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Paleolimnological assessment of human-induced impacts on Walden Pond (Massachusetts, USA) using diatoms and stable isotopes

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Multi-proxy analysis of a sediment core spanning 1600 years from Walden Pond, Massachusetts (USA), reveals substantial changes in the nutrient status over the past ∼250 years resulting from anthropogenic impacts on the lake and watershed. Following a period of environmental stability from about 430 AD to 1750 AD, the abundance of the diatom Cyclotella stelligera *increased, the chrysophyte cyst to diatom ratio decreased, organic content declined, bulk organic $\delta^{13}C$ decreased, and bulk organic $\delta^{15}N$ increased. These changes coincided with logging in the watershed, and are mainly attributed to an increase in detrital input of inorganic sediment and delivery of dissolved soil decomposition products from the watershed. With the beginning of intensive recreational development of Walden Pond in the early 20th century, oligotrophic diatom species were largely replaced by disturbance indicators and the diatom-inferred lake pH increased by 0.5 units, while the bulk organic carbon and nitrogen stable isotope composition markedly shifted to lower and higher values, respectively. These changes reflect inorganic inputs from erosion related to trails, beaches, and construction, as well as increased nutrient inputs by wastewater seepage into groundwater and extensive recreational usage. Diatom-inferred total phosphorus increased only slightly, probably because oligotrophic species still persist during spring and autumn, when Walden Pond has lower nutrient concentrations due to reduced recreational activity. During the last 25 years, diatom assemblages stabilized, suggesting that management measures have been effective in reducing the rate of eutrophication. Notably, the changes observed over the past 250 years are well beyond the range of natural variability of the past 1600 years, yet the pre-disturbance record provides a useful target for developing additional restoration and conservation measures to ensure future environmental protection of this historical site.*

Keywords: New England, chrysophytes, pH, total phosphorus, land-use history

Introduction

The evaluation of anthropogenic impacts on ecosystems and the development of effective and appropriate restoration and conservation management strategies require knowledge of natural pre-disturbance ecosystem structure. In New England, lakes have been subject to watershed disturbance since European settlement in the

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17th century, when woodlands were cleared for pasture, housing, and wood harvest (Foster, 1995). Logging, agriculture and urban development in the catchment as well as recreational use have affected water quality in many New England lakes (Siver et al., 1996; Dixit et al., 1999; Francis and Foster, 2001).

Walden Pond, Massachusetts, and its catchment have experienced multiple historical anthropogenic impacts. The site has attracted much attention since the publication of the American classic *Walden* by the natural philosopher Henry David Thoreau (Thoreau, 1854; Whitney and Davis, 1986). Despite the public interest in the protection of the lake as a natural and historical monument, few studies exist on the limnology of Walden Pond (Deevey, 1942; Winkler, 1993; Colman and Friesz, 2001) and no comprehensive study of the pre- and post-disturbance limnology of Walden Pond has been conducted. The comparison of historical and recent limnological data suggests that Walden Pond has become more eutrophic since the early 20th century, but there is insufficient data to estimate whether the trophic level has reached a steady state or eutrophication is continuing (Colman and Friesz, 2001).

Paleolimnological studies offer a well-established approach for acquiring pre-historical data on lake water quality (Pienitz and Vincent, 2003). The physical, chemical and biological information preserved in lake sediments provide insight into past events that have occurred within the catchment and their effects on the lake environment. Fossil diatoms, which are well preserved in lake sediments, are useful indicators of past environmental change, including lake trophic status (Moser et al., 1996). By relating limnological data such as total phosphorus (TP) and pH to modern diatom assemblages, diatom inference models have been developed and subsequently applied to fossil samples in order to reconstruct quantitatively past lake properties (Hall and Smol, 1999). Changes in sedimentary diatom composition have been shown to reflect nutrient enrichment following logging and subsequent urban development in the catchments of New England lakes (Davis and Norton, 1978; Engstrom et al., 1985). Diatom-based quantitative reconstructions have been used to infer increased P and nitrogen (N) concentrations (Siver et al., 1999; Dixit et al., 1999) and rising pH and alkalinity (Davis et al., 1994) in New England lakes since European settlement. The remains of chrysophytes, a group of fossilizing planktonic algae, are also well preserved in lake sediments and are useful indicators of water quality (Zeeb and Smol, 2001). They are used in paleolimnological studies to investigate lake acidification and eutrophication (e.g., Siver et al., 1999).

Lake sediment carbon and N elemental and stable isotope stratigraphy have been used extensively for assessing changes in lake water nutrient balance in response to the impact of human activities on watersheds. Forest clearance, agricultural activity and urban development in watersheds, for example, frequently lead to lake eutrophication, which is recorded by changes in the carbon (C) and N elemental and stable isotope composition in lake sediment cores (e.g., Schelske and Hodell, 1991, 1995; Hodell and Schelske, 1998; Brenner et al., 1999; Teranes and Bernasconi, 2000). In some cases, these data also reveal the extent of lake recovery if measures have been taken to reduce nutrient loading, thus serving to evaluate the effectiveness of management strategies (e.g., Schelske and Hodell, 1991, 1995; Hodell and Schelske, 1998).

Here we use a multi-proxy paleolimnological approach to assess the impact of human disturbances and of recently adopted management measures on the nutrient balance of Walden Pond within the context of natural conditions over the past 1600 years. Our efforts focus on 1) the pollen record to document the human impact on the regional vegetation, 2) lake sediment analysis of C and N elemental and isotope geochemistry to qualitatively assess nutrient balance history, 3) the fossil diatom record and diatom-based quantitative inferences for pH and TP to assess the biological response of autotrophic organisms to disturbance, and 4) an evaluation of current management strategies for continued environmental stewardship of Walden Pond based on the results of this study.

Study site and land-use history

Walden Pond is a 25-ha kettle hole lake in eastern Massachusetts, USA (42°26.3′N, 71°20.4′W; Figure 1a). The present climate is temperate with warm summers (mean July temperature: 21.9°C) and winters allowing the formation of ice cover (mean January temperature: −4.1°C). Presently, 86% of the watershed is covered with pine-oak forest, dominated by *Pinus strobus* and *P. rigida*, as well as *Quercus rubra, Q. velutina* and *Q. alba*. The lake consists of three main basins, the eastern shallow basin (max. depth: 18 m), the central basin (max. depth: 20 m) and the deep western basin (max. depth: 30.5 m) (Figure 1b). The watershed (38 ha) is small in relation to the surface of the lake and is characterized by sandy glacial outwash soils and glacial till on granitic bedrock (Barosh, 1993). The main water supply (55%) is groundwater, entering the lake at the eastern end and draining an area of 62.2 ha including a small lake. Precipitation contributes

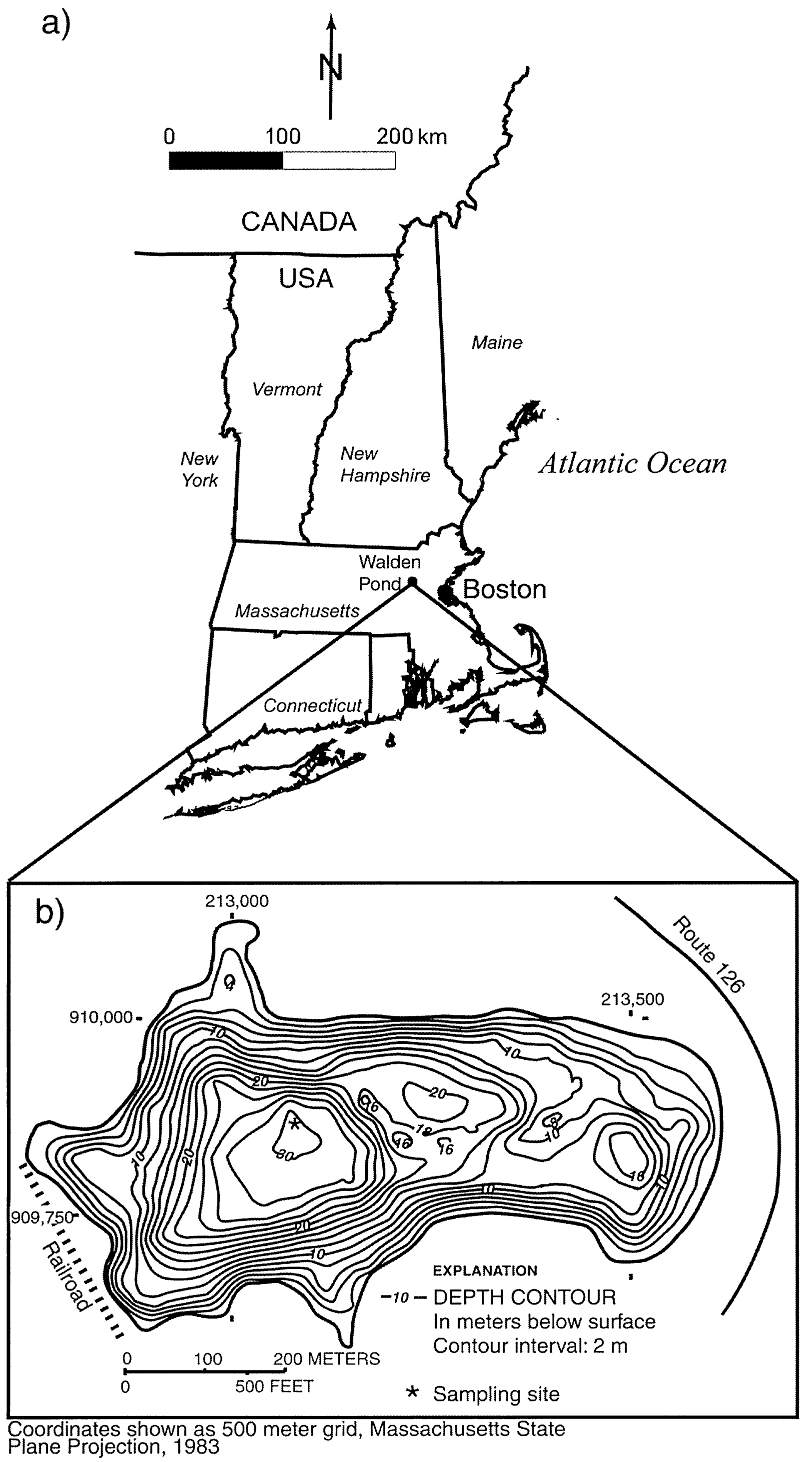

Figure 1. a) Map of the study region. b) Bathymetric map of Walden Pond with coring site. Modified from Coleman and Friesz (2001).

45% to the water balance (Colman and Friesz, 2001). The thermocline during summer stratification develops at ca. 15 m water depth. The forested, steep banks of the Walden Pond watershed and a short fetch help to keep the stratification until October or November, when turnover starts.

The area was settled at the beginning of the 17th century. The forest around Walden Pond was partly logged for timber harvest, with increasing intensity from the 17th to the 19th century (Brian Donahue, Brandeis University, pers. comm.). A slight decline in cutting occurred from 1850 to 1920 and a dramatic decline followed due to the donation of 80 acres surrounding the pond by the owners to the Commonwealth of Massachusetts for conservation and open space recreation. A railroad was built in 1844 near the southwestern end of the lake. In 1866, an excursion park was built on the shore, which burned down in 1902 and was not rebuilt. In the 1920s, a beach was created at the eastern shore, a bathhouse opened, an amusement park was established, and the number of visitors rose to 500,000 per year. In 1975, the Massachusetts Department of Environmental Management assumed responsibility for managing the park and implemented protection measures including the closure of the amusement park, trail improvement, control of access and improvement of facilities. Presently, the watershed is contains a well-developed series of hiking trails, and a public beach on the western shore is intensively used, attracting up to 100,000 visitors per month in the summer.

According to recent limnological surveys (Table 1), Walden Pond has been characterized as a mostly circumneutral, oligotrophic to mesotrophic lake with low conductivity (Colman and Friesz, 2001). The highest total phosphorus (TP) concentrations in Walden Pond were measured during summer (e.g., 140 μg l^{-1}, 6 September 1989 and 60 μg l^{-1}, 27 May 1998). Notably, these high values were measured on combined eastern and western basin samples, whereas the highest TP values measured between 1997 and 1999 were 22 μg l^{-1} (23 May 1998) and 19.5 μg l^{-1} (16 July 1998) in the western basin, thus indicating that the eastern basin has the highest TP concentrations. Nutrient budgets for the lake indicate that N inputs are dominated by groundwater, which is N-enriched by plume water from the septic leach field of the Walden Pond State Reservation headquarters and the bathhouse (30%), both located on the eastern shore of the lake, and recreational usage (34%) (Colman and Friesz, 2001). Phosphorus inputs are dominated by atmospheric dry deposition, background groundwater, and recreational usage, the latter representing more than 50% of the P load during summer (Colman and Friesz, 2001). The P budget calculations indicate that the present TP loading is classified between 'permissible' and 'critical load' according to the Vollenweider model (Colman and Friesz, 2001). The budgets include ground water, atmospheric deposition, swimmers, waterfowl, fish stocking, and direct runoff, but exclude internal nutrient recycling. Yet, high N and P concentrations near the bottom (max. 0.6 mg $l^{-1}$and 50 μg l^{-1}, respectively) as well as anoxic conditions in the hypolimnion during stratification reveal that nutrients are recycled from the sediments. Comparison with historical dissolved oxygen data collected in 1939 (Deevey, 1942), which recorded an oxygenated hypolimnion, indicates that eutrophication has occurred since then. In the early 1990s, there have been reports on algae accumulation at the surface and bloom-like conditions (Baystate Environmental Consultants, 1995).

Methods

Sampling and dating

On 24 February 2000, a 143 cm long sediment core was taken from the western basin of Walden Pond at a depth of 30 m (Figure 1b), using a simple-tube surface corer. The core was cut into 1 cm thick slices and sub-samples were used subsequently for the analyses of different proxy indicators and dating. The ^{210}Pb chronology (Binford, 1990) was established for the upper 14 cm of the core and by ^{14}C-AMS dating of bulk sediment (gyttja) at four horizons downcore. The European settlement horizon (ESH) was determined by pollen analysis and has been assigned to the historical recorded date 1635 AD for the foundation of the town Concord (Wheeler, 1967). The complete chronology was calculated by linear interpolation between the ^{14}C dates and by exponential trend lines between the oldest ^{210}Pb date, the ESH and the youngest ^{14}C date.

Sediment preparation of sub-samples for pollen analysis followed standard procedures (Faegri and Iversen, 1975). Pollen was counted to a total of 500 tree and shrub grains at 400× magnification. Pollen percentages are based on total terrestrial pollen grains, excluding aquatics, but including agricultural grains (i.e., herbs). Identification is based on standard taxonomic keys (McAndrews et al., 1973; Moore et al., 1991).

Organic matter was measured at 1 cm intervals using standard loss-on-ignition procedures (Dean, 1974). Approximately 1 cm^3 of wet sediment was dried overnight at 95°C and then weighed before and after combustion at 550°C for one hour.

Table 1. Limnological characteristics of Walden Pond. Data for 1994 were obtained at four sampling dates (January, May, June, and August, 1994). Samples were taken from the epilimnion (1 m depth) and the metalimnion (10 m depth) and combined from the eastern and western basins (Baystate Environmental Consultants 1995). Data for 1997–99 are measurements in the western basin: epilimnion and metalimnion (0–14 m depth), taken at 11 sampling dates (May–August, 1997; March-September, 1998; February, 1999) (Colman and Friesz, 2001). For calculating minimum (min), maximum (max) and mean values, each sample was used separately, including samples from different depths. The mean N:P ratio for 1997–1999 was calculated from mean total N and mean total P, while minimum and maximum were not calculated because of different sample numbers and depths. The 2001 measurement represents surface water.

Sample Date		12/2001	1997–1999			1994			1989 West & East		
Sampled Basin		West	West			West & East			(combined)		
No. of Samples		1	>44			16			8		
Characteristic	Unit		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Conductivity	μS cm^{-1}	93	83	92	n.d.	65	87	75	79	87	84
PH		6.9	6.4	9.4	7.7	6.5	7.3	6.8	6	7.7	7
Turbidity	NTU	n.d.	n.d.	n.d.	n.d.	0.43	1.7	1.1	n.d.	n.d.	n.d.
Alkalinity	μg l^{-1}	n.d.	n.d.	n.d.	n.d.	134	182	153	11	12	11
Total phosphorus	μg l^{-1}	5.3	1	22	8.4	10	60	19	10	140	60
Month				May			April			September	
Ammonia-N	mg l^{-1}	0.02	n.d.	n.d.	n.d.	<0.01	0.14	<0.03	0.02	0.02	0.02
Nitrate-N	mg l^{-1}	0.03	0.01	0.12	0.04	<0.01	0.05	<0.03	0.02	0.02	0.02
Total Nitrogen	mg l^{-1}	0.33	0.1*	0.57*	0.23*	0.21**	1.1**	0.41**	n.d.	n.d.	n.d.
Secchi Depth	M	8.5	2.5	7.5	5.2	4	9.3	6.8	n.d.	n.d.	n.d.
N:P Ratio		68:1	n.d.	n.d.	28:1	8.7:1	112:1	22:1	n.d.	n.d.	n.d.
Chlorophyll *a*	μg l^{-1}	2.2	0.1	8.2	2	2.3	3.73	3.1	n.d.	n.d.	n.d.

*Including ammonia.
**Excluding ammonia.
n.d. = no data.

Sediment sub-samples were analysed at 4 cm intervals for bulk organic C and N elemental and stable isotope composition. Samples were acid-washed in 10% HCl to remove carbonates, rinsed with de-ionized water and freeze-dried. Coarse-grained (>500 μm) sediments were removed by sieving. The fine-grained fraction was analysed for organic C and N percent and stable isotope composition using a Micromass Isochrom continuous flow mass spectrometer equipped with an elemental analyser at the University of Waterloo—Environmental Isotope Laboratory. Carbon and N isotope composition are reported in δ-notation, such that $\delta = [R_{sample}/R_{std} - 1] \times 1000$ where R is the $^{13}C/^{12}C$ and $^{15}N/^{14}N$ ratios in the sample and VPDB and AIR standards, respectively. Analytical uncertainty is ±0.03% for $\delta^{13}C$ and $\delta^{15}N$ based on repeated analyses of several samples.

Samples for diatom analysis were processed using standard procedures (Pienitz et al., 1995). A minimum of 500 valves per sample were counted and identified according to Camburn and Charles (2000), Krammer and Lange–Bertalot (1986–1991), and Fallu et al. (2000). The taxonomy of the fossil and the modern samples was matched by personal communication with S. Dixit and by comparing our photographs with figures presented in Camburn et al. (1984–86), as this was the main taxonomic reference used by Dixit et al. (1999) for the training set. Chrysophyte cysts were counted, but not identified, and the scales of synurophytes (a group of chrysophytes) were counted and partly identified on the same slides as the diatoms. The ratio of chrysophyte cysts and scales to diatom frustules are expressed as the percentage of the respective remains related to the sum of diatom frustules (= half of the diatom valve count) and the total count of chrysophyte remains.

Fossil diatom assemblages were subdivided into stratigraphic zones by optimal partitioning using the computer program ZONE (S. Juggins, unpublished program; Stephen.Juggins@ncl.ac.uk). The significant number of zones was estimated by the broken stick model (Bennett, 1996). However, this zonation technique separates groups at the midpoint of gradual

Table 2. Performance of the pH and TP models used for paleolimnological reconstructions in this study, based on diatom and environmental data from 82 New England lakes (Dixit et al., 1999).

Gradient	Method	r^2	RMSE	r^2_{jack}	RMSEP	max. bias
pH	WA inv.	0.87	0.24	0.82	0.30	0.37
TP	WA inv.	0.65	0.19	0.40	0.25	0.36

WA inv. = Weighted averaging with inverse deshrinking; RMSE = root mean squared error of prediction; RMSEP = jacknifed RMSE; r^2 = jacknifed coefficient of determination.

changes, which does not always reflect the exact timing of the onset of change. Therefore, we assigned the border between Zone II and Zone III to the level where the shift began (12 cm instead of the calculated 10 cm), in order to relate the start of this change to historically recorded human disturbances.

For quantitative reconstructions of pH and TP, we used transfer functions based on limnological and subfossil diatom data (Dixit et al., 1999) from 82 lakes located in the states of Vermont, New Hampshire, Massachusetts, and Connecticut (Köster et al., 2004). Details concerning numerical analyses of the data set, model development, and comparison of quantitative reconstructions with the instrumental record of Walden Pond are presented in Köster et al., 2004). Diatom-based inference models based on weighted averaging with inverse deshrinking (WAinv) were used for the reconstructions in this study (Table 2), as they represented the simplest models with good statistical performance (Köster et al., 2004). Model development, environmental reconstructions and calculation of sample-specific errors for the fossil samples were carried out using the program C^2 (Juggins, 2003). Errors were estimated by jacknifing, an intensive cross-validation procedure.

In order to test how well the fossil diatom assemblages are represented in the model data set, two methods of analog measures were applied. The coefficients of dissimilarity using chord distance (Overpeck et al., 1985) were calculated using the program ANALOG (H.J.B. Birks, University of Norway, Bergen, Norway and J.M. Line, Cambridge University, Cambridge, UK, unpubl. program). Based on the mean minimum dissimilarity coefficient (DC) within the model data, the 75 and 95% confidence intervals were calculated (Laird et al., 1998). Fossil samples with a DC lower than the 75% confidence interval were deemed to have good analogs in the calibration set, whereas DCs between 75 and 95% indicated poor analogs and DCs outside the 95% interval indicated no analogs (Laing et al., 1999). Furthermore, the 'goodness of fit' of the fossil assemblages to the reconstructed variables pH and TP was evaluated by a CCA with the first axis constrained to one variable and defining the modern and fossil samples as active and passive, respectively. Fossil samples having residual distances to the first axis outside the 95% confidence interval of the modern samples' distances were considered to have very poor fit (Birks, 1990).

Results

The chronology of the sediment core, based on ^{210}Pb and ^{14}C dates as well as the European settlement horizon (Table 3, Figure 2), indicates a sedimentation rate of about 0.13 cm yr^{-1} from ca. 430 to 1200 AD. From ca. 1200 to 1700 AD, sediment accumulation declined to 0.04 cm yr^{-1}, rising to an average rate of 0.09 cm yr^{-1} over the last 300 years.

The organic content of the sediments, inferred from loss-on-ignition, remained relatively constant with values around 40% from ∼430 AD to ∼1500 AD, except at ∼670 AD (100 cm) where a value of 49% was obtained (Figure 4a). From ∼1600 AD, the percentage of organic matter began to decline, until it reached about 25% at ∼1960 AD. Afterwards, the proportion of organic matter fluctuated between 25% and 40% with a tendency to higher levels in the most recent sediments.

Before European settlement, *Quercus* (oak), *Pinus* (pine) and *Betula* (birch) dominated the pollen stratigraphy, with about 15% aquatic macrophytes, and no

Table 3. ^{14}C dates for Walden Pond including AMS dates in years BP (ybp), calibrated dates (cal ybp) and calibrated dates converted to years BC/AD.

Depth (cm)	ybp	Calibrated ybp	Lab Error	2 Sigma Error	Cal ybp + 50	^{14}C Converted to Years BC/AD (2000 − Cal ybp + 50)
44–45	785	689	35	80	739	1261 ± 80
60–61	1084	970	35	110	1020	980 ± 110
90–91	1301	1261	36	120	1311	689 ± 120
124–125	1517	1396	38	96	1446	554 ± 96

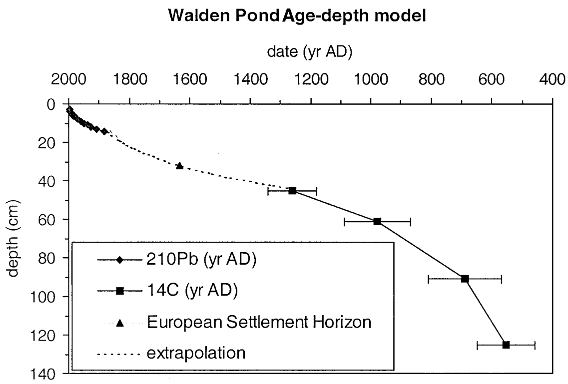

Figure 2. Age-depth model for Walden Pond.Dates were established by the ^{210}Pb and ^{14}C methods.The ESH (European settlement horizon) was determined by pollen analysis and assigned to the historical recorded date 1635 AD.

significant changes were observed (Figure 3). After settlement in the early 17th century, the proportion of *Pinus* increased from 15 to 25% and the amount of agricultural weeds (including Poaceae, *Ambrosia*, *Rumex,* etc.) started to increase. Between ca. 1840 and 1900 AD, the abundance of *Quercus* decreased by 20 to 30%, *Pinus* declined and agricultural weeds increased until they reached peak proportions of 28% at 1900 AD. In the early 20th century, *Betula* showed a maximum of 28% and the herbs declined sharply. Shortly afterwards, declines in *Betula* coincided with increases of *Quercus* and *Pinus*. *Fagus* (beech) and *Tsuga* (hemlock) pollen declined gradually from the early 18th century on until present. Between 10 and 8 cm (ca. 1940–1960 AD), the relative abundance of aquatic macrophytes, mainly *Isoëtes* (Quillworth), declined rapidly from 11 to 1.5%.

The C and N elemental and isotope composition of Walden Pond sediments was generally stable until marked changes occurred at the top of the core above ca. 24 cm depth (after ca. 1770 AD) corresponding with the main period of human disturbance in the catchment (Figure 4). Organic C and N contents in sediments below these strata were near constant with values of 20 and 2%, respectively (Figure 4b,c). Above this horizon, C and N rapidly declined to values as low as 16.8 and 1.2%, respectively, and then increased to values similar to those observed in the pre-1770 AD interval. A brief increase in % C at 12.5 cm depth (ca. 1910 AD) interrupted this general trend and corresponds to a horizon rich in charcoal fragments. Similarly, δ^{13}C and δ^{15}N were also generally stable in the lower strata with values of about −26.5 and 1.5‰, respectively (Figure 4e, f). Around 1770 AD, δ^{13}C values began to decline substantially to −30‰, whereas δ^{15}N values markedly began to increase to 5‰. Unlike the trends observed in the elemental profiles, the C and N isotope values did not return to values observed in the pre-1770 AD interval.

Three major periods with differing diatom assemblages were distinguished for the last ∼1600 years, including one zone preceding ∼1750 AD and two zones after ∼1750 AD, the latter two corresponding to human disturbance in the watershed (Figure 5).

Zone I (140–26 cm, ca. 430 to 1750 AD): In Zone I, the oligotrophic to mesotrophic and circumneutral to acidophilic species *Tabellaria flocculosa* (Roth) Kütz. str. IIIp sensu Koppen and *Cyclotella stelligera* (Cleve and Grunow) Van Heurck dominated. The acidobiontic diatom *Asterionella ralfsii* var. *americana* Körner was present at low abundance throughout this period. *Fragilaria nanana* Lange-Bertalot and *Cyclotella bodanica* aff. *lemanica* (Müller ex Schröter) Bachmann were present with abundances less than 10%. The ratio of synurophyte scales to diatom frustules varied between 9 and 29% (mean: 18%, Figure 5). The ratio of chrysophyte cysts to diatoms ranged from 7 to 21% (mean: 13%), with the highest values (18–20%) around 1700 AD.

Zone II (26–12 cm, ca. 1750 to 1920 AD): Around 1750 AD, the abundance of *T. flocculosa str. III p* started to decline, while *C. stelligera* increased by about 30%. *Cyclotella bodanica* aff. *lemanica* decreased from around 10% to very low abundance at ∼1860 AD. The synurophyte scales to diatom frustules ratio remained constant (mean: 21%), however, the mean relative abundance of chrysophyte cysts decreased from 13 to 8%.

Zone III (12–0 cm, ca. 1920 to 2000 AD): In the early 20th century, diatom assemblage composition showed a striking change. The abundances of the disturbance indicators *Asterionella formosa* Hassal and *Fragilaria nanana* increased from about 5% in the late 19th century to 50 and 35% respectively in the 1960s. Simultaneously, *C. stelligera* decreased rapidly, from a maximum abundance of 77% at ∼1900 AD to an average abundance of 3% after ∼1930 AD whereas *C. bodanica* aff. *lemanica* and *Tabellaria flocculosa* str. IIIp remained relatively constant at ca. 5% and 15%, respectively. *Asterionella ralfsii* var. *americana* disappeared around 1940 AD and was not subsequently recorded. From about 1980 to 2000 AD this new diatom assemblage stabilized.

The mean synurophyte scales to diatom frustules ratio increased to 43%, with a maximum of 64% in ∼1998. This increase was mainly caused by much higher abundances of scales of *Mallomonas crassisquama* (Asmund) Fott. The ratio of chrysophyte cysts to diatom frustules remained low with values

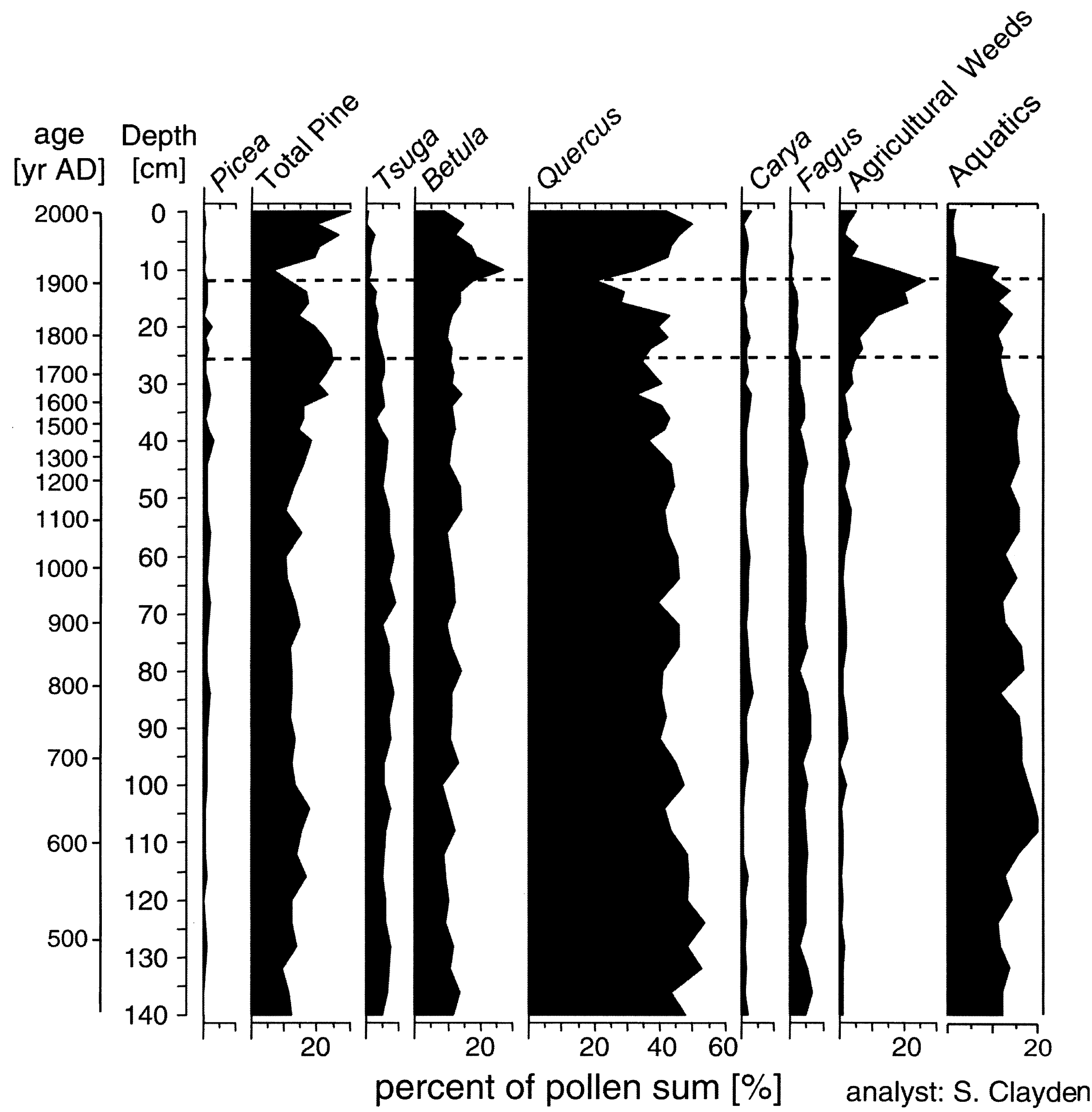

Figure 3. Pollen and spores stratigraphy of selected taxa in Walden Pond sediments. Abundances of aquatic taxa were calculated as percentage of total non-aquatic pollen and were not included in the calculation of pollen percentages. Dashed horizontal lines indicate the major diatom zones (see Figure 5).

around 8% until about 1997, and then increased to 10–20% in the upper three levels.

Two major periods with differing analog situations prevail in the sediment core (Figure 5). The samples between 140 cm and 9 cm (ca. 430 to 1950 AD) have dissimilarity coefficients lower than the 75% confidence limit, indicating that the fossil diatom species are well represented in the model data set. With the exception of the samples at 4, 3 and 0 cm, the recent samples between 8 and 0 cm (ca. 1950 to 2000 AD) have dissimilarity coefficients between the 75 and 95% critical values, indicating poor analogs (Figure 5). Similar patterns were obtained by the 'goodness of fit' analysis using CCA. The samples from 140 to 9 cm have a good fit to pH and TP, whereas the levels 8 to 0 cm lay outside the 95% confidence limit, indicating a poor fit of those samples to both variables.

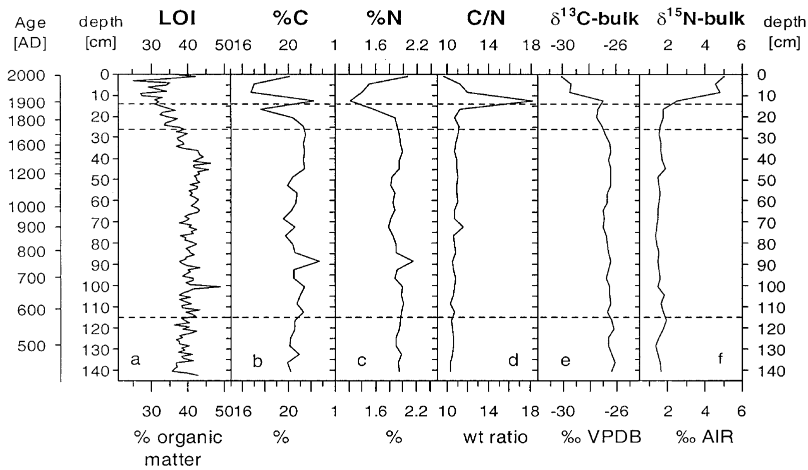

Figure 4. Loss-on-ignition (a), bulk organic carbon and nitrogen elemental (b, c, d) and stable isotope stratigraphy (e, f) for Walden Pond.Dashed horizontal lines indicate the major diatom zones (see Figure 5).

The diatom-inferred pH (DI-pH, Figure 5) remained stable from ca. 430 to 1880 AD, with values fluctuating around 7.3. Afterwards, the DI-pH sharply increased to 7.8 at ca. 1970 AD, after which values stabilized until the present day.

The diatom-inferred TP (DI-TP, Figure 5) followed similar trends as DI-pH, but increased with a time lag of about 50 years. DI-TP remained relatively stable with values around 6 μg l^{-1} in the lower levels until ca. 1930 AD. Thereafter, DI-TP continuously increased in

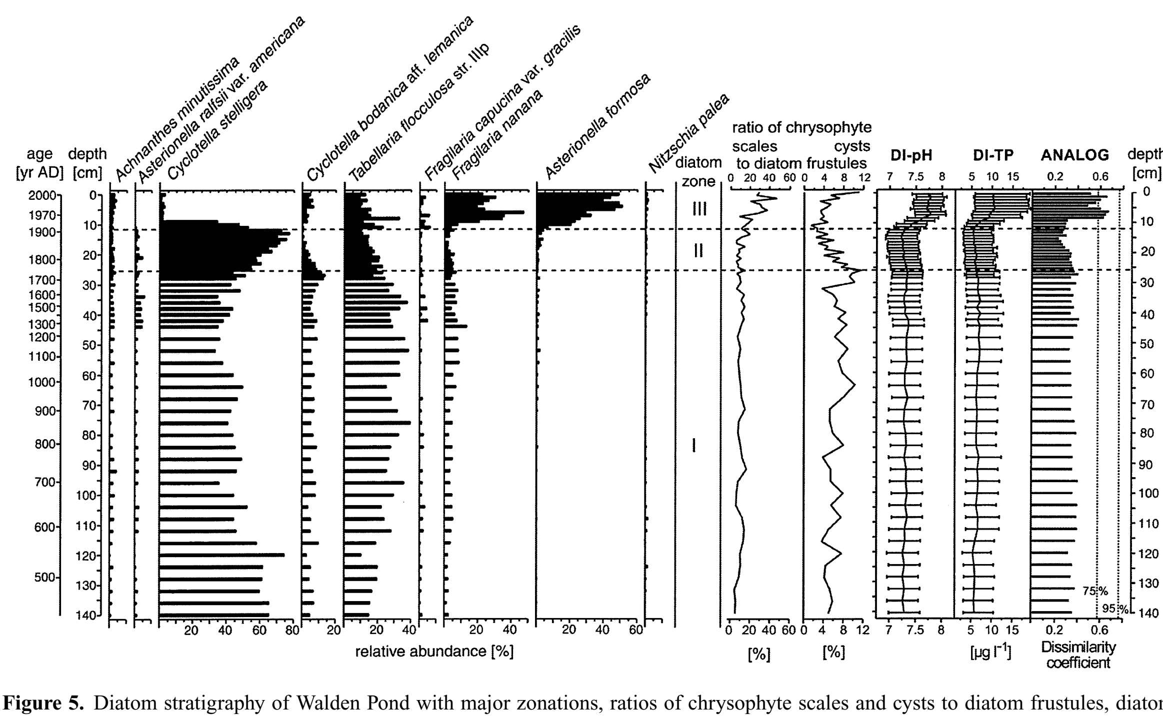

Figure 5. Diatom stratigraphy of Walden Pond with major zonations, ratios of chrysophyte scales and cysts to diatom frustules, diatom-inferred pH (DI-pH) and TP (DI-TP) and analysis of dissimilarity using the program ANALOG. The sample-specific error for DI-pH and DI-TP (for TP back-transformed to μg l^{-1}) is indicated by horizontal bars. Dashed vertical lines in the ANALOG graph indicate the 75% and 95% confidence limits.Values lower than the 75% limit indicate good analogs, values between the 75% and the 95% limits indicate poor analogs.

recent sediments, reaching a maximum of 10 $\mu g\, l^{-1}$ in the 1970s, and remained stable afterwards. The magnitude of these inferred changes, however, remained inside the error range of lower core samples.

Discussion

Major patterns in sedimentary pollen assemblages (Figure 3) reflect the regional land-use history. High abundances of agricultural weeds and parallel declines of tree species between ca. 1800 and 1900 AD are likely associated with the regional maximum deforestation. Pollen abundances of *Fagus* and *Tsuga* also decreased since the 18th century due to land clearance and fire. A peak of the pioneer tree birch in the early 20th century and a subsequent increase of dominant pre-disturbance species of the genera *Quercus* and *Pinus* reflect the regional re-growth of forest.

The clear decline of aquatic macrophytes (*Isoëtes*) spores between 1940 and 1960 AD may be related to changes in water transparency. Today, water transparency is moderate to high (Secchi depth: 2.5–9 m) thereby permitting growth of aquatic macrophytes, mainly the macroalga *Nitella*, between 6 and 13 m (Colman and Friesz, 2001). Deevey (1942) observed high water transparency in 1939, with aquatic mosses found at 15.7 m water depth. Therefore a moderate decline in transparency may have taken place since then.

Fundamental to the interpretation of organic geochemical records in lake sediments is knowledge of the origin of the organic matter. In the Walden Pond sediments, the fine-grained organic matter fraction is dominantly of aquatic origin based on the C/N ratios of near 10 throughout the record (cf., Meyers and Lallier-Verges, 1999). The only exception is the charcoal-rich horizon at 12 cm (~1910 AD), which correspondingly has an elevated C/N ratio of 18.2 and is consistent with organic matter derived from terrestrial sources (Figure 4d).

Human disturbance since about 1770 AD evidently has had a dramatic impact on the nutrient balance of Walden Pond. Large changes observed in the C and N elemental and stable isotope stratigraphy are clearly beyond the range of natural environmental variability observed over the last ~1600 years. Initial removal of catchment vegetation by logging appears to have resulted in an influx of primarily inorganic sediment, based on the decline in % C and % N (Figure 4b, c). Although the decline in organic content could also be interpreted as a reduction in lake productivity, this is less likely given the increase in catchment-derived nutrient loading that probably occurred during European settlement and which has been suggested elsewhere in the region (e.g., Kaushal and Binford, 1999; Hilfinger et al., 2001).

The subsequent increase in organic content at the top of the core may reflect a very recent increase in lake productivity. Alternatively, erosion protective measures in the catchment may be responsible for a reduction in the amount of inorganic sediment entering the lake or this sample may represent freshly deposited sediment that has not undergone degradation.

A number of factors can influence the C and N stable isotope composition of organic matter. For C, these are primarily processes that determine the C isotope composition of lake water dissolved inorganic carbon (DIC), the source of C for aquatic plants. These processes include the lake productivity-respiration balance, CO_2 exchange between the lake water DIC and the atmosphere, and the C isotope composition of DIC derived from soil respiration and bedrock weathering in the catchment (Boutton, 1991). The C isotope fractionation between the C source and aquatic plants can also vary depending on dissolved CO_2 concentrations and HCO_3^- uptake (Hodell and Schelske, 1998). Similarly, the N isotope composition of organic matter is dependent on several factors, including productivity, N transformations in the water column (e.g., denitrification, ammonium volatilization), and the N isotope composition of dissolved nutrients (Talbot, 2001).

Changes in C and N stable isotope records of lakes that have undergone catchment disturbance are frequently attributed to shifts in C and N cycling resulting from increased nutrient loading (Teranes and Bernasconi, 2000; Wolfe et al., 2000; Herczeg et al., 2001). Indeed, trends to lower $\delta^{13}C$ and higher $\delta^{15}N$ values in the initial post-1770 AD interval (Figure 4e, f) are also most likely associated with increased nutrient supply from removal of vegetation in the catchment and, in particular, increased delivery of ^{13}C-depleted dissolved CO_2 and ^{15}N-enriched NO_3^- from soil decomposition processes. Alternatively or in addition, productivity-driven enrichment of the dissolved inorganic nitrogen (DIN) with ^{15}N may have contributed to the positive shift in $\delta^{15}N$ in the lake sediment record. Evidently, similar productivity-driven enrichment of the DIC did not occur in Walden Pond perhaps due to a larger lake water reservoir of DIC compared to DIN. During the past 70 years, these trends have accelerated well beyond the range of natural variability observed over the past 1600 years and are possibly related to ^{13}C-depleted and ^{15}N-enriched wastewater seepage into the lake, although additional analysis of C and N isotope composition of the wastewater at Walden Pond is required to test this hypothesis.

The changes in fossil diatom and chrysophyte assemblages observed in Walden Pond sediments (Figure 5) are likely related to the human-induced changes in nutrient balance at Walden Pond over the past two centuries, as evidenced by comparison of biostratigraphic changes with those revealed by the C and N elemental and stable isotope record.

In Zone I (140–26 cm, ca. 430 to 1750 AD) the dominance of the diatom taxa *C. stelligera* and *Tabellaria flocculosa* str. III p and the presence of *Asterionella ralfsii* and *C. bodanica* aff. *lemanica* indicate that Walden Pond was an oligotrophic, circumneutral to slightly acidic lake between ca. 430 and 1750 AD. The low nutrient content can be explained by the naturally nutrient-poor soils in the catchment and the relatively small watershed from which not much terrestrial material is washed into the lake, as reflected by low C/N ratios. The fossil diatom flora consists mainly of planktonic species, which may be expected in a core taken from the deepest part of the lake. As the coring site is located at 30 m depth, there is likely a large area around the coring site that does not receive enough light to support a benthic diatom population.

In Zone II (26–12 cm, ca. 1750 to 1920 AD) the decrease of *Tabellaria flocculosa* str. III p and the increase of *C. stelligera* between ca. 1750 and 1900 AD coincide with the first known anthropogenic disturbance by timber harvesting in the Walden Pond watershed. The proportion of herbal pollen increased significantly at the same time, from 5 to 30% (Figure 3), indicating an opening of the forest vegetation in the region. Additionally, the decreases in sediment organic matter, % C, and % N (Figure 4a–c) suggest higher mineral inputs through soil erosion caused by logging activities.

Cyclotella stelligera similarly increased following forest clearance in the watershed of British Columbia lakes (Laird and Cumming, 2001), in Michigan lakes (Fritz et al., 1993) and in a Swiss lake (Lotter, 2001) as well as in Adirondack lakes (Rhodes, 1991). Logging in the watershed can lead to nutrient enrichment of lakes (Lott et al., 1994; Carignan et al., 2000). Engstrom et al. (1985) and Stoermer et al. (1985) related higher *Cyclotella* abundances, including *C. stelligera*, to nutrient enrichment. Other studies have indicated that *C. stelligera* may reflect re-oligotrophication (Clerk et al., 2000) and Brugam (1989) reported its decline after almost complete deforestation of Washington lake watersheds. These results suggest that the increasing abundance of *C. stelligera* after ca. 1750 AD reflects the removal of vegetation in the catchment of Walden Pond by logging activities, but that its abundance may decline with further nutrient enrichment.

The decrease in the chrysophyte cyst : diatom frustule ratio between ca. 1750 and 1920 supports the hypothesis of a slight nutrient enrichment. Decreasing abundances of chrysophyte cysts relative to diatoms in lake sediments have been proposed to accompany lake eutrophication (Smol, 1985).

In Zone III (12–0 cm, ca. 1920 to 2000 AD) the striking change from a diatom assemblage associated with oligotrophic conditions and with moderate catchment disturbance, such as discussed above, to one dominated by disturbance indicators, such as *Asterionella formosa* and *Fragilaria nanana,* is likely related to additional nutrient supply derived from increased activity in the watershed (i.e., trail and beach development, railway construction, wastewater seepage, and other recreation activities) over much of the past century. Nutrient-enriched lakes are often characterized by increased abundances of *Asterionella formosa* (e.g., Pennington, 1981; Bennion et al., 2000) and larger *Fragilariaceae*, such as *Synedra delicatissima* W. Smith (Brugam, 1978), *Fragilaria crotonensis* Kitton (Reavie, 2000; Lotter, 2001), *Fragilaria nanana*(Reavie et al., 1995), and *S. nana* Meister (Bennion et al., 2000).

The diatom species shift found in recent sediments probably relates to changes in summer conditions. According to a phytoplankton record of Walden Pond in 1995, *Asterionella formosa* and *Synedra* spp. (likely synonymous with *Fragilaria* spp.) grow during summer in this lake (Baystate Environmental Consultants, 1995). However, *Asterionella* and *Fragilaria* are also common during spring and autumn in lakes throughout North America. The explanation for this difference may be found in the combination of preservation and recreational use of Walden Pond, which is unusual for this region. During most of the year, the lake is almost undisturbed because of the forested watershed and the absence of private houses, whereas during few summer months there are thousands of visitors to the lake, who contribute approximately 27% of the annual P load and 64% of the annual N load (Colman and Friez, 2001). Continuing nutrient (e.g., P) availability and sufficient epilimnetic mixing throughout the summer may permit diatoms to form a richer summer population (Sommer et al., 1986). Maximum nutrient concentrations at Walden Pond were measured in summer in the eastern basin, close to the beach (Table 1). Therefore it is possible that recreational activities in summer were the source for nutrients that support a summer diatom population. This was likely different under the oligotrophic conditions that prevailed during periods preceding the anthropogenic disturbances, because P would have been largely consumed by the spring blooms.

Cyclotella stelligera is also a summer species, yet it is out-competed by *Asterionella formosa* and *Fragilaria* spp. which are good competitors for P (Van-Donk and Kilham, 1990) and which have been shown to be favoured by high total N:total P ratios (Interlandi et al., 1999). The high N:P ratio of 40:1 (average January to August values in the epilimnion and metalimnion, Baystate Environmental Consultants, 1995), indicates that phytoplankton growth is P-limited in Walden Pond. The proposed association between diatom disturbance indicators with summer conditions in Walden Pond (see above) requires testing from comprehensive phytoplankton surveys of the lake over several years and including all seasons. Also, as most nutrient inputs enter the lake on the eastern shore, a more detailed analysis of the eastern basin is necessary to completely characterize the lake's limnology.

The higher relative abundance of synurophyte scales in the recent sediments (Figure 5), mainly produced by *Mallomonas crassisquama,* supports the hypothesis of a nutrient enrichment of Walden Pond. This species also proliferated following nutrient addition to an Experimental Lake in western Ontario, Canada (Zeeb, 2004). Preliminary counts of synurophyte scales in another core, taken at Walden Pond in 1979, showed striking changes in species composition at about 1900 AD (John P. Smol, Queen's University, Kingston, ON, pers. comm.), coincident with the major change in the diatom assemblages in zone III. Taxa associated with undisturbed conditions and that are now quite rare, such as *M. lelymene* Harris and Bradley and *M. allorgei* (Deflandre) Conrad, dominated the pre-disturbance sediments. In the recent sediments, they were replaced by taxa indicating higher nutrient availability, such as *M. elongata* Reverdin and *M. caudate* Iwanoff. Thus, the changes in chrysophyte populations also reflect the nutrient enrichment of Walden Pond.

The chrysophyte cyst proportions remained lower during the 20th century than during pre-settlement times, indicating a higher trophic state. The upper three samples (1995–2000 AD) showed increasing proportions, indicating decreasing nutrient concentrations. The stability in chrysophyte cyst proportions during the early 20th century seems to contradict the increasing synurophyte scale:diatom ratio at the same time. The explanation may be that only the Synurophyceae bear scales, such as the dominant *M. crassisquama* in the recent sediments of Walden Pond. However, cysts are formed by scaled and non-scaled taxa from several chrysophyte groups. It is therefore possible that scales were more abundant due to this scaled species following nutrient enrichment, but that overall chrysophyte and cyst abundances (consisting mainly of oligotrophic species) remained low.

During the last ca. 20 years, diatom assemblages seem to have stabilized, probably indicating a reduced rate of eutrophication. As first management measures for water quality protection were implemented in 1975, these measures may have indeed reduced the nutrient loading to Walden Pond during summer.

Analog and Goodness-of-fit analyses have shown that the reconstructions are reliable for all levels, with the exception of levels 0–8 cm. Poor analogs and fit were detected for these uppermost levels, although all dominant fossil species are present in the model. The poor analogs result from high abundances of few species in our fossil samples (e.g., *Fragilaria nanana*, *Asterionella formosa)*, which is not the case in the training set lakes, where these species are present at lower abundances. This is likely due to higher relative abundances of benthic taxa in the training set lakes, which are generally shallower than Walden Pond. We assume that useful ecological parameters (species optimum and tolerance) have been estimated for the models and that they are therefore appropriate for inferring pH and TP in our sediment core.

From ca. 430 to 1880 AD (diatom zones I and II), diatom-inferred pH and TP remained constant, reflecting the stable diatom assemblages (Figure 5). The DI-TP of 5–6 $\mu g\ l^{-1}$ indicated oligotrophic conditions. The circumneutral character of the dominant species was reflected by the DI-pH, which fluctuates between 7.2 and 7.3.

A rapid increase in DI-pH by 0.5 units occurred between ca. 1920 and 1960 AD, reflecting the abrupt change in species composition from zones II to III. A rise in pH may indicate higher primary productivity in the lake. Phytoplankton and macrophytes remove CO_2 from the water column by photosynthetic assimilation, thereby driving the bicarbonate balance towards the alkaline end. PH measurements in recent years have shown peak values of 9 and more in the epilimnion during summer (Colman and Friesz, 2001), suggesting a temporally alkaline environment generated by high primary productivity.

Alternatively, pH can increase due to higher base cation concentrations (i.e., higher alkalinity). The source of such ions can be diverse: soluble inorganic material (Mg^{2+}, Ca^{2+}) may be washed into the lake by runoff over eroded soils, as suggested by lower organic N and C contents in the sediments beginning in zone II and persisting through zone III. An explanation for an increase in alkalinity may also be the higher in-lake productivity attributable to higher nutrient levels from logging and recreational use as discussed above. Increased deposition of organic material causes oxygen depletion in the hypolimnion of Walden Pond during late summer and autumn (Baystate Environmental Consultants, 1995; Colman and Friesz, 2001; Köster, unpubl. data) permitting sulphate reduction and denitrification in the hypolimnion, as well as release of base cations from sediments (Schindler, 1986; Psenner, 1988). Manganese, Fe, P and ammonia concentrations were high in the hypolimnion near the sediments in late summer (Colman and Friesz, 2001), indicating that alkalinity was in fact generated in the anoxic hypolimnion and at the sediment/water interface.

Higher DI-TP values in the top of the core support the evidence of rising nutrient levels at Walden Pond, which was provided by stable isotopes and chrysophytes. However, this change is subtle with 5 μg l^{-1}. Given the drastic changes in diatom species composition, and changes in geochemistry and stable isotope composition that were attributed to an increase in nutrient loading, the small increase in diatom-inferred TP is surprising. However, the reconstructions correspond well with the instrumentally recorded mean annual TP levels in the western basin that remained below 10 μg l^{-1} between 1997 and 1999 (Table 1). Yet, some summer samples during this time show a deviation from the mean (ca. 20 μg l^{-1}; Table 1). The shift in the diatom community of the western basin to one dominated by species typical of nutrient-enriched waters is probably due to these moderate seasonal P maxima, as discussed above. During seasons when Walden Pond is not subject to intense recreational use (e.g., spring and autumn) the lake water returns to lower nutrient concentrations ($<$10 μg l^{-1}), probably allowing proliferation of diatoms with low TP optima, such as *Cyclotella bodanica* and *Tabellaria flocculosa* str. III p. For quantitative reconstructions based on fossil samples that integrate all seasons, this means that species with low-TP optima may partly balance out the effects of species with high TP optima growing during summer.

Although the lake is presently considered to be oligo- to mesotrophic and its clear water suggests a 'natural state,' the geochemical and diatom records in the sediments of Walden Pond indicate substantial changes in the nutrient balance of the lake due to human impact during the last three centuries. The low susceptibility of the lake to exhibit evident signs of eutrophication, such as turbid water caused by phytoplankton blooms may be due to its great depth, its small watershed, and the fact that it is mainly fed by groundwater. Human-derived nutrients added to the lake in the summer may be used up by planktonic organisms, which subsequently transfer the nutrients by sedimentation to the lake bottom. However, increased nutrient inputs to Walden Pond through erosion and recreational use during much of the 20th century have left a signature in the lake sediments, which have the potential of being recycled into the lake water column. Active bacteriological decomposition of organic matter leads to oxygen-depleted conditions in the hypolimnion of the lake in late summer and autumn, permitting recycling of sedimentary nutrients to the water column and up-welling during full circulation periods. If high nutrient inputs during summer persist, past and present nutrient loads may lead to further eutrophication of Walden Pond.

Stable diatom assemblages and increasing chrysophyte cyst proportions in the uppermost sediments suggest that initial management practices applied in the 1970s have halted the process of eutrophication. Current preventive measures to reduce nutrient loading including the monitoring of groundwater down gradient from the septic leach field and of oxygen content in the hypolimnion, storm water runoff control, and public awareness activities (Colman and Friesz, 2001) should therefore continue. Given the difficult interpretation of the available limnological records due to highly variable sampling protocols, continued monitoring using standardized sampling and analysis methods are of great importance. If signs of further eutrophication, such as more frequent anoxia in the hypolimnion, are observed, or if nutrient contamination of the groundwater starts to increase, more effective wastewater treatment and reduced recreational usage may be necessary to protect Walden Pond from further water quality deterioration.

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