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Response of three paleo-primary production proxy measures to development of an urban estuary

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Abstract

In this study we present a novel comparison of three proxy indicators of paleoproductivity, pigments, biogenic silica (BSi), and cysts of autotrophic dinoflagellates measured in cored sediments from New Bedford Harbor, Massachusetts. In addition to detailed historical reports we use palynological signals of land clearance, changes in the ratio of centric and pennate diatoms, sedimentary organic carbon and stable carbon isotopes to constrain our interpretations. Our study spans the period from prior to European settlement to ~1977, during which watersheds were cleared, port development occurred and much of the coastal property became industrialized. The combined effects of nutrient loading from watershed clearance and urban sewage on the estuarine ecosystem shifted not only levels of primary production, but also the nature of the production. Our proxies show that when European colonists first arrived the estuarine production was benthic-dominated, but eventually became pelagic-dominated. Importance of water column production (by diatoms and dinoflagellates) rapidly increased as soil nitrogen was released following forest clearance. Stabilization in rates of forest clearance is reflected as a decline in production. However, population increases in the urbanizing watershed brought new sources of nutrients through direct sewage discharge, apparently again stimulating primary production. We assume that early 20th century changes in sewage discharge and introduction of heavy metals into Harbor waters caused a temporary reduction in primary production. The introduction of a new sewer outfall near the core site and changes in estuarine hydrography due to construction of a hurricane barrier across the mouth of the harbor are reflected by renewed water column production, but decreases in the population of diatoms and dinoflagellates. Fossil pigments suggest renewed water column production in the latest years recorded by our sediment core. However, the sediment record also suggests decreased populations of diatoms and dinoflagellates. These most recent changes are probably associated with introduction of a new sewage outfall near the core site a hurricane barrier, which altered hydrographic conditions.

Keywords: Buzzards Bay; Urbanization; Forest clearance; Industrialization; Algal blooms; Pollution; Phytoplankton; Benthic algae

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1. Introduction

Studies of paleoproductivity have been used to document human and climatic impacts on lake and marine ecosystems. Four indicators have been used for paleo-primary productivity: sedimentary concentrations of diatoms, dinoflagellate cysts, biogenic silica (BSi), and degradation products of algal pigments (fossil pigments). Perhaps the most commonly used indicator of paleoproductivity is the accumulation of frustules of diatoms, an important autotroph in aquatic systems, in the sediment record. Concentrations of BSi have been shown to closely correlate to diatom cell counts in lakes (Schelske et al., 1983) and have been used to demonstrate impacts of nutrient loading in Chesapeake Bay (Cooper, 1995), the Gulf of Mexico (Turner and Rabalais, 1994), and in the Weddell Sea (Shimmield et al., 1994). However, under continued high loading of nitrogen in marine waters or phosphorus in lakes, diatom production may become limited by available dissolved silica in the water column (Conley et al., 1993) and be replaced by autotrophic dinoflagellates or nanoplankton. In such situations, a record of increased autotrophic production is no longer recorded by diatom cell counts or BSi deposited from the diatom population.

If dissolved silica becomes limiting, shifts in phytoplankton communities may favor dinoflagellates (Hecky and Kilham, 1988). The increased problem of dinoflagellate blooms in the late 20th century has been attributed in part, to degradation of coastal water quality (Paerl, 1988; Anderson et al., 2002). During sexual reproduction some dinoflagellate species produce a dormant cyst that is readily preserved as a fossil record of that portion of the living population (Dale, 1996). Unlike pigments, that may be subject to degradation, or BSi, that can be subject to dissolution from sediments (e.g. Yamada and D'Elia, 1984; Conley and Schelske, 1989) many dinoflagellate cyst taxa are relatively robust with respect to diagenetic processes. The most common studies of dinoflagellate cysts are found in paleoceanographic research where they have been used as an indicator of climate change (e.g. de Vernal et al., 1991b; Sawada et al., 1999). However, variability in sedimentary concentrations of cysts also has been the basis for inference of increased dinoflagellate production in estuarine (de Vernal et al., 1991a) and marine (e.g. de Vernal and Mudie, 1992) environments. Their use as indicators of changes in water quality is rare with reported studies limited to Norwegian fjords (e.g. Dale et al., 1999), Tokyo Bay (Matsuoka, 1999, 2001) and most recently Buzzards Bay, Massachusetts (Pospelova et al., 2002). We have not located any paleoceanographic or estuarine studies that compare cyst concentrations to other proxy measures of paleoproductivity in a single core.

Aquatic sediments accumulate pigments from all photosynthetic autotrophs (Sanger, 1988). The pigment record could thus indicate continuous diatom production if preservation of siliceous frustules is prevented by a silica limitation or replacement of diatoms by other autotrophs when BSi or diatom records show a decline in production of that portion of the phytoplankton. However, preservation of the pigment record can be problematic as photodegradation can occur in the water column (Carpenter et al., 1986) and diagenesis will occur in toxic sediments (Gorham et al., 1974). Despite these problems, Brush (1984b) demonstrated that algal pigments (chlorophyll degradation products) preserved in sediments reflected water quality changes in the upper Chesapeake Bay where pigment flux increased by an order of magnitude at the time of introduction of urban sewage.

In this study we make a novel comparison of three proxy measures of estuarine primary productivity: pigments, BSi, and dinoflagellate cysts. By examining them in the context of a detailed historical record we can determine if they reflect predictable responses to inputs of nutrients and toxins over the history of a notoriously polluted estuary, New Bedford Harbor, Massachusetts. In addition, to detailed historical reports we use palynological signals of land clearance, changes in the ratio of centric and pennate diatoms, changes in dinoflagellate cyst taxa, sedimentary organic carbon, and stable carbon isotopes to constrain our interpretations. As this is the first study (of which we are aware) that compares the response of all three indicators of paleo-primary productivity in either freshwater or marine ecosystems—we assess the veracity and practicality of the proxies.

2. Study area

2.1. The estuary and watershed

New Bedford Harbor is situated in the lower reaches of the Acushnet River estuary. The estuary is a relatively small system with a surface area of 73.3 km^2 and a watershed area of 69.5 km^2 (Fig. 1).

This region was subject to Wisconsinan glaciation and soils are derived from till or glacial outwash. Upland soils of the watershed are comprised of either Hinckley (a sandy Entisol), Paxton (a coarse-loamy Spodosol), or Woodbridge and Whitman (both coarse-loamy Inceptisols) soil series (Roffinoli and Fletcher, 1981). The Hinckley soils, found in the upper reaches of the watershed, are derived from glacial outwash. These are excessively drained, with an average clay content of $<1\%$ and as much as 75% sand. In the lower basin Paxton, Woodbridge, and Whitman soils are derived from compact glacial tills, relatively impervious to percolation. These soils are shallow with maximum depth of 33–76 cm, and coarse-grained with average clay content $<5\%$.

2.2. The harbor ecosystem

Turner et al. (2000) conducted a 9-year program (141 cruises from October 1987 to September 1998) monitoring environmental parameters around Buzzards Bay. Their sample station 8 is in the area of our core sample site in New Bedford Harbor, and we use their results to characterize water chemistry and phytoplankton of the waters. In New Bedford Harbor waters are shallow and well mixed. Over the sampling period salinity was generally 30 ppt, but did decrease immediately after rain events. Surface temperatures vary seasonally, ranging from -2 to 27 °C. Of all Buzzards Bay sample stations the New Bedford Harbor station has the highest average chlorophyll a concentration (12.84 mg l^{-1}) and second highest total ammonium (4.09 μM), phosphate (1.67 μM) and dissolved silicate (8.63 μM) levels.

By using Utermols iodine solution as a preservative for phytoplankton samples, Turner et al. (2000) avoided the disintegration of microflagellate that commonly occurs when conventional formalin-based preservatives are used. As at most stations sampled in Buzzards Bay, they found that microflagellates and phytoflagellates dominated (by cell count) the phytoplankton assemblage of New Bedford Harbor with phytoplankton in the following abundance: 74% microflagellates, 17% phytoflagellates, 8% diatoms, and 1% dinoflagellates. Bacterioplankton densities were second highest of all staions sampled, 3.46×10^6 cells ml^{-1}.

Eelgrass (*Zostera marina*) is virtually absent from New Bedford Harbor, but is common in the waters of Buzzards Bay where it accounts for as much as 11–40% of production when it is present in shallow embayments (Costa, 1988). There is little information on the historical distribution of eelgrass in New Bedford Harbor, specifically, but salinity, temperature and water depths are not limiting to its growth (Costa, 1988) so we can assume that it was an important component of the estuarine habitat prior to harbor development. In his review of the historical distribution of eelgrass in Buzzards Bay Costa (1988) notes that after the devastating wasting disease of 1931–1932, recolonization of eelgrass in New Bedford Harbor was limited compared to other parts of the Bay, presumably due to human modifications of the harbor environment. The few remnant eelgrass beds present disappeared after construction of the hurricane barrier in the 1960s.

2.3. Harbor history

Comprehensive histories of harbor use and watershed development are available in reports by Voyer et al. (2000) and Pesch and Garber (2001). Some of the salient details from their histories are reported here.

When Bartholomew Gosnold landed on the shores of New Bedford Harbor in 1602 he reported the presence of a large native population. In the following years, European settlements in the region were small and scattered. The first permanent settlement of the New Bedford Harbor watershed followed the conclusion of King Philip’s War in

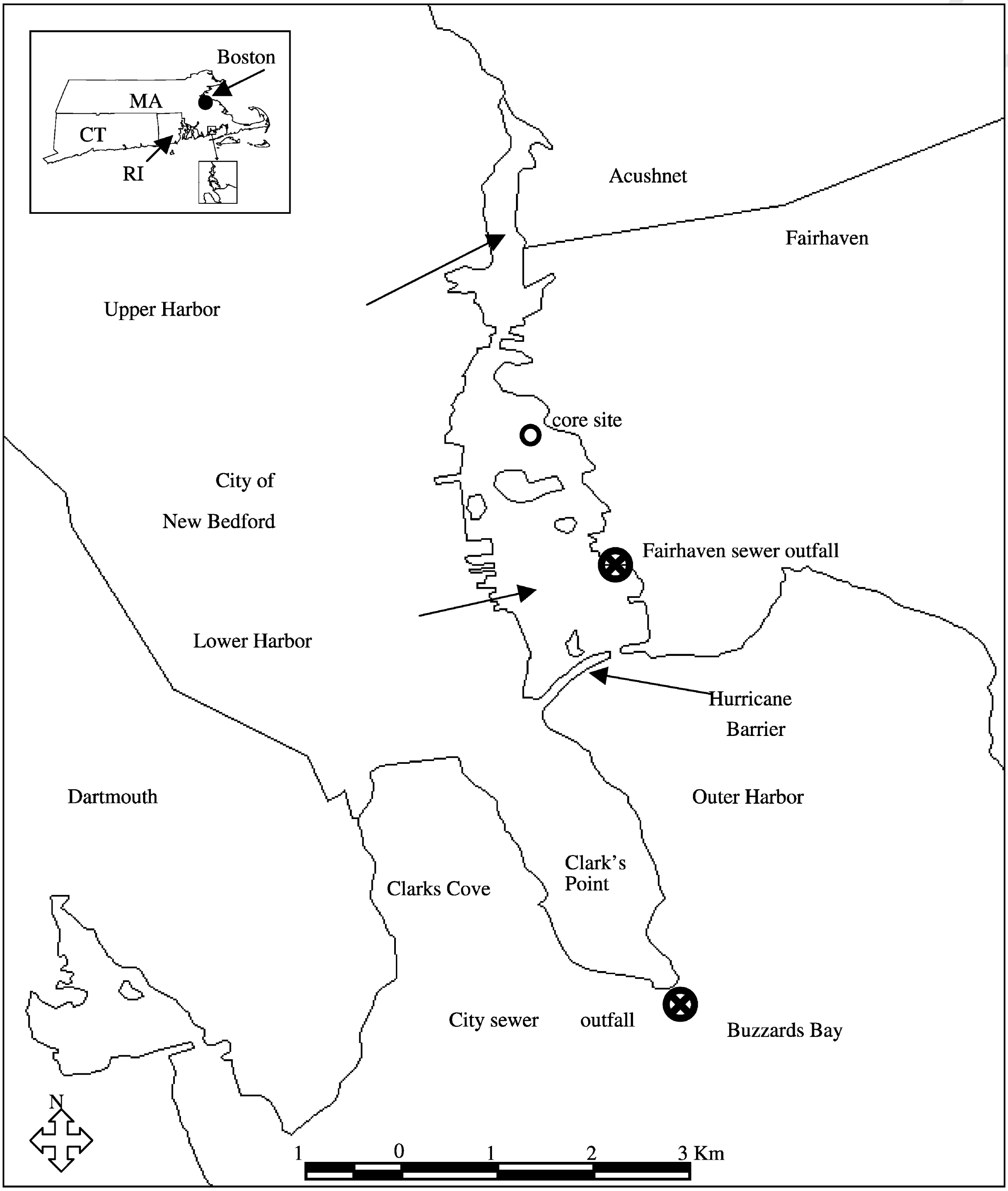

Fig. 1. Map of New Bedford Harbor and Buzzards Bay. Inset map shows general location.

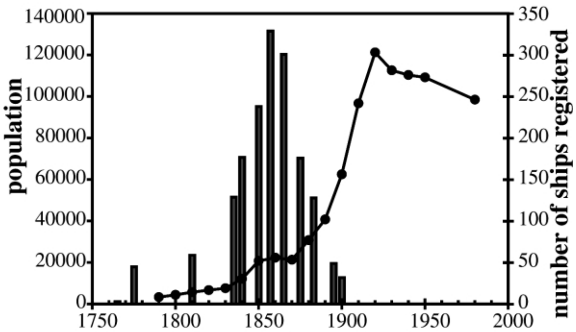

Fig. 2. Historical record of number inhabitants (black dots) in the New Bedford area and ships registered in the port (columns).

1676 when native raids on local colonist settlements subsided (Voyer et al., 2000; Pesch and Garber, 2001).

At the time of first European settlement terrestrial vegetation was dominated by oak forest, typical of southern New England. Until the middle of the 18th century the primary activity in the watershed was subsistence farming and, based on the size of the typical New England farm, Pesch and Garber (2001) estimate roughly 4% of the forested watershed was cleared. The importance of farming decreased as New Bedford's harbor became an important port for whaling vessels.

From 1750 to 1850 New Bedford grew to become the world's largest whaling port (Voyer et al., 2000). By the mid 18th century, growth of the whaling industry brought major changes to the harbor and its watershed. Bridges and wharves were constructed (wharf area = 37 acres), changing the hydrographic properties of the estuary (Voyer et al., 2000). Local construction of ships registered in the Harbor (Fig. 2) and wharves created a demand for lumber so that by 1834 the wooded area of the watershed was reduced by 50%. Because of the resultant sediment accumulation the US Army Corps of Engineers began to dredge ship channels in 1839.

As petroleum replaced whale oil the economy of the city shifted to one based on textile industries, and the number of whaling ships registered in the harbor dramatically declined. From 1890 to 1920 the number of mills and population grew steadily until 1920. It is likely that discharges from these mills were minor, as their major functions were spinning and weaving, rather than dyeing and finishing—the latter two notorious for release of chemical discharges into waterways. However, the construction of mills led to the loss of 0.54 km^2 of wetlands in the watershed and sewage from the burgeoning population was discharged directly into the harbor. By the late 19th century sewage was a major health issue and in 1912 the city of New Bedford began construction of an interceptor sewer line, which directed discharge off Clark's Point, outside the harbor (Fig. 1). In 1969 a wastewater treatment facility built to handle sewage from the town of Fairhaven, on the eastern side of the harbor, began to discharge into the lower harbor (Fig. 1).

During the 20th century additional industrial development resulted in discharges of a variety of heavy metals and organic chemicals into the Harbor. Use of polychlorinated biphenyls (PCBs) by local manufacturers of electrical capacitors resulted in the release of large quantities of PCBs into the Harbor. Because of the high concentration of PCBs in harbor sediments, New Bedford Harbor was placed on the US Environmental Protection Agency's National Priority List for cleanup in 1982 (Nelson et al., 1996).

2.4. Climate

The 30-year (1951–1980) average annual monthly air temperature at New Bedford is 11.3 °C (Environmental Data and Information Service, 1983). Mean monthly temperatures are above 0 °C 12 months of the year, but minimum temperatures are below 0 °C from December to February, with the lowest monthly mean in January (−4.0 °C). The Upper Harbor freezes for some period during most winters.

Baron and Gordon (1985) used a combination of historical and instrumental records to reconstruct climate parameters in eastern Massachusetts over the period 1600–1980. They provide a reconstruction of winter air temperatures for 1742–1980, but the record is incomplete, missing the period 1780–1825. From 1742 to 1895 average winter temperatures were below 0 °C. After this period, winter temperatures were more variable, but remained above 0 °C for 19 years of their record.

3. Methods

3.1. Core collection and storage

In 1998 sediments were collected from a boat by pushing a core tube into the sediment in water depths of 2.3 m of lower New Bedford Harbor (Fig. 1). Geographic coordinates of the core site are 41.65° N and 70.92° W. After collection, the core was brought to the laboratory and immediately frozen and stored at −20 °C. The core was then thawed under controlled temperature (4 °C), extruded and sectioned into 1–3-cm intervals. Core samples to be used for pigment analysis were placed in glass vials, purged with nitrogen, sealed with Teflon caps and frozen at −20 °C. Sediments were subsampled in sections ranging from 1 to 3 cm thick. This core, NBH5C, was collected as part of a larger study described by Latimer et al. (in press), but was the only core retrieved that included extensive sediments deposited before European settlement, and the only core with sediment storage appropriate for pigment analysis.

3.2. Pigments

Prior to pigment extraction the samples were freeze-dried in the dark for 24 h. Freeze-dried sediments (0.5–1 g) were transferred to 20 ml glass vials containing 3 ml of 100% cold acetone. Pigments were extracted three times by sonication in a water bath at 4 °C. The combined solvent extracts were evaporated under a stream of N_2 to a final volume of 3 ml and filtered through a 0.45 μm acrodisc PTFE membrane filter for instrument analysis.

Quantitative analysis of all pigments was conducted with a Waters 2690 HPLC separation module coupled with 996 photodiode array detector (PDA) and a 474 fluorescence detector with excitation set at 410 nm and emission at 660 nm. The PDA detector was operated at 665 and 410 nm. A chromatographic procedure was developed for the analysis of fossil chlorophyllous pigments (FCPs) based on a reverse-phase YMC carotenoid column (4.6×250 mm, with 5 μm particle size). The elution gradient has been adapted from that of Wright et al. (1991) and modified for the analysis of polar and non-polar FCPs. The elution gradient program (1 ml min^{-1}) began with 40% solvent A (methanol), 40% solvent B (acetonitrile), and 20% solvent C (1 M aqueous ammonium acetate, pH 7.2). It was then ramped to 80% A, 10% B, and 10% C in 3 min, with an isocratic hold for an additional 10 min. Next, it was changed to 20% A, 20% B and 60% D (ethyl acetate) in 20 min followed by a linear ramping to 10% A and 90% D in 25 min. The column was re-equilibrated between samples by linear ramping to the initial conditions over 5 min and maintenance for another 5 min. Aliquots of 100 μl were mixed with 50 μl of 1 M aqueous ammonium acetate before analysis.

FCPs were identified by photodiode spectra and fluorescence data. The concentration was calculated from the summed absorbances at 665 nm of all the individual chlorophyll derivatives identified by HPLC and expressed as equivalents of ZN (II) pyropheophorbide octadecyl ester per gram of dry sediment (Villanueva and Hastings, 2000). The standard ZN (II) pyropheophorbide octadecyl ester was chosen in this case due to its structural parallels to the chlorophyll derivatives, good chemical stability and availability at our lab.

3.3. Biogenic silica

Concentrations of biogenic silica (BSi) were determined using a wet alkaline extraction technique (Conley, 1988). Three replicate extractions were run on each sample. With each set of replicates we included a standard sample from oligotrophic Still Pond, Chesapeake Bay (Conley, 1998). Our measurement of BSi concentrations of this standard averaged 2.57±0.32 mg g^{-1}.

3.4. Diatoms

Diatom extraction was performed using Jerković's (1977) adaptation of a method developed by Houstedt in 1930 (cited by Jerković, 1977), in which samples are chemically treated with H_2SO_4, $KMnO_4$, $(COOH)_2 \cdot 2H_2O$ and H_2O_2 interspersed with washing and rinsing steps. The diatom fraction was then separated from the coarse sand fraction using settling techniques.

After the chemical treatment each sample was diluted with distilled water to achieve approximately equivalent densities of diatoms. A small quantity of the suspension was mounted on a glass slide with Naphrax. Diatoms were counted as pennate or centric on the basis of the shape of the frustule. This was done using a 630× magnification objective and by making transects equally distributed along the slides. A minimum of 604 frustules (302 diatoms) was counted for each sample. The relative abundance of these two groups were compared and expressed as the C:P ratio.

Centric diatoms are generally pelagic and pennate forms are predominantly found in benthic habitats: growing on the sediment surface (epipelic) or as epiphytes on submerged aquatic vegetation. Thus, the C:P ratio reflects the relative populations in pelagic and benthic systems (Cooper, 1995).

3.5. Pollen and dinoflagellate cysts

Samples for pollen and dinoflagellate cysts were treated using a standard protocol described by Pospelova et al. (2002). Calibrated tablets of *Lycopodium* spores (Stockmarr, 1977), added during processing, allowed for calculation of dinoflagellate cyst concentrations based on the dry weight of sediments.

Aliquots were mounted on glass slides with glycerin jelly. Pollen was identified with reference to published keys (e.g. McAndrews et al., 1973; Moore et al., 1991) and the reference collection of the McGill Geography Department. Identification of dinoflagellate cysts was made on the basis of published descriptions in accordance with taxonomy given in Lentin and Williams (1993), Head (1996), Rochon et al. (1999) and Head et al. (2001) and Pospelova and Head (2002).

3.6. Sediment carbon

Stable carbon isotopes and percentage of organic carbon were measured by continuous flow elemental analysis/isotope ratio mass spectrometry (EA/IRMS) as described by Latimer et al. (in press).

Table 1
Rate of sediment accumulation in New Bedford Harbor core 5C, determined through radionuclide profiles and chemical and pollen stratigraphies

Depth cm	Accumulation rate cm year^{-1}	Age per cm year	Flux g cm^{-2} year^{-1}
0–1	0.39	2.6	0.17
1–6	0.38	2.6	0.23
6–16	0.34	2.9	0.21
16–100.5	0.33	3.0	0.18
100.5+	0.07–0.09	11.1–15.2	0.06

3.7. Dating

The top 16 cm of core was dated using the radionuclides lead-210 and cesium-137 as described by Latimer et al. (in press). Rates, shown in Table 1, were constrained by the sedimentary profiles of PCBs and total lead. Dating indicated that the top layers were lost in coring and that surface sediments (our 0 cm-depth) correspond to ~1973. Cesium-137 cannot date sediments older than 1953 and lead-210 generally cannot date sediments older than 100 years due to lower concentrations in marine sediments, thus other dating methods are needed for the lower section of the core.

When landscape or vegetation change can be associated with a known time period, stratigraphic pollen profiles can be used to develop a chronology. In North America the forest clearance associated with European settlement can be detected by an increase in weed pollen, particularly ragweed (*Ambrosia*) in sediments deposited during that period (e.g. Brugham, 1978; Brush, 1984a). If the early history of the area is known, then the pollen stratigraphy provides a dating tool.

In New Bedford sediments the percentage of ragweed pollen fluctuates, but increases consistently above 90.5 cm (Fig. 3). We associate the consistent production of ragweed pollen with 1676 when Europeans became established in the local area (Pesch and Garber, 2001) and in previous reports on our studies of New Bedford Harbor we have designated the age of the 90.5 depth as 1676

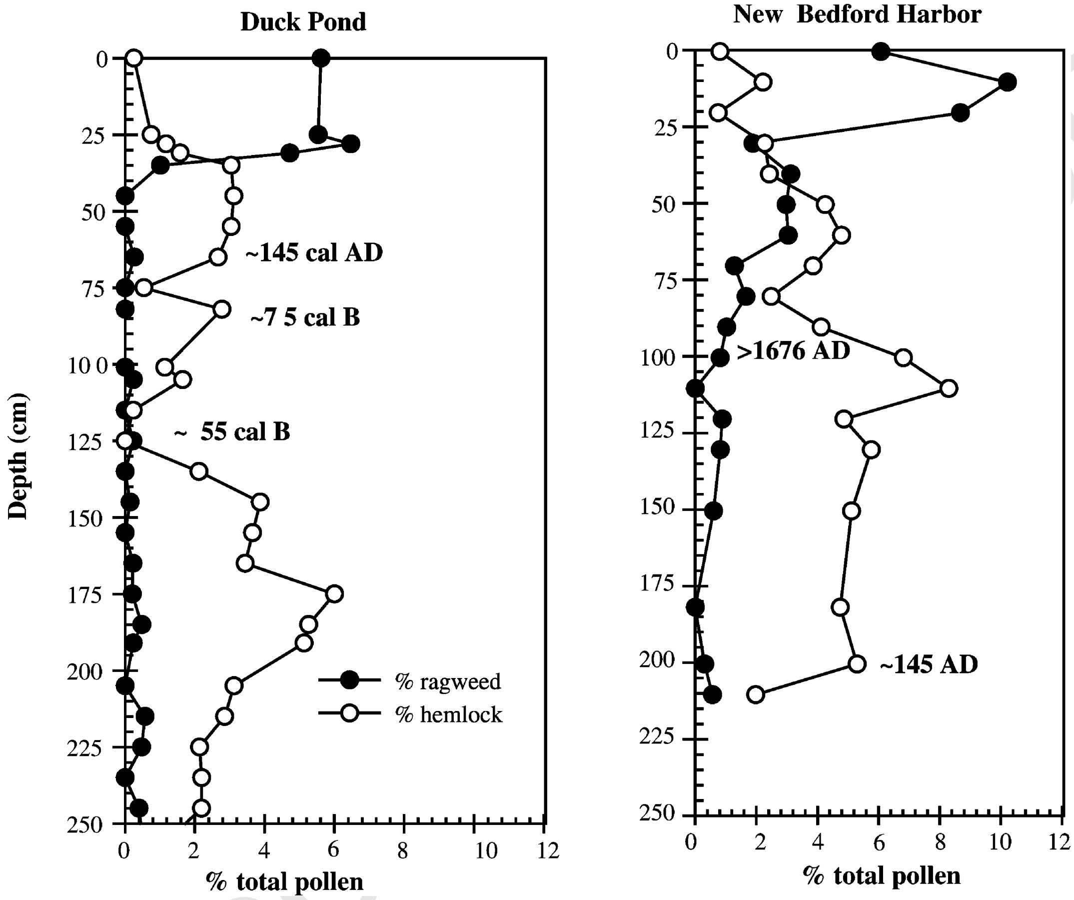

Fig. 3. Percent ragweed and hemlock pollen with depth in cores from Duck Pond, (Winkler, 1985) and New Bedford Harbor, Massachusetts. Duck Pond pollen data were obtained from the global pollen database (www.ngdc.noaa.gov/paleo/gpd.html).

(Latimer et al., in press; Pospelova et al., 2002). However, in a recent report Swales et al. (2002) detected lag in transport of pollen from watershed to estuary. Changes in relative abundance of dinoflagellate cyst taxa suggest that environmental change is recorded at the 100 cm depth (Pospelova et al., 2002). For instance, the percentage of *Spiniferites bentorii* and *Dubridinium* spp. is higher at 100 cm than at any previous level thus, earlier period (Fig. 4). Both taxa continue to increase with shallower depths. *Alexandrium tamarense*, noted for production of harmful algal blooms, occurs for the first time at ~100 cm depth. Finally, the relative abundance of *Lingulodinium machaerophorum* begins a decline at this same level. Thus, we make the assumption that there was a lag in transport and deposition of ragweed pollen and that 100.5 cm more closely corresponds to 1676, but present both chronologies in graphs of the data.

Below 100-cm depth, fluctuations are probably associated with natural variability in vegetation cover, earlier unsuccessful settlements, or small-scale native clearing (Cronon, 1983). A constant presence of ragweed pollen above 100 cm indicates that forest regrowth was prevented (Chmura et al., 2000), consistent with the local settlement pattern.

We could not isolate enough terrestrial carbon from lower sediments to perform carbon-14 dating. To extrapolate below the settlement horizon requires that we assume sedimentation rates before human settlement are equivalent to those following, despite dramatic land cover change. Such an assumption would be contrary to findings in other regions (e.g. Brush, 1984a).

We can employ pollen stratigraphies to constrain the time of deposition of the lowermost sediments by comparing the New Bedford Harbor pollen record to a dated pollen record from the region. The nearest dated pollen record with adequate resolution, dating control and site characteristics is from Duck Pond (41°55′N, 70°00′W) on Cape Cod. Winkler (1985) performed carbon-14 dating at seven different depths of her 428-cm deep core. Her pollen stratigraphy shows presence of hemlock above 250 cm, but a temporary decline of hemlock pollen by 125-cm depth (Fig. 3). Davis (1981) pointed out that the decline of hemlock was a rapid phenomenon occurring throughout the eastern United States. Annually laminated deposits from Pout Pond, New Hampshire showed that it took 1900 year for hemlock pollen to recover from its pre-decline levels (Allison et al., 1986).

To constrain dating of earliest sediments from our New Bedford Harbor core we compare its pollen stratigraphy to the one from Duck Pond. Since Winkler's original report new techniques for calibration of carbon-14 dates have been made available. We have recalibrated her original dates using OxCal version 3.5 (Bronk Ramsey, 1995) and present the equivalent calendar years in Table 2. Rates between dated levels are calculated by linear extrapolation.

Table 2
Radiocarbon dates (Winkler, 1985) for Duck Pond sediments. Modern calibrations calculated in this study using OxCal (Bronk Ramsey, 1995)

Depth (cm)	Lab no.	Radiocarbon age		Calibrated age	
		year	S.D.	year	error
52.5	WIS-1300	1280	70	770 AD	260
137.5	WIS-1270	4650	70	3425 BC	125
251.0	WIS-1391	8230	90	7270 BC	210

The New Bedford Harbor pollen stratigraphy shows a decline of hemlock concurrent with a ragweed increase, attributable to the impact of European forest clearance, but no major decline prior (Fig. 3). Thus, the core bottom is most likely

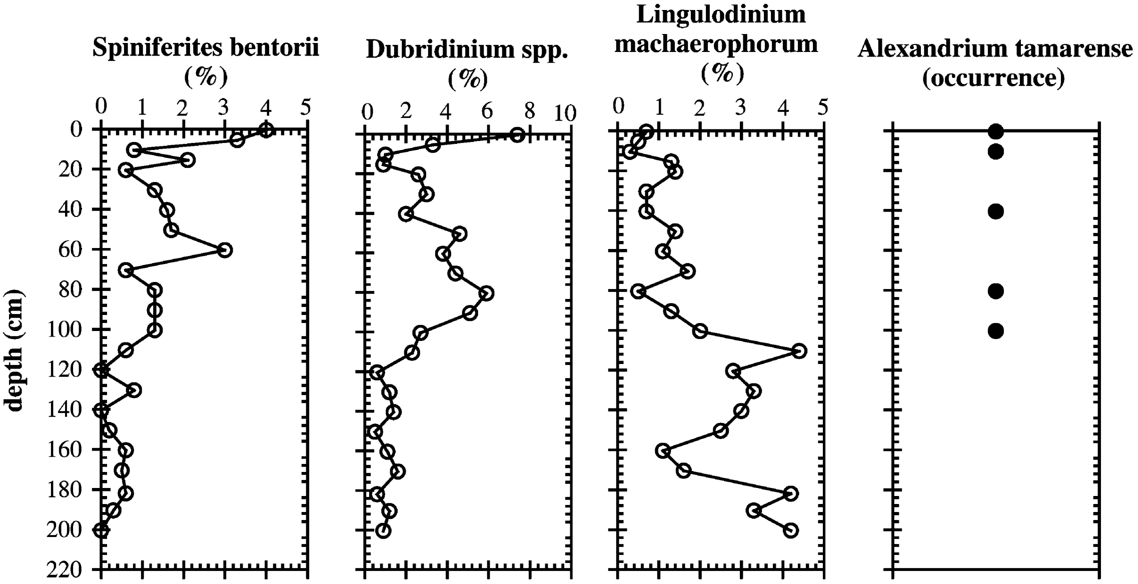

Fig. 4. Proportions of three dinoflagellate cyst taxa in core 5C, New Bedford Harbor. The fourth plot, for *A. tamarense*, represents simply presence or absence of these cysts in slide counts.

younger than 2855 cal BC, the time of hemlock decline at Duck Pond. The lowest two samples in the New Bedford Harbor core show a large increase in hemlock pollen that could represent recovery after the hemlock decline or simply a fluctuation after the regional recovery. If the increase in hemlock just above the bottom of the New Bedford Harbor core (from 210.5 to 200.5 cm) is concurrent with the initial recovery that peaked at 82-cm depth at Duck Pond, an appropriate age for the 200.5-cm depth in the New Bedford Harbor would be 705 cal. BC. It is more likely that the hemlock increase at New Bedford is concurrent with the Duck Pond increase that occurs at 65-cm depth. Thus, the *maximum* age attributable to the 200.5-cm depth at New Bedford is probably around cal AD 145, providing an accretion rate prior to European settlement of 0.07 cm year^{-1}, one-fourth that occurring after settlement. Considering that the carbon-14 date used to calculate this rate has an error of 260 years, we recognize that sediment accumulation rates (at depths $>$100.5 cm) based upon this maximum possible age ranges from 0.07 to 0.09 cm year^{-1}. Thus, a single centimeter in this lowermost section may represent 15.2–11.1 year and less.

We use the results from radionuclide and pollen dating to calculate total flux, or accumulation rate (cm^{-2} year^{-1}) of each parameter, which is the product of the concentration (number or mass per unit of dry wt of sediment), the sedimentation rate (cm year^{-1}), and the dry sediment bulk density (g cm^{-3}). Examples of ages various sediment depths are provided in Table 3. Measurements of bulk density were not available for all depths, thus were estimated based upon available measurements.

Table 3
Ages of selected core depths

Depth (cm)	Age (year AD)
2	1970
7	1957
9	1952
11	1947
21	1916
31	1886
41	1856
51	1826
61	1796
71	1766
81	1736
91	1706
101	1676
121	1372
141	1070
161	766
201	158

4. Results

4.1. Pigments

Pigment concentrations vary little from the core bottom (at 219 cm) to 90.5-cm depth at which point there is a 50% increase over the previous highest concentration (Fig. 5a). From this depth and above, pigment concentrations vary from 18.43 to 57.56 nmoles g^{-1} dry wt, with additional maxima at 70.5 cm, 20.5 cm and at the surface. Transformation of pigment concentrations to flux values removes the local maxima at 90.5 cm, but has little effect on the pattern shown in concentrations above this depth (Fig. 5b).

4.2. Diatoms: BSi and centric/pennate ratios

Concentrations of biogenic silica range from a low of 4.3% dry wt at the surface to a high of 6.3% at 79.5 cm-depth (Fig. 5a). A nearly equivalent peak in concentration occurs at 25.5 cm and lesser maxima at 56.0, 109.5 and 159.5 cm depth.

The pattern of BSi flux differs from concentration (Fig. 5b). Throughout the earliest period of the core record BSi flux remains low, under 2.4 mg cm^{-2} year^{-1}. By ~1770 flux increases more than three-fold. The BSi flux declines during the 19th century, although rates are higher than those recorded during the earlier history. A second peak in BSi flux, nearly equivalent in magnitude, occurs at ~1913. This rise is followed by a decrease in BSI flux in the 1960s and 1970s.

Through most of the core history, the centric/pennate diatom ratio remains below one, with the exception of the uppermost sample, corresponding to ~1970 (Fig. 6b). Prior to 1700, the proportion of pelagic diatoms was only 30–60% of that of

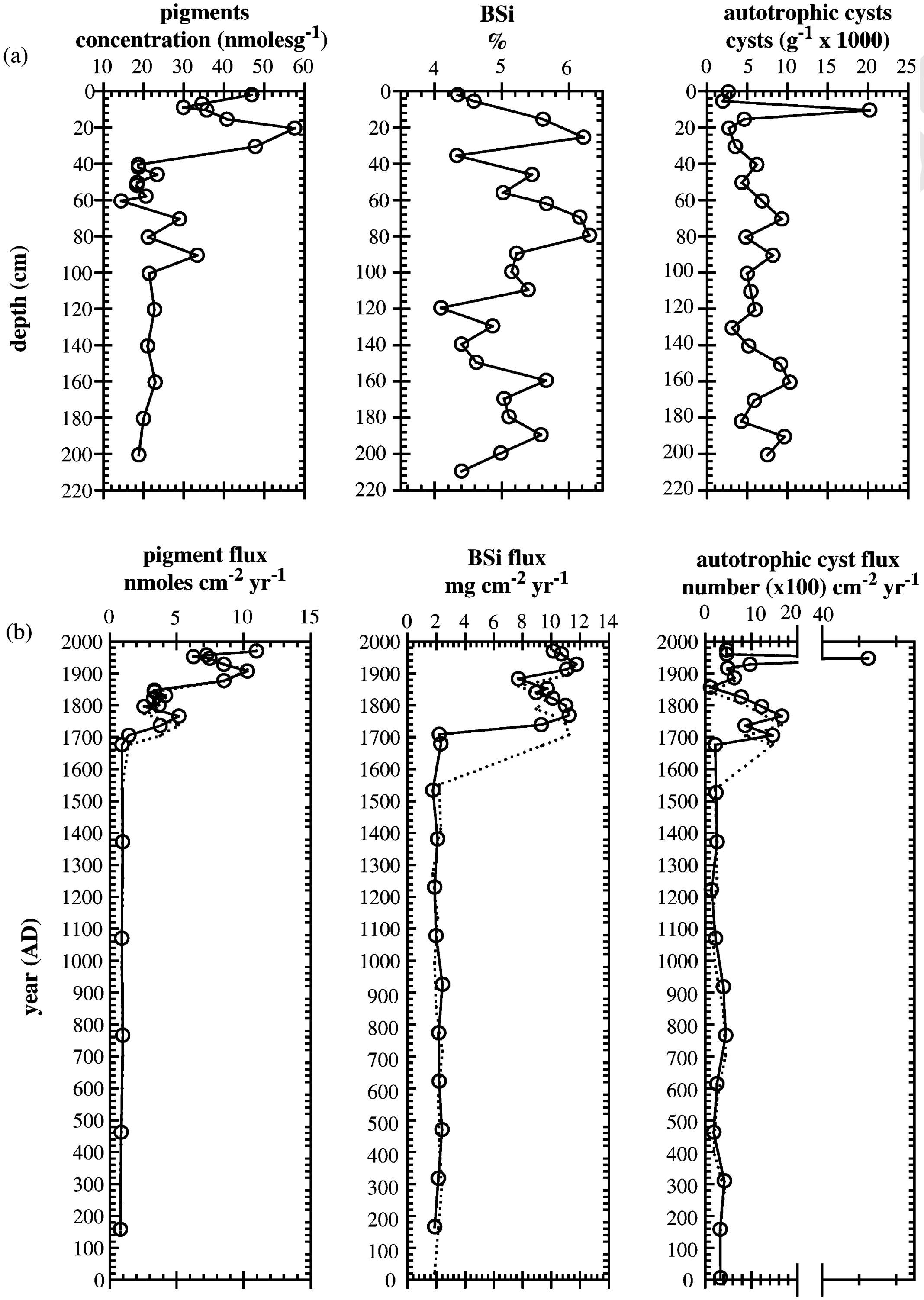

Fig. 5. Pattern of pigments, BSi, and cysts of autotrophic dinoflagellates in sediment core 5C, New Bedford Harbor. (a) Concentrations with respect to depth. (b) Fluxes over time. Soild lines and circles represent chronology assuming that 100.5 cm-depth corresponds to ~1676 AD. Dotted line represents chronology with assumption that 90.5 cm corresponds to ~1676 AD.

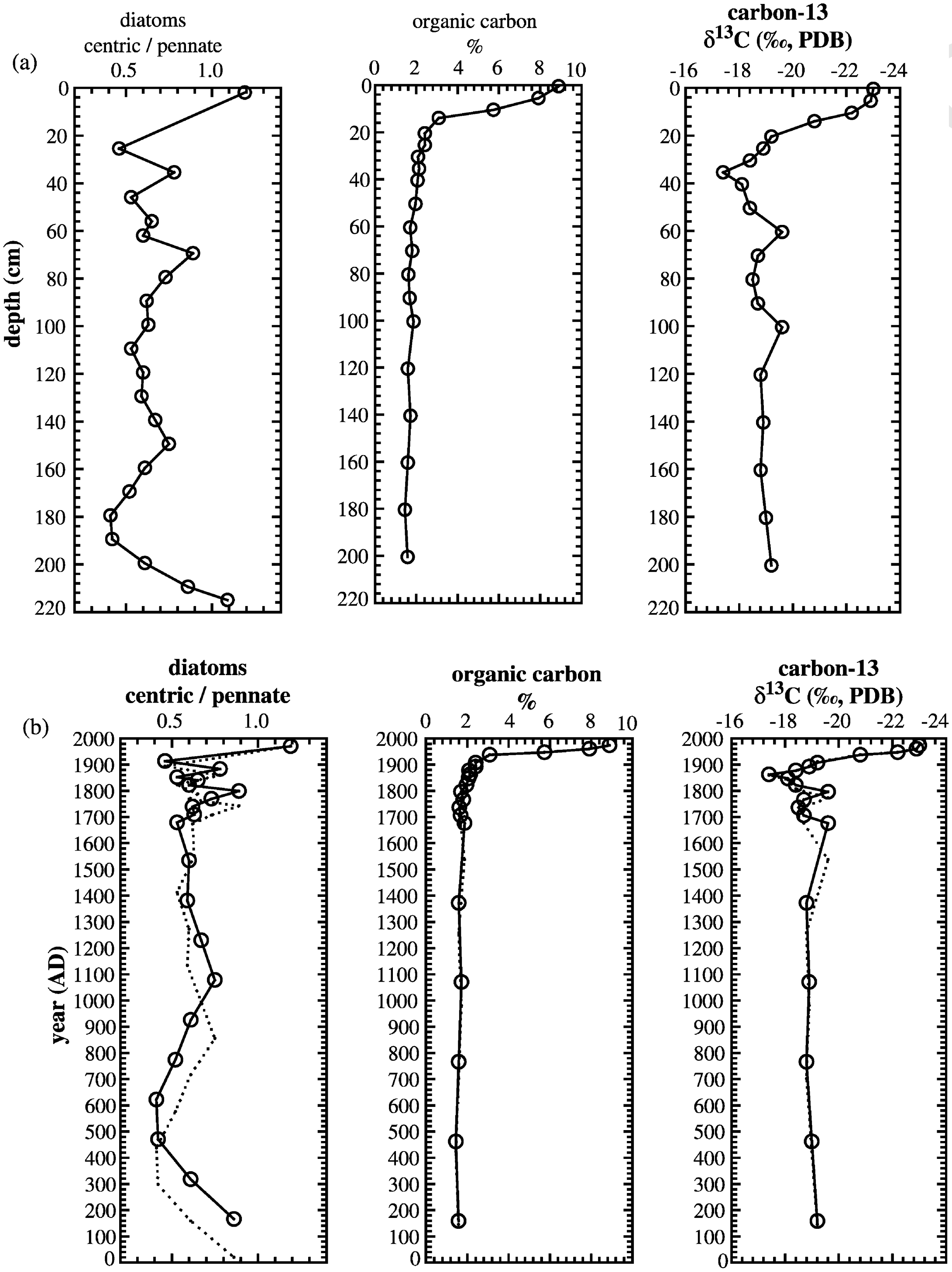

Fig. 6. Pattern of ratios of centric to pennate diatoms, flux and $\delta^{13}C$ of sedimentary carbon in sediment core 5C, New Bedford Harbor. (a) Values with respect to depth. (b) Values plotted over time. Soild lines and circles represent chronology assuming that 100.5 cm-depth corresponds to ∼1676 AD. Dotted line represents chronology with assumption that 90.5 cm corresponds to ∼1676 AD.

benthic diatoms. By the late 1700s the pelagic component increased to 90% of the benthic, but declined to near historical lows approximately 1852 and again in 1913 (Fig. 6b). In the most recent sediment sampled, the proportion of pelagic diatoms is 20% greater than benthic.

4.3. Dinoflagellate cysts

Dinoflagellate cyst concentrations vary over an order of magnitude, from 1997 to 20 204 cysts g^{-1} dry wt (Fig. 5a). The maximum concentration, occurring at 10.5-cm depth, is twice as large as three other maxima (approx. 9000 to 10 000 cysts g^{-1} dry wt) that are found at 190.5, 160.5–150.5, and 70.5 cm. The flux of cysts is consistently low (<697 cysts cm^{-2} $year^{-1}$) prior to ~1700 (Fig. 5b). At 100.5 cm, fluxes become variable and, as with concentrations, the maximum flux (more than twice that of the next highest value) occurs at 10.5 cm, thus at ~1947. A detailed discussion of the pattern of fluxes of dinoflagellate cyst taxa after European settlement is given in Pospelova et al. (2002).

4.4. Sedimentary carbon

Sources of sedimentary carbon are indicated by the $\delta^{13}C$ signature (e.g. Chmura and Aharon, 1995) which differentiates among terrestrial (−26‰, PDB), saltmarsh (−16‰, PDB), eelgrass (−10‰, PDB), or marine (phytoplankton, −20‰, PDB) sources. We assume that human sewage carries the signal of terrestrial carbon. From about 1860 on there is a decline (from > −18 to −23‰) in the $\delta^{13}C$ of sedimentary carbon in New Bedford Harbour (Fig. 6b). The decline is probably due to the saltmarsh loss documented during this period, as well as the loss of eelgrass beds, presumed to have been once extensive in the Harbor. During the same period carbon concentration increases, probably due in part to increased phytoplankton production and decreased decomposition rates, but the low $\delta^{13}C$ indicates that terrestrial carbon sources are clearly increasing. The terrestrial component is from human sewage (freshwater inputs are minor here), a problem recognized throughout the history of the City (Pesch and Garber, 2001).

5. Discussion

5.1. Pre-colonial to 1750

Fluxes of pigments, BSi and dinoflagellate cysts show little variability in the pre-European settlement history of New Bedford Harbor. This and lack of appropriate dating control in lower sediments make it difficult to detect any climate perturbations that may be associated with climatic events, such as the Medieval Optimum or Little Ice Age (Mann et al., 1999).

Peak concentrations of pigments, BSi, and dinoflagellate cysts occur after European occupation of the watershed and all fluxes are distinctly higher in the post settlement period. Consistently low concentrations of pigments in the lower portion of the core (corresponding to the pre-settlement period) are likely a result of lower inputs of pigments and higher rates of degradation of those present. Before European settlement, the Acushnet River estuary is assumed to have been an oligotrophic system with abundant eelgrass beds (Voyer et al., 2000). Under such conditions waters would be clear, promoting photodegradation of pigments. Oxygen released during photosynthesis of eelgrass and benthic algae would enhance toxic conditions at the sediment/water interface further promoting high rates of pigment degradation. Thus, we would not expect to find much eelgrass pigment preserved in the sediment record. In this oligotrophic system, lower water column production also would have allowed for higher light intensities, thus enhanced rates of photodegradation. Accelerated sediment accumulation rates and increased phytoplankton production (reducing the potential for photodegradation) associated with land clearance would help to preserve the record of enhanced production. The higher flux of dinoflagellate cysts, which are less susceptible to degradation, supports the conclusion that increases in pigments and BSi are due not simply to better preservation.

All measures of primary production-BSi, pigments, and dinoflagellate cysts show a response to early European settlement of the New Bedford

Harbor watershed, associated with forest clearance detected by the rise in ragweed pollen. Changes in taxa of dinoflagellate cysts, prior to production increases suggests that ecological shifts were already occurring in the aquatic ecosystem.

Variability in concentrations of BSi and cysts of autotrophic dinoflagellates below 100-cm depth (Fig. 5a) suggests that either sediment accumulation rates were variable or environmental conditions varied. It is likely that both occurred, to some degree. The lack of variability in pigment concentrations before increased sediment accumulation rates also suggests that, as expected, this indicator is not a reliable proxy for paleo-primary productivity in shallow, clear, oxygenated estuarine waters. However, in a eutrophic system with high sediment accumulation rates, such as an urbanized estuary, it becomes a sensitive proxy.

Marine coastal ecosystems, particularly those without nutrient enrichment, are nitrogen limited (e.g. Boynton et al., 1982; Oviatt et al., 1995). Increased fluxes of all three paleo-productivity measures are concurrent with or immediately follow the ragweed rise that signals the early forest clearance. Studies of the impact of forest clearance in watersheds at Hubbard Brook, New Hampshire showed that forest clearance resulted in a ten-fold increase in nitrogen runoff, as compared to the watershed used as a control site (Likens et al., 1978). Assuming a similar response in the New Bedford watershed, the seemingly minor clearance of 4% of forest in the early years of the New Bedford settlement would result in nearly a 50% increase of the nitrogen released from the watershed. Acushnet watershed soils would rapidly transport mobile nutrients through the watershed, as they are either highly permeable or shallow and situated above nearly impermeable, compacted till.

The impact of simple forest clearance on water column production has been noted in paleoecological studies of Chesapeake Bay (Cooper, 1995) and in lakes. Little et al. (2000) found clearance of mixed forest associated with European settlement around Lake Muskoka, Ontario caused ‘profound impacts’ in the diatom population of Gravenhurst Bay. The importance of the loss of forest cover, separate from other human influences, also was demonstrated by Hall and Smol (1993) who showed a response of phytoplankton communities to prehistoric hemlock decline around lakes in Ontario.

5.2. 1750–1850

During the latter half of the 18th century the increased flux of pigments, BSi, and dinoflagellate cysts (Fig. 5b) indicates shifts in the magnitude of production while C/P ratios and $\delta^{13}C$ indicate shifts in the source of primary production shortly after (Fig. 6b). We assume that primary production of the harbor increased or maintained relatively high levels from 1700 to ~1775. Throughout this period continued watershed clearance, indicated by an overall increase in abundance of ragweed pollen from 100 to 60 cm (Fig. 3), was presumably the major forcing of nutrient increases as population numbers were still low (Fig. 2). Increases in production were first in the benthic community, then primarily in the water column as pelagic diatom abundance increases and the decrease in $\delta^{13}C$ of sedimentary carbon can be explained by an increase in carbon from phytoplankton relative to eelgrass and saltmarshes. Contributions of terrestrial carbon eroded from the farmed soils also are likely to have contributed to this signal. The increased flux of cysts indicates that higher production rates were not limited to the diatom component of the phytoplankton.

From the late 1700s to the mid 1800s the pigment flux and C–P ratio suggest that water column production declined, but system production probably remained higher than in pre-settlement times (Fig. 5b and Fig. 6b). The decline in the proportion of centric diatoms and enrichment in the $\delta^{13}C$ of sedimentary carbon (from −19.6 to −17.4‰) suggests an increase in the relative importance of eelgrass and epiphytic diatoms.

5.3. 1850–1960

By the mid 1800s, ship and wharf construction had peaked, and the need for lumber. Our records of watershed clearance are not sufficiently detailed, but we assume that its rate declined over this period as the abundance of ragweed pollen (Fig. 2) remains relatively stable over the same period (corresponding to approx. 60-30 cm depth). As the release of nitrogen from newly cleared forest soils subsides within 5 years (Likens et al., 1978), its input to the estuary would have also declined.

After the mid 1800s fluxes of pigments and BSi show that water column production increased to levels equal to or greater than any previous period in the estuary's history (Fig. 5b and Fig. 6b). The importance of production in the water column is indicated by the increased proportion of centric diatoms ~1883 and a depletion of the $\delta^{13}C$ of the sedimentary carbon.

During this second pulse the stimulus for increased production would have been the growing population of the City of New Bedford (Fig. 2). In 1852, the City's first sewer lines were constructed, channeling untreated human waste directly into the estuary. The magnitude of sewage eventually was so great that it became a point of litigation as a public nuisance, as well as a health hazard (Pesch and Garber, 2001).

The second decline in primary production, in the 20th century, would be expected simply due to local improvements in sewage disposal practices, but difficult to separate from possible effects of toxic substances now being released into the estuary. By the 1920s an interceptor sewer line was partially completed, channeling much of the City's sewage outside the Harbor to an outfall off the end of Clarks Point (Fig. 1). However, during high rainfall events combined sewer overflows released sewage to many locations throughout the harbor and Latimer et al. (in press) show substantial increases in sediment concentrations of heavy metals, such as chromium, silver, lead, cadmium and copper in the early 20th century. We assume that inputs of heavy metals contributed to the decline in production—an assumption supported by experiments with estuarine mesocosms to which various mixes of nutrients and heavy metals were added (Breitburg et al. 1999). Introduction of trace metals to the mesocosms produced a mix of positive and negative responses among algal taxa. There was additional variability with respect to introduction of nutrients and timing of additions. In the mesocosm experiment some responses were a decline in overall phytoplankton production, a decrease in density of larger centric diatoms, in pennate diatoms, and a three order of magnitude increase density of small-celled chlorophytes.

5.4. Post 1960

The final shift in primary production recorded is indicated by an increase in pigment flux ~1960, but with no corresponding increase in flux of BSi or dinoflagellate cysts (Fig. 5b and Fig. 6b). Although overall diatom production continually decreased, the production of pelagic diatoms surpassed benthic and epiphytic for the first time in the estuary's history—suggesting a precipitous decline in benthic primary production. These production shifts can be explained by the construction of the hurricane barrier across the mouth of the Harbor in 1964–1965. The barrier increased residence time of estuarine waters by 30% and resulted in loss of the Harbor's remaining eelgrass beds, the host for epiphytic diatoms. Increased carbon accumulation may have resulted in lower dissolved oxygen levels in bottom waters and sediments, further reducing bioturbation, as benthic faunal populations would probably have declined. The added shelter of the hurricane barrier would also have reduced the occurrence of wind-driven waves. With the quiescent conditions created by the hurricane barrier (Pritchard and Schubel, 1981) recycling of BSi from sediments would be much reduced. Under conditions of excessive nitrogen loading diatoms can become silica-limited (Conley and Malone, 1992) and reduction in sediment resuspension may have contributed to reduced overall diatom production.

Preceding this most recent decline is an unprecedented peak in the flux of dinoflagellates (Fig. 5b), composed primarily of *Gonyaulax* species (Pospelova et al., 2002). This discrete increase may be due to a bloom, perhaps an initial response to changes in water chemistry that caused a shift in phytoplankton community structure.

Decreased diatom and dinoflagellate production, but high pigment flux suggests that populations of other autotrophs have increased in these last two decades. Phytoplankton studies in the late 1980s have shown that tiny micro- and phytoflagellates dominate the phytoplankton of New Bedford Harbor. Could this dominance of nanoplankton be a result of the perturbations in the nutrient regime during the late 20th century?

The larger cells of many diatoms and dinoflagellates are likely to contain an order of magnitude more pigment than the tiny nanoplankton cells (e.g. Stromski et al., 2001) but, when very abundant nanoplankton can contribute a substantial portion of the pigment concentration measured in some marine and estuarine systems. The seasonal contribution of picoplankton to total chlorophyll *a* has been as high as 40% in the Urdaibai estuary (Ansotegui et al., 2003), 50% of the total pigment measured in waters of a ria on the Spanish coast (F. Rodríguez, personal communication), and up to 61% in continental shelf waters of the Bay of Biscay (Rodríguez et al., 2003).

Some investigators suggest that nutrient enrichment results in a gradual decrease in size-class structure of phytoplankton with eventual dominance of nanoplankton (Vilicic, 1989; Kimor, 1992). Our results seem to support this hypothesis, but our pigment record does not discriminate between these algal groups so we cannot make definitive statements about the historical importance of the nanoplankton.

6. Summary and conclusions

Our paleoproductivity records show four major changes in the aquatic ecosystem of New Bedford Harbor. These changes can be attributed to human perturbations of the estuarine watershed and waters. Early forest clearance increased nutrient loading to the estuary. This process was enhanced by soil characteristics of the watershed. Major increases in production by dinoflagellates, diatoms, and probably other autotrophs occurred at this time. Production continued to be stimulated as rates of watershed clearance (indicated by the% of ragweed pollen) increased until the 19th century. The subsequent decline in production corresponds to a deceleration or hiatus in forest clearance.

A second pulse in production was stimulated by introduction of nutrients with discharge of sewage to the harbor. Most of the increased production occurred within the water column. Although later declines in production seem to correspond to ‘improvements’ in sewage disposal practices (i.e. diversion of discharge to water outside the harbor), impacts from the introduction of toxic substances from local industries cannot be discounted.

A third increase in production is reflected solely by increased pigment flux in the last years of our record, but preceded by a dinoflagellate bloom. Immediately following, dinoflagellate and diatom production decreased, with a precipitous decline in benthic primary production. Changes in harbor hydrography had occurred as construction of a hurricane barrier increased residence time (Abdelrhman, 2002) and reduced wave energy, therefore, surface mixing. This likely reduced the recycling of BSi from sediments, thus diatom production. We assume that increased pigment flux is due to increases in other aquatic autotrophs, likely the micro- and phytoflagellates that presently dominate the phytoplankton of New Bedford Harbor.

7. Uncited reference

Brush and Davis, 1984; Arantza et al., 2003

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