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## A palaeolimnological record of human disturbance from Harvey's Lake, Vermont: geochemistry, pigments and diatoms

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**SUMMARY.** 1. Stratigraphic analyses of inorganic geochemistry, pigments and fossil diatoms in a 0.7 m core of profundal sediments are used to reconstruct the limnological history of Harvey's Lake, Vermont, over the last 1000 years. The lake is moderately productive, deep (44 m) and clear, and the phytoplankton today is dominated by the blue-green alga, *Oscillatoria rubescens*. Sedimentary pigments unique to blue-green algae, oscillaxanthin and myxoxanthophyll, provide a detailed history of changes in the *O. rubescens* population. Accurate sediment chronology is derived from  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$  and  $^{14}\text{C}$  dating and from the stratigraphy of pollen and sawmill wastes.

2. Primary production increased in Harvey's Lake in 1780 following European settlement and again after 1945, as shown by greater accumulation of sedimentary pigments and diatom frustules, and changes in fossil algal assemblages. Blue-green algae first appeared in abundance about 1945, indicating nutrient enrichment from dairy wastes and shoreline development. Increased deposition of elements associated with clastic minerals also suggests greater soil erosion during both of these intervals.

3. Two episodes of increased sedimentary anoxia (1820–1920 and 1945–present) are marked in the sedimentary record by enhanced pigment preservation, changes in authigenic Fe and Mn stratigraphy, and the development of laminated sediments. The earlier episode of oxygen depletion is correlated with the discharge of sawmill wastes into the lake, and the later episode is associated with increased primary production.

4. Based on these data a new model for Fe and Mn sediment stratigraphy is proposed for lakes that do not undergo complete hypolimnetic anoxia.

5. Fine-scale resolution of recent diatom and oscillaxanthin stratigraphy provides historical evidence for a long-term negative interaction between diatom and blue-green algal populations in Harvey's Lake.

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## Introduction

Concern for water quality conditions in Harvey's Lake, Vermont, began in the mid 1970s when fishermen reported red algal scums emerging from holes bored through the ice. Subsequent investigations by the Vermont Department of Water Resources (1977) revealed that the phytoplankton community of the lake was dominated year-round by the blue-green alga *Oscillatoria rubescens* Decandolle (= *Microcoleus lyngbyaceus* (Kützing) Crouan, according to Drouet, 1968). Because *Oscillatoria* has appeared in many lakes worldwide that were undergoing a transition from oligotrophic to eutrophic conditions (Edmondson, 1968; Skulberg, 1978), its presence in a historically clear unproductive lake such as Harvey's was viewed with alarm (Enright & Smeltzer, 1983). As a result, this palaeolimnological study was initiated to address specific questions about the trophic development of the lake: (1) were the *O. rubescens* populations a natural or anthropogenic phenomenon, (2) had productivity increased recently, (3) had diatom populations declined as a result of blue-green algal dominance, (4) had the hypolimnetic oxygen regime been different in the past, and (5) could evidence of past changes in water quality be correlated with known land-use changes in the catchment over the 200 years of intensive human activity?

In this study the limnological history of Harvey's Lake is reconstructed through the integration of several independent palaeolimnological techniques. The abundance of *Oscillatoria rubescens* was traced through oscillaxanthin, a pigment unique to the Oscillatoriaceae that is preserved in lake sediments (e.g. Griffiths & Edmondson, 1975; Züllig, 1982). The composition and productivity of past diatom populations was reconstructed from the stratigraphy of fossil diatom frustules. Geochemical analysis of redox-sensitive elements provides information about changes in hypolimnetic oxygen regime, and sediments were corroboratively dated by several independent methods including  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$  and pollen analysis.

### Modern limnology

Harvey's Lake is a relatively deep ( $Z_{\text{max}} = 44$  m,  $A_0 = 142$  ha), dimictic lake valued for its

trout fishery. The lake has been studied since autumn 1976 by the Vermont Department of Water Resources, from which virtually all of the data on modern limnology and land-use history is derived (State of Vermont, 1977; Enright & Smeltzer, 1981, 1982, 1983).

*Oscillatoria rubescens* constitutes more than 90% of the phytoplankton biomass year-round and, during stratification, is concentrated in a layer several metres thick near the thermocline. The *O. rubescens* layer is sometimes in the hypolimnion (e.g. 1980) and sometimes in the metalimnion (e.g. 1981). It produces an oxygen maximum of up to  $17 \text{ mg l}^{-1}$ ; hence, its vertical placement may affect the degree of hypolimnetic oxygen depletion (profundal concentrations are less than  $2 \text{ mg l}^{-1}$  by the end of the summer, although anoxia does not occur). From 1978 to 1981, mean annual areal hypolimnetic oxygen depletion rates varied between 280 and  $581 \text{ mg O}_2 \text{ m}^{-2} \text{ day}^{-1}$ , suggesting that *Oscillatoria* placement below the thermocline introduces substantial quantities of oxygen into the hypolimnion.

Between 1977 and 1981 total phosphorus concentrations at spring overturn increased monotonically from 10 to  $20 \mu\text{g l}^{-1}$ . Most of the phosphorus becomes concentrated in the *Oscillatoria* during spring and is subsequently kept out of the epilimnion all summer. As a result, epilimnetic phytoplankton biomass is low, producing a correspondingly deep average Secchi disk depth, 6.7 m (compared to an expected depth of 2.6 m if the  $20 \mu\text{g l}^{-1}$  phosphorus were manifest as epilimnetic phytoplankton; Carlson, 1977).

Two separate catchments contribute water to the lake. The primary catchment (2024 ha) is largely (71%) forested with most of the balance (20%) used as cropland and grassland. The catchment of South Peacham Brook, which is both larger (3212 ha) and has more agricultural land (32%) than the primary basin, occasionally contributes water to Harvey's Lake (Fig. 1). Over the past 200 years there has been a succession of dams on the Stevens River below the outlet from Harvey's Lake and its confluence with South Peacham Brook. During periods of high discharge the present dam causes a backflow into Harvey's Lake.

The major anthropogenic sources of phosphorus to the lake are the dairy operations in

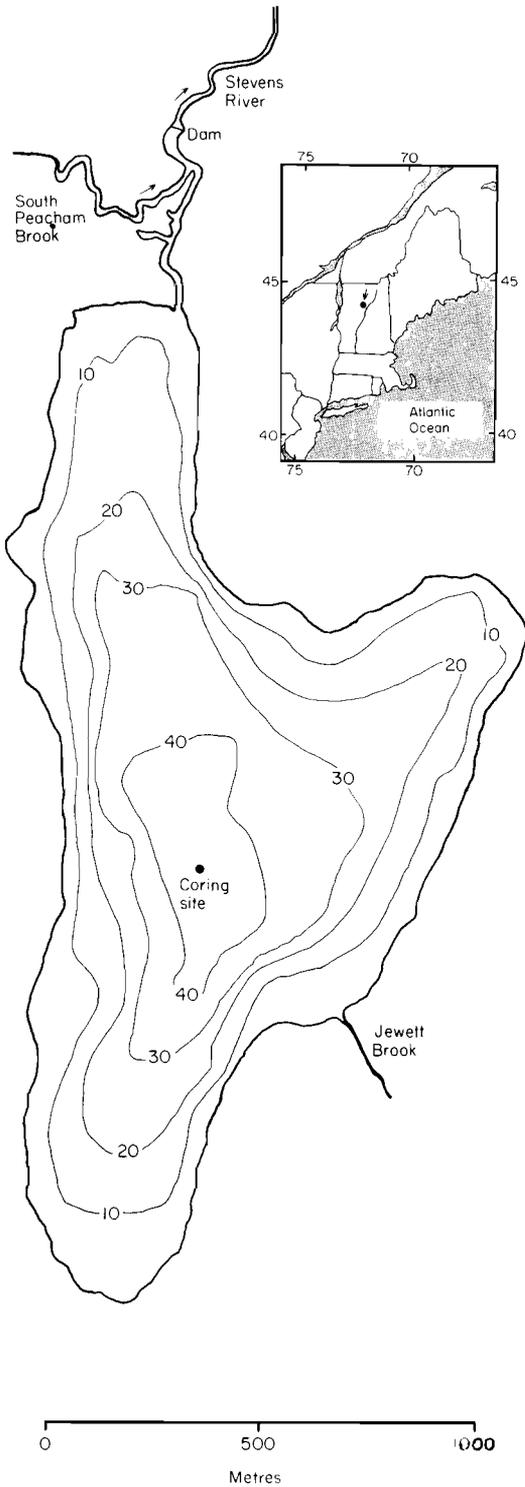


FIG. 1. Harvey's Lake bathymetry. Contour interval in metres.

the primary catchment, the backflow of South Peacham Brook, possibly the septic systems of the 101 shore-line cottages, and enhanced internal release from anoxic sediments.

Dissolved silica in the epilimnetic waters of the lake varies seasonally with diatom production from 5.5 mg l<sup>-1</sup> at autumn turnover (mid-November) to a minimum of 3.5 mg l<sup>-1</sup> during midsummer (July–August). Recent silica enrichment experiments in Harvey's Lake (Enright & Smeltzer (1983) indicate that diatom production does not appear to be silica limited. The pH varies seasonally between 7.0 (at spring turnover) and 8.5 (during peak summer photosynthesis); alkalinity averages 1.2 meq l<sup>-1</sup>.

#### Land-use history

Prior to European settlement in the Harvey's Lake region, human impact on the lake by native Indians was probably insignificant; the area was only seasonally occupied for hunting and fishing. This situation changed dramatically after 1775 when the Town of Barnet, in which the lake is situated, was settled by a Scottish emigration company. Forest clearance began that same year. In 1780 a sawmill was built on Jewett Brook and sawdust from the mill was discharged into the lake until about 1920. Much of the timber for the mill was cut locally.

In 1908 a new dam was constructed on the Stevens River just below the outlet from Harvey's Lake (Fig. 1) and until 1927 lake levels were drawn down seasonally to provide water for a hydroelectric plant in Barnet 10 km downstream. The periodic backflow into Harvey's Lake probably began with the construction of this dam, and has been aggravated by the 1982 channelization of South Peacham Brook.

In recent years the area of cleared land in the Harvey's Lake catchment has apparently declined, following land-use trends for the State of Vermont in general. However, the number of active dairy farms have gradually expanded their production since 1945 so that the impact of present-day agriculture on the lake may be greater than in the past. The use of chemical phosphorus fertilizers by local farms began about 1950, and in 1953 farmland on the east slope of the catchment was fitted

with a drainage system and the runoff was diverted directly into the lake.

Prior to 1945 there were approximately ten houses along the shoreline of Harvey's Lake, but active construction over the last 35 years has raised that number to 101. All rely on individual septic systems, for which the compact soils and steep shoreline are not well suited.

## Methods

### Coring

Coring was conducted during September 1981 at a site near the deepest part of the lake, 42 m in depth (Fig. 1). A cable-operated lead-weighted piston corer modified from Digerfeldt (1978) and equipped with a 10 cm plexiglass core-barrel was used to raise the upper 0.8 m section of sediments. These were extruded vertically in the field and sectioned into 1 cm increments upon which all subsequent analyses were performed. In addition, a freeze-core (Wright, 1980) was taken from the same location and used for visual inspection of sediment structure and lithology.

### Pollen

Sediment samples (1 cm<sup>3</sup>) were processed from fifteen core levels for pollen analysis by the methods of Faegri & Iversen (1975) as modified by E. J. Cushing (unpublished). *Eucalyptus* pollen was added as an exotic marker to determine pollen concentrations, and at least 500 fossil grains were identified and counted from each level. All stratigraphic data were plotted with the graphics program POLDATA (E. J. Cushing, pers. comm.) on the University of Minnesota's CDC Cyber 730 and Varian-Statos plotter.

### Woodchips

At twenty-eight levels woodchips were washed from 10 g aliquots of wet sediment through 864  $\mu$ m and 210  $\mu$ m sieves. The chips were dried at 110°C and weighed, and identification was provided by J. L. Bowyer (University of Minnesota Department of Forest Products) and D. J. Christensen (U.S. Forest Products Laboratory, Madison, Wisconsin).

### Lead-210

Lead-210 activity was determined through the extraction and counting of a daughter isotope, polonium-210. Extraction of <sup>210</sup>Po was done with methods developed by Flynn (1968) and modified by Evans (1980). The <sup>210</sup>Po and a <sup>208</sup>Po internal tracer were plated onto silver planchets and counted on an Ortec 576 alpha spectrometer. Supported <sup>210</sup>Pb was calculated from the <sup>210</sup>Pb activity of five deep samples (44–68 cm). The average supported activity ( $\pm$ S.D.) per gram dry matter (6.8 dpm $\pm$ 0.9) was subtracted from the total activity in each of the twenty-three shallow samples.

### Cesium-137

Cesium-137 activity was determined by non-destructive gamma counting. For each of nineteen levels, 50 g wet sediment samples were counted for a least 12 h with a GeLi detector with a Canberra Series 40 multichannel analyser. Calibration was done with a standard of the same geometry as the samples.

### Geochemistry

Sediments were analysed at twenty-five stratigraphic levels by D.C.-Argon plasma spectroscopy for a suite of eight major elements (K, Mg, Ca, Mn, Fe, Al, Si, P). Prior to analysis, wet-chemical extraction techniques were utilized to separate an acid-soluble 'authigenic fraction' and biogenic (diatom) silica from a clastic mineral 'allogenic fraction', the elemental composition of each fraction was determined separately. Engstrom & Wright (1984) have shown that this separation is often necessary in order to elucidate geochemical history from the heterogeneous sediments of small lakes, because different environmental information is contained within each fraction. Authigenic materials are those formed within the lake or the sediments and include biochemically precipitated carbonates, metal oxyhydroxides, sulphides, phosphates, and sorbed or co-precipitated elements. In contrast, the allogenic fraction consists largely of mineral particles resulting from the erosion of catchment soils.

The extraction procedure used in this study was modified only slightly from that proposed

by Engstrom & Wright (1984). Samples (1.0 g wet) were first treated with 30% hydrogen peroxide to destroy organic matter and release organically bound cations, followed by 1 M hydroxylamine hydrochloride/25% acetic acid (Chester & Hughes, 1967) to dissolve metal hydroxides, carbonates and adsorbed components. Biogenic silica was then selectively dissolved with 0.2 N NaOH (Krause, Schelske & Davis, 1983) and the remaining clastic residue was fused in lithium borate (Suhr & Ingamells, 1966) to complete the digestion. The hydroxylamine reagent, substituted for 0.3 N HCl used by Engstrom & Wright (1984), proved to be an equally efficient extractant to which allogenetic silicates were somewhat more resistant.

### Pigments

Pigments were extracted in 100 ml 90% acetone (final concentration) from samples (10 g wet) at thirty-eight levels by techniques modified from Lorenzen (1967), Sanger & Gorham (1972) and Griffiths (1978), and described in detail by Swain (1985). Chlorophyll derivatives (CD) were measured as the absorbance of the raw acetone extract at 665 nm and expressed in relative units where one unit is equal to an absorbance of 1.0 in a 10 cm cell when dissolved in 100 ml of solvent. Percent native chlorophyll is the proportion of chlorophyll not degraded to pheopigments, measured through acidification to 0.003 M H<sup>+</sup> so that

$$\% \text{ native chlorophyll} = \frac{665B - 665A}{0.7(665A)} \times 100$$

where 665B is absorbance before acidification and 665A absorbance after.

Total carotenoids (TC) were determined by first saponifying a 20 ml aliquot of the acetone extract with 10 ml of 20% KOH in methanol (w/v) for 2 h. Most of the carotenoids were then isolated from the saponified chlorophyll derivatives in a separatory funnel by the addition of 30 ml Petroleum ether (30–60° b.p.). The absorbance of the carotenoids at 448 nm was then expressed in units analogous to those for chlorophyll (above).

Oscillaxanthin and myxoxanthophyll were measured by phase separation and trichromatic equations. First, 40 ml petroleum ether was added to a 70 ml aliquant of the acetone

extract in a separatory funnel and swirled vigorously. The hypophase was then removed and dried in a 25°C water bath under an air-jet and re-dissolved in 5 ml absolute ethanol. Absorbance was read at 412, 504 and 529 nm and weight of each blue-green algal pigment present in the original acetone extract was calculated so that

$$\mu\text{g oscillaxanthin} = 79.202 A_{529} - 13.701 A_{504} - 5.067 A_{412}$$

and

$$\mu\text{g myxoxanthophyll} = 55.428 A_{504} - 53.387 A_{529} - 1.265 A_{412},$$

where A<sub>x</sub> is the absorbance in a 1 cm cell at wavelength x (these methods were evaluated with liquid chromatography by Swain, 1985).

### Diatoms

Sediment subsamples of known weight from twenty-five levels were processed for diatom analysis by aqueous combustion in 30% hydrogen peroxide and potassium dichromate catalyst. The catalyst was removed by settling and decanting, and coverslips were prepared and settling trays for quantitative analysis (Battarbee, 1973). Coverslips were mounted on Naphrax (R.I.=1.7) and specimens were identified and counted under oil immersion objectives (N.A.=1.30). Over 500 valves were counted at each depth, and counts were processed with the phytoplankton program FIDIC (T. B. Ladewski, pers. comm.).

## Results and Discussion

### Lithology

The sediment core was composed entirely of brown to black fine-grained gyttja (Ld<sup>04</sup>, in the terminology of Troels-Smith, 1955), and was diffusely banded or mottled throughout. The freeze-core revealed fine light-dark laminations in two sections of the profile; 0–9 cm and 21–28 cm (Fig. 2). Sediment structure between the laminated sections was homogeneous.

Mid-core sediments contained coarse wood fragments, representing sawmill wastes discharged into Harvey's Lake from the Jewell Brook sawmill between 1780 and 1920. Up to thirty-six woodchips of various size were found

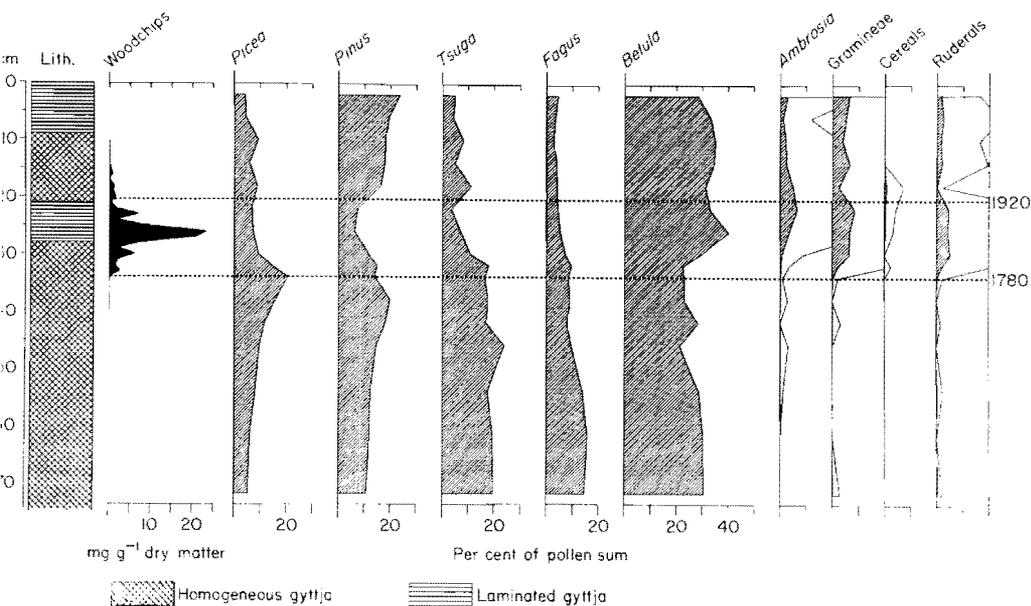


FIG. 2. Pollen diagram of the Harvey's Lake core including lithology and woodchip stratigraphy. Open curve represents  $10\times$  exaggeration. Ruderals composed of the following taxa: *Rumex*, *Plantago*, *Chenopod./Amaranth.*, *Cruciferae*, *Artemisia*, *Leguminosae*, *Tubuliflorae*, *Liguliflorae*.

per 10 g of wet sediment, many cleanly cut across the grain, as if with a saw. These cross-cut woodchips were of uniform length, 10.0 mm measured with the grain, and of variable width up to 5 mm. Some, apparently cut with the grain, were between 10 and 15 mm long. A small selection of these wood fragments were identified as *Tsuga canadensis* (L.) Carr. (eastern hemlock), *Thuja occidentalis* L. (northern white cedar), *Pinus strobus* L. (eastern white pine) and *Picea* sp. (spruce).

A concentration profile for woodchips shows that they first appear at 33 cm, peak between 18 and 23 cm and disappear above 20 cm (Fig. 2). The historical dates for the inception and end of the sawdust discharge are almost identical with radiometric dates for these same levels (see below). This suggests that the concentration of these relatively large wood fragments represents the loading of sawmill wastes, including fine particles since decomposed. Peak woodchip concentrations closely correspond to the older (deeper) set of laminations at 21–28 cm. Laminations are thought to occur when profundal oxygen concentration is reduced to such low levels that sediment-mixing by benthic animals is virtually eliminated (Davis, 1974). If so, then these sediment

laminations probably correspond to profundal anoxia resulting from increased biological oxygen consumption induced by loading of the sawmill wastes. Culver (1975) attributed the onset of biogenic meromixis in Hall Lake, Washington, to the biological oxygen demand caused by a similar introduction of sawdust.

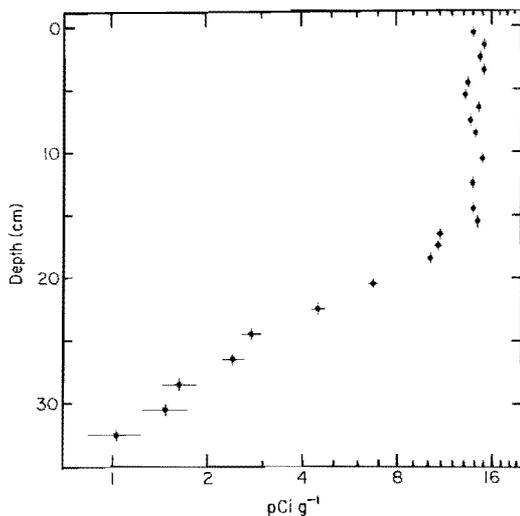


FIG. 3. Unsupported  $^{210}\text{Pb}$  stratigraphy.  $^{210}\text{Pb}$  activity in picocuries per gram dry matter.

## Dating and sediment accumulation

The chronology of post-settlement sediments from Harvey's Lake is based primarily on close-interval  $^{210}\text{Pb}$  dating. Unsupported  $^{210}\text{Pb}$  activity was determined at twenty-three levels to a depth of 34 cm. Plotted against sediment depth (or cumulative dry-sediment weight),  $^{210}\text{Pb}$  activity exhibits an exponential decline below 16 cm, whereas in the upper sediments lead activity is nearly constant (Fig. 3). The flat portion of the activity curve cannot be explained by surface mixing or a single depositional event because fine laminations, which would be destroyed by such processes, occur

red in this section of the core. This pattern indicates that the rate of sediment accumulation has varied over time so that the constant flux-constant sedimentation model for  $^{210}\text{Pb}$  cannot be used (Robbins & Edgington, 1975). The constant initial concentration (c.i.c.) model is also inappropriate here because it requires a monotonic decline in  $^{210}\text{Pb}$  activity with depth (Appleby & Oldfield, 1983). Instead sediment age was calculated using the model of Appleby & Oldfield (1978) which assumes constant rate of supply (c.r.s.) of unsupported  $^{210}\text{Pb}$  to the sediments but allows sediment flux to vary. This model provides a reasonable explanation of the  $^{210}\text{Pb}$  activity profile from

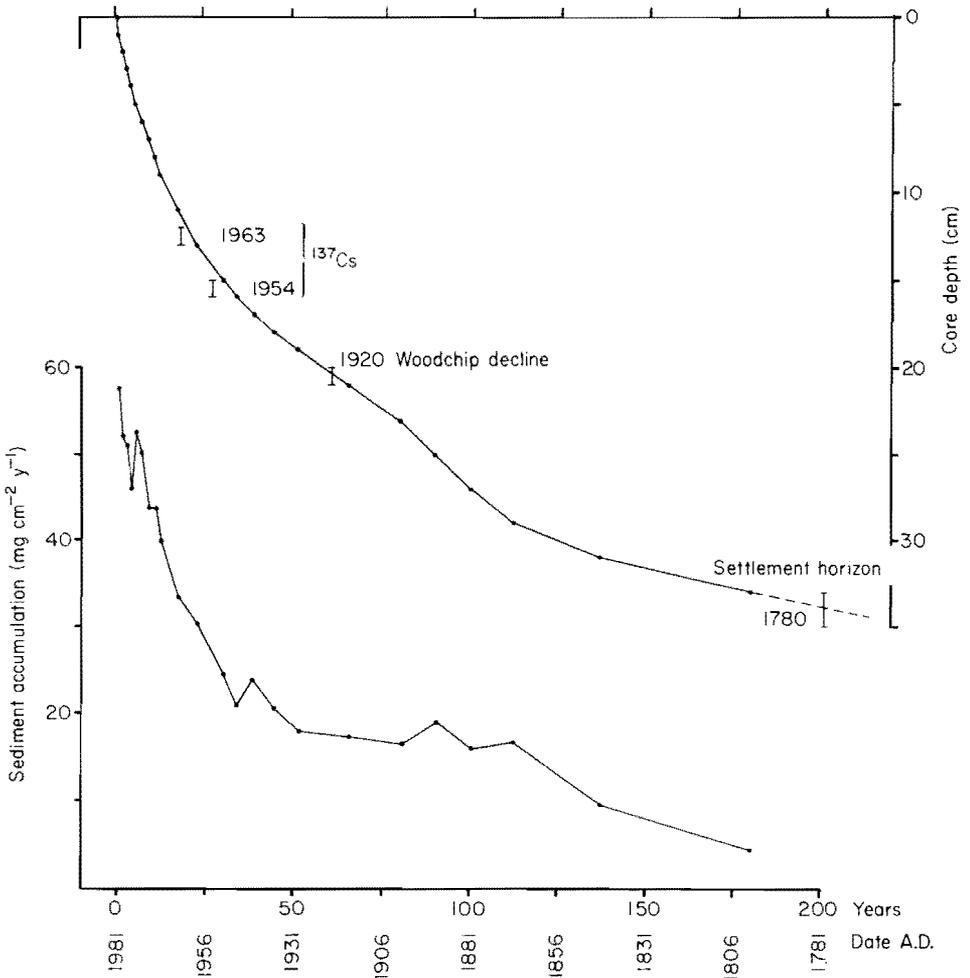


FIG. 4. Age-depth relationship (above) and sediment accumulation rate (below) in the Harvey's Lake core as determined by  $^{210}\text{Pb}$ .

Harvey's Lake. Sediment accumulation rates have accelerated over time, diluting  $^{210}\text{Pb}$  concentrations apace with the rate of lead decay. This is clearly illustrated in Fig. 4 where c.r.s. calculations of sediment accumulation and age-depth relationships are plotted.

An abrupt increase in sediment accumulation rate begins at 16 cm (dated to 1948) and is sustained to the core-top, where a maximum rate of  $60 \text{ mg cm}^{-2} \text{ y}^{-1}$  occurs. This interval corresponds to the flat section of the lead activity profile (Fig. 3). The transition at 16 cm correlates with the post-1945 increase in summer-home construction, which undoubtedly contributed to accelerated sediment loading to the lake. The lowest section of the  $^{210}\text{Pb}$  profile also shows gradual acceleration of sedimentation rates up-core, which probably began with European settlement in the catchment. The rate of sediment accumulation is constant at  $20 \text{ mg cm}^{-2} \text{ y}^{-1}$  between 30 cm (1860) and 19 cm (1930). This interval represents the section of exponential decline on the  $^{210}\text{Pb}$  activity plot.

Three dated stratigraphic markers in the Harvey's Lake core provide independent evidence of the accuracy of our  $^{210}\text{Pb}$  chronology. First, the stratigraphy of cesium-137 identifies sediments from the era of atmospheric nuclear-weapons testing (Fig. 5). A maximum concentration of  $^{137}\text{Cs}$  was found at 13 cm, and the onset of deposition appears below at 16 cm (low levels of  $^{137}\text{Cs}$  below 16 cm are attributed to downward mixing or diffusion). The dates of 1963 and 1954 are placed, respectively, on these levels, based on the historical pattern of atmospheric fallout (Health and Safety Laboratory, 1977). These dates fall reasonably close to the  $^{210}\text{Pb}$  age-depth curve (Fig. 4), thus supporting the high rates of recent sediment accumulation calculated from the c.r.s.  $^{210}\text{Pb}$  model. While the 1963 maximum might also be assigned to a second  $^{137}\text{Cs}$  peak at 10 cm, this point is equally close to the  $^{210}\text{Pb}$  curve and thus does not change our conclusion.

The decline in woodchip concentrations at 20 cm (Fig. 2) indicates the termination of sawdust discharge from the Jewett Brook mill in 1920 and provides a second dating horizon nearly synchronous with  $^{210}\text{Pb}$  chronology. A 'tail' of low woodchip values above 20 cm is presumably a result of redeposition from lit-

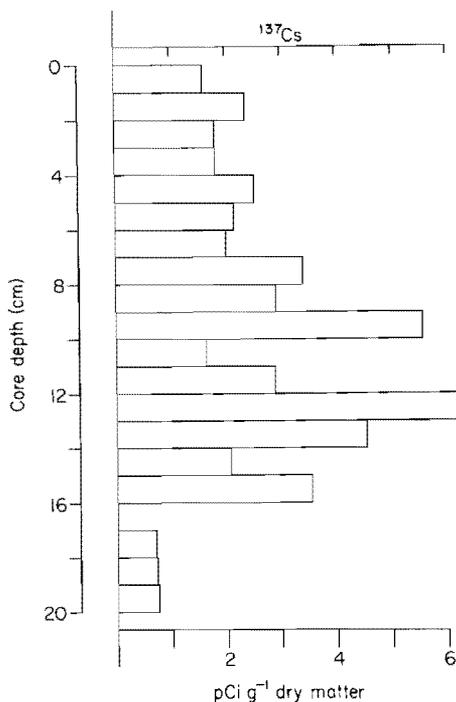


FIG. 5. Cesium-137 activity in the Harvey's Lake core.

toral deposits that form a delta at the mouth of Jewett Brook.

Vegetational changes associated with the onset of European settlement in the Harvey's Lake region mark the oldest dating horizon, at 32–34 cm. This is revealed through pollen analysis as an increase in plants associated with land clearance including *Ambrosia*, *Artemisia*, grasses, and European adventives such as *Plantago*, *Brassica* and *Trifolium* (Fig. 2). Forest cutting is indicated by the drop in arboreal pollen, notably *Picea*, *Pinus*, *Tsuga* and *Fagus* and a subsequent rise in *Betula*, presumably due to secondary succession. The first appearance of woodchips from the Jewett Brook sawmill also occurs at 33 cm. Written historical records place the start of this event around 1780 for the Harvey's Lake catchment. While this settlement horizon lies below the last datable  $^{210}\text{Pb}$  sample at 33 cm, the age-depth curve may be extrapolated downward to 34 cm on the basis of the sediment accumulation rate at the 33 cm level. If this is done, the

projected line passes directly through the pollen date (Fig. 4).

A single radiocarbon date of  $800 \pm 60$  years B.P. at 63–65 cm (UM-2643) provides the basis for pre-settlement sediment chronology. By extrapolating upward to the bottom of the  $^{210}\text{Pb}$  curve, this date yields a mean sediment accumulation rate of  $5.2 \text{ mg cm}^{-2} \text{ y}^{-1}$ . This value is similar to the rate calculated for the lowest lead date ( $4.4 \text{ mg cm}^{-2} \text{ y}^{-1}$ ), which lends additional support to the c.r.s. lead calculations, even for the base of the  $^{210}\text{Pb}$  profile where potential error is greatest. Thus, all dating procedures used for the Harvey's Lake core are broadly corroborative, and taken together they provide a reliable and detailed chronology.

Even with accurate sediment dating, sediment accumulation rates from a single core do not necessarily reflect sediment loading for the lake as a whole. Changing patterns of sediment deposition across the basin and particularly changes in the intensity of sediment focusing can confound single-core depositional records (Davis, Moeller & Ford, 1984). Davis & Ford (1982) suggest that changes in sediment focusing may be evaluated by calculations of pollen influx. Assuming a constant regional pollen-rain, pollen accumulation at an individual core-site should not change substantially unless the pattern of sediment deposition in the basin shifts. Lake-wide changes in sediment loading alone should only affect pollen concentration and not influx.

In our core from Harvey's Lake, pollen influx is virtually constant ( $1.53 \pm 0.36 \times 10^4$  grains  $\text{cm}^{-2} \text{ y}^{-1}$ ;  $\bar{x} \pm \text{SD}$ ) from pre-settlement sediments to 14 cm. At 10 and 6 cm levels this value rises to  $2.5 \times 10^4$  and at 2 cm to  $3.6 \times 10^4$ . It appears from these data that sediment deposition patterns were fairly constant until 1955 (14 cm) when some increase in focusing to the core site may have occurred.

On the other hand, serious changes in sediment redeposition should have altered the flux of  $^{210}\text{Pb}$  to our core site, violating a primary assumption of the c.r.s. model (Appleby & Oldfield, 1978). The accuracy of our  $^{210}\text{Pb}$  chronology argues against any major shift in sediment focusing. Instead the change in pollen influx may represent a recent increase in stream-borne pollen from the backflow of South Peacham Brook.

## Geochemistry

*Authigenic Fe and Mn.* Concentration curves for authigenic Fe and Mn (Fig. 6) exhibit minimum values at 31 cm, just above the settlement horizon, followed by peaks between 29 and 21 cm. Mn then increases sharply to maximum values above 16 cm (1945 A.D.) while Fe remains low. Because accumulation rates for the sediment matrix change markedly following settlement, concentration profiles do not accurately reflect the flux of Fe and Mn to the core-site. This is particularly true in the case of Fe, where increasing deposition of other sedimentary components since 1945 has diminished Fe concentration despite increasing Fe accumulation rates during this interval. Accumulation profiles, which are independent of such dilution effects, are similar for Fe and Mn; precultural rates are lowest, rates above 16 cm are highest, and a small peak occurs between 29 and 23 cm (about 1850–1900).

Authigenic Mn concentrations throughout the core are extremely high compared to values reported elsewhere for organic, fine-grained lacustrine sediments (Gorham & Swaine, 1965; Sasseville & Norton, 1975; Engstrom & Wright, 1984). In Harvey's Lake the lowest Mn content in pre-settlement sediment ( $10 \text{ mg g}^{-1}$  dry sediment) exceeds maximum concentrations at most other sites, and Mn values above 15 cm ( $50\text{--}90 \text{ mg g}^{-1}$  dry sediment) are as high as those reported for some oxidate crusts and ferromanganese nodules (cf. Jones & Bowser, 1978). Authigenic Fe content, however, is similar to that reported from other locations.

The high Mn content of the Harvey's Lake core cannot be attributed to a Mn-rich source in the catchment. The geologic formations in the drainage basin are not unusually rich in Mn-bearing minerals (Hall, 1959), and the allogenic fraction of the sediments, representing terrigenous clastics, has a mean Mn content of only 0.08%. Likewise post-settlement depositional migration of Mn within the sediment column is also an unlikely source, because enrichment under such conditions would be limited to the oxidized microzone (usually the upper 1 cm or less of sediment). Instead Mn-enrichment through selective transport within the lake itself is a more probable explanation. In many lakes Mn and Fe sedi-

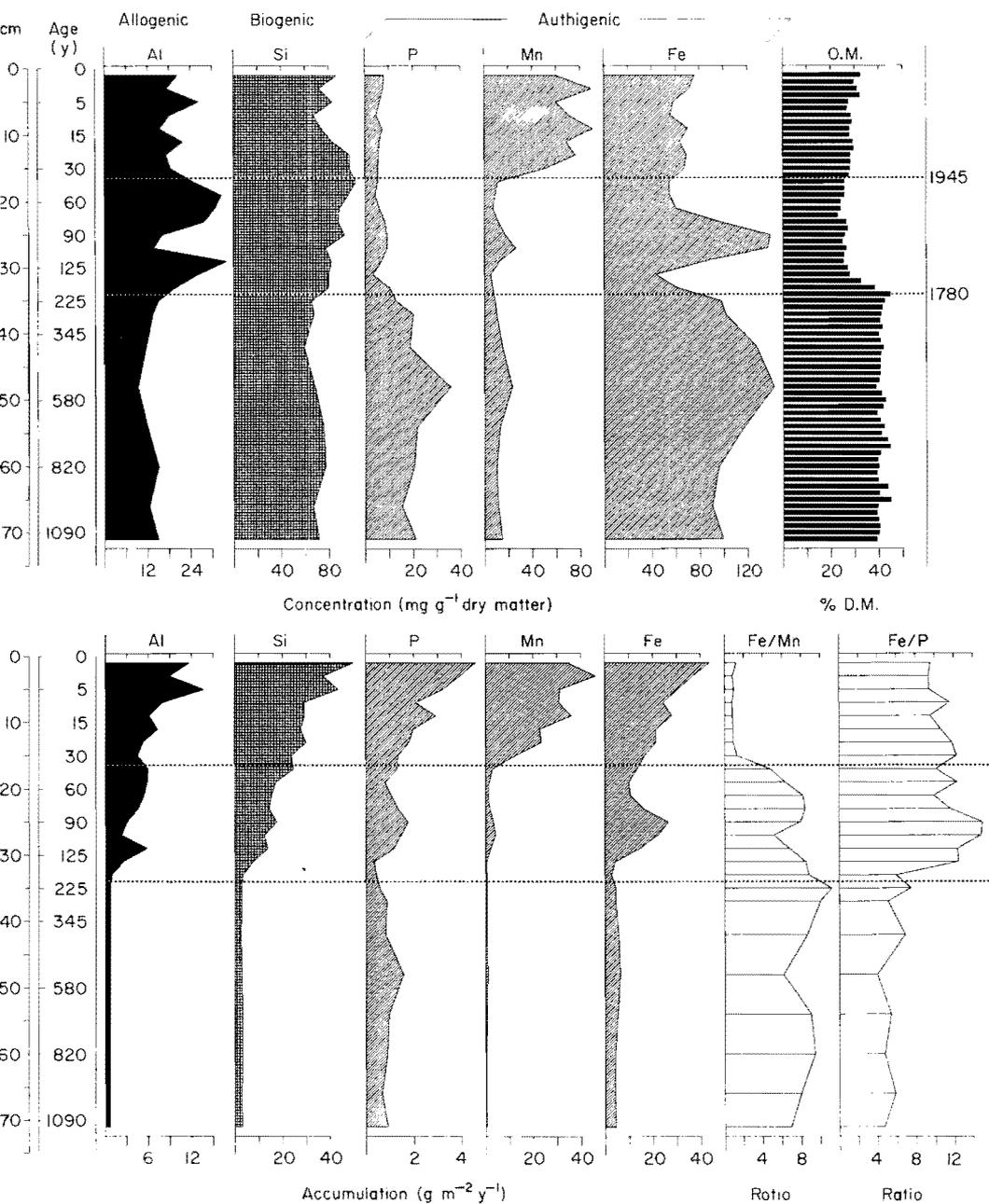


FIG. 6. Selected geochemical profiles for the Harvey's Lake core as concentration (above) and accumulation rate (below), except as noted. D.M.=dry matter; O.M.=organic matter. Age in years before 1981.

ment concentrations tend to increase with increasing water depth because of the selective transport of fine-grained Mn and Fe precipitates to deeper, more protected regions of the

bottom (Syers, Harris & Armstrong, 1973). Harvey's Lake is a deep, steep-sided basin (relative depth=3.3%) in which down-slope transport of fine particulates should be effec-

tive. Some slopes of the deep basin are barren of fine-grained deposits, which have been winnowed into deeper water.

The resuspension and transport of Fe and Mn particulates may also be enhanced by redox cycling at the sediment-water interface. Both Fe and Mn are highly insoluble in oxidized form, but they are readily mobilized from the sediments as dissolved species if the interface becomes reduced through oxygen depletion (Mortimer, 1941, 1942). Precipitation and re-deposition of Fe and Mn oxyhydroxides may follow as upward-diffusing ions of Fe(II) and Mn(II) encounter oxygen in the overlying water column. In this cyclical pattern of dissolution and redeposition (the ferrous and manganous 'wheels' of Campbell & Torgersen (1980) and Mayer, Liotta & Norton (1982), respectively) Fe and Mn may be mobilized from surficial sediments on the slope of the lake basin and transported into profundal regions as fine particulates by wave and current action, or as dissolved species in a density current as proposed by Tessenow (1975). Mn may be selectively enriched in Harvey's Lake sediments because it dissolves at higher redox potential and tends to remain in solution longer than Fe (cf. Jones & Bowser, 1978).

Because Fe and Mn mobility is redox-dependent, the stratigraphy of these elements in lake sediment cores may be used to reconstruct long-term changes in hypolimnetic oxygen conditions. A widely accepted model for sedimentary Fe and Mn proposed by Mackereth (1966) predicts lowered concentration and accumulation of these metals under locally reducing conditions. This model assumes that a portion of the Fe and Mn mobilized from anoxic sediments is mixed into the water column during turnover and flushed from the lake or redeposited across the entire basin.

However, throughout the Harvey's Lake core, the highest Fe and Mn accumulation occurs during periods when independent evidence indicates lowered sedimentary redox potential, contrary to Mackereth's model. Maximum accumulation rates for these elements occur above 16 cm (after 1945) and correspond to a period of maximum primary productivity according to pigment and diatom data. Greater oxygen consumption at the sediment surface from increased organic loading would be expected during this interval.

Furthermore, the presence of fine laminations above 9 cm suggests that hypolimnetic anoxia was sufficiently severe or prolonged to eliminate benthic invertebrates whose burrowing activities normally homogenize sedimentary layers. Increased sedimentary anoxia since 1945 is also indicated by a higher percentage of native chlorophyll in sediments above 16 cm.

A second but much lower peak in Fe and Mn accumulation, between 23 and 29 cm, is likewise correlated with a band of laminated sediments (21-28 cm) and increased preservation of sedimentary chlorophylls. In this case oxygen depletion from the microbial decay of sawmill wastes is the probable cause of lowered sedimentary redox potential. By contrast, the slowest rates of Fe and Mn accumulation (for Mn lower than modern rates by two orders of magnitude) are recorded during pre-settlement times when diatom and pigment stratigraphy indicate relatively low primary productivity. The correspondingly low rates of sedimentation and organic loading probably promoted higher sedimentary redox potential during this period.

Mackereth's model also predicts an increase in the Fe:Mn ratio during periods of hypolimnetic anoxia because of the greater mobility of Mn in mildly reducing environments. Yet again, the opposite pattern is evident in the Harvey's Lake core. The Fe:Mn ratio is highest throughout the presettlement interval when sedimentary redox potential was probably highest, and is lowest above 16 cm (1945) when profundal sediments were almost certainly more reduced.

Although the results from Harvey's Lake do not conform to Mackereth's hypothesis, changes in Fe and Mn stratigraphy are nevertheless correlated with independent evidence for shifts in sedimentary redox potential. It appears that historical changes in oxygen regime are manifest in the Fe and Mn stratigraphy even though the trends are opposite to that expected. An alternative explanation for these patterns follows from our previous suggestion that redox cycling across the sediment-water interface may enhance the transport of Fe and particularly Mn into profundal regions. An increased flux of Fe and Mn from reduced sediments during summer stratification should increase the physical transport and redeposition of Fe and Mn

particulates at autumn turnover. We contend that the direction of this redeposition will be downslope so long as profundal environments are sufficiently oxygenated to prevent dissolution. If so, then maxima in Fe and Mn accumulation should indicate periods of greater oxygen depletion in surficial sediments, whereas minima should correspond to periods of higher sedimentary redox potential. This is the observed pattern in Harvey's Lake. Because the coring site corresponds to the deepest part of the basin, the source of Fe and Mn must necessarily be upslope. Clearly, severe hypolimnetic anoxia can diminish Mn accumulation in profundal sediments if release from redox cycling exceeds gains from particulate deposition at that location (Davison, Woof & Rigg, 1982). Under less extreme conditions, however, the increased loading of Fe and Mn particulates from upslope deposits may be effectively preserved in deep water sediments so that net accumulation is increased. A similar argument has been advanced by Davison *et al.* (1985) to explain Mn distribution in sediments of Coniston Water in the English Lake District.

Both Mackereth's model and our interpretations assume greater Fe and Mn mobility in reducing environments. However, it is clear from this study that, once mobilized, the fate of Fe and Mn can be strikingly different in certain waters. Two factors appear to separate Harvey's Lake from sites that conform to Mackereth's hypothesis. First, in deep protected basins such as Harvey's Lake, wave and current action at depth is weak, so that the flushing of hypolimnetic solutes and fine particulates during turnover should be less pronounced than in shallow basins. Second, mild oxygen depletion rather than complete hypolimnetic anoxia may be critical in preventing a net loss of Mn and Fe from profundal sediments during stratification. If the water column above the sediments always retains some oxygen (as in present-day Harvey's Lake) the migration of dissolved Fe and Mn into the hypolimnion and subsequent loss through mixing should be minimal.

Lake hydrodynamics as well as oxygen regime can influence the pattern of Fe and Mn deposition across the lake bottom. Similar changes in sedimentary redox potential can produce very different stratigraphy between

lakes and presumably even at different sites within the same basin.

**Phosphorus.** The concentration of authigenic P in Harvey's Lake sediments exhibits a marked decline upward across the settlement horizon at 34 cm (Fig. 6). However, P accumulation rates generally increase up-core, indicating that the lowered P content of post-settlement sediments is a result of accelerated dilution by other inputs to the sediments. The profile of P accumulation is similar to that for authigenic Fe: a small peak occurs between 29 and 21 cm, followed by progressively higher rates above 16 cm (1945).

Sedimentary P is frequently used to reconstruct past rates of P loading and related changes in primary productivity (e.g. Shapiro, Edmondson & Allison, 1971; Williams, Murphy & Mayer, 1976). Although lake sediments serve as an effective sink for inorganic P, deposition and retention of P in the bottom sediments is strongly controlled by redox potential and authigenic iron chemistry (Shukla *et al.*, 1971; Syers *et al.*, 1973), as well as temperature, pH and sediment mixing (Kamp-Nielsen, 1974; Holdren & Armstrong, 1980). Variations in P retention are frequently more important than changes in P inputs in determining phosphorus stratigraphy.

Our first impression from the profile of phosphorus accumulation is that of increased P loading to Harvey's Lake since 1945. This interpretation fits well with diatom and pigment stratigraphy and with the chronology of events that could have increased P inputs from the catchment. Alternatively, the significant correlation between Fe and P concentrations in the Harvey's core ( $r=0.71$ ;  $N=25$ ;  $P<0.001$ ) suggests that increased deposition of Fe-oxyhydroxides, with which inorganic P is closely associated in lake sediments, may have increased P deposition during this interval. Studies by Shukla *et al.* (1971) and Williams *et al.* (1971) indicate that the ability of sediments to sorb inorganic P and the concentration of P found in most lake sediments are closely related to authigenic Fe content. If Fe accumulation increased at the core site in response to lowered sedimentary redox potential caused by accelerated organic deposition, as proposed, then greater P accumulation may be an indirect consequence of increased primary productivity and the resulting deposition of or-

ganic matter, rather than a direct measure of P levels in the water column.

These alternative hypotheses can be partially resolved by comparing the recent increase in P accumulation with that occurring between 29 and 21 cm (1870–1915). During this older phosphorus peak, Fe accumulation increased even more than P, as shown by the sharp rise in the Fe:P ratio from pre-settlement values (Fig. 6). Accelerated P deposition during this interval can be attributed largely to Fe deposition, because pigment and diatom profiles do not indicate any peak in lake productivity that would accompany temporarily greater P loading. In contrast, the P increase since the 1945 horizon has exceeded that of Fe, as shown by a decline in the Fe:P ratio, despite even greater Fe accumulation rates and lower redox potential during this recent interval compared to the preceding one. Thus a portion of the phosphorus increase that begins about 16 cm represents accelerated P inputs to Harvey's Lake in recent times, resulting in greater saturation of the sedimentary Fe–P complex. Because of changes in Fe accumulation, however, the magnitude of this increase in P loading is difficult to assess.

**Biogenic silica.** Biogenic silica concentrations are relatively constant throughout the entire Harvey's core with a mean content of 17% as SiO<sub>2</sub> (80 mg Si g<sup>-1</sup> dry sediment). Diatom concentrations determined from counts at the same levels are moderately correlated with biogenic silica concentrations ( $r=0.51$ ;  $N=25$ ;  $P<0.01$ ) despite major taxonomic shifts in fossil assemblages; correlation is not higher because the concentration profiles are nearly constant. The number of diatom valves equivalent to 1 g of SiO<sub>2</sub> equals  $3.5 \times 10^9$  in these sediments, which is similar to values reported for Prästjön by Renberg (1976) and Lough Neagh by Flower (1980): roughly  $3 \times 10^9$  for both studies. The deletion of levels where microscopic inspection revealed poor preservation did not substantially change the regression or improve the correlation.

The deposition of biogenic silica has generally kept pace with the increased inputs of other sedimentary components following settlement, so that silica does not show declining concentrations up-core as does authigenic P, for example. Accumulation rates for silica rise five-fold between 34 and 29 cm (1780–1870)

and then double above 16 cm (1945). This pattern indicates major increases in primary productivity following settlement and again after 1945.

**Allogenic clastics.** The stratigraphy of elements associated with clastic minerals is often used as an index of past soil erosion rates (e.g. Mackereth, 1966; Sasseville & Norton, 1975; Huttunen & Tolonen, 1977). Typically these interpretations are confined to K, Na and Mg when sediments are digested in bulk, because for other elements the authigenic and biogenic contributions are significant. However, the fractionation technique used in this study allows us to estimate allogenic Fe, Al, Si and Ca as well, without the confounding influence of non-clastic components.

In the Harvey's Lake core all elements of the allogenic fraction are highly correlated ( $r>0.95$  except for Mn) so that stratigraphic trends for the fraction as a whole may be represented by a single profile; in this case we have selected Al (Fig. 6). Both the concentration and accumulation rate of Al increase upwards across the settlement horizon at 34 cm (1780), concurrent with a drop in the organic content of the sediment. Because allogenic Al is derived solely from terrigenous clastics, increased soil erosion in the catchment is indicated. The drop in organic content results from increased dilution by these eroded inputs. The trend in Al is interrupted up-core at 27 cm (1880) by a drop in concentration and accumulation rate, while the overall sediment accumulation rate also stabilizes at this level. Both indices suggest stabilization of catchment soils. From this point upwards Al accumulation accelerates approximately corresponding with the gross rate of sediment accumulation. Aluminium concentration, on the other hand, declines to pre-settlement values above 17 cm (1940) as a result of dilution by other sedimentary components, notably authigenic Mn and organic matter.

We contend that the Al stratigraphy primarily represents erosional intensity in the catchment and that this has generally increased from pre-settlement values up to the present. However, it must be stressed that our interpretation is based on accumulation rates at a single core site and that changes in the pattern of clastic deposition across the lake bottom could also be an important factor controlling

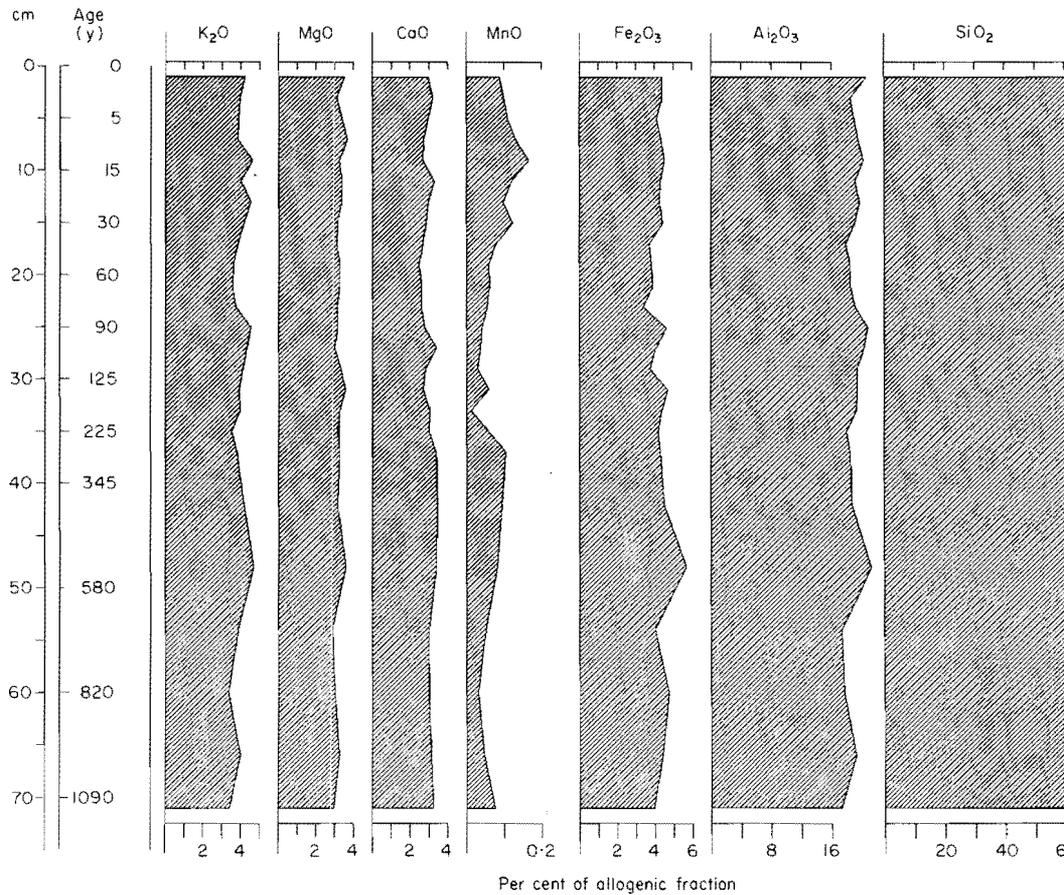


FIG. 7. Stratigraphic composition of allogenic fraction. All elements represented as common oxides.

Al stratigraphy. Nevertheless, good correspondence between the Al profiles and historical patterns of human agricultural activity in the catchment indicate that the erosional interpretation is broadly correct.

The elemental composition of lake sediments has also been used to estimate the relative intensity of soil weathering in the past (e.g. Mackereth, 1966; Pennington *et al.*, 1972; Guppy & Haphey-Wood, 1980). These studies argue that mineral matter from rapidly eroded soils should be less highly leached of base metals (Na, K, Mg, Ca) than clastics derived from stabilized soils. However, Engstrom & Wright (1984) contend that these interpretations may be incorrect because the supporting geochemical evidence is based on the elemental composition of the inorganic ash, which includes biogenic Si and authigenic oxides, rather than allogenic minerals alone.

Results from the Harvey's Lake core in which the allogenic fraction was analysed separately support this position. In these sediments the elemental composition (as weight per cent by common oxide) is virtually constant throughout (Fig. 7). These results indicate that there has been no measurable change in the chemical composition of the allogenic clastic throughout the millennium represented by this core, despite major shifts in erosional intensity, catchment vegetation and land use. Although weathering intensity may well have varied during this time, a record of such changes is not preserved in the sediments of Harvey's Lake.

#### Pigments

*Blue-green algal pigments and per cent native chlorophyll.* Oscillaxanthin is a pigment

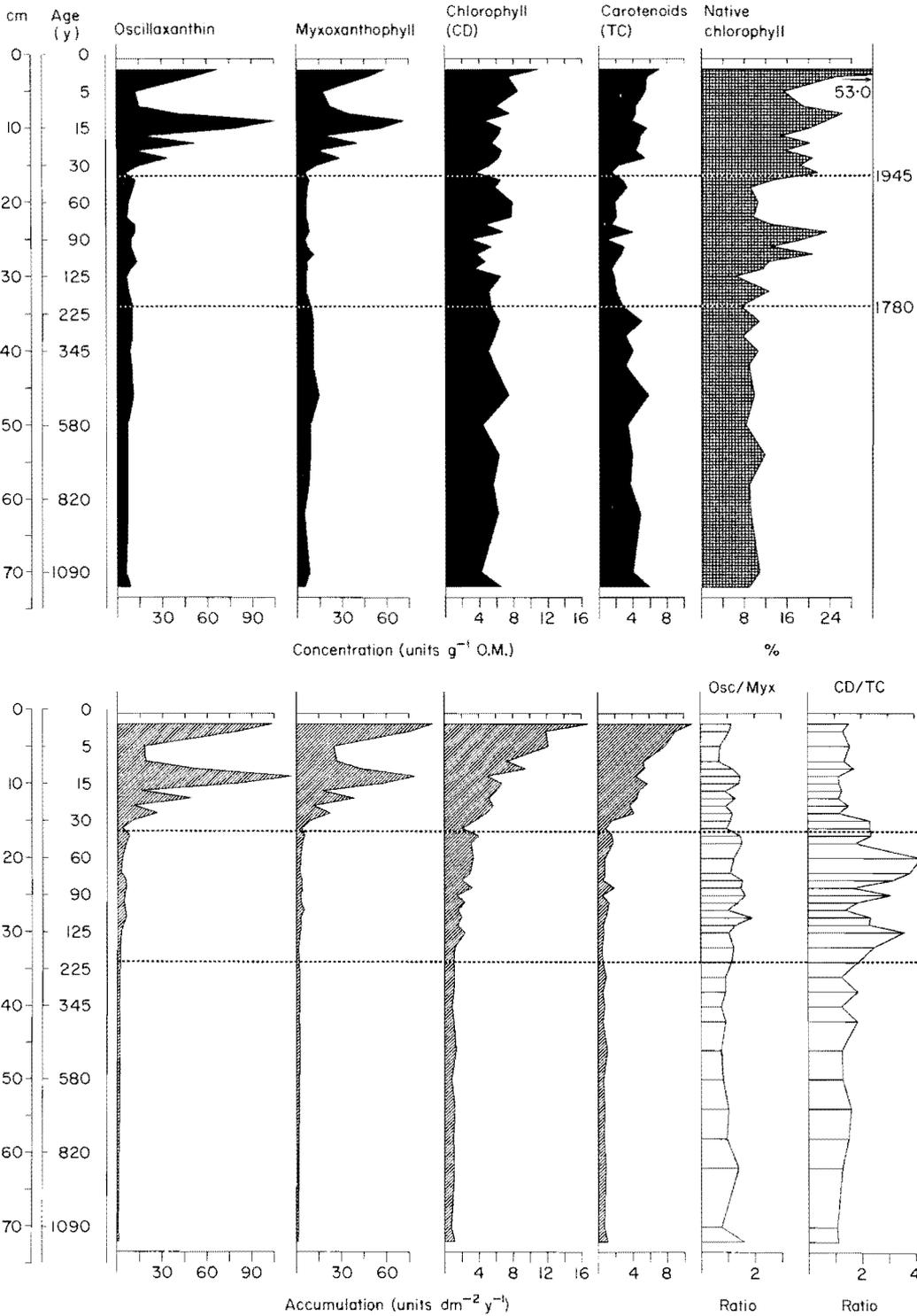


FIG. 8. Pigments in the Harvey's Lake core calculated as concentration (above) and accumulation rate (below), except as noted. O.M.=organic matter. Units for blue-green algal pigments are  $\mu g$  and for chlorophyll and carotenoids are standard absorbance units.

unique to the Oscillatoriaceae and has been found in only one genus apart from *Oscillatoria*. In contrast, myxoxanthophyll is found in most blue-green algal genera and in all six families examined (Hertzberg, Liaaen-Jensen & Siegelman, 1971).

In the Harvey's Lake core, the most obvious stratigraphic change in pigment concentration is the dramatic rise in oscillaxanthin and myxoxanthophyll beginning at 15 cm (Fig. 8). Because pigments are labile compounds this increase can indicate either better preservation through sedimentary anoxia or increased production by blue-green algae. These two factors are not mutually exclusive, because a shift in trophic state that increases blue-green algal abundance is usually associated with hypolimnetic oxygen depletion from increased organic loading (Walker, 1979). However, any cause of hypolimnetic oxygen depletion, including increased primary production by algae other than blue-greens, could produce a stratigraphic increase in oscillaxanthin or myxoxanthophyll. Therefore an independent measure of pigment preservation is needed in order to distinguish increased pigment production from enhanced preservation. Swain (1985) presents evidence that the proportion of sedimentary chlorophyll not degraded to pheopigments (per cent native chlorophyll) provides such a measure.

In the Harvey's Lake core, per cent native chlorophyll increases about the same time as do oscillaxanthin and myxoxanthophyll. However, in this case, two pieces of evidence indicate that the increase in blue-green algal pigments is largely the result of increased production, rather than enhanced preservation. First, chlorophyll preservation increases 2 cm below the rise in blue-green algal pigments. Second, there is an earlier period of equally good preservation (23–32 cm) during which blue-green algal pigment concentrations change little. Because oscillaxanthin and myxoxanthophyll do not increase during these first episodes of enhanced preservation, their recent rise must have resulted largely from increased production.

Züllig (1982) demonstrated broad agreement between oscillaxanthin stratigraphy in a core from Baldeggersee and the historical record of *Oscillatoria rubescens* in plankton counts. In this case the entire core was laminated, sug-

gesting that preservation conditions had been similar during variations in the *O. rubescens* population.

Although oscillaxanthin and myxoxanthophyll are relatively sensitive to preservation conditions, they degrade at almost exactly the same rate (Swain, 1985), so that the ratio between them (OSC/MYX) is actually independent of preservation. The OSC:MYX ratio is therefore a measure of the relative production of these pigments, where higher values (usually  $\geq 1.0$ ) indicate *Oscillatoria* dominance of the blue-green algal flora (Swain, 1985). Pre-settlement OSC/MYX values from Harvey's Lake average 0.9 (SD =  $\pm 0.2$ ), while post-settlement values are 1.3 ( $\pm 0.2$ ), excluding low values of 0.7 at 5 and 7 cm. *Oscillatoria* has therefore been more important in the blue-green algal flora since settlement, except possibly the period between 5 and 7 cm. A major bloom of *Anabaena* occurred in 1977, the first year of lake monitoring, but has not reappeared since (1977 corresponds to a core depth of 5 cm).

*Chlorophyll and carotenoids.* Chlorophyll derivatives (CD) and total carotenoids (TC) are frequently used in palaeolimnology to reconstruct past levels of primary productivity (Wetzel, 1970; Sanger & Gorham, 1972; Manny, Wetzel & Bailey, 1978). However, in most such studies pigment stratigraphy has been expressed as concentration, usually in units per gram organic matter, the interpretation of which may be difficult if the flux of the organic matrix also changes. This problem is quite evident in the Harvey's Lake core in which CD and TC concentrations do not increase in the top 15 cm where blue-green algal pigments indicate increasing eutrophy and where higher per cent native chlorophyll marks enhanced pigment preservation (Fig. 8). Both of these factors should favour greater inputs of CD and TC to the sediments. However, pigment concentrations do not increase because accelerated erosion of pigment-poor allochthonous organics has held CD and TC concentrations constant through dilution.

When the effects of dilution are removed by calculation of accumulation rates (pigment  $\text{cm}^{-2} \text{y}^{-1}$ ) CD and TC values increase steadily, beginning about 17 cm (Fig. 8). If CD and TC accumulation rates are proportional to primary production, then in Harvey's Lake primary

production has increased continuously from about 1945 to the present. In addition, CD accumulation rises from an average of 1.04 (SD= $\pm 0.03$ ) to 2.25 ( $\pm 0.77$ ) following settlement. TC accumulation increases less dramatically across this horizon, from 0.75 ( $\pm 0.03$ ) to 0.94 ( $\pm 0.47$ ).

CD and TC accumulation rates thus reveal a moderate increase in primary production after settlement and a major increase after 1945, while CD and TC concentrations reflect no changes throughout. Pigment concentrations here do not reveal trophic shifts where net accumulation rate does (corroborated by diatom, geochemistry, and blue-green algal pigment data). In this case, pigment accumulation rates demonstrate clear advantages over expression as concentration.

*Ratio of CD to TC.* Because carotenoids degrade faster than chlorophylls, the ratio of chlorophyll derivatives to total carotenoids (CD/TC) has been used both as an index of the quality of preservation in profundal sediments and as an index of the relative input of allochthonous organics, in which pigments are poorly preserved (Sanger & Gorham, 1972). High CD/TC values are expected in oligotrophic lakes, because poor preservation and relatively high allochthonous inputs tend to be correlated with oligotrophy. Indeed, oligotrophic lakes exhibit high ratios and eutrophic lakes low (Gorham *et al.*, 1974; Santelmann, 1981; Swain, 1985).

However, Swain (1985) presents evidence that relatively more carotenoids than chlorophyll are actually produced in eutrophic lakes, suggesting that the ratio at production may be the most important factor influencing the final CD/TC values found in sediments. In addition, there is evidence that the quality of preservation within a lake modifies the initial CD:TC ratio from production only to a limited extent.

The marked increase in CD/TC values above 34 cm (after settlement; 1780) can be attributed to a basic change in the relative production of these pigments in the lake. The initial increase in CD/TC occurs when per cent native chlorophyll has not changed, so that the rise in ratio cannot have been caused by poorer preservation conditions in the lake. Furthermore, the moderate increase in the accumulation rate of organic matter following settlement, even if entirely allochthonous, cannot

account for the CD/TC increase (Swain, 1985). The only alternative is the conclusion that the relative production of these pigments changed.

The CD/TC values associated with production are higher above the settlement horizon than below, but were apparently modified by preservation conditions so that above 34 cm native chlorophyll and CD/TC are mirror images (Fig. 8). During periods of better preservation, CD:TC ratios drop to values nearly equal to those before settlement. The shift to higher CD/TC values at settlement is correlated with a change in diatom composition from dominance by benthic to planktonic species (see below). These fundamentally different growth forms might be expected to produce a different complement of pigments, but whether this diatom shift caused the CD:TC increase is open to speculation.

### Diatoms

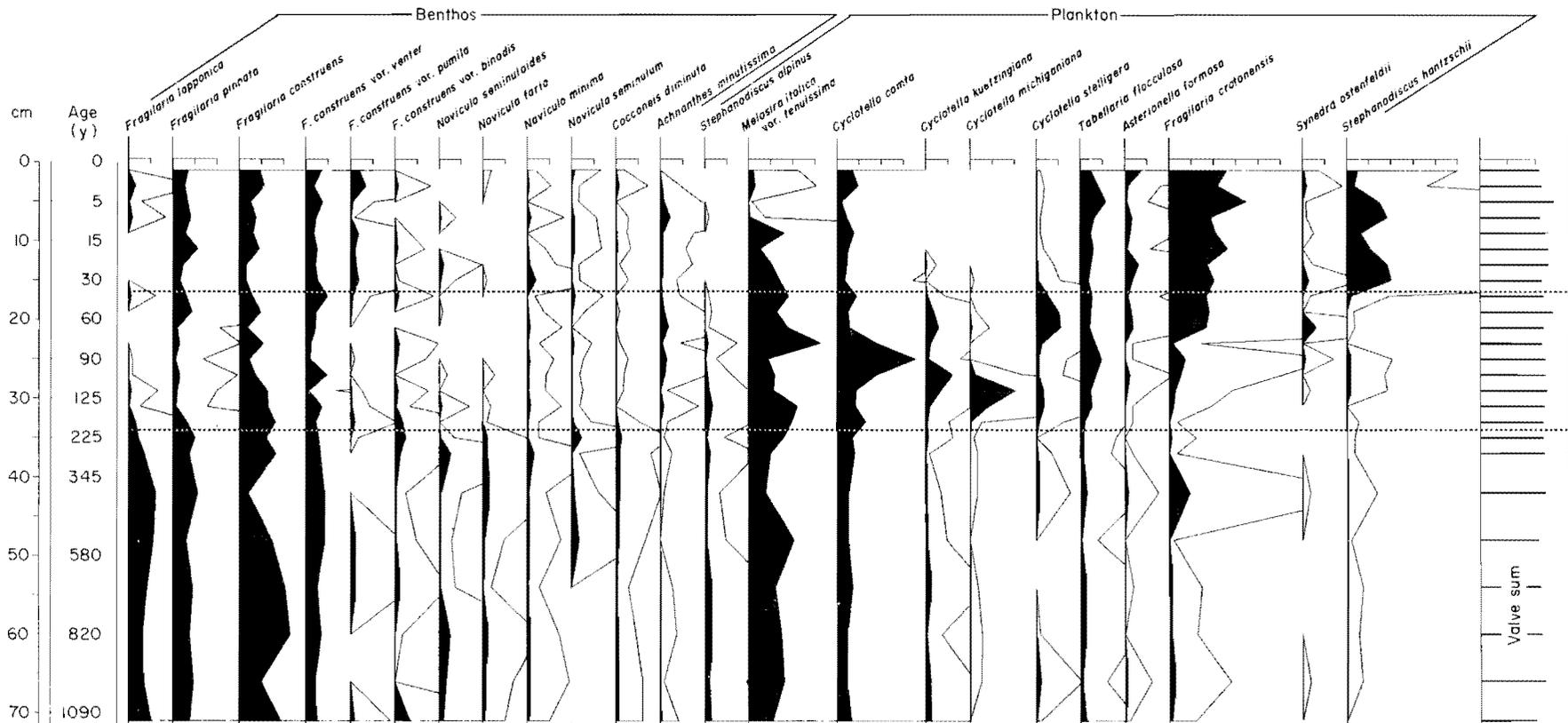
The diatom flora of Harvey's Lake is characteristic of deep, mesotrophic, circumneutral to basic temperate lakes (e.g. Stoermer, 1977), and in fact the flora bears a striking resemblance to those of the upper Laurentian Great Lakes (Stoermer & Yang, 1969; Stoermer, 1980). In the present study, 321 taxonomic

TABLE 1. List of the twenty-three most common diatom taxa (with authorities) in the Harvey's Lake core

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<i>Achnanthes minutissima</i> Kütz.
<i>Asterionella formosa</i> Hass.
<i>Cocconeis diminuta</i> Pant.
<i>Cyclotella comta</i> (Ehr.) Kütz.
<i>Cyclotella kuetzingiana</i> Thw.
<i>Cyclotella michiganiana</i> Skv.
<i>Cyclotella stelligera</i> (Cleve & Grun.) V.H.
<i>Fragilaria construens</i> (Ehr.) Grun.
<i>Fragilaria construens</i> var. <i>binodis</i> (Ehr.) Grun.
<i>Fragilaria construens</i> var. <i>pumila</i> Grun.
<i>Fragilaria construens</i> var. <i>venter</i> (Ehr.) Grun.
<i>Fragilaria crotonensis</i> Kitton
<i>Fragilaria lapponica</i> Grun.
<i>Fragilaria pinnata</i> Ehr.
<i>Melosira italica</i> var. <i>tenuissima</i> (Grun.) O. Müll.
<i>Navicula farta</i> Hust.
<i>Navicula minima</i> Grun.
<i>Navicula seminuloides</i> Hust.
<i>Navicula seminulum</i> Grun.
<i>Stephanodiscus alpinus</i> Hust. ex Huber-Pest.
<i>Stephanodiscus hantzschii</i> Grun.
<i>Synedra ostenfeldii</i> (Krieg.) A. Cl.
<i>Tabellaria flocculosa</i> (Roth) Kütz.

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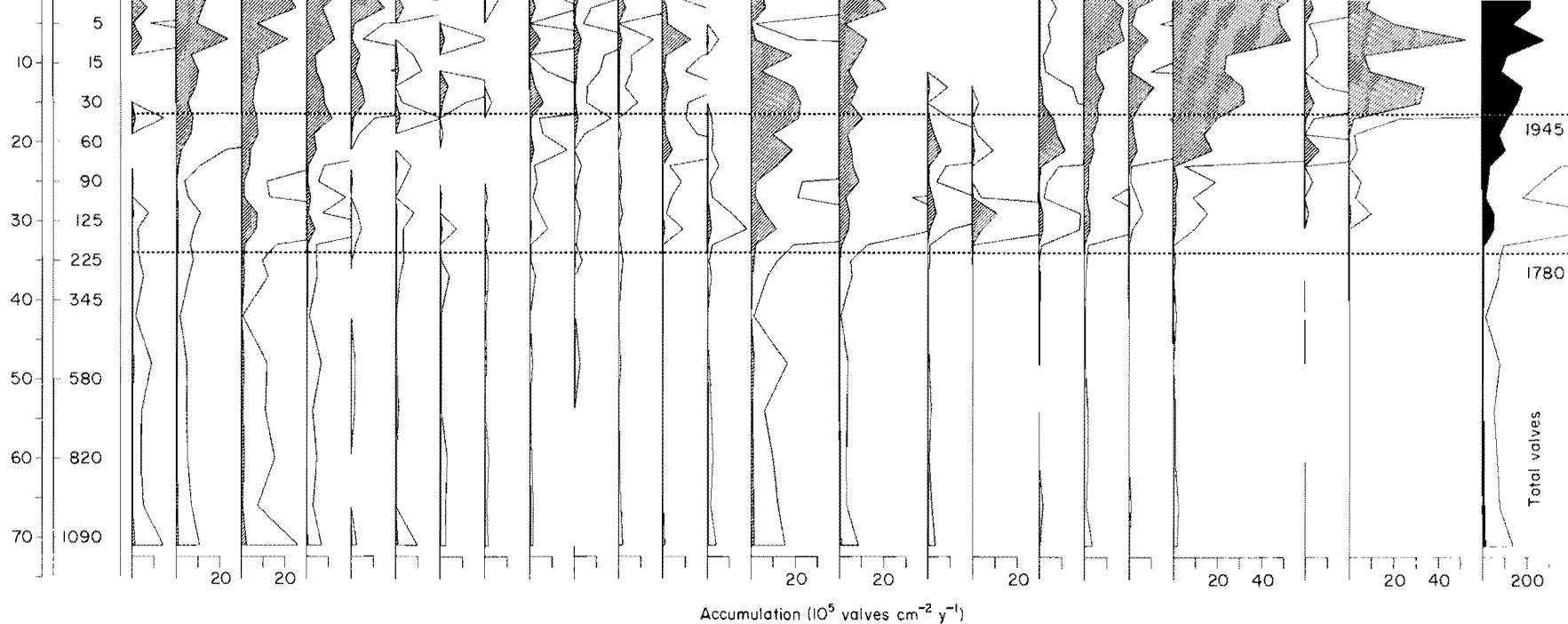


FIG. 9. The twenty-three most common diatom taxa in the Harvey's Lake core calculated as relative abundance (above) and accumulation rate (below). Benthic/tychoplanktonic species *C. stelligera* and *T. flocculosa* are placed with the plankton. Open curves represent 10× exaggeration.

entities have been identified, representing thirty-seven diatom genera. The twenty-three most common taxa are listed in Table 1, and their relative abundance and net accumulation are presented in Fig. 9. Major changes in the diatom flora occur at two horizons in the core, just after the onset of logging (34 cm) and at the dramatic rise in oscillaxanthin (15 cm).

*Relative abundance.* Most of the common taxa are present throughout the core, even across the settlement horizon (Fig. 9). Benthic taxa are well represented at all strata, indicating that no major deterioration of water transparency occurred in the time period represented by the core. Species that decline in relative abundance above the settlement horizon include *Fragilaria lapponica*, *Navicula farta*, *Cocconeis diminuta*, *Navicula seminuloides* and *Stephanodiscus alpinus*. The first four of these are benthic forms that prefer sandy substrates and intermediate to deep water depths (2–30 m; Kingston, 1980; Stoermer, 1980), and the last is a planktonic species that prefers cold water but is not stenothermal (Theriot & Stoermer, 1982). Four *Cyclotella* species common in oligotrophic habitats (Stoermer & Yang, 1969; Bradbury, 1975) have abundance peaks between the 1780 settlement horizon and the 1945 level. *Cyclotella comta*, a warm-season plankter (Stoermer and Ladewski, 1976) that is common throughout the core, has its highest percentage abundance at 25 cm (1890). *Cyclotella michiganiana*, *C. kuetzingiana* and *C. stelligera* (a tycho planktonic species) also have their maximum relative abundances between the two horizons.

The increase in these *Cyclotella* species presents a significant change in plankton composition from the pre-settlement dominance of *Melosira italica* var. *tenuissima* and *Stephanodiscus alpinus*. *Cyclotella* dominance in Harvey's Lake was apparently a response to nutrient enrichment caused by post-logging soil erosion and early agricultural activity. In lakes with higher background nutrient concentrations, these same *Cyclotella* species are often abundant prior to European settlement (Bradbury, 1975; Carney, 1982). The benthic species *Fragilaria pinnata* and *F. lapponica* decline in relative abundance at the same sediment depths where *Cyclotella* species predominate (34–16 cm).

*Achnanthes minutissima*, *Synedra ostenfeldii*,

*Asterionella formosa*, *Fragilaria crotonensis* and *Tabellaria flocculosa* begin increasing in relative abundance between the two horizons and continue to increase above 16 cm. These are all widely occurring diatoms that are favoured by high nutrient concentrations.

The only common diatom species that has its percentage abundance peak after the blue-green algal increase is *Stephanodiscus hantzschii*, and its dominance indicates further nutrient enrichment and probable eutrophy (Lowe, 1974). Other palaeolimnological studies have shown that increases in *S. hantzschii* often occur later than increases in *Fragilaria crotonensis*, and the rise in *S. hantzschii* abundance has been correlated with increased P loading from sewage and livestock wastes (Bradbury, 1975; Carney, 1982). *F. crotonensis*, on the other hand, apparently responds to nutrient increases from diverse sources including soil erosion. Nutrient enrichment experiments with natural phytoplankton assemblages from northern Lake Michigan (Stoermer, Ladewshi & Schelske, 1978) also support the conclusion that *S. hantzschii* blooms in response to increased micronutrients.

A dramatic change in the relative amounts of planktonic and benthic diatoms occurs at the settlement horizon. Below 34 cm (1780) valves from planktonic species account for only 25–35% of each assemblage. The 33 cm depth has a transitional value of 41% plankton, and all younger assemblages contain 50–74% plankton (Fig. 10). This shift in life-form composition of the diatom assemblages is consistent with the expected nutrient increase to the lake after 1780.

*Accumulation.* The net accumulation diagram (Fig. 9) shows the quantitative accumulation for the same twenty-three taxa represented in terms of relative abundance. The total accumulation of diatom valves generally increases from the settlement horizon to the top of the core. This large increase in diatom accumulation rate after logging, apart from any floral changes, probably documents increased diatom production due to nutrient additions to the lake caused by soil erosion and inflow of animal and human wastes. This same kind of evidence for eutrophication has been well documented for Irish lakes (Battarbee, 1973, 1978a, b). The accumulation rates of

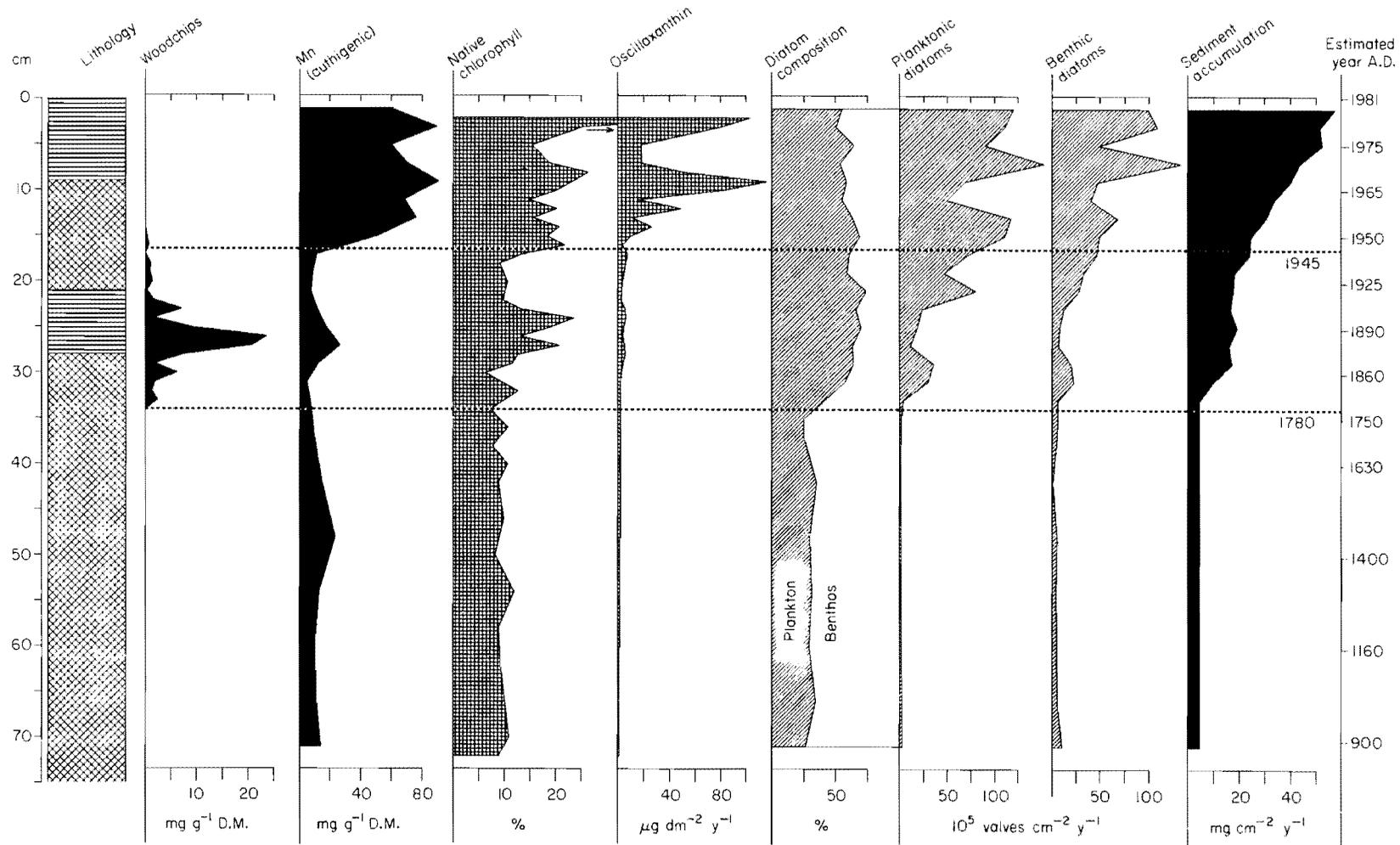


FIG. 10. Summary diagram of selected parameters.

planktonic and benthic diatoms show the same trend of a general increase above the settlement horizon (Fig. 10).

The diatoms with the highest pre-settlement accumulation rates are some of the *Fragilaria* taxa, *Melosira italica* var. *tenuissima*, *Cyclotella comta* and *Navicula seminuloides* (Fig. 9). *Fragilaria lapponica*, *N. farta* and *N. seminuloides* have low accumulations above the settlement horizon, but marked increases above 16 cm (1945) may indicate some recovery of benthic community composition. The decline of these taxa between the two horizons contrasts with large gains in accumulation by several *Cyclotella* species during the same interval.

Most species, including some that show no change in relative abundance (Fig. 9), exhibit increasing accumulation rates above the settlement horizon to the top of the core. Many littoral species are included in this group, which indicates that phytoplankton never became sufficiently abundant to reduce the productivity of littoral species through shading. A continuous increase in benthic production during eutrophication may be a phenomenon associated with lakes where the additional nutrients are expressed as a metalimnetic *Oscillatoria* population, rather than as epilimnetic algal populations.

The change in dominant plankton species below, between and above the two horizons is indicative of a gradual but continuous anthropogenic modification of lake water chemistry. The dramatic accumulation increases of *Fragilaria crotonensis*, *Synedra ostenfeldii* and *Stephanodiscus hantzschii* indicate that the diatom plankton, and thus shading of the benthos, have been increasing substantially in the last few decades. The decline of *Cyclotella* species and *Stephanodiscus alpinus* indicates a shift toward greater eutrophy. The only possible indication that the nutrient loading has abated or that the flora is stabilizing is the recent return and increase of some benthic taxa (*Fragilaria lapponica*, *Navicula farta*, *N. seminuloides*, *Cocconeis diminuta*) that thrive with good water transparency. This increase may indicate a shift from epilimnetic phytoplankton, which shade the benthos, to metalimnetic *Oscillatoria* populations.

Two of the low points in the total valve accumulation curve (Fig. 9), at 42 cm and at

23–27 cm, correspond to episodes of poor valve preservation subjectively noted during counting at those levels. We have no explanation for the pre-settlement episode, but the post-settlement episode corresponds with good pigment preservation and iron and manganese mobilization in the sediments, indicating a period of higher organic-matter deposition and/or low oxygen concentration at the coring site. Both of these diatom dissolution levels are reflected in the accumulation curves for individual taxa. It is unlikely that the total valve accumulation rate curve is highly distorted by silica dissolution (cf. Renberg, 1976; Brugam, 1980), because both of the microscopically identified core segments with poor preservation are easily recognized on the total accumulation curve. There is no reason to expect that other dissolution events went undetected.

## Synthesis

The millennium of sediment accumulation represented in the Harvey's Lake core can be divided into three periods of contrasting limnological development. A summary of the history is provided by a composite diagram of key stratigraphic variables in Fig. 10.

### Pre-settlement

The oldest period from the base of the core to 34 cm (estimated dates of 850–1780 A.D.) is indicative of highly stable conditions, relative to subsequent periods, during which time only minor fluctuations are observed in sediment chemistry, pigments or fossil diatoms. Oscillaxanthin accumulation is very low, and diatom assemblages are dominated by benthic forms (65–75% of total valves). By all indications, pre-settlement Harvey's Lake was a clear-water oligotrophic system in which blue-green algae figured in only a minor way. Gradual shifts in the surrounding vegetation, particularly a regional increase in spruce (Fig. 2) are not reflected in other aspects of sediment stratigraphy.

### Post-settlement: 1780–1945

Beginning at the settlement horizon (1780), however, there is evidence of a major depart-

ture from stability. This shift is marked by the first appearance of woodchips from the Jewett Brook sawmill and the sudden change in pollen composition that resulted from the inception of logging and agricultural activity. In the immediate post-settlement interval total sediment accumulation increases four-fold over pre-settlement rates, primarily because of increased soil erosion following land clearance. At the same time, net accumulation of both benthic and planktonic diatoms increases, though the plankton at a higher rate, so that the diatom assemblage shifts markedly to one dominated by planktonic forms, particularly *Cyclotella* spp. We interpret this shift to represent increased diatom production caused by an accelerated influx of nutrients from agricultural activity in the catchment.

The direct dumping of sawmill wastes into Harvey's Lake, a practice that continued until 1920, is manifest in the stratigraphic profiles of authigenic manganese and native chlorophyll as well as the presence of laminated sediments during this interval. The striking correlation between woodchip concentration and these three variables provides strong evidence for an early episode of increased sedimentary anoxia in the post-settlement period of lake development that resulted from bacterial degradation of sawdust. The anoxia increased Mn deposition at the core-site through redox mobilization and focusing, enhanced chlorophyll preservation, and caused laminations to be preserved through the elimination of sediment mixing by benthic invertebrates. A decline in Mn and per cent native chlorophyll and the disappearance of laminations correspond to the cessation of sawdust discharge in 1920 and indicate a return to lowered rates of hypolimnetic oxygen depletion at that time. Sawdust discharge itself does not appear to have increased overall diatom productivity, as valve accumulation rates decline slightly during peak woodchip deposition (although poor preservation may figure here), and pigment accumulation rates also show no change (Fig. 8).

Despite these various perturbations, the accumulation of blue-green algal pigments does not increase significantly during this second period of the lake's history (1780–1945). Throughout most of the interval before 17 cm (1940), sediment accumulation remains nearly constant, although elevated above pre-

settlement rates. The lake appears to have remained oligotrophic throughout. Increases in productivity during the first 165 years after settlement were probably small relative to more recent increases. During the episode of increased sedimentary anoxia the hypolimnion probably remained largely oxygenated during stratification as it does today.

#### *Recent: 1945–81*

The most recent phase in the history of Harvey's Lake, which began about 1945, is marked by three independent events documented in the sedimentary record: (1) a second and perhaps more severe episode of sedimentary anoxia as indicated by the massive increase in Mn deposition and rise in chlorophyll preservation; (2) the first appearance of *Stephanodiscus hantzschii* and substantial quantities of blue-green algal pigments which signals the transition to a eutrophic phytoplankton community; (3) the rapid acceleration of sediment accumulation that continues unabated to the present.

The return to more reduced sediments suggests that oxygen depletion from organic loading to the hypolimnion increased markedly at this time. This condition has persisted to the present and is also marked by the reappearance of laminations above 9 cm. Historical trends in the hypolimnetic oxygen depletion rate calculated from direct measurement of oxygen profiles substantiate our conclusion from the sedimentary record. From 1978 to 1981 depletion rates ranged from 280 to 381 kg d<sup>-1</sup>, whereas for 1939 (the only year for which historical data are available) an oxygen depletion rate of 90 kg d<sup>-1</sup> was calculated (Enright & Smeltzer, 1982).

The 1945 increase in hypolimnetic oxygen depletion appears to have resulted from increased autochthonous production, unlike the earlier episode where allochthonous organic matter in the form of wood fibre was the cause. The earlier episode provides a controlled experiment whereby the stratigraphic changes in pigments and geochemistry associated with increased primary production can be separated from changes resulting from anoxia alone. This allows us to conclude that the sharp rise in oscillaxanthin above 16 cm (1945) is not an artefact of enhanced preservation

but actually marks the first appearance of the large populations of *Oscillatoria rubescens* that dominate the phytoplankton today. Actually *O. rubescens* production may not have initiated sedimentary anoxia, as the latter predates the oscillaxanthin increase by several years. Increased productivity by other phytoplankton, particularly diatoms, which rise concurrently with Mn and native chlorophyll, probably was responsible for the initial shift in oxygen depletion.

Elevated primary production after 1945 almost certainly resulted from increased nutrient flux to the lake, and two historically simultaneous events in the catchment were the likely source of these inputs. First, the expansion of dairy farming and the channelization of farm-waste runoff into Harvey's Lake about 1950 are the most probable causes for nutrient enhancement of algal production. The proliferation of summer homes along the shoreline, each with individual septic systems, represents a second potential source of nutrient enrichment. Moreover, the continuous acceleration in overall sediment accumulation since 1945 can largely be attributed to increasing erosion caused by excavation and land clearance during home-building near the lake shore.

Certain changes in the diatom assemblages precede the 1945 horizon. In particular, nutrient-enrichment indicators such as *Asterionella formosa* and *Fragilaria crotonensis* increase at 20 cm (about 1920) and contribute to the rise in planktonic diatom accumulation rates at that time. Land-use history for the Harvey's Lake catchment is incomplete for this period, so that anthropogenic influence is difficult to assess. Nonetheless, sedimentary evidence for productivity changes after 1945 is most striking, and the development of large populations of eutrophic indicators such as *Stephanodiscus hantzschii* and *Oscillatoria* (Fig. 10) attests to the major impact of events after 1945.

#### Diatom–*Oscillatoria* interactions

While planktonic and benthic diatoms, as well as oscillaxanthin, all exhibit trends of increasing accumulation since the 1945 horizon, there exist marked fluctuations in each of these profiles up to the present. Oscillaxanthin has distinct peaks in the intervals correspond-

ing to 1965–70 and 1978–80, whereas the diatoms are sparse at these strata but common in between. Chlorophyll derivatives, on the other hand, show a steady increase in accumulation throughout. Because both blue-green algae and diatoms produce chlorophyll, the fluctuations in fossil diatoms and blue-green algal pigments apparently resulted from changes in algal composition rather than shifts in overall primary production.

The inverse relationship between oscillaxanthin and planktonic diatoms is particularly striking in this regard and provides historical evidence for the kind of long-term negative interaction between blue-green algae and diatoms documented by Keating (1978). In addition, the percentage of planktonic diatoms in the total sedimentary assemblage declines slightly at strata where peak blue-green algal pigment accumulation occurs. Any negative influence of large *Oscillatoria* populations should most affect planktonic diatoms, which these data indicate. A similar stratigraphic record suggesting diatom–*Oscillatoria* antagonism is evident in Züllig's (1982) profiles from Baldeggersee.

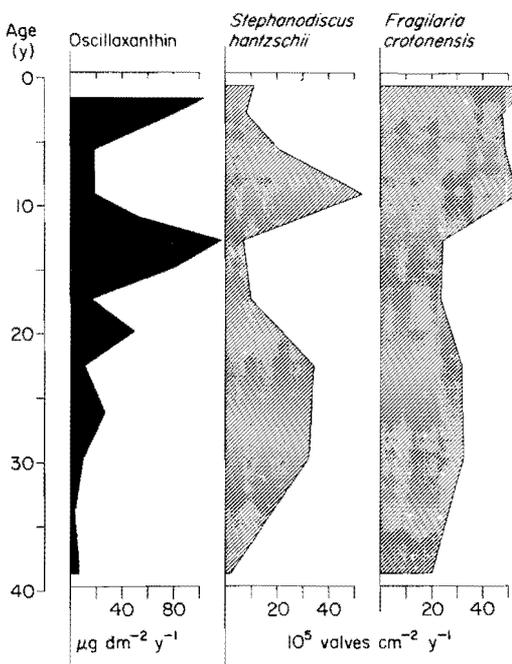


FIG. 11. Accumulation rates for oscillaxanthin and the two dominant planktonic diatoms during the past 40 years. Age in years before 1981.

Even among planktonic diatoms, the pattern varies between species, as shown in Fig. 11, where *Stephanodiscus hantzschii* and *Fragilaria crotonensis*, the two dominant diatom plankters in recent sediments, are plotted along with oscillaxanthin. The inverse nature of *S. hantzschii* and *Oscillatoria* populations is striking, whereas there is no clear relationship between *F. crotonensis* and *Oscillatoria*. The seasonality of these two diatom species may offer an explanation for their contrasting stratigraphy: *S. hantzschii* characteristically blooms during mixing in late winter and early spring (Carney, 1982), when *Oscillatoria* occupies the mixed layer of the lake; *F. crotonensis*, on the other hand, blooms in mid-summer and is often common through autumn (Stoermer & Ladewski, 1976; Stoermer *et al.*, 1978), when *Oscillatoria* is concentrated in the metalimnion. Thus the opportunity for negative interaction between diatoms and blue-green algal populations is greater for *S. hantzschii* than for *F. crotonensis*. Another reason that *F. crotonensis* might not be affected by *Oscillatoria* abundance when *S. hantzschii* is lies in Keating's (1978) suggestion that the Fragilariaceae may be less susceptible than other diatoms to blue-green algal allelopathy.

Evidence has recently been gathered from *in situ* bag experiments conducted in Harvey's Lake that support our historical interpretation of reciprocating diatom-*Oscillatoria* populations (Enright & Smeltzer, 1983). In these studies the growth rate of diatom populations in epilimnetic enclosures declined significantly with the introduction of metalimnetic waters, filtered or unfiltered, in which dense *Oscillatoria* populations were growing. These results imply that *Oscillatoria* may inhibit diatom production, possibly through allelopathy, thus providing a mechanism for the alternating oscillaxanthin-diatom stratigraphy in the core. The proximate cause for such fluctuations may relate to variations in nutrient inputs, seasonal circulation patterns, or other unknown factors.

### Conclusions

The recent limnological trend in Harvey's Lake revealed by the sedimentary record is one of increasing eutrophy, hypolimnetic oxygen depletion and *Oscillatoria* dominance of the phytoplankton. Production by diatom

populations, including benthic forms, has also increased, which indicates that water clarity has not seriously diminished. Present-day transparency in Harvey's Lake is anomalous, high relative to other lakes with similar loading, because much of the mid-summer biomass resides in the metalimnion. However this present condition has developed only in recent years and may represent a transitional stage in water quality that could be succeeded by epilimnetic blue-green algal populations if nutrient loading continues to accelerate (Edmondson, 1968; Reynolds & Walsby, 1975). From the sedimentary record we see no evidence that nutrient enrichment has abated. Water quality monitoring has revealed increasing phosphorus levels in the lake from 1977 to 1982 (Enright & Smeltzer, 1983).

Our stratigraphic analysis of Harvey's Lake sediments clearly shows that limnological conditions today are radically different from the oligotrophic state that existed prior to settlement and that much of the change occurred very recently. The anthropogenic eutrophication of Harvey's Lake is not, in itself, a unique story, but our reconstruction of this history is unusually detailed and unambiguous because it integrates several stratigraphic analyses and precise sediment dating.

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