estimate of 19^{th} century discharge.

Second, there is some uncertainty in dating the sediment, due to both the dating models themselves and to the fluctuating sediment provenance and accumulation rates in this lake. High sediment accumulation rates and variable supported ^{210}Pb activities in transects 2, 3 and 4 cause unacceptably large errors in the CRS ^{210}Pb model. This problem was overcome in transect 4 by directly measuring supported and unsupported ^{210}Pb with gamma spectrometry. In transects 2 and 3, dates were obtained by correlating magnetic susceptibility features from cores 2B and 3B to dated cores in adjacent transects. With only 4-5 known (dated) points for cores 2B and 3B, there is more uncertainty in the timing of specific events, such as the first increase in total-P_{sed}. Coarser temporal resolution may also mask short, intense fluxes of sediment. The most significant consequence for this study is that the timing and duration of the large sediment fluxes to sub-basins A and B cannot be constrained to better than a two- or three-decade interval. Nevertheless, dating detail is sufficient to distinguish very significant changes in sediment accumulation, and to integrate these two cores into the whole-lake flux calculations.

Third, the total-P_{lake} reconstruction using a diatom inference model entails some uncertainty. The diatom inference model is constructed from a lacustrine dataset, whereas it is applied here to the riverine system of Lake St. Croix. Furthermore, while the model itself is statistically robust, hypereutrophic lakes are under-represented in the calibration lake set, so diatom-inferred TP reconstructions greater than 85 µg L^{-1} are not possible. This may explain some of the discordance between diatom TP and monitoring records of total-P_{lake} from the 1960s and early 1970s when measured total-P_{lake} values in Lake St. Croix were higher than the reconstructed TP values. Thus, the historical TP outflow from Lake St. Croix inferred from the diatoms and historical flows during these time periods are likely conservative.

Conclusions

The unique geomorphic history of the Upper Mississippi River created Lake St. Croix at the terminus of the St. Croix River. This geologic idiosyncrasy allowed us to successfully apply paleolimnological techniques within a whole-basin context to quantitatively reconstruct pre-historical water quality in a large riverine system. The lake sediments describe changes occurring throughout the St. Croix watershed and constrain the list of historic events that had significant influence on water quality. The chronologies developed here make it clear that the earliest European settlement activities caused only modest increases in sediment loading to the river and did not affect nutrient levels appreciably. Major changes occurred in the mid-1900s, and Lake St. Croix is now far from its natural state in terms of sediment and phosphorus loads and algal ecology. This study provides historical context for citizens and policy-makers as they decide what level of lake/watershed management and restoration is desirable and achievable.

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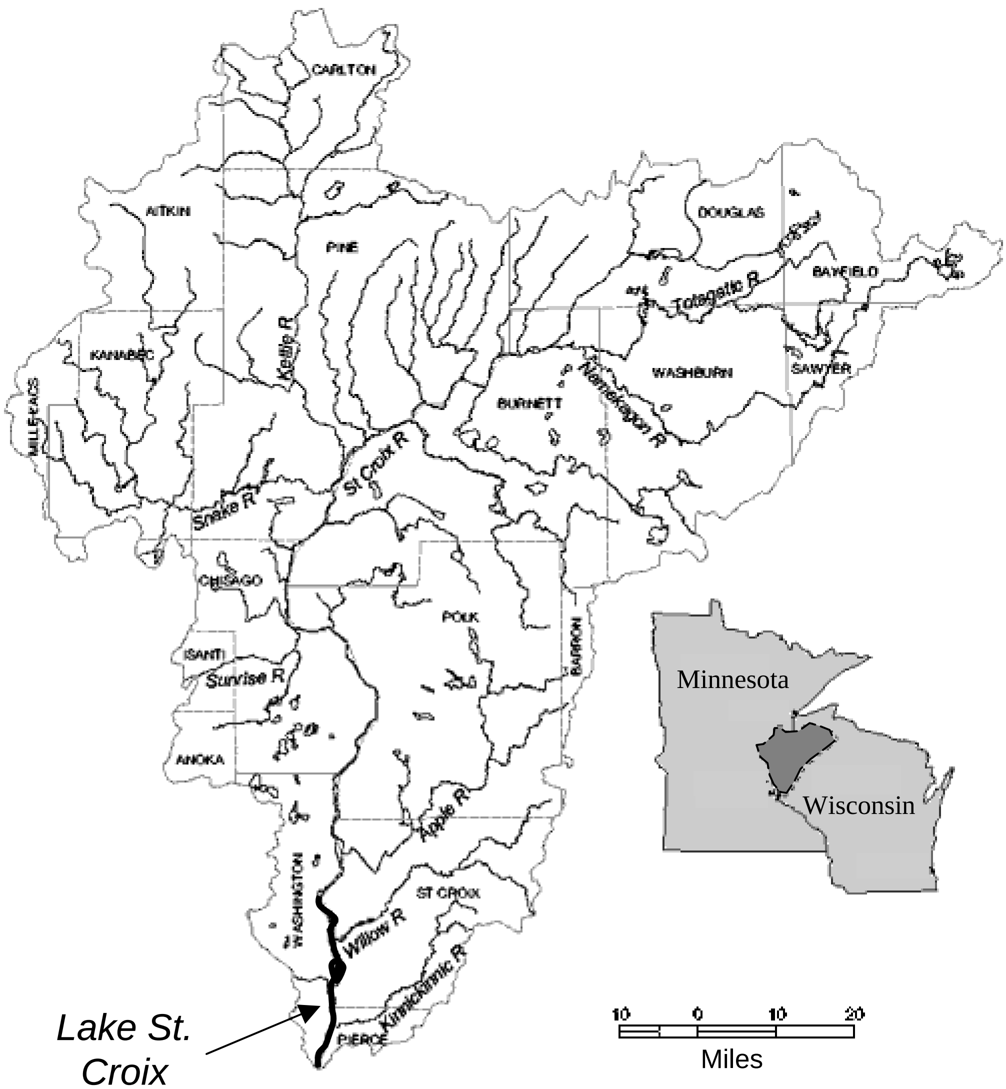
Figure 1 The St. Croix River watershed in Minnesota and Wisconsin.



Map from the Minnesota Pollution Control Agency, http://www.pca.state.mn.us

Figure 2 Lake St. Croix from Stillwater, Minnesota, to the Mississippi River. The lake is divided into four sub-basins (A-D) by the deltas of side-stream tributaries. Core transects are labeled 1-8 going upstream.

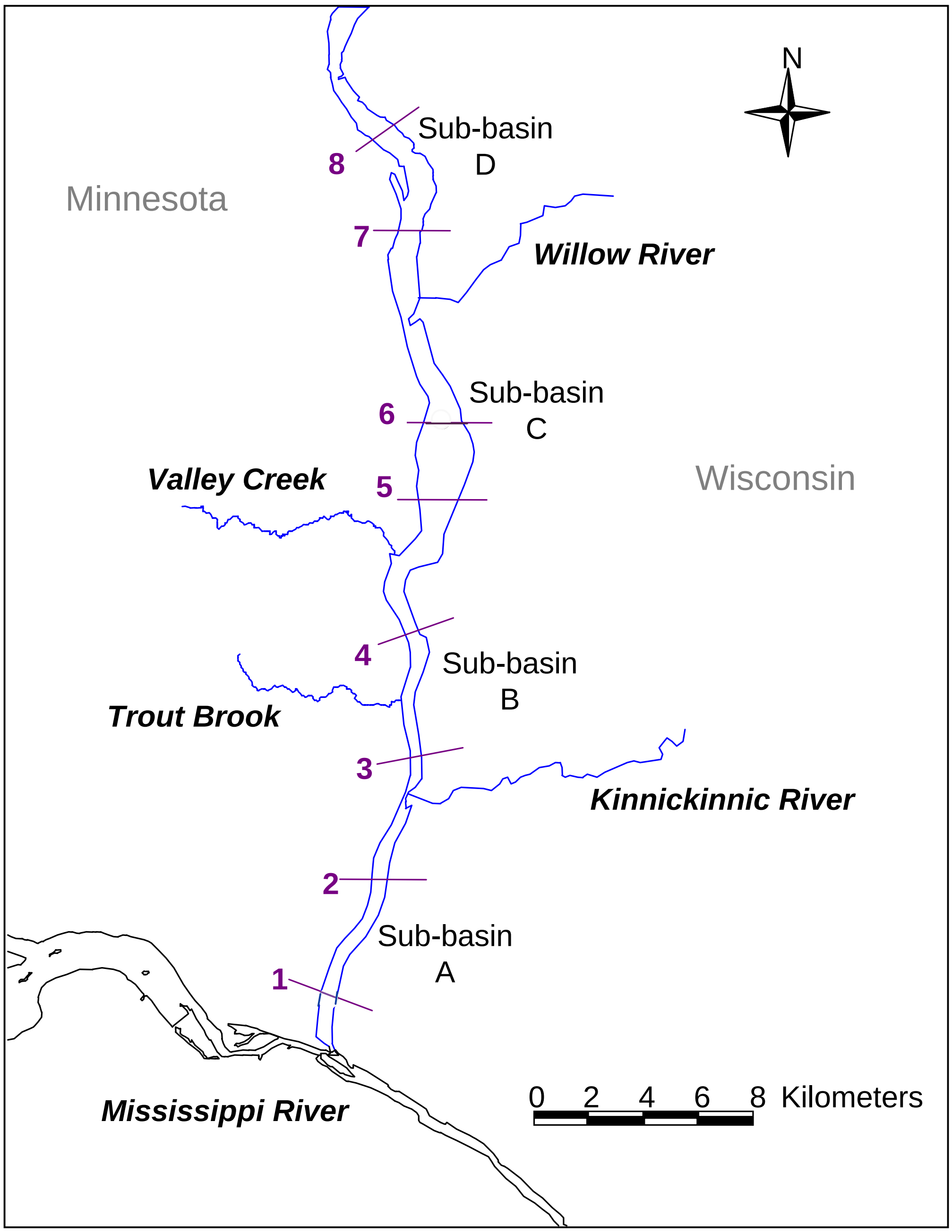


Figure 3 Magnetic susceptibility versus depth for the twenty-four cores. Three cores were collected along each of eight transects.

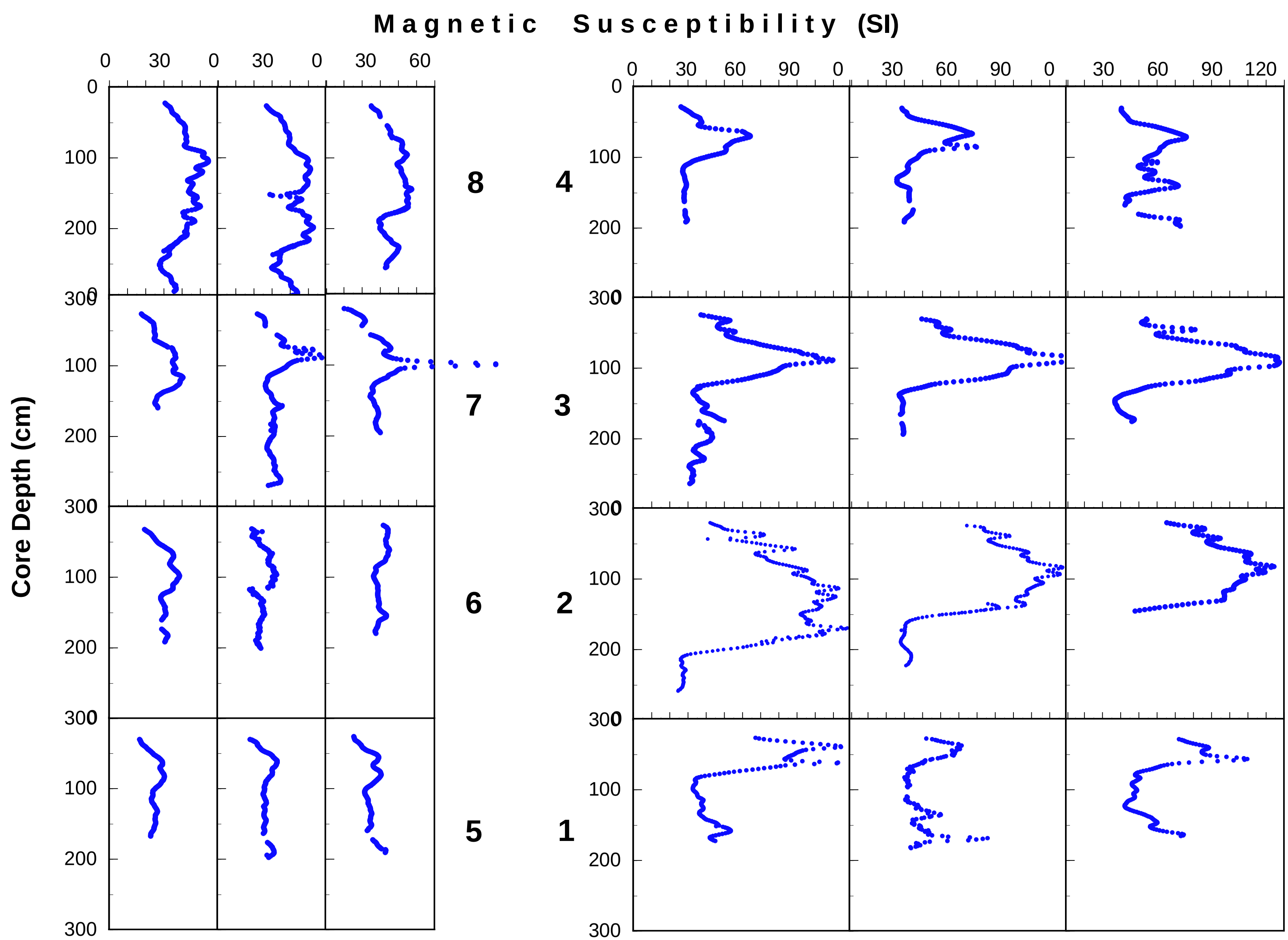


Figure 4 Percent composition of sediment in the eight primary cores, as determined by loss-on-ignition analysis.

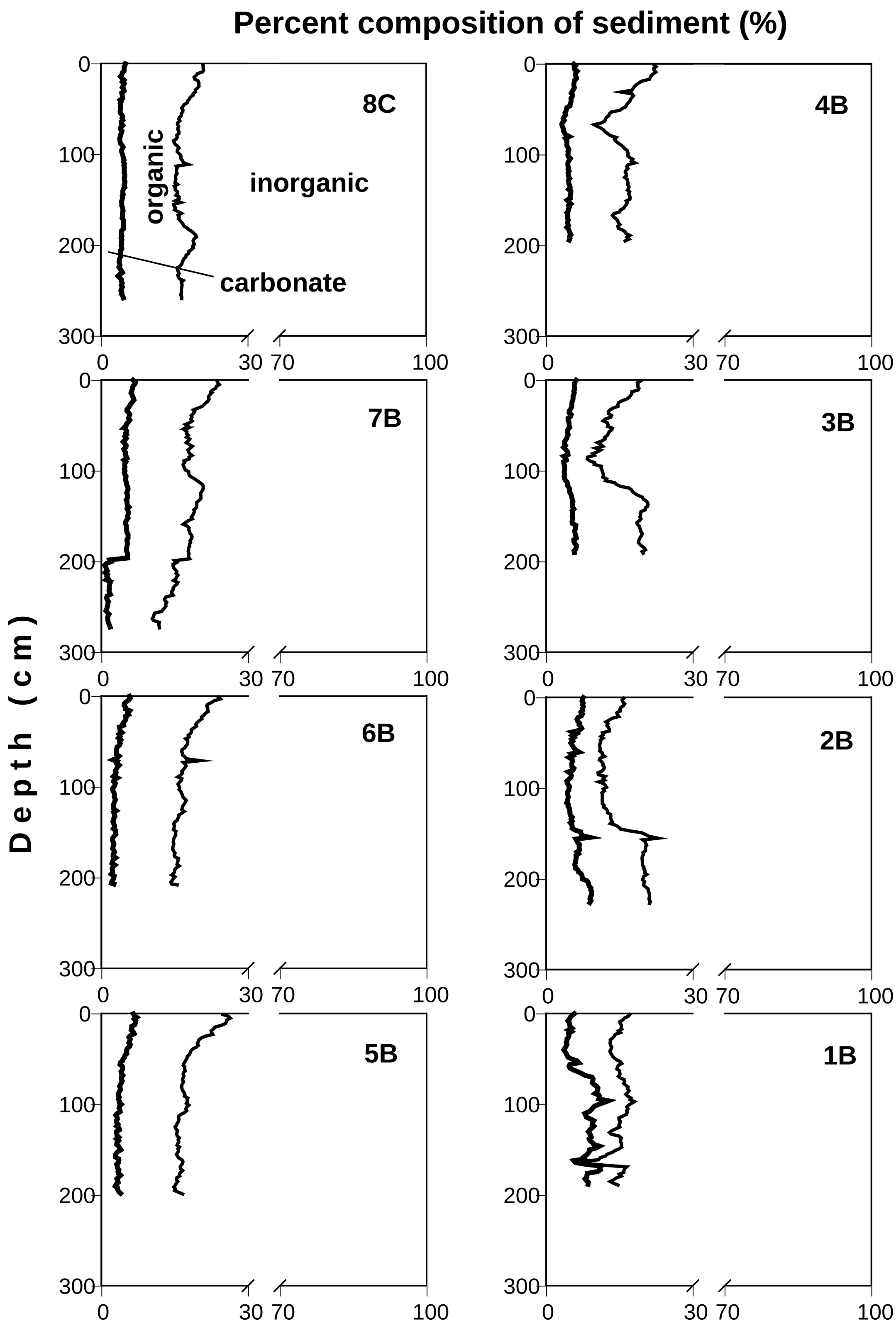


Figure 5 Median grain size versus date for the eight primary cores

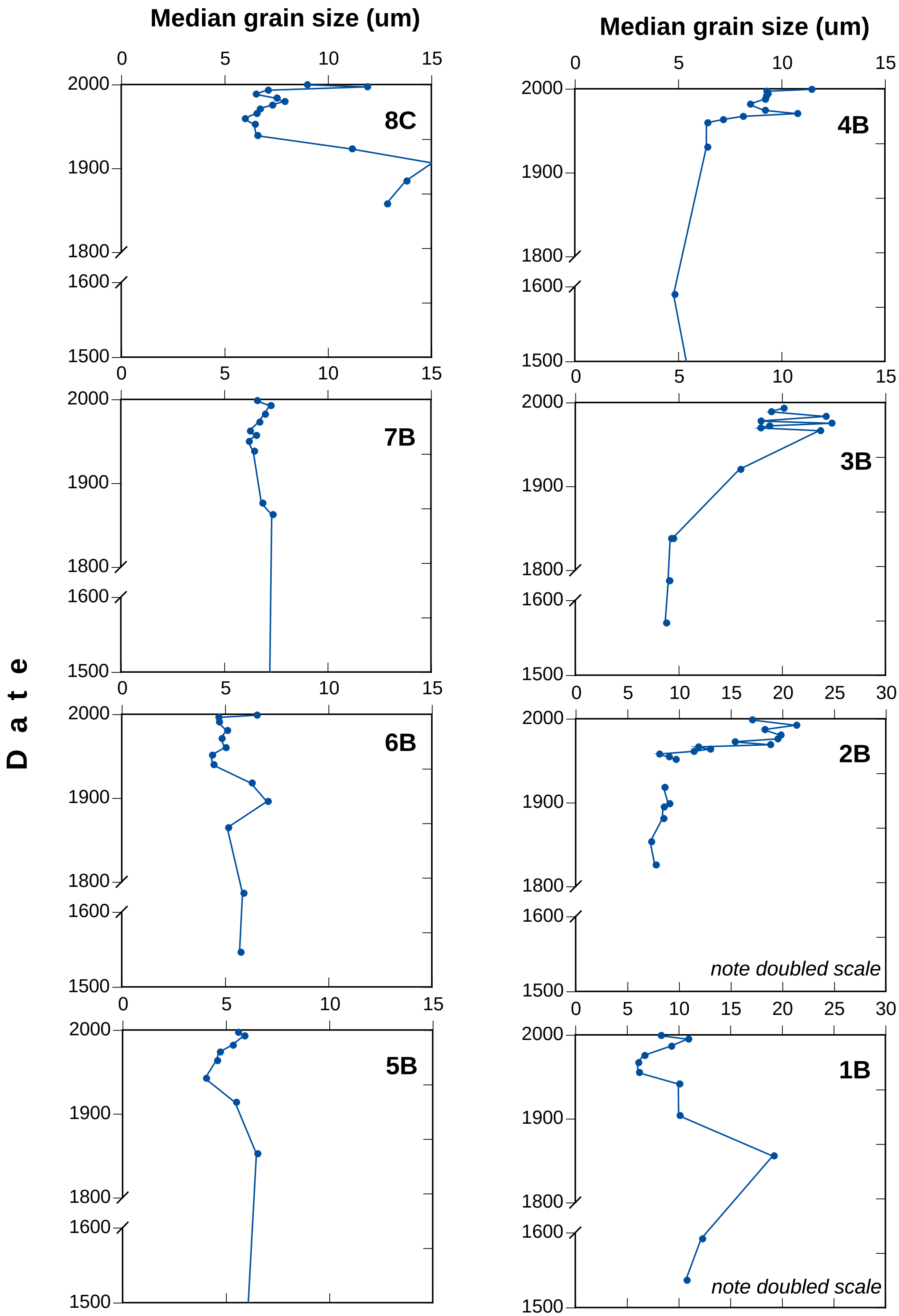


Figure 6 Activity profiles for 137Cs versus depth in the eight primary cores; peaks correspond to 1963-1964 maximum in atmospheric nuclear testing.

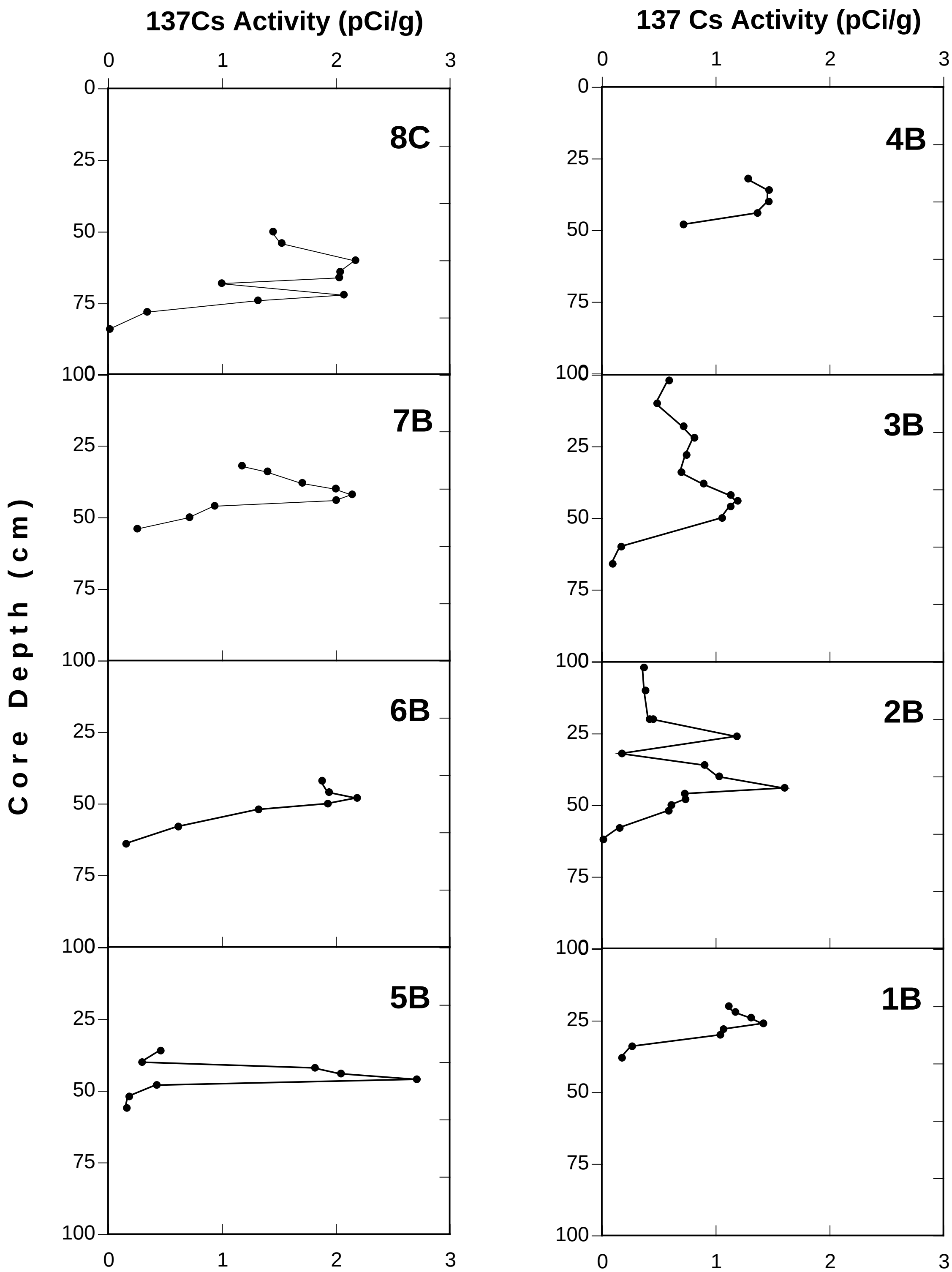


Figure 7 Activity profiles for total 210Pb versus depth in the eight primary cores; error bars represent +/- 1 s.d. from counting uncertainty.

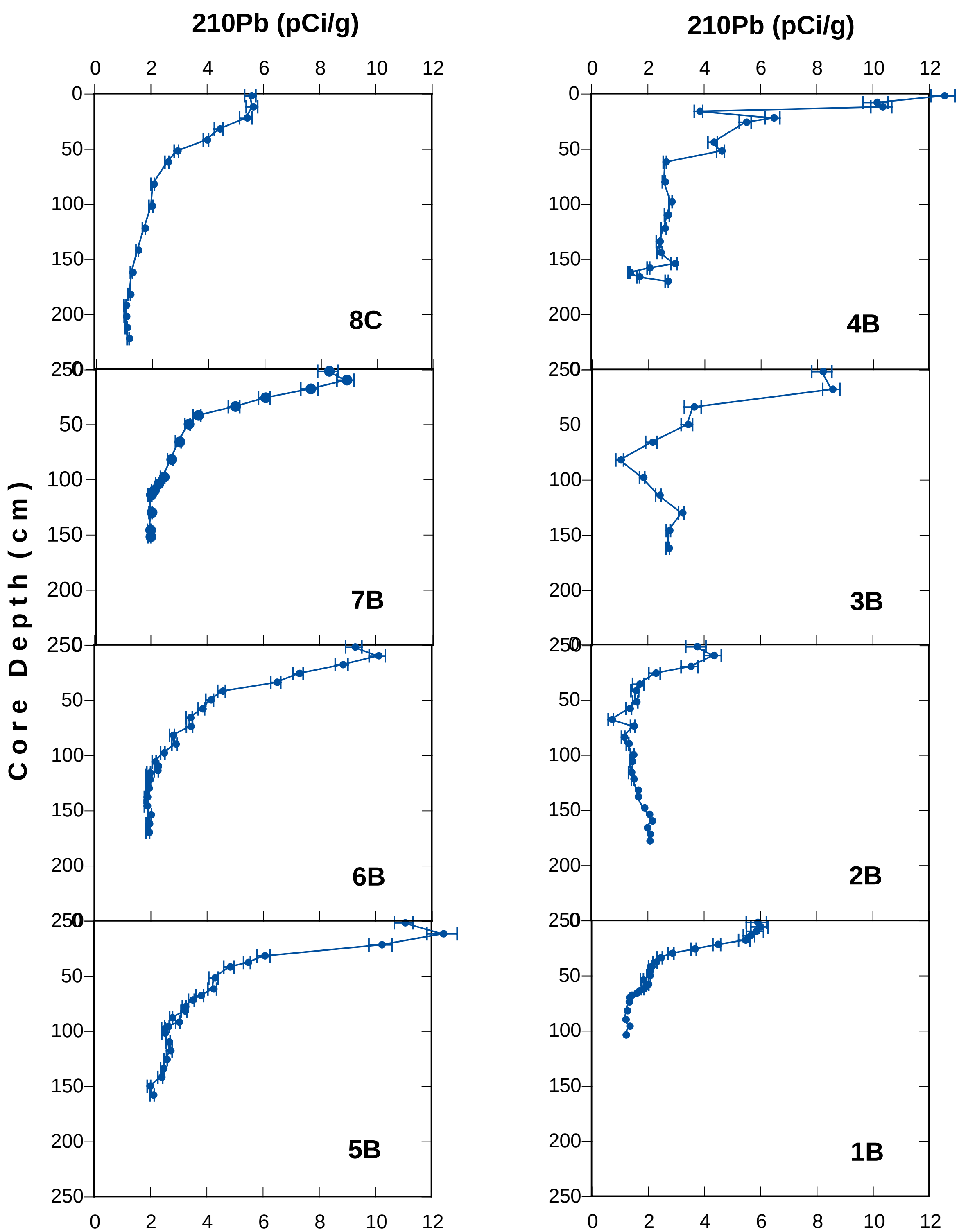


Figure 8 Lead-210 dates of the 137Cs activity peaks (1963-1964); error bars represent +/- 1 s.d. from counting uncertainty.

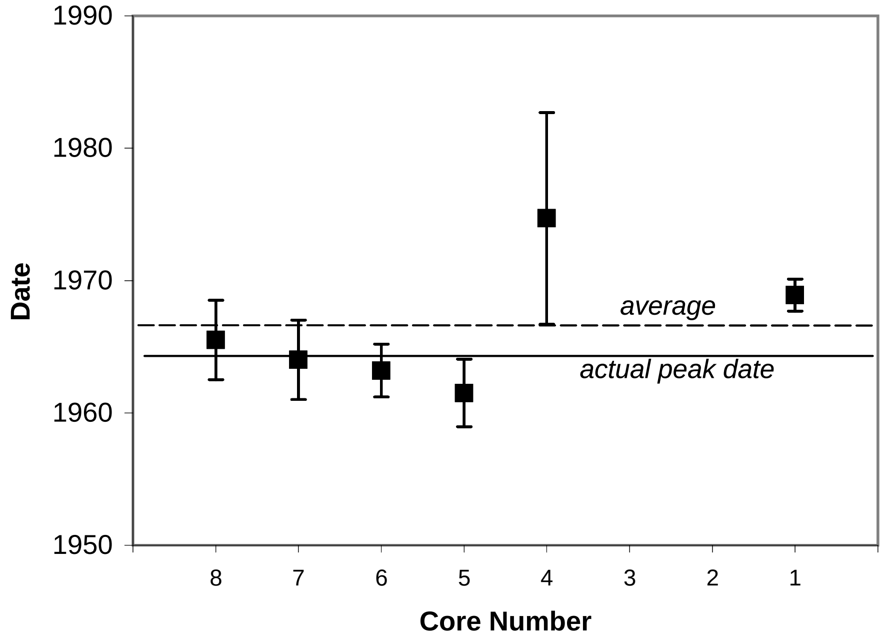


Figure 9 Lead-210 dates of the initial rise in magnetic susceptibility

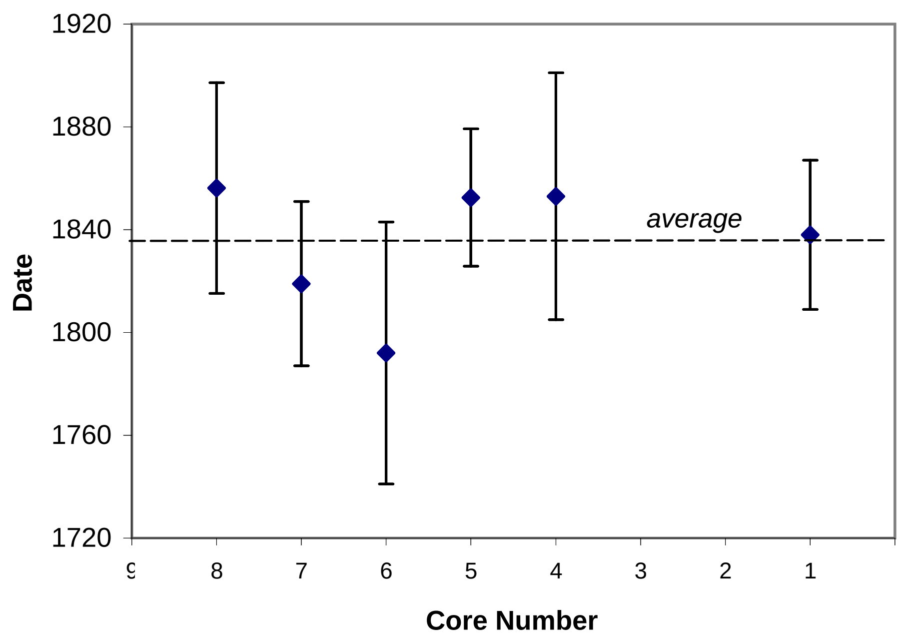


Figure 10 Lead-210 activity as measured by gamma spectrometry in primary cores from transects 2, 3 and 4. Unsupported 210Pb is the difference between total 210Pb and supported 210Pb (as measured by 214Pb) for each depth interval.

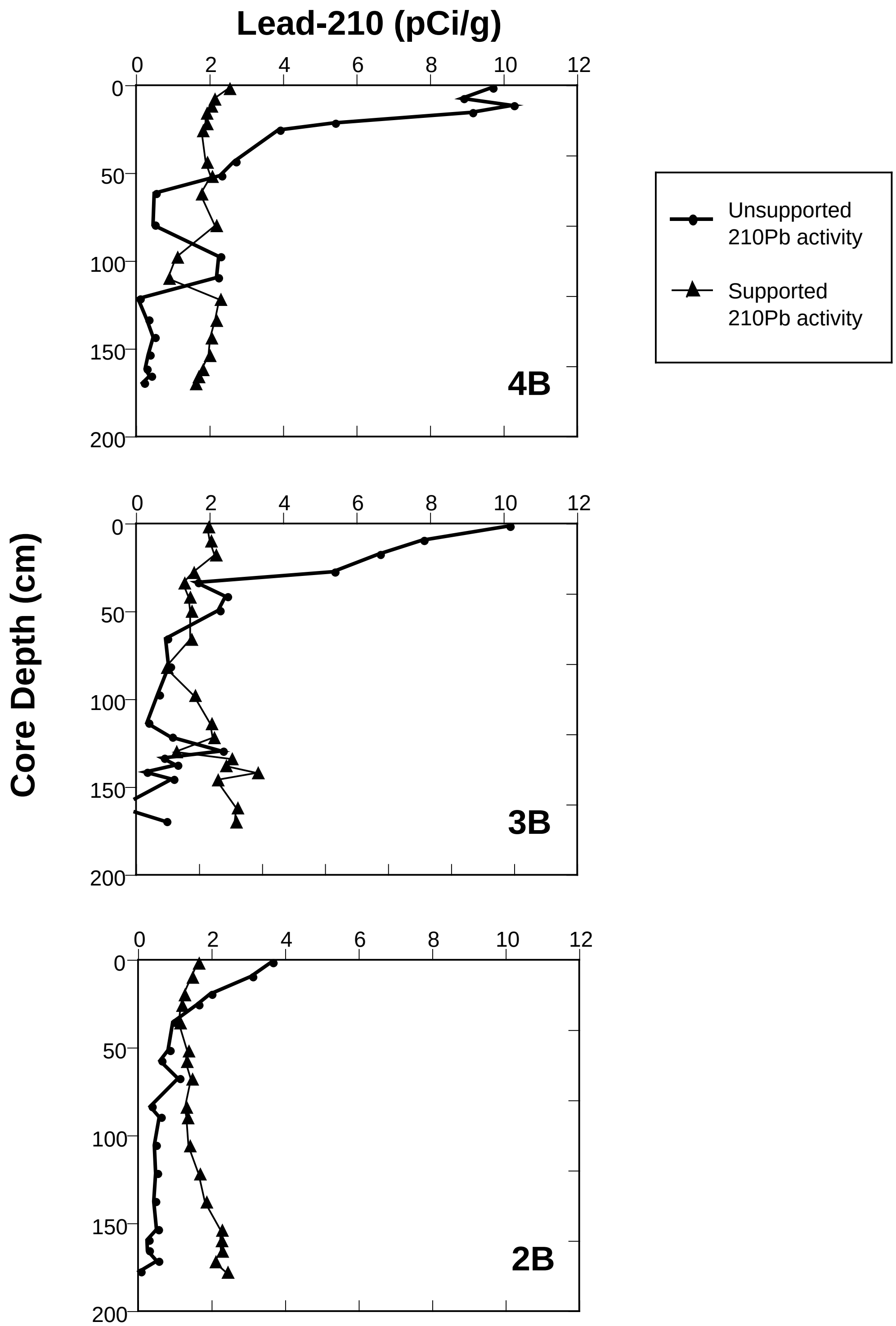


Figure 11 Cross-correlation of magnetic features for cores 2B and 3B, which could not be dated with 210Pb methods. Dated intervals from adjacent transects (1B and 4B) were correlated to 2B and 3B, respectively, using common magnetic susceptibility features.

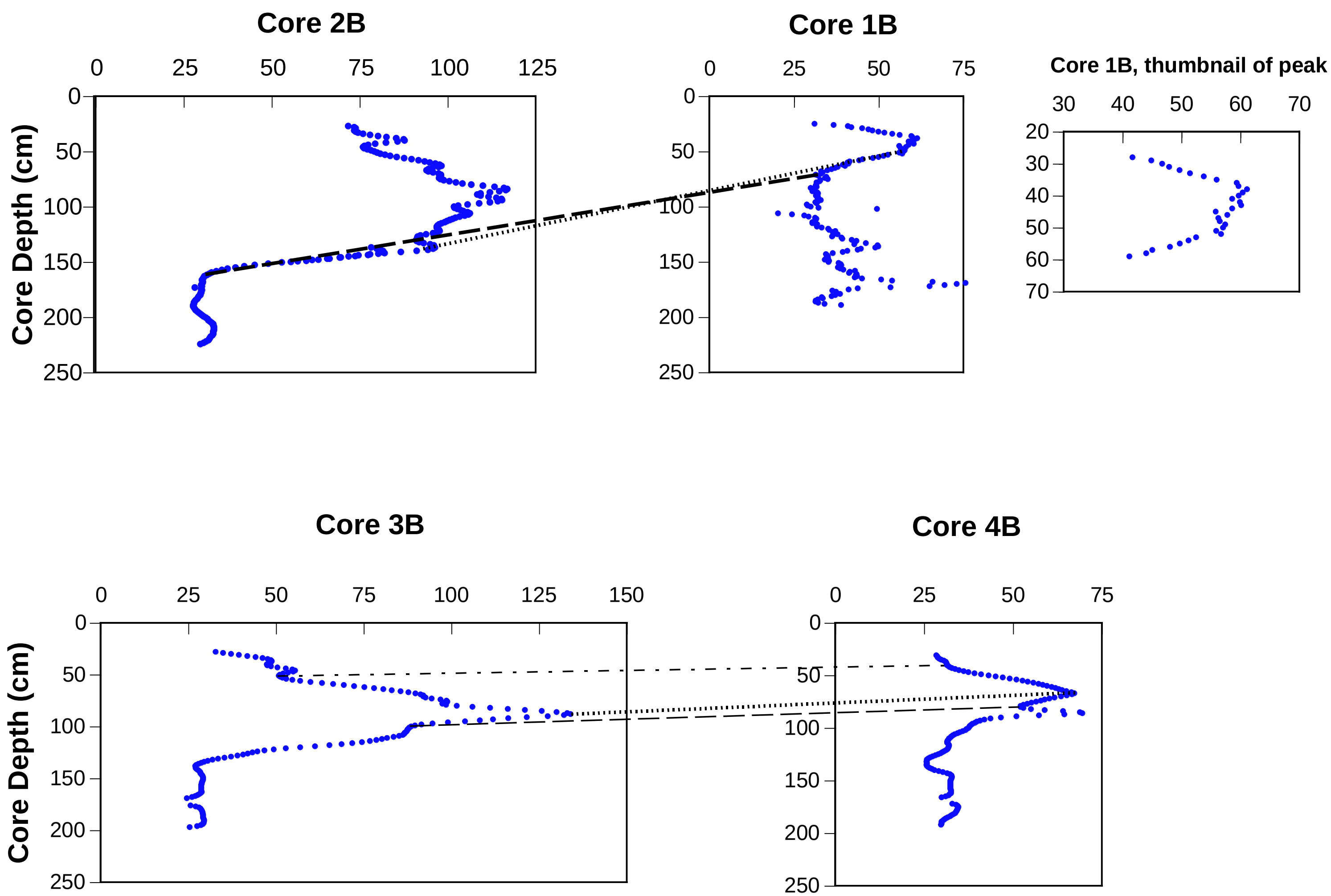


Figure 12 Sediment accumulation rates in the eight primary cores over the last two centuries. Error bars are calculated from the uncertainty in the CRS 210Pb dating model. Cores 3B and 2B were dated by magnetic correlation and drawn without error bars.

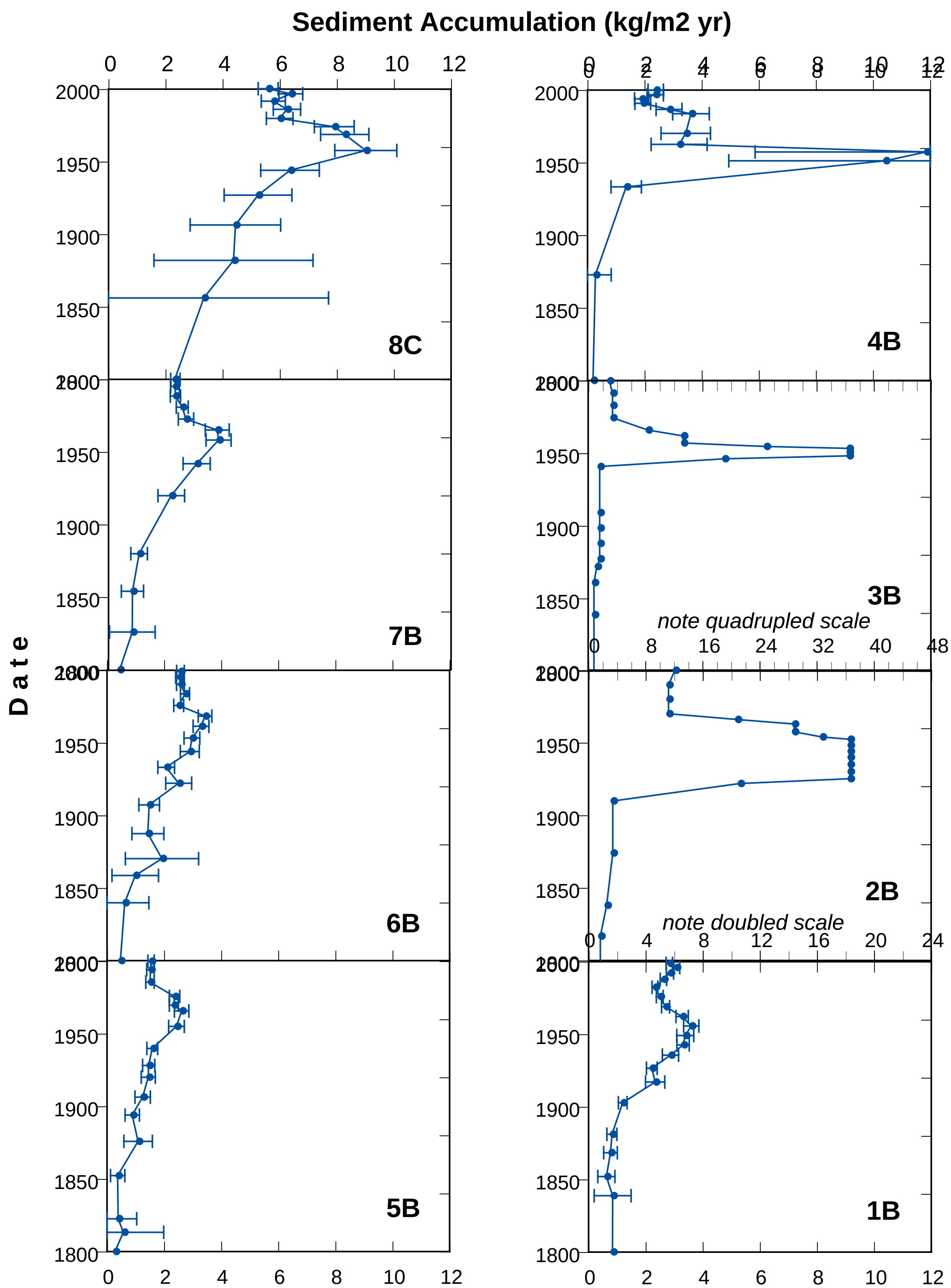


Figure 13 Sediment P concentration versus date in the eight primary cores. NaOH-P is iron- and aluminum-bound P, HCl-P is calcium-bound P, and Organic-P is bound to organic matter.

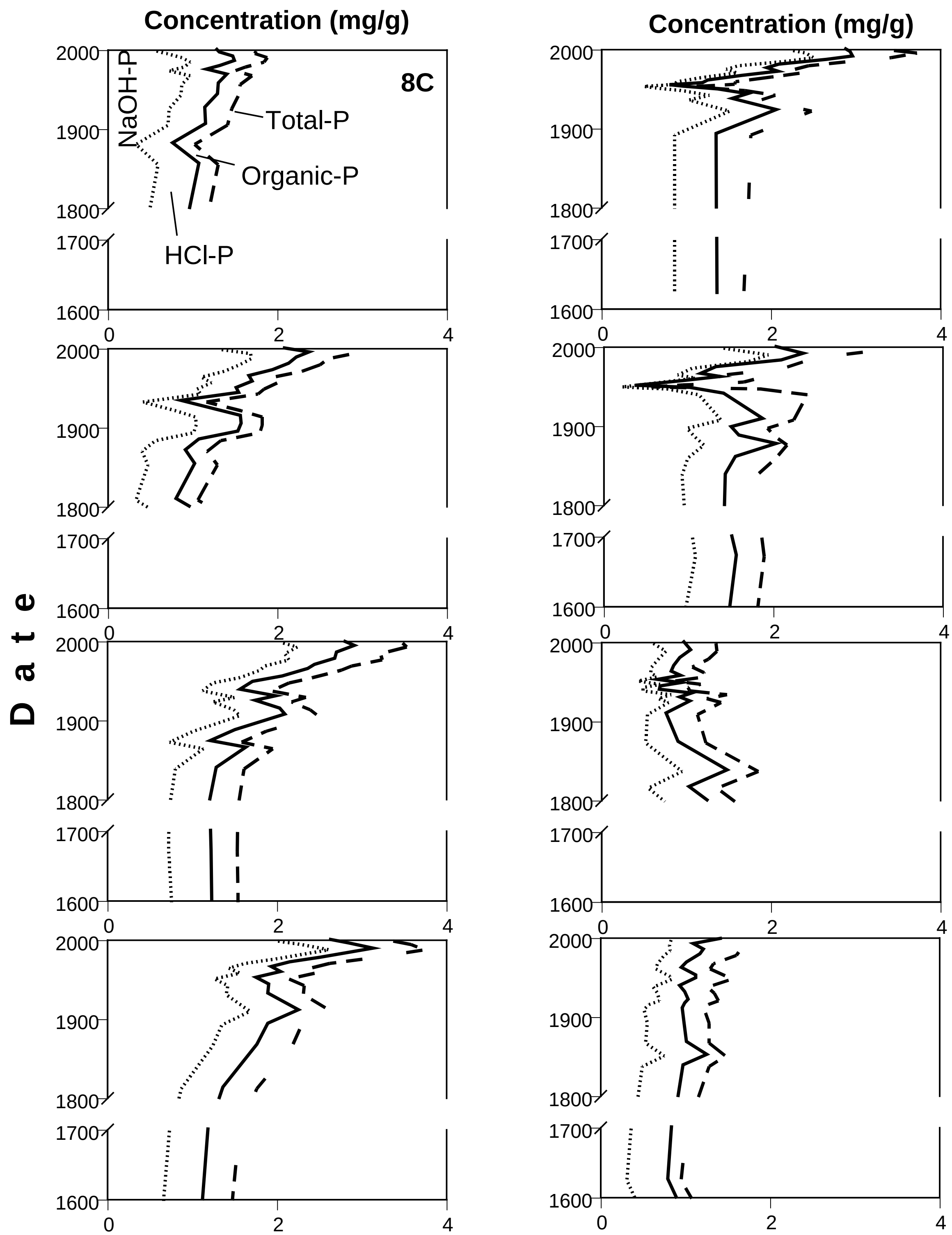


Figure 14 Biogenic silica (bSi) concentration versus date in the eight primary cores.

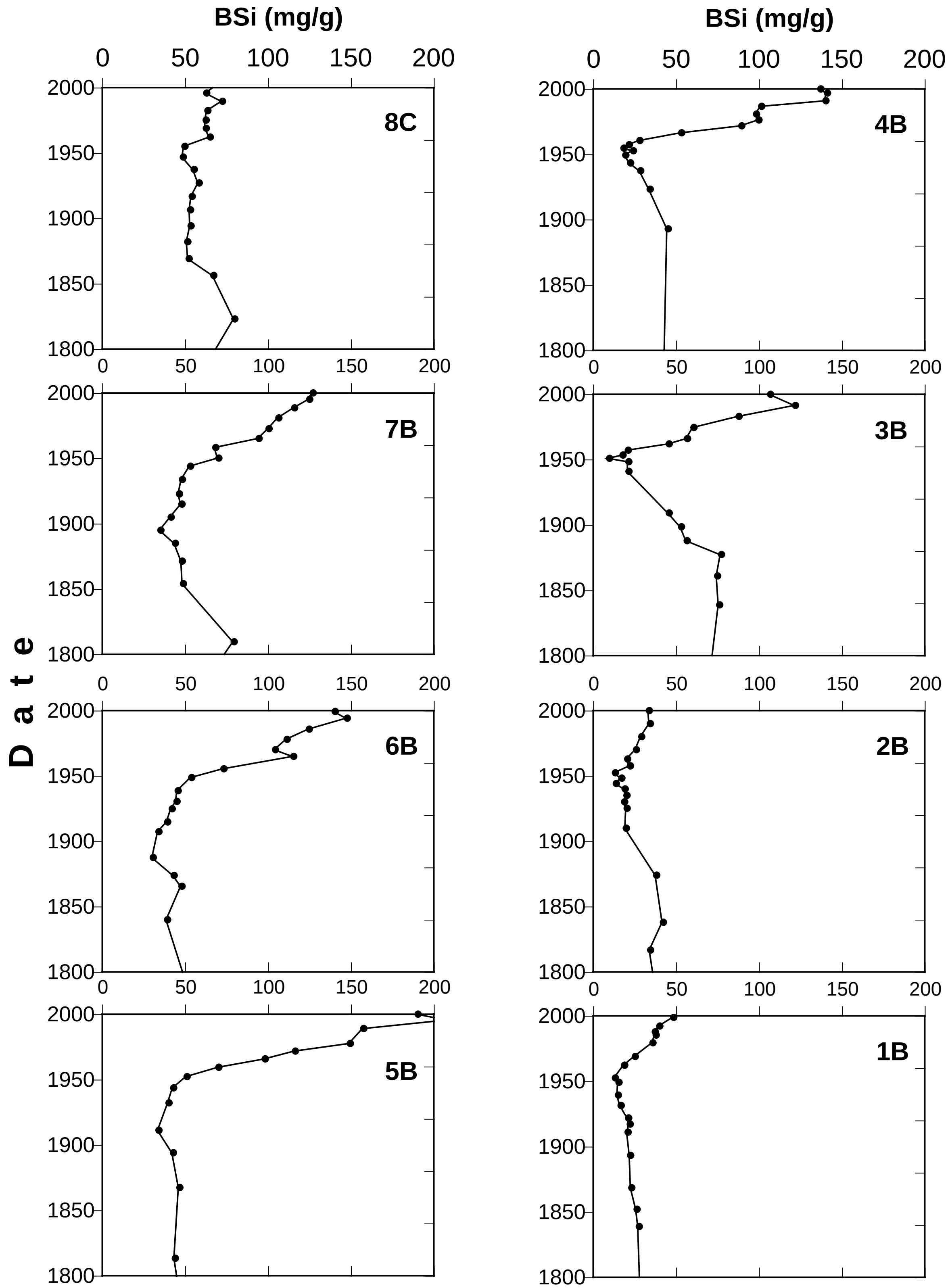


Figure 15 Fossil pigment concentrations (nmole/g org C) in secondary cores from transects 1 and 6; primary cores from these transects were used for diatom analysis.

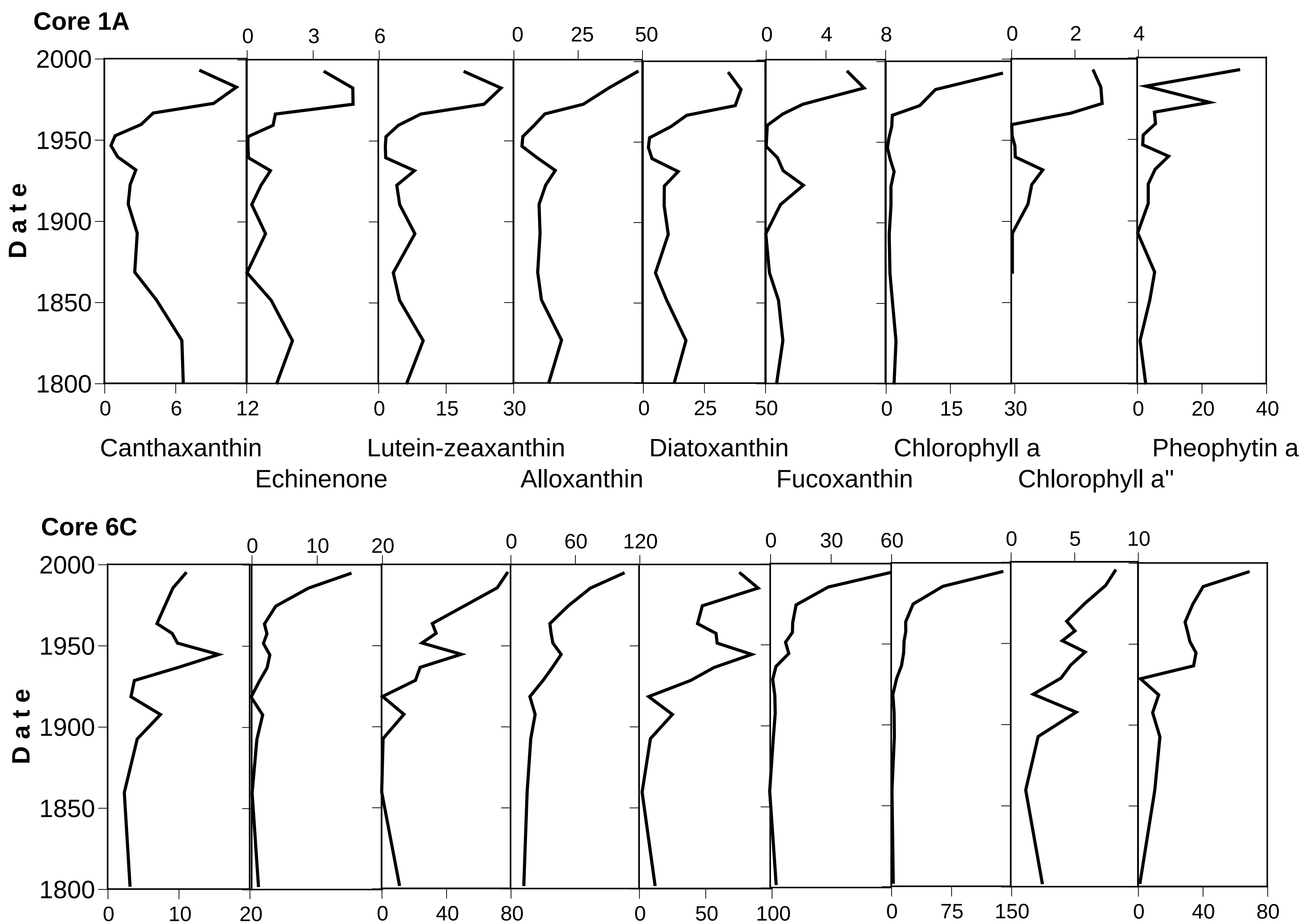


Figure 16 Whole lake sediment accumulation rates versus date

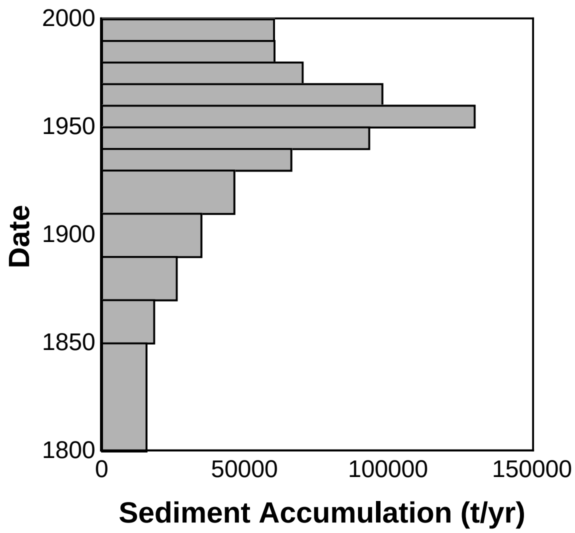


Figure 17 Whole-lake accumulation of phosphorus in the sediment of Lake St. Croix over the last two centuries.

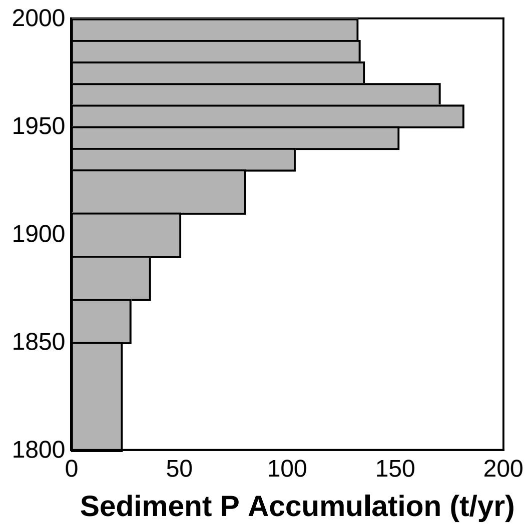


Figure 18 Accumulation of P in sediment compared to whole-lake sediment accumulation. Before 1950, the correlation coefficient of this relationship was 0.98; after 1950, there is an excess of P relative to total sediment.

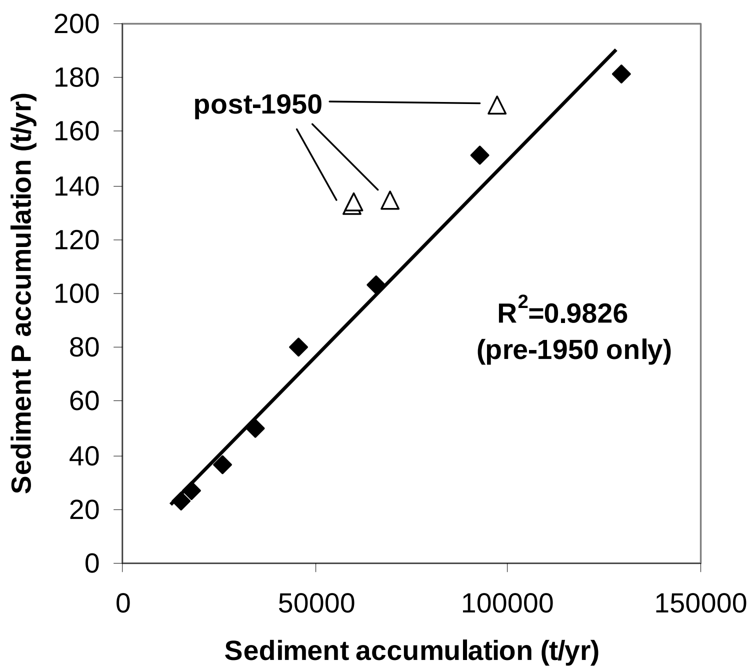


Figure 19 (a) Accumulation of diatoms and chrysophyte cysts in core 1B

(b) Relative abundance of benthic and planktic diatoms

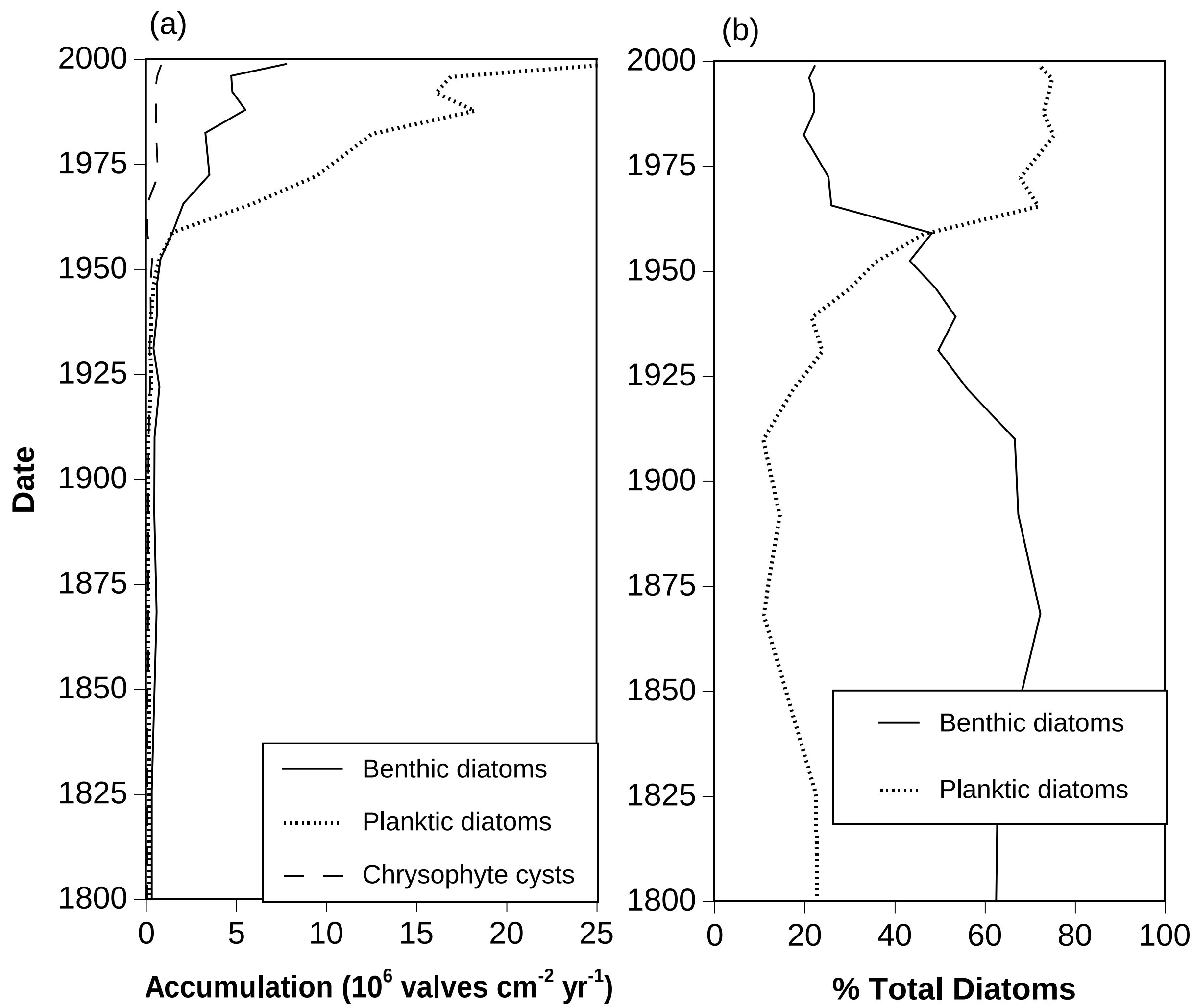


Figure 20 Lakewater total P concentrations reconstructed from fossil diatom assemblages in core 1B using a diatom-TP inferrence model (from Edlund and Engstrom, 2001)

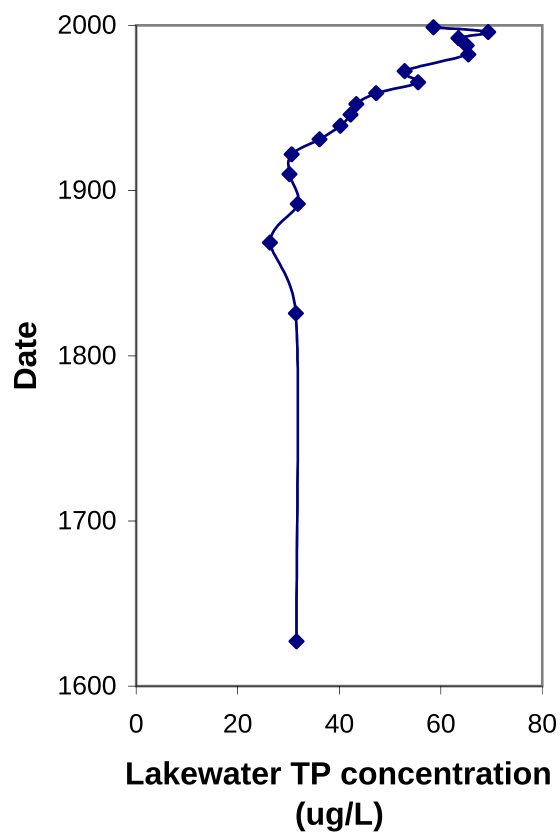


Figure 21 St. Croix flow at USGS gauging station in St. Croix Falls, WI. Regression of data from 1940-2000 shows no significant trend.

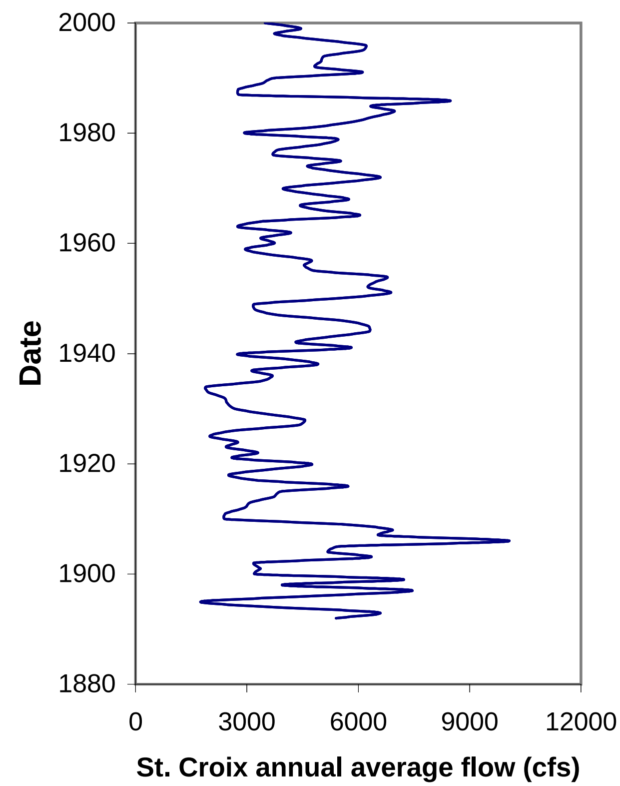


Figure 22 Whole-lake P mass balance for Lake St. Croix calculated by summing the P in the lakewater outflow and the P trapped in lake sediments to arrive at the total P load to the lake over the last two centuries.

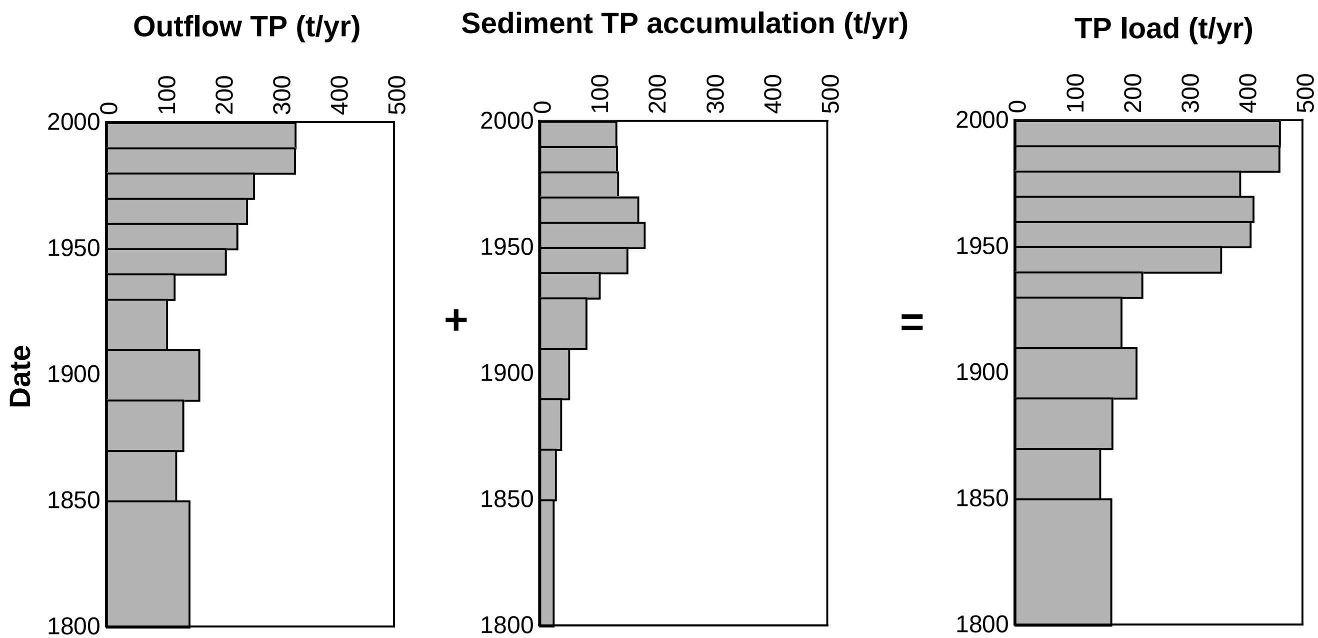


Figure 23 The proportion of the total P load to Lake St. Croix trapped in sediments over the last two centuries.

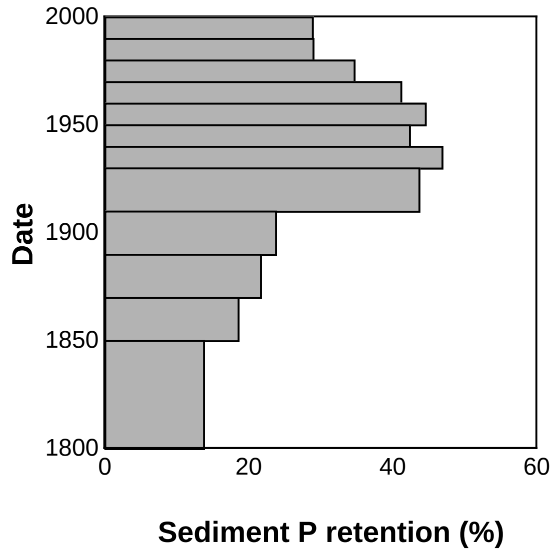


Figure 24 (a) Percent of the whole-lake sediment load accumulated in each sub-basin.
(b) Sediment accumulation rate of each sub-basin normalized by sub-basin depositional area.