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Environmental stress and recovery: the geochemical record of human disturbance in New Bedford Harbor and Apponagansett Bay, Massachusetts (USA)

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Abstract

Sediments record the history of contamination to estuaries. Analysis of the concentrations of toxic organic compounds, contaminant and crustal metals, organic carbon content and isotopic composition in sediment cores from two estuarine systems in Buzzards Bay allowed reconstruction of human impacts over 350 years. Vertical distributions of the contaminants correlate with changes in the nature of watershed/estuarine activities. All contaminants were highly enriched (tens to hundreds times background) in modern New Bedford Harbor sediments. Enrichment began around the turn of the 20th century for all but PCBs, which were first synthesized in the 1930s. An increase in organic carbon content and a shift of carbon isotopes toward a more terrestrial signature illustrates increasing anthropogenic impact in New Bedford as population grew along with the industrial base. Institution of environmental protection measures in the late 20th century was reflected in decreased, although still substantially elevated, concentrations of contaminants. A lack of industrial development in Apponagansett Bay resulted in much lower concentrations of the same indicators, although specific contaminants related to the early whaling industry increased significantly above background as early as the late 18th century. The similarity of indicators in older portions of cores from NBH and unimpacted Apponagansett Bay demonstrates that cores can be used to establish reference conditions as successfully as using separate sites judged *a priori* to represent the reference state. The historical reconstruction approach provides the basis for establishing relationships between environmental stressors and factors that drive the stressors, as well as a framework for the assessment of ecological response(s) to environmental stressors over a range of time and/or exposure scales.

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1. Introduction

The major problems in marine coastal environmental science revolve around the intersection of humans and the environment. Pollution problems are correlated with population density, which has driven significant efforts to monitor estuaries in order to assess their status. These monitoring efforts are important because they allow scientists and managers to begin to relate drivers, stressors and effects. Establishing the relationships between drivers, stressors and effects provides managers with a sound scientific basis on which to build consensus on solutions to problems. Environmental remediation and restoration activities are often based on the assumption that removal of anthropogenic stressors will result in a return of the system to optimum ecological integrity. The ecological condition of a system is a function of physical, chemical, and biological processes, most of which are affected by anthropogenic and natural stressors. Without long-term data from the analysis of biological and chemical indicators in sediment cores and an understanding of historical human activities, it is difficult to assess ecosystem integrity.

This paper describes the characterization of historical trends of toxic chemical stressors (Table 1) in the New Bedford Harbor and Apponagansett Bay estuaries. It is part of a series of papers detailing impacts of urbanization on New Bedford Harbor and Apponagansett Bay through analysis of dinoflagellate cysts (Pospelova et al., 2002), foraminifera (Scott et al., 2002) and pigments, diatoms and biogenic silica (Chmura et al., in press). These companion papers report on the system effects using biotic response indicators analyzed in the same sediment cores. The purpose of the paper is to report on whether: (1) indicators in sediment cores can be used to determine trends in stressors; (2) indicators in sediment cores, coupled with anthropological data on watershed activities, can yield information on watershed driver–stressor relationships; and (3) indicators in sediment cores can be used to establish reference or background stressor conditions.

2. Methods and materials

2.1. Environmental history

New Bedford Harbor (NBH) (Fig. 1, Table 2), part of the Buzzard's Bay estuary, is a relatively shallow system with a modest freshwater source and generally well mixed and unstratified water column (Turner et al., 2000). The harbor is divided into two areas, the Upper and Lower Harbor segments; the Lower Harbor (south of the I-195 and Coggeshall Street Bridges) is significantly wider and deeper than the Upper Harbor. Portions of NBH are listed on the Environmental Protection Agency's National Priorities List for cleanup (Bergen et al., 1998), primarily because of polychlorinated biphenyl (PCB) contamination. It is also contaminated with metals and other organic chemicals (Pruell et al., 1990; Shine et al., 1995) and considered to be eutrophic (Costa and Howes, 1996). NBH has a highly urbanized watershed and its developmental history is well documented (Pesch and Garber, 2001; Voyer et al., 2000). Historical human impact on the environment of NBH can be divided into five overlapping periods, each defined by the dominant economic and social activities that took place in and around the harbor: agricultural (1676–1780), whaling (1750–1900), textile (1880–1940), post textile (1940–1970), and environmental awareness (1970–present). Characteristic watershed and waterbody activities of these periods are listed in Table 3.

The Apponagansett Bay estuary is also an embayment of Buzzard's Bay (Fig. 1), but with a much smaller watershed area than NBH (Table 2). Due to its restricted geomorphology and watershed loading, inner Apponagansett Bay is one of the most eutrophic embayments of Buzzard's Bay (Howes et al., 1999). Outer Apponagansett Bay is better flushed and shows moderate eutrophication (Howes et al., 1999). Historical development in the Apponagansett Bay watershed is not as well known but was similar to that in NBH during the agricultural and whaling periods, albeit smaller in scale. As in NBH, the shoreline of Apponagansett Bay was altered (but to a much lesser extent than NBH) by wharf and bridge construction as the

Table 1
Stressor indicators measured in sediment cores

Polychlorinated biphenyls (PCBs) (18 indicator congeners of the 209 possible congeners from 2–10 chlorines per molecule)	Total Aliphatic hydrocarbons (TAHs) (Major constituents of petroleum hydrocarbons; also derived from plant organic matter)	Polycyclic aromatic hydrocarbons (PAHs) (constituents of petroleum; also derived from combustion of organic matter) priority* pollutant PAHs	Metals **contaminant metals ^crustal metals
CB008 (2,4'-dichlorobiphenyl)	nC-10 (Decane)	Fluorene*	Zinc**
CB018 (2,2',5-trichlorobiphenyl)	nC-11 (Undecane)	Phenanthrene*	Copper**
CB028 (2,4,4'-trichlorobiphenyl)	nC-12 (Dodecane)	Anthracene*	Lead**
CB052 (2,2',5,5'-tetrachlorobiphenyl)	nC-13 (Tridecane)	Sum C-1 Phen./Anthracenes	Chromium**
CB044 (2,2',3,5-tetrachlorobiphenyl)	nC-14 (Tetradecane)	Sum C-2 Phen./Anthracenes	Nickel**
CB066 (2,3',4,4'-tetrachlorobiphenyl)	nC-15 (Pentadecane)	Sum C-3 Phen./Anthracenes	Cadmium**
CB101 (2,2',4,5,5'-pentachlorobiphenyl)	nC-16 (Hexadecane)	Sum C-4 Phen./Anthracenes	Silver**
CB118 (2,3',4,4',5-pentachlorobiphenyl)	nC-17 (Heptadecane)	Fluoranthene*	Manganese^
CB153 (2,2',4,4',5,5'-hexachlorobiphenyl)	Pristane	Pyrene*	Iron^
CB105 (2,3,3',4,4'-pentachlorobiphenyl)	nC-18 (Octadecane)	Benz[a]anthracene*	Aluminum^
CB138 (2,2',3,4,4',5'-hexachlorobiphenyl)	Phytane	Chrysene*	
CB187 (2,2',3,4',5,5',6-heptachlorobiphenyl)	nC-19 (Nonadecane)	Sum C1,C2 Chrysenes	
CB128 (2,2',3,3',4,4'-hexachlorobiphenyl)	nC-20 (Eicosane)	Sum Benzofluoranthenes*	
CB180 (2,2',3,4,4',5,5'-heptachlorobiphenyl)	nC-21 (Heneicosane)	Benzo[e]pyrene	
CB170 (2,2',3,3',4,4',5-heptachlorobiphenyl)	nC-22 (Docosane)	Benzo[a]pyrene*	
CB195 (2,2',3,3',4,4',5,6-octachlorobiphenyl)	nC-23 (Tricosane)	Perylene	
CB206 (2,2',3,3',4,4',5,5',6-nonachlorobiphenyl)	nC-24 (Tetracosane)	Indeno[123-cd]pyrene*	
CB209 (2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl)	nC-25 (Pentacosane)	Dibenz[ah]anthracene*	
Sum of measured congeners (Σ CBs)	nC-26 (Hexacosane)	Benzo[ghi]perylene*	
$2 \times \Sigma$ CBs ~ total PCBs	nC-27 (Heptacosane)	Coronene	
	nC-28 (Octacosane)	Sum of priority pollutant PAHs	
	nC-29 (Nonacosane)		
	nC-30 (Triacontane)		
	nC-31 (Hentriacontane)		
	nC-32 (Dotriacontane)		
	nC-33 (Tritriacontane)		
	nC-34 (Tetratriacontane)		
	Total Aliphatic Hydrocarbons (total of resolved and unresolved constituents)		

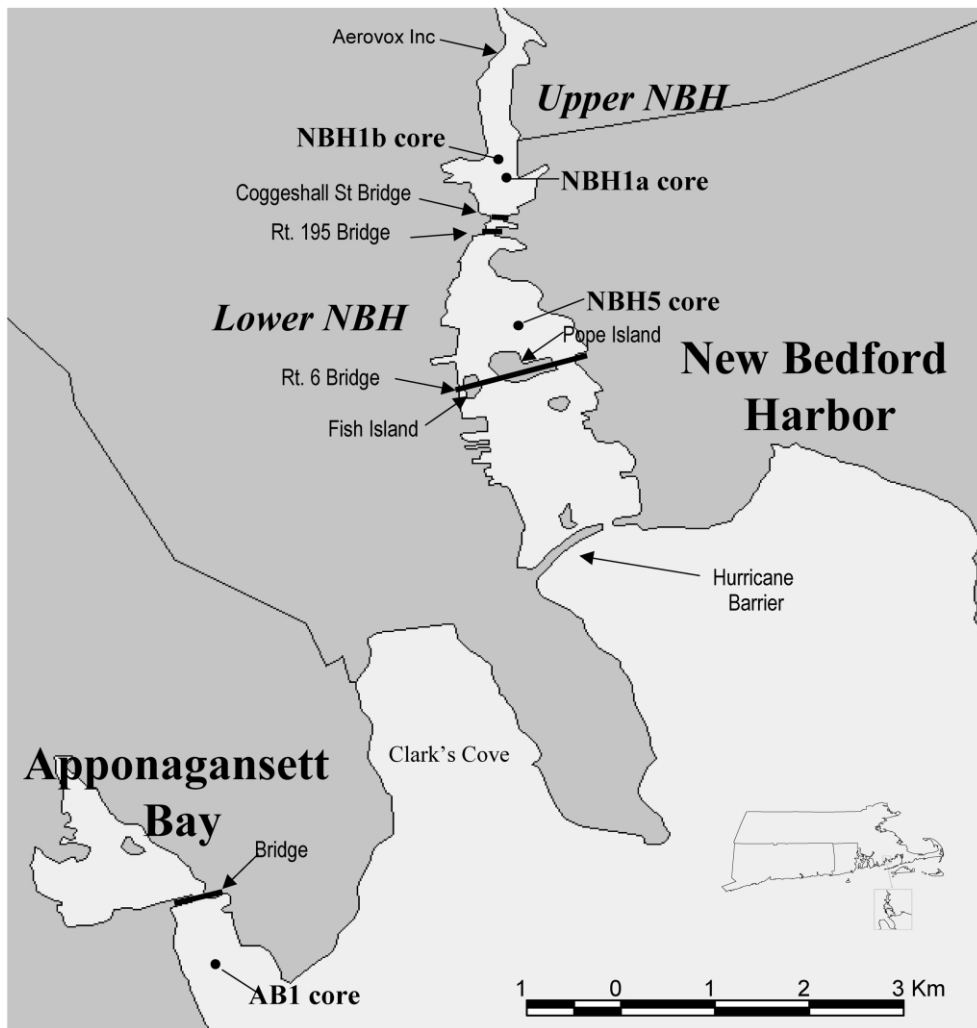


Fig. 1. Locations of New Bedford Harbor and Apponagansett Bay sediment core sampling sites and other important sites throughout the systems.

population around it increased (Buck, 1964; Glennon, 2001). However, the level of commerce and industrialization in the Apponagansett Bay watershed was markedly less than in the nearby New Bedford Harbor watershed. Thus, we consider Apponagansett Bay to be a suitable reference site to compare with New Bedford Harbor.

2.2. Sampling

Sediment cores were collected from three sites in New Bedford Harbor and one from Apponagan-

sett Bay (Fig. 1). Core samples were collected either by pressing a core liner into the sediments (hand piston corer, cores NBH1a, 1b, 5) or by using a gravity coring device (Benthos Model 2171 ID: 67 mm, OD: 73 mm, core AB1). Upon collection, cores were immediately transported to the laboratory upright and stored at 4 °C in the dark until processing. Cores were split lengthwise at the University of Rhode Island's Marine Geological Samples Laboratory. Cores were visually inspected for bedding, based on color, lithology

Table 2
Comparison of current oceanographic and other characteristics of Apponagansett Bay and New Bedford Harbor

	Apponagansett Bay	New Bedford Harbor
Depth (mean half tide, m) ¹	2.3	4.2
Saltwater flushing time (days) ²	1.3	2.1
Area of embayment (km ²) ³	2.93	10.73
Area of watershed (km ²) ⁴	21.61	68.99
Dominant land use (type%) ⁴	Forest 32% Residential 34% Urban 6%	forest 39% residential 23% urban 12%
Dominant water use ⁵	Recreational Boating	Commercial Fishing
Population	28 503 ⁶	96 353 ⁷
Watershed population	1319	1397
Density (persons/km ²)		
Area watershed/embayment	7	6

¹ Source: (Aubrey, 1995).

² Calculated using a tidal prism model. Source: *ibid.*

³ Source: *ibid.*

⁴ Source: <http://www.buzzardsbay.org/download/buzzbaylanduse.xls> (downloaded 04/28/00).

⁵ Source: (Howes et al., 1999).

⁶ Source: <http://www.state.ma.us/scripts/dls/databank/indiv1.cgi?report3> (Town of Dartmouth, 1998; downloaded 04/28/00).

⁷ Source: <http://www.state.ma.us/scripts/dls/databank/indiv1.cgi?report3> (City of New Bedford, 1998; downloaded 04/28/00).

and sedimentary structures, in order to assess coring disturbance and sedimentary characteristics. The cores were sealed in plastic liners, with half stored at 4 °C and half at –20 °C. Cores were X-rayed to characterize them beyond visual means,

then sectioned into 1- or 2-cm sections and analyzed for the constituents listed in Table 1. Selected samples were analyzed for excess ²¹⁰Pb, ¹³⁷Cs and pollen to aid in core dating and determination of sedimentation rates.

Table 3
Developmental periods for New Bedford Harbor

Development period	Drivers: Watershed/Harbor Activities
Agricultural (1676–1780)	Minimal land clearance (~4%), farming Sparsely populated
Whaling (1750–1900)	Wharf and bridge construction Industries Significant land clearance for building (up to 50% by 1815–1834)
Textile (1880–1940)	Wetland filling (mill construction) Dramatic population increases Industries
Post-textile (1940–1970)	Electronics industry Other industries Hurricane barrier construction Stable/decreasing population
Environmental Awareness (1970–present)	Industrial pretreatment/Clean industry/POTW treatment Improvement Clean Water Act, Clean Air Act, RCRA, CERCLA designation Urban sprawl/ increased impermeability of watershed

Source (except for the environmental awareness period): (Pesch and Garber, 2001; Voyer et al., 2000).

Table 4
Summary of quality assurance procedures and criteria for organics and metals

Purpose	Process	Sample frequency	Criteria	
			Organics	Metals
Instrumental analysis				
Precision	Replicate solution	every 15		≤ 15% rsd
Accuracy	Calibration solution	every 6–15	< 25% error	< 15% error
Matrix effects	Spike/ISTD recovery	every 20	60–120% recovery	85–115% recovery
Overall analysis				
Precision	Replicate samples	every 20	< 15% rsd	< 30% rsd
Accuracy	SRM/CRM	every 20	85–120% recovery	60–140% recovery
Contamination	Procedural blank	Every 20	< 3× detection limit	< 1% of sample concentration

2.3. Analytical

2.3.1. Organic toxicants

Extractions of organic toxicants were done using a MES-1000 microwave sample extraction system (CEM Corp., Matthews, NC). Sediment samples were extracted with organic solvents and purified by column chromatography. Details of moisture standardization, microwave extraction parameters and silica gel column chromatography have been reported elsewhere (Jayaraman et al., 2001). PCBs (18 congeners, Table 1) were analyzed by gas chromatography with an electron capture detector using a 30-m DB-5M fused silica capillary column. Congener identities were confirmed using SRM2262, National Institute of Standards and Technology; PCB198 was used as an internal standard. Signal integration and calculations were performed using HP Chem Station® software. Samples were analyzed for individual PAHs and aliphatic hydrocarbons on a Hewlett–Packard 5890 Series II Gas Chromatograph® equipped with a split/splitless injection port, a 60 m fused silica column (0.25 mm id) coated with 0.25 μm DB-5 (J&W Scientific®, Folsom, CA), and a Hewlett–Packard 5971A Mass Selective Detector operated in the selected ion monitoring mode. Data were collected and analyzed using Hewlett–Packard MS/Chem Station® software. Quality assurance procedures and criteria are summarized in Table 4. All contaminant concentrations are reported on a dry weight basis. Organic carbon normalization

was evaluated but made little difference in the core profile trends.

2.3.2. Contaminant and crustal metals

Sediment samples were digested by microwave heating in pressurized, Teflon-lined digestion vessels (CEM Corp., Matthews, NC) with a mixture of concentrated acids, following EPA method 3052. Sediment digestate solutions were analyzed for crustal and contaminant metals (Table 1) by inductively coupled plasma atomic emission and graphite furnace atomic absorption spectrophotometry. Quality assurance procedures and criteria are summarized in Table 4.

2.3.3. Stable carbon isotopic composition and organic carbon content

Particulate organic matter in estuaries is a mixture of terrestrial, fluvial and marine components, consisting of phytoplankton cells, organic debris and eroded material from soils, marshes, peats and sediments. To distinguish between marine, marsh, and terrestrial components, we use stable carbon isotope ratios in the organic material. Marine phytoplankton usually have a different stable carbon isotope ratio (–21‰) than terrestrial plants (–26‰), which are different from marsh derived organic matter (–16‰). We assume that the stable isotopic value of the organic matter of a given sample will be the result of a mixture of the three types of sources. Sediment samples were analyzed for organic carbon content and stable carbon iso-

tope ratio ($\delta^{13}\text{C}$) by continuous flow elemental analysis/isotope ratio mass spectrometry. The reference gases are calibrated relative to primary references traceable to international standards. The isotopic composition of several standard reference materials are routinely measured to assure that our laboratory scale is consistent with the accepted international scale. The percent organic carbon is determined from the same gases produced during the analysis for stable isotopes.

2.3.4. Radionuclides

The radionuclides ^{210}Pb , ^{137}Cs and ^{226}Ra or ^{214}Pb were analyzed in selected core samples by direct gamma assay at the University of Rhode Island Graduate School of Oceanography (cores NBH1a and NBH5) and the Liverpool University Environmental Radioactivity Laboratory (core AB1). Excess, or unsupported, ^{210}Pb activity was calculated as the difference between the measured activities of total ^{210}Pb and parent nuclides ^{214}Pb or ^{226}Ra , the parent nuclide activities serving to estimate the supported ^{210}Pb activity. Sedimentation rates and ages of sediment core sections were calculated by fitting vertical profiles of excess ^{210}Pb activity to two different models: the constant initial concentration (CIC) model assumes a rate of supply of ^{210}Pb to the sediments proportional to the sedimentation rate, resulting in a constant mass concentration of ^{210}Pb in freshly deposited sediments, whereas the constant rate of supply (CRS) model assumes a constant flux of ^{210}Pb from the water column to the sediments regardless of sedimentation rates (Appleby and Oldfield, 1978).

The distribution of ^{137}Cs in the cores was used to evaluate dates assigned to core sections, the expectation being that ^{137}Cs activity should reach a maximum in sediments deposited approximately 1963, when atmospheric weapons testing was at its greatest, and would be insignificant in sediments deposited much before the initiation of atmospheric testing in the early 1950s. The decline in concentrations of total stable lead in sediments was used as a stratigraphic marker for the early to mid 1970s (Owens and Cornwell, 1995; Santschi et al., 2001; Trefry et al., 1985). Similarly, the onset of polychlorinated biphenyls was used as a

stratigraphic marker for 1930 (Latimer and Quinn, 1996).

The lengths of cores NBH5 and AB1 were well suited to evaluate much older time periods. Pollen analyses were used to estimate the age of deeper sections in these cores (since ^{210}Pb is only suitable for the last 100 years) following techniques used to date cores from the Potomac River, Chesapeake Bay and Connecticut (Brugham, 1978; Brush and Brush, 1994; Brush et al., 1982). Pollen stratigraphy was used because it reflects aspects of the land use in the surrounding watershed. Pollen analyses were performed using published techniques (Pospelova et al., 2002). Previous work has shown sedimentation rates outside the harbor and within the harbor in the earlier half of the 20th century were approximately 0.2–0.3 cm/year (Summerhayes et al., 1985), so rates estimated for deeper samples were constrained within this range.

3. Results and discussion

3.1. Chronology

3.1.1. New Bedford Harbor cores

Vertical profiles of radionuclide activities in core NBH1a (Fig. 2a) reveal a mixed layer approximately 5 cm deep and steadily decreasing excess ^{210}Pb activity below. Vertical resolution of the ^{137}Cs data was insufficient to distinguish a clear peak, but the distribution suggested the maximum concentration, corresponding to approximately 1963, would occur at or just above the 12–13 cm horizon. The first occurrence of ^{137}Cs activity, corresponding to the onset of atmospheric testing in 1953, would be found somewhere between 13 and 18 cm depth. Applying the CIC model to the ^{210}Pb activity between 5 and 21 cm depth and constrained by the limits of the ^{137}Cs data, we calculated a sedimentation rate of 0.24 cm/year, with good correlation between $\log^{210}\text{Pb}$ activity and depth ($r^2=0.992$), and approximately 4 years accumulation of sediment in the mixed layer. The second Upper Harbor core (NBH1b) was not dated using radiometric methods; but its close proximity to core NBH1a suggested similar depositional history. Comparing depths of peak and background concentrations of contaminants in the two cores,

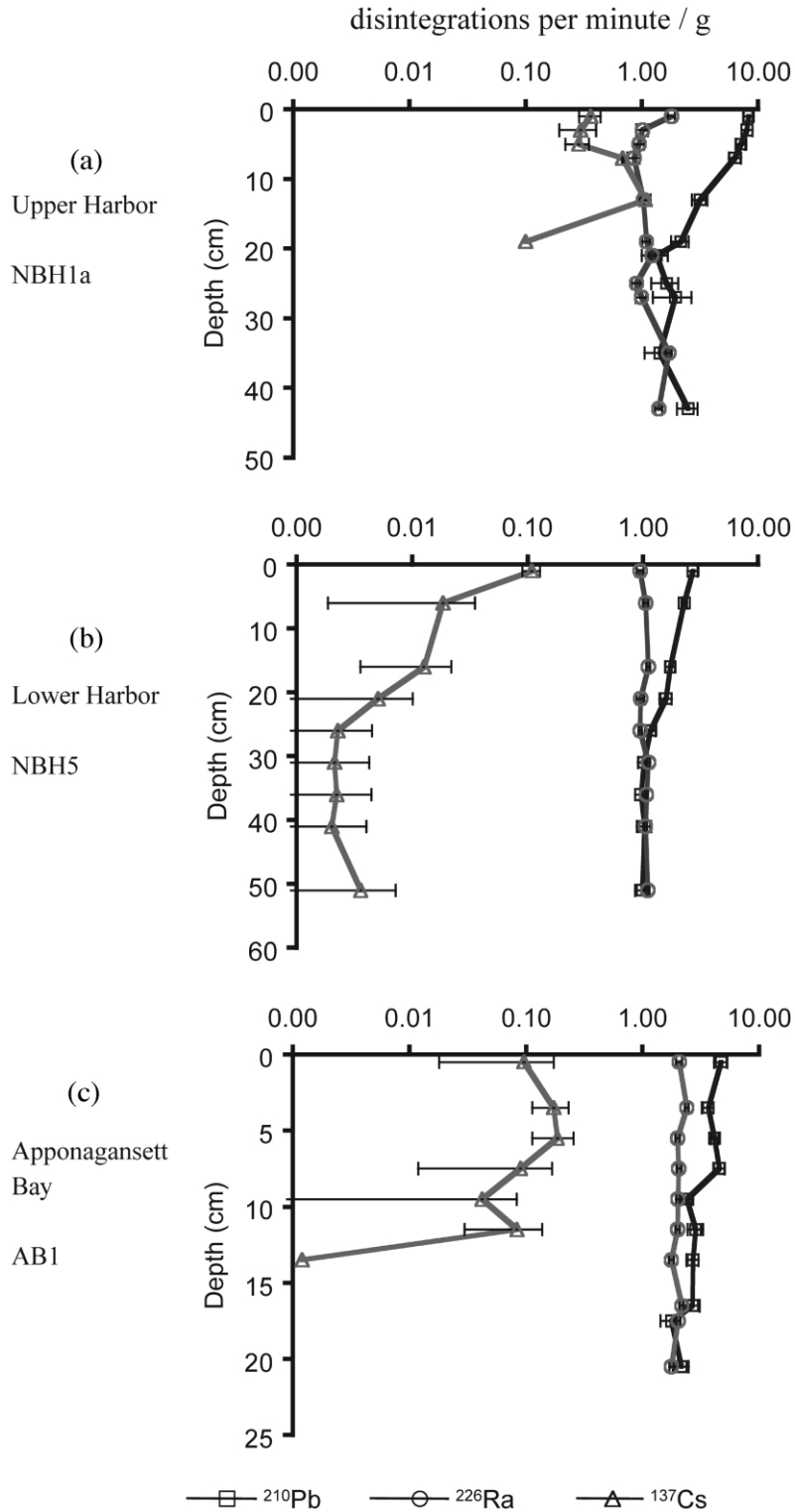


Fig. 2. Profiles of activities of radionuclides used for dating New Bedford Harbor (NBH1a, A; NBH5, B) and Apponagansett Bay (AB1, C) sediment cores.

the sedimentation rate in core NBH1b was estimated to be 0.36 cm/year, approximately 50% higher than in NBH1a, with the top 7 cm a mixed layer encompassing approximately 3–4 years accumulation of sediment.

In core NBH5 from the Lower Harbor ^{210}Pb activity decreased monotonically with depth in the upper 25–30 cm (Fig. 2b). Both models estimated elevated sedimentation rates in sediments near the top of the core and a slower rate below. The CRS model gave the best fit with rates of 0.34–0.39 cm/year near the top of the core and 0.11 cm/year below.

The profiles of ^{137}Cs and total lead in the NBH5 core made it apparent that some surficial sediments were not retained in the core liner when the core was collected. ^{137}Cs activity was highest in the uppermost sediments and significant in only one other horizon (5–6 cm), constraining the date of the 5–6 cm horizon to sometime between the initiation and maximum periods of atmospheric testing, 1954 and 1963, respectively. Concentrations of lead were also highest in the uppermost sediments rather than subsurface, meaning sediments at the top of the core were deposited no later than 1973. The deepest horizon in which concentrations of total PCBs increased significantly above background, 11–13 cm, must have been deposited after 1930. Within these constraints, the CRS model gave the best fit, with 1973 as the estimated date of the top of the core, and was used to develop the chronology for the NBH5 core. The model was applied only to the upper portion of the core (0–16 cm), where ^{210}Pb activity was significantly above the supported background. The uncertainty in the chronology introduced by the loss of the surface sediments was less than 5 years and only affects dating in the upper portion of the core; the effect was minimal on dating estimates for the lower part of the core which constituted the majority of the analysis.

For the lower portion of core NBH5, the sedimentation rate was estimated using pollen analyses (Brugham, 1978; Brush and Brush, 1994; Brush et al., 1982). Initial European settlement and consequent clearance of forested land resulted in a decrease in the predominant oak pollen and concomitant increase in ragweed pollen. The fraction

of the pollen assemblage comprised of ragweed pollen began to increase above background ($\sim 1\%$) at 90–91 cm depth, indicating land clearance corresponding to European settlement in New Bedford approximately 1676 (Pesch and Garber, 2001; Voyer et al., 2000) (Fig. 3a). Similarly, the ratio of oak pollen to ragweed pollen decreasing to ~ 5 indicates land clearance of 40–50% (Brush and Brush, 1994; Brush et al., 1982), which in New Bedford occurred between 1815 and 1834 (Voyer et al., 2000); in this core, this ratio was found at a depth of 50–51 cm (Fig. 3a). Using these two dated horizons and 1928 as the date for the 15–16 cm horizon, as determined from the ^{210}Pb data, we calculated a long-term mean sedimentation rate of 0.29 cm/year. This rate is only slightly lower than that determined for the more recent sediments using the CRS model and is consistent with rates estimated in the lower portion of other cores within NBH and in Buzzard's Bay (Summerhayes et al., 1985).

3.1.2. Apponagansett Bay core

Excess ^{210}Pb activity in core AB1 was highly variable (Fig. 2c), suggesting that historical sedimentation rates were variable, making use of the CIC model inappropriate. Chronology based on the CRS model (Peter G. Appleby, Environmental Radioactivity Research Center, University of Liverpool, personal communication) indicated sedimentation rates were somewhat higher (0.3 cm/year) in recent times than in the past (0.1–0.2 cm/year). CRS model calculations suggested at least two episodes of rapid sedimentation during the past 60 years, in the early 1960s, and again in the mid 1980s. The onset of ^{137}Cs activity at 11–12 cm may be estimated as occurring around 1954, but a decrease in ^{137}Cs activity at 9–10 cm, similar to a feature in the ^{210}Pb profile, likely reflects dilution due to an episode of rapid sedimentation; therefore, the maximum at 5–6 cm may not be a reliable indicator of the 1963 fallout maximum. Concentrations of lead in core AB1 were scarcely above background for the entire core. The absence of a distinct lead maximum precluded use of the stable lead to calibrate the chronology. However, in sections from the uppermost 7 cm of the core, which correspond to post-1970 according the CRS

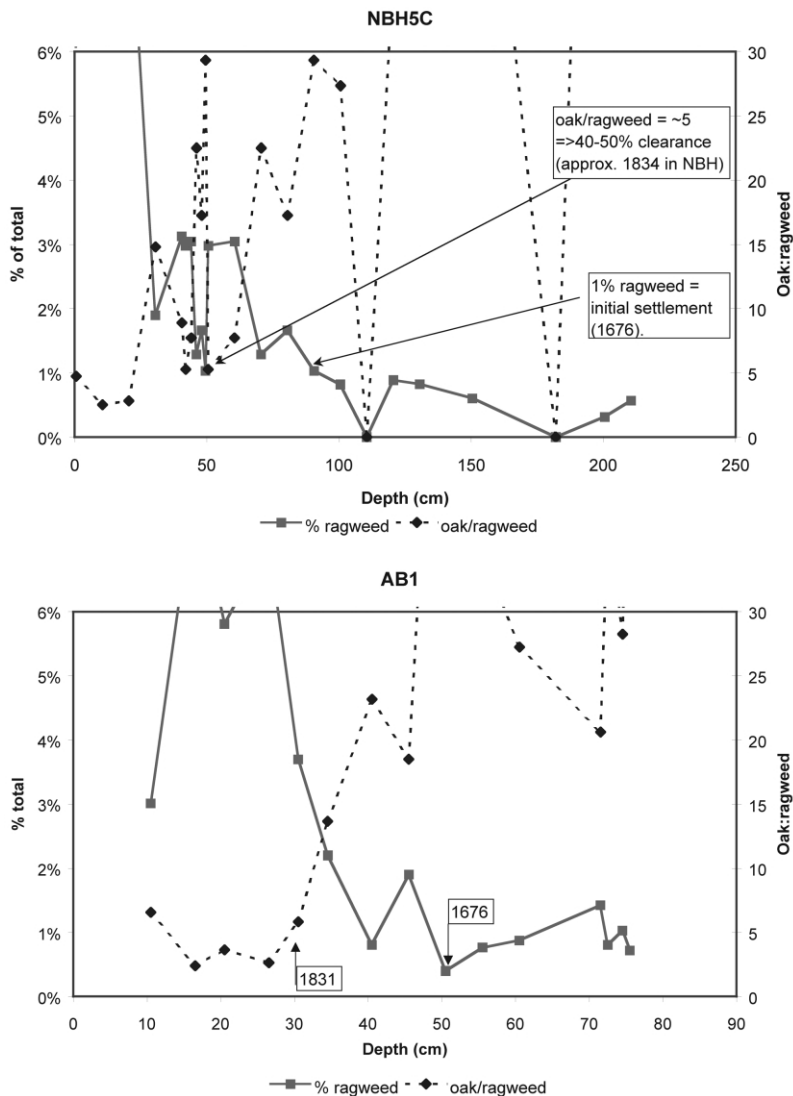


Fig. 3. Distribution of % ragweed pollen and oak/ragweed pollen ratios with depth in the NBH5c (A) and AB1 (B) cores.

model chronology, lead concentrations were lower by a factor of 2 than in underlying sediments, consistent with the trends previously noted (Owens and Cornwell, 1995; Santschi et al., 2001; Trefry et al., 1985). Similarly, PCBs were not found in any horizons with dates estimated at 1934 or earlier.

As with core NBH5, we used pollen to estimate the age of the deeper sections of core AB1 (Fig. 3b). Ragweed concentrations varied between 0.4

and 1.4% in horizons from 50–51 cm and below, and increased rapidly to values as high as almost 8% above 50 cm. This distribution was consistent with the history of early settlement in the Appogansett Bay watershed: settlers arrived as early as 1657, but substantial population growth did not take place until after the end of the King Philip's War in 1676. Analysis of an 1831 map of the area revealed that approximately 51% of the watershed was cleared by that time (C. Pesch, unpublished

Table 5
Summary of sedimentation rates for sediment cores

Core	Depth (cm)	Sedimentation rate (cm/year)	Comments
NBH1a	0–5	0	
	5–21	0.24	CIC model
	21–43	0.24	Extrapolated
NBH1b	0–7	0	
	7–50	0.36	Estimated
NBH5	0–1	0.39	CRS model
	1–6	0.38	
	6–16	0.34	
	16–21	0.11	
	21–91	0.29	Pollen
AB1	91–217	0.29	Extrapolated
	0–1	0.31	CRS model
	1–4	0.36–0.42	
	4–8	0.15–0.28	
	8–10	0.57–0.60	
	10–12	0.24–0.38	
	12–13	0.20–0.23	
	16–51	0.13	Pollen
51–79	0.13	Extrapolated	

data); the corresponding decrease of the ratio of oak pollen to ragweed pollen to ~ 5 occurred at or above the 30–31 cm horizon in core AB1. Using dates of 1676 for the 50–51 cm horizon, the last horizon in which measured ragweed concentrations remained near background, 1831 for the 30–31 cm horizons, and 1931 for the 16–17 cm horizon (the bottom of the ^{210}Pb record), we calculated a mean sedimentation rate of 0.13 cm/year for the lower portion of core AB1. Table 5 summarizes the estimated sedimentation rates for all of the cores.

3.2. Effects of socioeconomic trends in New Bedford Harbor

Due to the limited number of people and farms, the period from pre-European settlement to the first settlement through the agricultural phase (1600s–1780) was not expected to extensively affect the aquatic environment of New Bedford Harbor. It is estimated that only approximately 4% of land in the watershed was cleared during this time, so surface runoff of sediment and pollutants would not have been large (Pesch and Garber, 2001; Voyer et al., 2000). The bottom portion of

the Lower Harbor core, NBH5, where the PAH record extends to well before European settlement, contains a small peak in concentrations (barely discernable in Fig. 4). This peak, although within the statistical definition of background, nevertheless likely reflects the burning of wood near the harbor from pre-European settlement through 1780. Native Americans burned the under-brush in coastal woods of New England prior to European settlement (Cronon, 1983; Howes, 1923).

Concentrations of metals in the Lower Harbor core were no different in sediments deposited during the agricultural period than in those predating European Settlement (Fig. 5a,b). If anything, concentrations of aluminum, iron and manganese were less variable during the agricultural period (Fig. 5b). Since these metals usually reflect the fine particle content of sediments, this suggests that grain size was more consistent during that time. Concentrations of organic carbon range from 1.5 to 1.9% in these sediments, with stable carbon isotope ratios ($\delta^{13}\text{C}$) of -18.5 to -19.6‰ , a signal midway between a system dominated by saltmarsh (-16‰) and marine (-21‰) carbon (Fig. 4).

With the onset of the whaling period around 1750, the watershed began to change as the original farms were subdivided, population began to increase, and industries that supported the whaling effort contributed contaminants to NBH (Voyer et al., 2000). The manufacture of goods such as copper sheathing for the bottoms of ships, try pots, pumps, fittings, and ship bells added metals, PAHs, solvents, grease, and acids to the harbor (Pesch and Garber, 2001; Voyer et al., 2000). The increase in concentrations of priority pollutant PAHs in core NBH5 (barely visible at the scale in Fig. 4) corresponds with the rise of industrial activity during the whaling period. These pyrogenically derived PAHs confirm that activities in the watershed during this period were detectable in the harbor, although the level was small compared to later time periods.

Unlike PAHs, concentrations of most metals in Lower Harbor sediments did not increase during the whaling era, except for copper and lead (Fig. 5a). Copper and lead increased above background in core NBH5 beginning in the late 1780s and

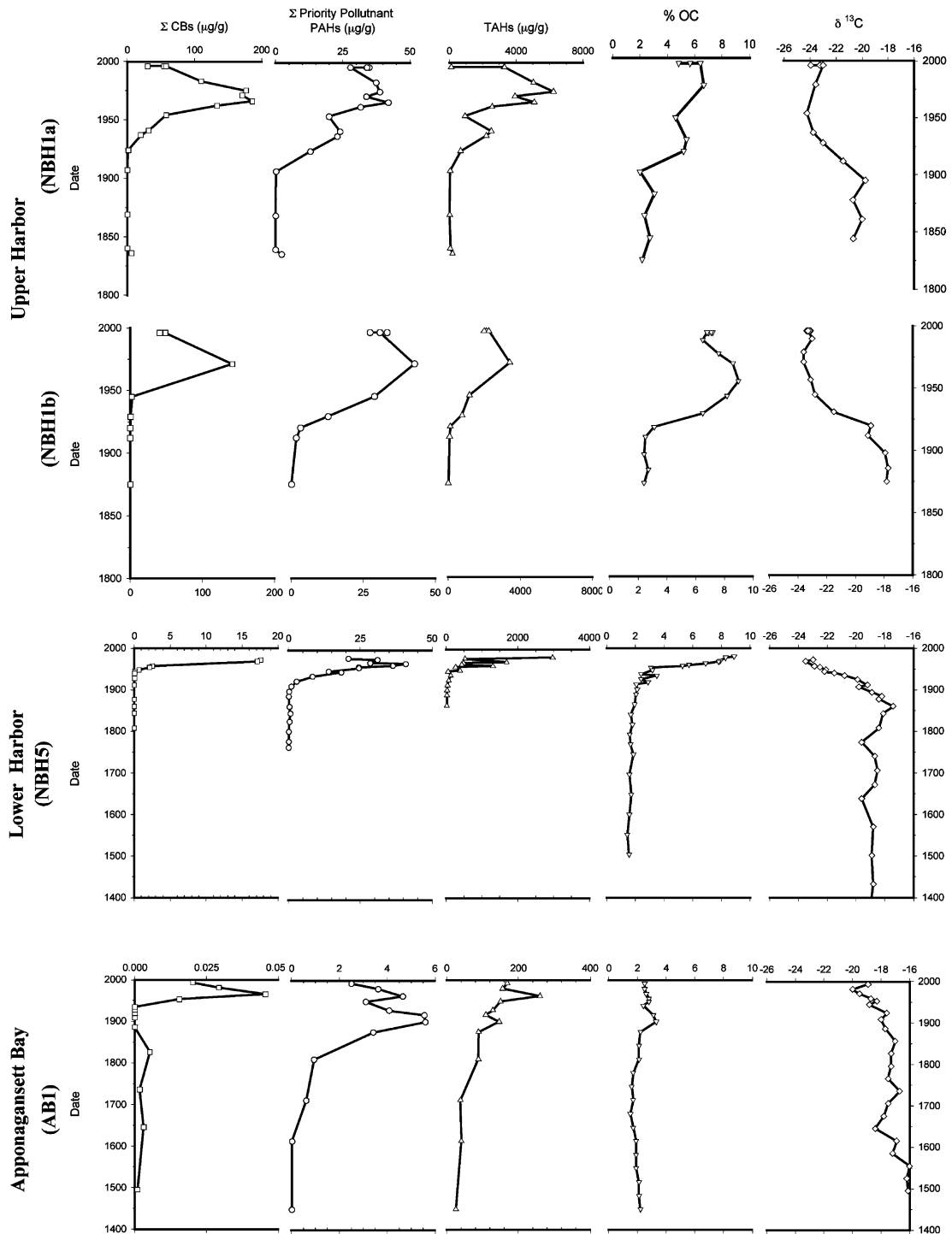


Fig. 4. Profiles of chlorinated biphenyls (CBs), priority pollutant PAHs, total aliphatic hydrocarbons (TAHs), organic carbon content, and carbon isotopic ratios in New Bedford Harbor and Apponagansett Bay sediment cores.

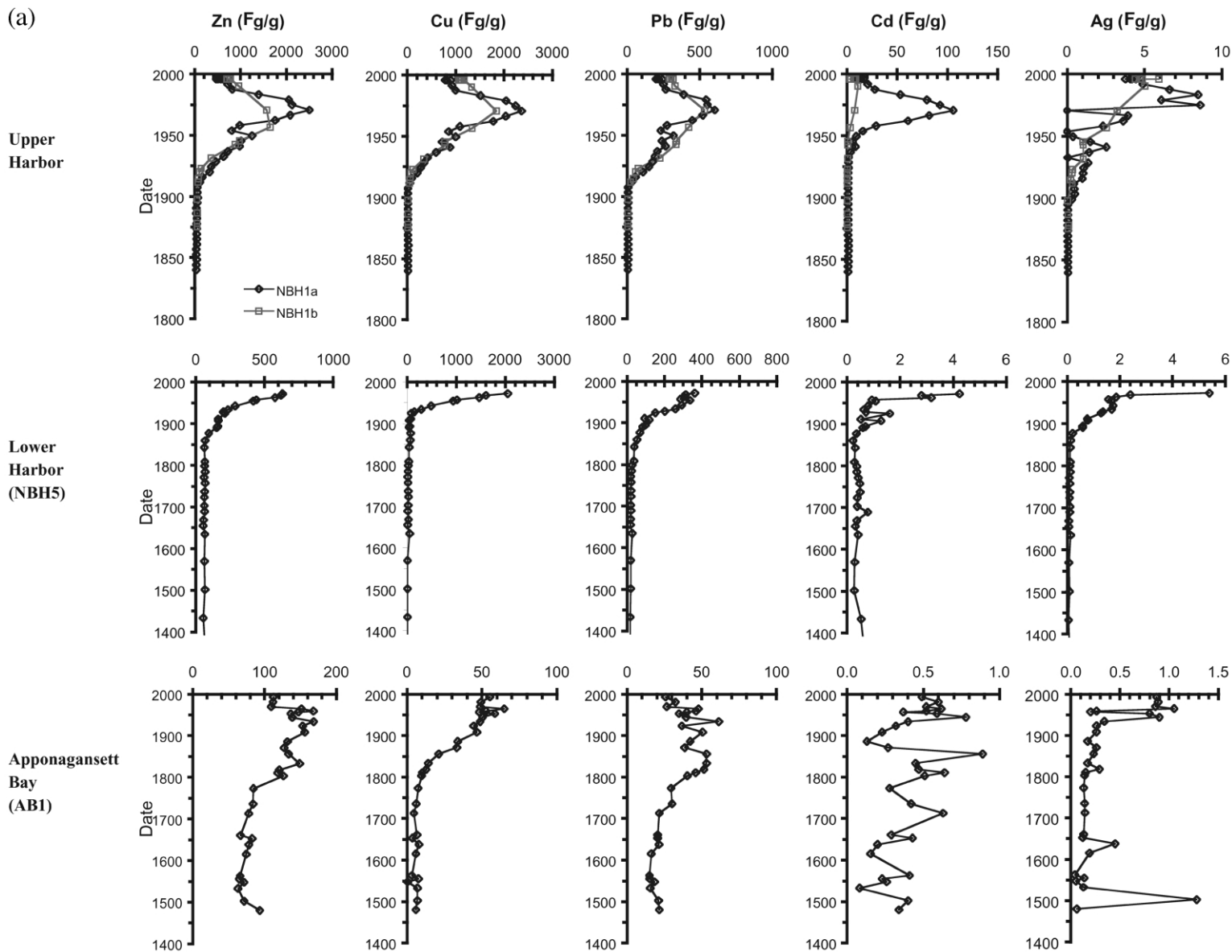


Fig. 5. (a) Profiles of Zn, Cu, Pb, Cd and Ag in New Bedford Harbor and Apponagansett Bay sediment cores (note that scales are different for different metals and different cores). (b) Profiles of Cr, Ni, Mn, Fe and Al in New Bedford Harbor and Apponagansett Bay sediment cores (note that scales are different for different metals and different cores).

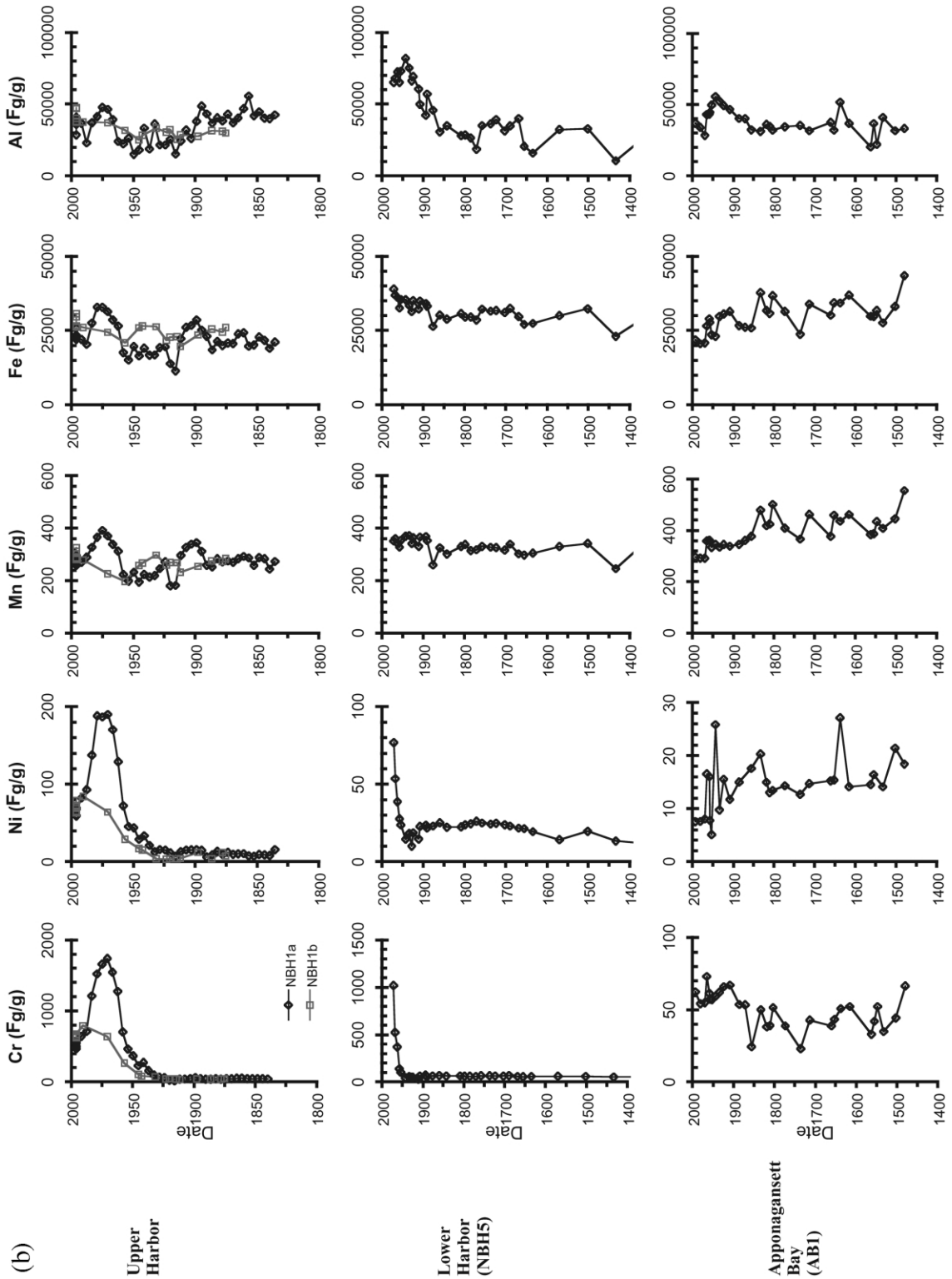


Fig. 5 (Continued).

1790s, although as with PAHs, the increase was small (~50% of background) compared to increases during subsequent years. These metals most likely came from the metal-working industries (foundries, machine shops, metal-working shops) that provided metal goods to support the whaling industry (Pesch and Garber, 2001; Voyer et al., 2000).

The sediment record in the Upper Harbor cores (NBH1a and NBH1b) shows that the late whaling period had little effect on contaminant levels in this portion of the harbor. Except for the beginning of a rise in PAHs, organic contaminants remained at background concentrations throughout this period (Fig. 4). Likewise, the increase in copper and lead concentrations was confined to the Lower Harbor area and is not seen in Upper Harbor sediments of this period. Most metal-working and whaling-related industries of this period were located on the shore of the Lower Harbor, and the contamination derived from them was apparently not severe enough to be transported to the Upper Harbor in significant amounts.

Organic carbon concentrations in sediments from the whaling period ranged between 1.8 and 2.5%, while stable carbon isotope ratios ranged from -17.4 to -20.6‰ (Fig. 4). These values were slightly higher but not dramatically different from those from the agricultural period and before. An analysis of population trends by Voyer calculated that New Bedford Harbor changed from oligotrophic to mesotrophic around 1835 and from mesotrophic to eutrophic around 1905 (Voyer et al., 2000). Thus, the changes in organic carbon amount and character observed in the cores from both the Upper and Lower Harbor at the end of the 19th century record the beginning of significant human activities that marked the end of the whaling and the beginning of the textile periods.

In summary, the activities associated with whaling (increasing population, wharf and bridge construction, significant land clearing, industrial operations) contributed only small amounts of toxics to the harbor sediments. Small, but significant, increases in copper, lead, and pyrogenically derived PAHs were detected in the early part of the whaling period. However, increasing population in the watershed clearly began to push the

harbor over a threshold from mesotrophy to eutrophy. It was at the end of the whaling and the beginning of the textile period that the harbor began to exhibit strong and progressive increases in the levels of contaminants due to human activities.

The textile period ushered in extensive changes in NBH, including substantial filling of wetlands for the construction of the textile mills, expansion of industrial activity both in numbers and spatial extent, and a dramatic increase in population. By 1920, 120 000 people were living in New Bedford, an increase of a factor of 4.5 over the population in 1880 (Pesch and Garber, 2001). Not surprisingly, a transition in contaminant trends was observed starting around the beginning of the 20th century. Population growth resulted in increased sewage delivered to NBH and greatly increased amounts of nutrients and organic carbon entering the harbor (Pesch and Garber, 2001). The amount of toxic substances released directly from the mills was probably not substantial because the operations were mainly spinning and weaving of cloth, not bleaching and dyeing of material. However, concentrations of many organic toxicants did begin to depart from background during the period from 1880 to 1940 (Fig. 4). The first significant appearance of organic toxicants, except for PCBs, was in the time period 1907–1929. In fact, PAH and TAH concentrations reached a relative maximum at the end of the textile period (~1940) in the NBH1a core (Fig. 4), declining slightly before increasing again in the post-textile period (1940–1970). PCBs began to increase in all of the cores in the period from 1937 to 1945; this is consistent with their first use in New Bedford (Schloss, 1985). Concentrations of contaminant metals also increased: for most, concentrations first increased significantly above background in the period 1880–1916, and continued increasing throughout the period (Fig. 5a).

The amount and type of organic carbon loading to the harbor changed dramatically during this period. Concentrations of organic carbon increased from a background of approximately 2% to greater than 5%, with a concomitant shift in the isotopic ratio. Consistent with the burgeoning population of New Bedford Harbor, a major change began to

take place around 1895 in the Upper Harbor; the stable carbon isotope signal changed from a system dominated by marsh/marine carbon toward a system dominated by terrestrial and marine carbon ($\sim -23.4\text{‰}$). The Lower Harbor core, NBH5, showed a similar trend with the shift from marsh/marine to terrestrial/marine beginning at 1900. The filling of wetlands for construction of textile mills (Pesch and Garber, 2001; Voyer et al., 2000) explains the continued shift in $\delta^{13}\text{C}$ values away from a marsh dominated system (Fig. 4). The increasing inputs from human waste, which would increase both the terrestrial signal by direct discharge of labile organic matter (human and animal sewage), and the marine signal by an increase in nutrients, which stimulate both water column (phytoplankton) and benthic production (macroalgae), explains the shift of the isotopic ratio toward an estuary dominated by terrestrial and marine organic material. This change represented a major state change or threshold from a system dominated by the ocean to one dominated by what was happening on the land.

The trends of contamination in NBH evident in the textile period continued into the post-textile period. The economic base began to diversify significantly in order to blunt the effects of the declining textile industry. Manufacturing companies moved into vacant buildings where textile mills once thrived. These new activities continued and even increased the contamination of the harbor and introduced new types of contaminants, such as PCBs. This period marked the most rapid increases in toxic contaminant levels in the sediment cores over the entire developmental history of New Bedford Harbor.

Notable during this period was the growth of Aerovox Incorporated, an electrical components manufacturing firm, located along the shores of the Upper Harbor, that used PCBs in their processing (Fig. 1). In the Upper Harbor, maximum concentrations of total PCBs between 280 and 350 $\mu\text{g/g}$ occurred in sediments from the period 1966–1975, decreasing to current concentrations of approximately 92 $\mu\text{g/g}$. These trends reflect both the local and national sales records of Monsanto (national producer of PCBs) and Aerovox (Monsanto, 1979; Schloss, 1985).

It is clear from the sediment profiles in the two Upper Harbor cores, however, that the current PCB contamination is a factor of 3–4 less than the maximum concentrations observed for the early 1970s. This decrease of approximately 3% per year over the past 25 years (from 1971–1996) most probably resulted from the burial of the PCB-contaminated sediment with less contaminated material due to source reductions. Because the harbor is regularly affected by storms and tides, this process is likely to involve a continual influx of clean sediment, resuspension of contaminated sediments, mixing and burial of sediments with greater contamination. This dynamic interaction is exemplified by the mixed layer in the two cores in the Upper Harbor, estimated to be 5–7 cm thick. This layer is probably resuspended on a regular basis during storms and strong tides. Despite the reduction in concentrations of PCBs in sediments over the past 30 years, maximum concentrations are still only 12–16 cm below the surface in the Upper Harbor and may still affect the water column and biota living there.

While the PCB contamination of New Bedford Harbor is unprecedented for marine waters, other industrial activities in and around the harbor affected the level of contamination in the system. Increased use of the internal combustion engine in ships allowed the revival of commercial fishing. By 1984 the port led the nation in fish landings (Massachusetts Division of Marine Fisheries, 1985), and fish-related processing and infrastructure thrived after the decline of textile mills. Pollution from diverse industries continued to cause increased PAH and TAH concentrations in the sediments of the harbor throughout this period (Fig. 4). Concentrations of contaminant metals, already increased significantly above background by 1940, increased by factors of 2 to more than 10 between 1940 and 1970. Concentrations of some metals declined slightly between 1950 and 1954 (as reflected in one of the Upper Harbor cores), but increased sharply again from 1954 to 1971–1975, when they reached their maximum values. Similarly, organic carbon concentrations increased during this period from approximately 5% to as much as 9% by 1970, although the $\delta^{13}\text{C}$ isotopic signal did not shift much further.

Previous historical analyses of New Bedford Harbor did not separate the environmental awareness period from the post-textile period (Pesch and Garber, 2001; Voyer et al., 2000). However, increasing public awareness of environmental degradation brought about cultural changes that warrant characterization and discussion of the last thirty years separately. Significant improvements in the environment resulted from major legislative action; while some environmental laws existed before 1970, most extensive legislative action aimed at improving the environment was initiated between 1970 and the present.

In 1983, New Bedford Harbor and 17 000 acres of adjacent Buzzards Bay were placed on the US Environmental Protection Agency's National Priority List as a Superfund site because of PCB contamination. From April 1994 through September 1995, the most contaminated sediments in the Upper Harbor were dredged and placed in a nearby interim shoreline confined disposal facility. Eventually, PCB-contaminated sediment will be removed from most areas of the Upper Harbor. Implementation of legislative actions at the local level also resulted in reductions in the concentrations of other contaminants in New Bedford Harbor. For example, the Clean Water Act required states to set limits on all point sources to coastal waters, and as a result, construction of the Fairhaven wastewater treatment facility and upgrades to the New Bedford wastewater treatment facility were completed. Pretreatment of point sources before discharge into a public wastewater treatment facility was also implemented in 1987 (Voyer et al., 2000). These environmental regulations have reduced point source inputs of toxics. Metals in surficial sediments of the Upper Harbor have decreased 50–90% from the maxima in the early 1970s, and we have documented reductions of 15–30% in PAHs and TAHs in the harbor sediments. It is worth noting that reductions of PAHs and TAHs are not as marked as those of PCBs, most likely because sources of these constituents, combustion of fossil fuels including transportation sources, have not decreased as much as pollutants from industrial sources. Concentrations of organic carbon, derived primarily from carbon and nutrient inputs from wastewater, urban runoff, and com-

bined sewer overflows, have also not decreased significantly.

Because rates of contaminant accumulation might be expected to more closely reflect anthropogenic activities than concentrations, we calculated accumulation rates from measured contaminant concentrations, bulk density and estimated sedimentation rates. The spatial and temporal trends of accumulation in the New Bedford Harbor cores paralleled those of concentrations of contaminants. In core NBH5, slightly higher sedimentation rates in near surface sediments caused slight variation between profiles of contaminant concentration and accumulation. Comparative accumulation rates at the 3 sites were in relatively good agreement: accumulation rates in the background portion of the cores agreed within a factor of 2–6 for all contaminants and maximum accumulation rates agreed within a factor of 4 or less except for cadmium and chlorinated biphenyls (Table 6). The higher accumulation rates for CBs in the Upper Harbor is understandable, as the major point source of these compounds was located in the Upper Harbor; the reason for much higher Cd in NBH1a is not clear. It can be seen that, even with diminished inputs in recent times, rates of contaminant accumulation in NBH are still exceptionally high compared with other US waterways (Table 6).

3.3. *Effects of socioeconomic trends in Apponagansett Bay*

Apponagansett Bay was selected, *a priori*, as a reference site because of the absence of large-scale industrial development within its watershed. Its geochemical record was expected to share similar background conditions with that of New Bedford, but without strong local inputs, thus reflecting more regional processes such as atmospheric deposition or input from Buzzards Bay. Local non-point sources resulting from the less dramatic growth and development within the Apponagansett Bay watershed were also expected to be reflected in the sedimentary record.

Examination of organic carbon and stable carbon isotope records in the core revealed that this system has changed only slightly from the late

Table 6
Contaminant accumulation rates

	Zn ($\mu\text{g}/\text{cm}^2/\text{year}$)	Cu	Cr	Pb	Ni	Cd	Ag	CBs	PAHs	TAHs	OC*
NBH1a											
Surface	87	140	86	38	11	2	0.7	5	6	21	10
Maximum	400	377	277	96	30	17	1.3	29	7	920	13
Background	9	2	10	1.4	2	0.2	0.08		0.03	17	6
NBH1b											
Surface	197	298	175	83	20	0.9	1.2	12	9	560	18
Maximum	554	514	257	149	27	3.5	2.0	39	12	950	30
Background	26	14	17	9	3	0.09	0.06		0.03	6	9
NBH5											
Surface [^]	129	419	208	74	16	0.9	1.1	4	4	600	18
Maximum	147	419	208	80	16	0.9	1.1	4	10	600	22
Background	13	4	13	5	4	0.09	0.02		0.01	4	4
AB1											
Surface	39	19	22	9	3	0.2	0.3	0.007	0.9	59	9
Maximum	55	19	22	15	4	0.2	0.3	0.01	1.3	59	9
Background	9	0.6	5	2	2	0.04	0.03		0.002	3.8	2
Rates of accumulation of contaminants from other US waterways (from Santschi et al., 2001)											
Galveston Bay	18	2.4	12	4.5	–	0.03	0.03	0.001	0.054	–	–
Mississippi River Delta	55	8.1	27	10	–	0.07	0.06	0.001	0.25	–	–
Tampa Bay	42	13	28	22	–	0.36	0.17	0.02	8.67	–	–

*Units for organic carbon are $\text{mg}/\text{cm}^2/\text{year}$; [^] reflects up to 1973.

1500s to the present (Fig. 4). The concentration of organic carbon remained in the range of 1.8–2.6%, which indicates a system with minimal eutrophication. Although organic carbon concentrations rose slightly in the period 1920 to 1928, possibly indicating impacts of anthropogenic activities, concentrations were still less than 3.5%. The noticeable shift in $\delta^{13}\text{C}$ from a marsh to a marine type signal during the 20th century likely reflects the gradual human influence on the watershed that increased the amount of terrestrial organic matter (from runoff), marine organic matter (derived from increased nutrients and associated phytoplankton biomass), or reduced the magnitude of eelgrass carbon ($\delta^{13}\text{C} \sim 10\text{‰}$) in the estuary (Costa, 1988). Loss of shoreline marsh by residential development could explain the $\delta^{13}\text{C}$ signal; however, comparisons of historical to present day wetland areas showed no significant wetland losses. Although the inner portion of Apponagansett Bay has been identified as ‘one of the most nutrient overloaded embayments of Buzzards Bay,’ the outer Bay (where the core was taken) has been only moder-

ately impacted from inputs of excess nutrients and labile organic matter (Howes et al., 1999).

Input of PCBs to Apponagansett Bay were also minimal (Fig. 4). Maximum concentrations were 4000 times less than maxima observed in New Bedford Harbor. The timing of maximum PCB concentrations in Apponagansett Bay was roughly consistent with that in New Bedford Harbor and reflected national PCB sales. The low concentrations in Apponagansett Bay indicate that local sources of PCBs were negligible and most PCBs were likely to have been derived from regional atmospheric deposition (Latimer, 1997).

Profiles of PAHs in the Apponagansett Bay core revealed much lower concentrations compared to New Bedford Harbor (Fig. 4). The first significant concentrations were observed at depths corresponding to 1891, and the maximum concentration, deposited around 1920, was only approximately 17% of that in New Bedford Harbor. This suggests a local source of PAHs, during the early phases of the industrial revolution, probably due to the burning of coal and petroleum. This source is consistent

with the signal observed in TAHs, major constituents of petroleum products, which began to increase from background in the mid 1800s. A second PAH maximum, occurring around 1965, was similar to trends observed in New Bedford Harbor and may be the result of increased non-point transportation sources. These sources decreased after passage of the Clean Air Act in 1970 and concentrations continued to decrease to the present. It is interesting to note that concentrations of some metals (Zn, Cu and Pb) also increased in Apponagansett Bay sediments around 1770–1805. These increases could be related to the shipbuilding established in the mid-18th century, but as with PCBs and PAHs, the concentrations are very small compared to New Bedford Harbor.

As in the New Bedford Harbor cores, trends of contaminant accumulation rates in Apponagansett Bay generally paralleled those of contaminant concentrations, but because of varying sedimentation rates, profiles of accumulation rates were somewhat different. Increased rates of sediment accumulation in surficial (0–5 cm) and near-surface (10–12 cm) sediments caused contaminant accumulation rates to be significantly increased compared to adjacent horizons, whereas concentrations were relatively constant. Thus, maximum accumulation rates of several contaminants (e.g. Cu, Cr, Cd, Ag, TAHs and organic carbon) occurred in surficial sediments (Table 6). Conversely, low sediment accumulation rates deeper in the core (17–20 cm) resulted in higher concentrations of metals, but decreased accumulations. Again it should be noted, however, that even the maximum contaminant accumulation rates in Apponagansett Bay, comparable to those in other US waterways, were still far less than those determined for New Bedford Harbor (Table 6).

3.4. Establishment of reference conditions

A reference location or system is often chosen to compare against a given site or system in order to assess the effects of stressors. To be useful, the reference site should share as many common characteristics as possible with the investigated site, while remaining free from the stressors being

considered. In this study, the Apponagansett Bay site met these requirements; the contaminant profiles indicated that anthropogenic activities have contributed little in the way of contamination to the outer portion of the Bay. Although the geochemical record showed evidence of some anthropogenic activities, the degree of contamination or inferred eutrophication is slight when compared to New Bedford Harbor. The fairly consistent temporal record also shows that similar conditions have been maintained over hundreds of years. Consequently, outer Apponagansett Bay provided a valid reference location against which to compare the findings in New Bedford Harbor.

Statistical analyses were performed to determine the depth in each core at which concentrations of analytes increased above baseline or reference conditions. Starting from the bottom of each core, concentrations in each core horizon were compared against those measured in all underlying horizons (*t*-test, $P=0.05$). The depths at which concentrations significantly exceeded underlying concentrations were noted for each substance, and the underlying horizons were designated as representing background conditions. Background concentrations were then estimated for those depths at which all of the analytes were at background levels by calculating the mean and 95% confidence interval concentrations of each analyte in each core. All analyses were performed using SAS Statistical software (Release 6.12, SAS Institute Inc., Cary, NC, USA). Assuming that the underlying sediments represent background conditions, mean concentrations were calculated for each contaminant (or class of contaminants) in the background portion of each core (Table 7). Because PCBs were not synthesized until the 1930s, there was no background concentration for these compounds. Mean background concentrations were very similar in all the cores, both within and outside NBH, suggesting a common signature of contaminant concentrations in background sediments; they were also equal to or approximately half of background concentrations determined by Summerhayes in NBH (Summerhayes et al., 1985). Equally important, background concentrations found in the NBH cores differ by less than a factor of 2 from those in the top 5 cm (a depth interval typical for

Table 7

Concentrations of contaminants in background sediments and reference site surficial sediments ($\mu\text{g/g}$)

Location	Station		Zn	Cu	Cr	Pb	Ni	Cd	Ag	PAHs	TAHs	% OC Carbon	$\delta^{13}\text{C}$
Upper Harbor	NBH1a		42	10	48	<7	11	1.1	0.4	0.1	48	2.6	-20.3
		±	20	9	14		7	0.4	0.4	0.4	77	1.3	1.5
Upper Harbor	NBH1b		55	18	45	<7	9	0.2	0.1	0.1	16	2.5	-17.8
		±	5	2	6		12	0.2	0.1			0.8	0.6
Lower Harbor	NBH5		60	14	59	20	20	0.4	0.1	0.2	ns	1.7	-19.0
		±	14	17	14	6	11	0.3	0.1	0.7	ns	0.3	0.8
NBH mean background			51	13	52	12	15	0.7	0.1	0.2	40	2.0	-19.1
		±	16	12	13	4	9	0.3	0.1	0.5	40	0.5	0.8
Apponagansett Bay mean background	AB1		74	5	46	19	17	0.3	0.1	0.02	33	1.9	-17.0
		±	20	5	21	6	9	0.3	0.3	0.06	136	0.6	2.1
Apponagansett Bay surficial sediments	0–1 cm		112	55	63	26	7.5	0.5	0.9	2.5	169	2.5	-18.9
	4–5 cm		112	49	54	32	7.6	0.6	0.9	3.6	156	2.5	-20.0

Note: background PCB concentration is undetectable; ns = background not sampled in this core (estimated at 26, $\text{CI} \pm 8.6 \mu\text{g/g}$). Concentrations are means and 95% confidence intervals for all samples determined as representing background, that is, when none of the analytes were above background. For samples where analyte concentrations were below detection limit, the method detection limit was substituted for purposes of calculations.

reference assessments) of the Apponagansett Bay core, except for Cu and Ag, which were approximately 4 and 7 times higher, respectively, in Apponagansett Bay surficial sediments than the NBH background. Thus the background portion of the New Bedford Harbor cores provides nearly the same information that would be provided by analysis of the top 5 cm of the Apponagansett Bay core. This demonstrates the use of cores to self-reference, that is, to provide information about reference conditions without having to select an external reference site.

It should be noted that the statistical determination of what constitutes reference conditions was accomplished independent of any dating information, and indicates that reference conditions can be characterized without the need for detailed core analysis (Dixit et al., 1999). In the absence of such detailed analytical data, the self-referencing approach can be used to establish reference conditions, provided the investigator has some knowledge of: (a) historical land use and anthropogenic activities in the watershed to establish dates for background conditions; and (b) sedimentation rates in the water body to estimate the depth in the sediment column corresponding to the dates determined.

3.5. Driver–stressor relationships

Among the many possible drivers of ecological stress in New Bedford Harbor, population is primary, more so than particular industries or sources. The population of New Bedford rose rapidly in the late 19th and early 20th century, increasing by approximately 500% from 1870 to a maximum around 1920, and subsequently decreasing slightly (~20%) between 1920 and 2000 (Fig. 6). Contaminant levels increased between 1910 and 1970. Furthermore, despite significant changes in both the intensity and types of industrial activity in the harbor area concentrations of contaminants were all highly correlated in the NBH cores. If contamination in NBH was linked to specific industries or activities, it might be expected that the recorded impact of contaminants specific to those particular industries might follow the rise and decline of the industries.

Population is not the sole driver responsible for the temporal distribution of chemical and geochemical stressors. The increase of contaminant concentrations lags behind the explosion of population by 40–50 years, not reaching the maximum until early in the 1970s. Moreover, contaminant concentrations have decreased significantly in the

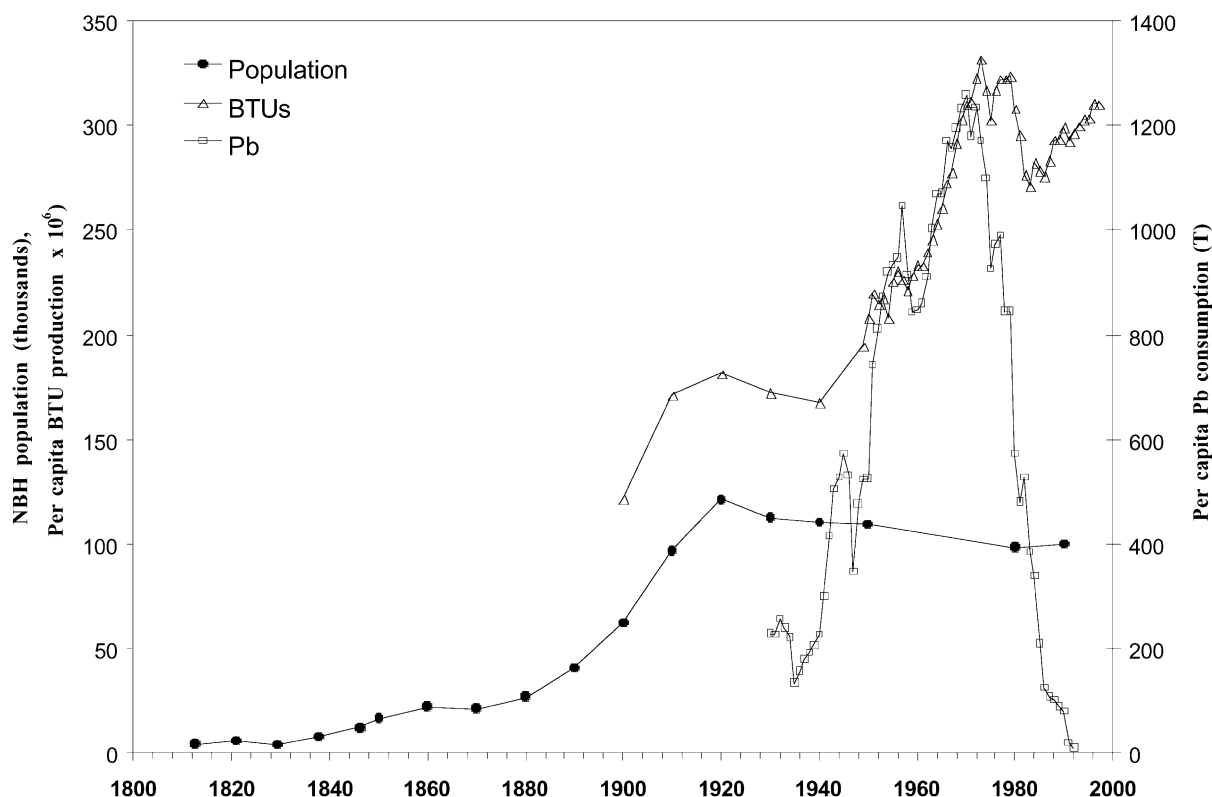


Fig. 6. NBH population, national per capita BTU production, and Pb consumption by year. (data sources: BTUs: 1900–1940 data from (Hottel and Howard, 1971); 1949–1997 data from the Energy Information Administration, <http://www.eia.doe.gov/historic.html>; Pb in gasoline data from <http://minerals.usgs.gov/minerals/pubs/commodity/lead/stat/tbl2.txt>; population data from US Census Bureau, Population Division, Population Distribution Branch, <http://www.census.gov/population/www/estimates/uspop.html>).

last 30–40 years, while the New Bedford population has decreased only slightly. Clearly, other factors influence the contamination of the harbor.

A second factor operating is what we refer to as the societal use factor, the amount of potential emissions to the environment generated per capita. This factor increased substantially during the industrialization taking place during the 20th century. For example, per capita national energy production (as BTUs), remained relatively constant between 1910 and 1940, and then almost doubled from 1940 to 1973 (Fig. 6). Even more telling is the dramatic rise in the consumption of lead in the production of gasoline; per capita consumption of lead increased by more than 450% between 1930 and 1970. These data serve to indicate that poten-

tial emissions to the environment increased substantially as industrialization progressed in America throughout the 20th century.

The rapid growth in emissions was subsequently limited in part by a third factor, which we refer to as the environmental control factor. As noted earlier, beginning in approximately 1970, increased environmental awareness led to the implementation of environmental regulations that markedly reduced point sources and emissions of contaminants to the environment. As prevalence of these controls increased, net emissions decreased. For example, as rapidly as per capita consumption of lead increased from 1930 to 1970, it decreased from 1970 on, as regulations phased out the use of lead in gasoline. However, not all controls have

been equally successful; while per capita energy production decreased between 1973 and 1983, it has risen consistently since.

We submit that net emissions to the environment reflect the product of these three factors. In New Bedford Harbor, population increased in the early 20th century, but the societal use factor was low, so there was little increase in the levels of contamination. With increasing industrialization, the societal use factor increased; each person on average used, consumed, and emitted more substances into the environment, so overall emissions to NBH increased. This was seen in the rapid increase of metals, PAHs, and organic carbon between 1920 and 1970. With the onset of environmental awareness and regulation in the early 1970s came both decreased societal use and increased environmental control factors, which resulted in decreased net emissions. This again was reflected in the core profiles of most contaminants. Concentrations of these contaminants were greatly reduced in surface sediments of NBH relative to the maximum concentrations measured in subsurface sediments. The exceptions to this observation were the profiles of PAHs and organic carbon in NBH, which showed no, or only moderate, decreases (15–25%) in recent sediments relative to subsurface maxima. These contaminants are tied directly to drivers that don't have strong environmental controls, namely, fossil fuel use and non-point inputs of nutrients from the watershed.

4. Conclusions

The watersheds of New Bedford Harbor and Apponagansett Bay share similar regional characteristics, but have undergone very different developmental histories. Apponagansett Bay has maintained a basically rural, now suburban, residential environment, while New Bedford has experienced industrial development extending back hundreds of years. Analysis of geochemical indicators in sediment cores from these two systems allows the reconstruction of historical inputs of toxic substances. The similarity of indicators in the deeper, older portion of NBH cores with those in relatively unimpacted Apponagansett Bay dem-

onstrates that cores can be used to establish reference conditions for a site as successfully as using separate sites judged *a priori* to represent the reference state. The advantage of the core method is that the impacted and reference periods have all non-experimental factors (e.g. hydrodynamics) in common, whereas a spatially distinct reference site, if one exists at all, may have different factors influencing the endpoints of interest. Reference conditions will always exist in cores, provided the cores are long (old) enough. Combining the chronological record of indicators in cores with extensive knowledge of anthropogenic activities and land use within a watershed enables assessment of the relative extent and impact of human activities on an estuary. This approach also provides the basis for establishing relationships between environmental stressors and factors that drive the stressors. Finally, this approach provides a framework for the assessment of ecological response(s) to environmental stressors over a range of time and/or exposure scales.

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